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RESEARCH ARTICLE

Antifouling paint biocides (Irgarol 1051 and diuron) in the selected ports of Peninsular Malaysia: occurrence, seasonal variation, and ecological risk assessment

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Abstract

Irgarol 1051 and diuron are photosystem II inhibitors in agricultural activities and antifouling paints in the shipping sector. This study focused on three major ports (western, southern, and eastern) surrounding Peninsular Malaysia to construct the distribution of both biocides on the basis of the seasonal and geographical changes. Surface seawater samples were collected from November 2011 to April 2012 and pretreated using the solid-phase extraction technique followed by quantification with GC-MS and LC-MS-MS for Irgarol 1051 and diuron, respectively. Generally, the distribution of Irgarol 1051 was lowest during November 2011 and highest during April 2012, and similar patterns were observed at all ports, whereas the distribution of diuron was rather vague. The increasing pattern of Irgarol 1051 from time to time is probably related to its accumulation in the seawater as a result of its half-life and consistent utilization. On the basis of the discriminant analysis, the temporal distribution of Irgarol 1051 varied at Klang North Port, Klang South Port, and Pasir Gudang Port, whereas diuron was temporally varied only at Kemaman Port. Furthermore, Irgarol 1051 was spatially varied during November 2011, whereas diuron did not show any significant changes throughout all sampling periods. Ecological risk assessment exhibited a high risk for diuron and Irgarol 1051, but Irgarol 1051 should be of greater concern because of its higher risk compared to that of diuron. Thus, it is recommended that the current Malaysian guidelines and regulations of biocide application should be reevaluated and improved to protect the ecosystem, as well as to prevent ecological risks to the aquatic environment.

Keywords Antifouling biocides · Diuron · Irgarol 1051 · Ecological risk assessment · Seasonal distribution · Discriminant analysis

Introduction

Marine biofoulers are organisms on submerged structures such as a ship's hull, an oil rig stand, and a fish cage (Shevalkar et al. 2020). The colonization of these organisms poses a severe concern, especially to the shipping industry. Biofoulers tend to increase the ship's fuel consumption since their attachment increases the hull's friction; therefore, extra fuel is needed to maintain the normal ship's speed (Abbot et al. 2000; Evans et al. 2000). Besides that, the attachment of biofoulers also put an extra cost in maintaining the ship's hull as they need to be cleaned up periodically. Owing to this concern, antifouling coating paints have been widely used to incapacitate marine biofouling in improving the shipping industry.

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An antifouling paint is a coating paint that is frequently applied on underwater hulls to inhibit the growth as well as detach marine biofoulers from submerged structures. Historically, numerous types of chemicals such as organotin (OT) compounds, organo-mercury compounds, and DDT have been widely used as antifouling compounds in underwater coating paints. Nonetheless, such compounds cause deleterious effects on the environment and human health; therefore, they were banned in the shipping industrial sector and were replaced by OT compounds such as tributyltin and triphenyltin (Mukhtar et al. 2019). However, in the early twenty-first century, after being used as antifouling paints, OT compounds have been also banned because of their acute toxicity, persistence, and poor biodegradability (Macken et al. 2008; Kucuksezgin et al. 2011; Tsunemasa and Okamura 2011).

Banning OT compounds as antifouling paints led to using biocide compounds as alternative antifouling agents in coating paints (Hanapiah et al. 2017). Booster biocides were selected because of their low persistence and high degradability characteristics (Mukhtar et al. 2019). Biocides are chemical compounds or microorganisms that are being used to kill, prevent, or harm any harmful entity or pest. The most common booster biocides, which have been widely used in antifouling paints, are Irgarol 1051 and diuron. Both biocides are extensively being used in agricultural activities as photosystem II inhibitor herbicides (Girling et al. 2015). According to Dafforn et al. (2011), the half-life for Irgarol 1051 and diuron is in the range of 100 to 350 days and 1 to 12 months, respectively. Conversely, both biocides also pose some threat to the non-targeted organisms such as benthic organisms and seagrass (Magnusson et al. 2013; Fernandez and Gardinali 2016; Kaonga et al., 2015).

In Malaysia, Irgarol 1051 and diuron are knowingly being utilized in both shipping and agricultural activities. The occurrence and distribution of diuron in the water column of Peninsular Malaysia ports were reported by Ali et al. (2014). Diuron was found in all collected samples without any apparent distribution trend. The concentration of diuron in all sampling stations was less than the permissible limit, guided by the Dutch National Institute of Public Health and the Environment. In the meantime, Irgarol 1051 was claimed to have contaminated the Peninsular Malaysia water ecosystem (Ali et al. 2013). Generally, the highest concentration of Irgarol 1051, recorded at Klang West Port, exceeded by 84-fold its permissible limit in water according to Dutch authorities. The present study is performed to investigate the influence of seasonal and geographical changes on the distribution of both biocides in the seawater, as well as to evaluate their ecological risk. Three out of seven major ports surrounding Peninsular Malaysia have been selected. The selected ports are Kemaman Port, Pasir Gudang Port, and Klang Port, which represent the east, south, and west parts of Peninsular Malaysia, respectively.

Materials and methods

Generally, this study has manipulated the secondary data, published by Ali et al. (2013) and Ali et al. (2014) for further risk assessment and chemometric analysis. Samples were collected and analyzed in 2012 and no new sample analyses are performed for this study. The purpose of this study is to further evaluate the influence of seasonal and geographic changes on the distribution of Irgarol 1051 and diuron in the major ports of Peninsular Malaysia, as well as the ecological threat they pose.

Sample collection

Sampling activities were conducted in the period of November 2011 to April 2012, to have a better view of the effect of seasonal changes on Irgarol 1051 and diuron distribution in the marine ecosystem. Generally, the climatic condition in Peninsular Malaysia is characterized by monsoon seasons, which are known as the southwest monsoon (May to September), northeast monsoon (November to March), and two shorter periods of inter-monsoon seasons (April and October) (Roseli and Akhir 2019). The increasing trends in both the total amount of rainfall and the frequency of wet days were recorded during the northeast monsoon, which gives rise to the increasing trend of rainfall intensity (Wong et al. 2016). December/January is the peak of the northeast monsoon period with heavy rains in Malaysia. In contrast, the trend of the total amount of rainfall and the frequency of wet days decreases during the southwest monsoon. Besides rainfall patterns, port vessel traffic and agricultural activities have significant roles in chemical contamination in the marine environment. It should be noted also that Malaysia uses biocides as main pesticides in palm oil plantations Muhamad et al. (2010). Lewis et al. (2009) reported maximum concentrations of pollutants around the Great Barrier Reef lagoon, Australia, during intensive rainfall events. Furthermore, on the basis of Malaysia Port Statistics (https://www.ceicdata.com), data on Malaysia's monthly vessel traffic (arrivals) at Peninsular Malaysia Port indicates heavy traffic in November and December (e.g., January 1997 to March 2018).

Surface seawater samples were collected during November 2011, January 2012, and April 2012 at three

Fig. 1 Sampling location at three major ports in Peninsular Malaysia

major ports in Peninsular Malaysia. The selected ports are Kemaman Port, Pasir Gudang Port, and Klang Port (Fig. 1). The Klang Port is divided into three sub-ports: North Klang Port, South Klang Port, and West Klang Port. Four liters of seawater samples were collected into a clean acetone-washed amber bottle and kept at the lowest temperature in an icebox, prior to transportation to the laboratory.

Analytical procedure and chromatographic analysis

The solid-phase extraction (SPE) technique was used to extract Irgarol 1051 from water samples. The extraction procedure was previously described by Sheikh et al. (2009) and Ali et al. (2015). In brief, Isolute Triazine SPE cartridge conditioning was carried out by eluting 10 mL of methanol followed by 10 mL of Milli-Q water. Two liters of seawater samples was loaded into the SPE cartridge at a constant flow rate of 20 mL/min. The cartridges were subjected to washing using 10 mL of Milli-Q water and subsequently dried under vacuum for 45 min before eluting with 5 mL of ethyl acetate-acetone (1:1) through an anhydrous sodium sulfate column. An internal standard, *p*-terphenyl-d_{14} (200 μL of 50 μg/L), was added into the extracts before the combined extract was blown down using nitrogen gas to about 200 μL. The final extracts were analyzed using gas a chromatography-mass spectrometry (GC-MS) instrument (QP 2010, Shimadzu, Japan). Separation of the targeted analyte was accomplished using a DB-5 MS capillary column. The GC-MS settings such as injection temperature, column oven temperature, temperature program, and ion source temperature were previously described in Ali et al. (2015).

Diuron was pre-concentrated using a PLS-3 SPE cartridge column, as adapted from Sheikh et al. (2009). The cartridge was first conditioned using acetonitrile, methanol, and Milli-Q water, in respective order. Prior to loading, the pH of 1 L of water samples was maintained at 3.5 by adding 10 mL of 0.2 M EDTA followed by the addition of 1 mL of 1 mg/L diuron D-6 ($C_9H_4Cl_2D_6N_2O$) as a surrogate standard. The analysis of diuron was carried out using LC-MS/MS with an Agilent ZORBAX Eclipse XDB-C18 column, as described by Ali et al. (2014).

The accuracy and precision of the extraction method were determined by investigating their linearity and recovery. For linearity, a series of standards for each analyte was prepared, and the standards were extracted via the SPE cartridges. The calibration curves were constructed, and the value of linear regression was obtained. The limit of detection (LOD) was calculated using the formula adapted from Miller and Miller (2010). The LOD value obtained for Irgarol 1051 was 1.0 ng/L, whereas that for diuron was 0.5 ng/L.

Recovery tests were also conducted for the purpose of monitoring the efficiency of the methodology. For Irgarol 1051, 2 L of water samples collected from remote areas was spiked with 4 ng/L and went through the optimized SPE protocol ($n = 4$). A similar process was carried out for diuron with 1 L of water samples. The percentage of recovery for both Irgarol 1051 and diuron was >90% with a %RSD value of <10%.

Statistical analysis

Discriminant analysis (DA) is a statistical approach that has been widely used to classify a set of observed data into pre-defined classes. It is commonly utilized to discriminate the variables between two or more sample groups (Adiana et al. 2017). In the present study, DA was applied to a raw dataset by using standard, stepwise forward, and stepwise backward methods to construct discriminant functions (DFA) for spatial and temporal variations of biocides in the water column of major ports in Peninsular Malaysia. DA was carried out using XLSTAT 2014.5.03 software. In the stepwise forward mode, variables are introduced step-by-step starting from the most significant variables until no significant changes are obtained; meanwhile, in the stepwise backward mode, variables are removed step-by-step starting with the least significant variables until no significant changes are obtained (Chabukdhara and Nema 2012; Juahir et al. 2019).

Ecological risk assessment

Ecological risk assessment was carried out on the basis of the procedure described by the European Chemicals Agency (ECHA 2017) and according to the Technical Guidance Document on Risk Assessment (TGD) (European Commission 2003). The risk factor, also known as the risk quotient (RQ), is calculated as follows:

$$RQ = \frac{MEC}{PNEC} \tag{1}$$

where MEC is the measured concentration of biocides in the surface water and PNEC is the predicted no-effect concentration of biocides in the ecosystem. The PNEC values were obtained from the ecotoxicity endpoint (LC50/EC50) of chemicals for the respective species in the relevant environment and using an appropriate assessment factor as outlined in the TGD guidelines. PNEC is calculated as follows:

$$PNEC = \frac{LC50\ 0r\ EC50}{1000} \tag{2}$$

Three standard test species, namely, algae, daphnids, and fish, corresponding to three different trophic levels, were evaluated. The ecotoxicity endpoint of the selected biocides for those three test species was obtained from the ECOSAR database (USEPA 2011). Risks are classified into four levels: negligible ($RQ < 0.01$), low ($0.01 \leq RQ < 0.1$), medium ($0.1 \leq RQ < 1$), and high ($RQ > 1$) (Palma et al. 2014).

Results and discussion

The average distribution of Irgarol 1051 and diuron in seawater, collected at the major ports of Peninsular Malaysia, is shown in Fig. 2. Throughout November 2011, January 2012, and April 2012, the distribution of Irgarol 1051 shows similar increasing patterns at all ports, where the concentration of Irgarol 1051 was the lowest in November 2011 and highest in April 2012. However, the distribution of diuron was indistinguishable, as each port has recorded a different period with high and low concentrations of diuron.

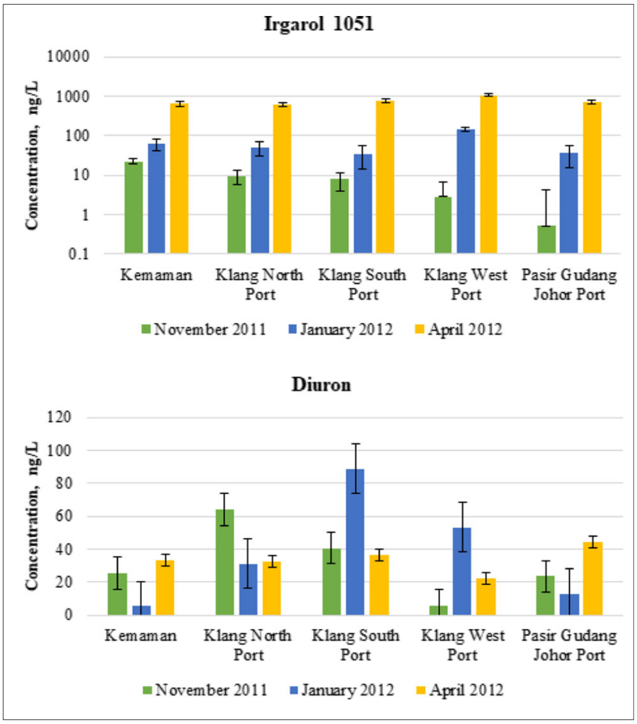


Fig. 2 Distribution of Irgarol 1051 and diuron in the seawater of major ports in Peninsular Malaysia

The distribution pattern of Irgarol 1051 is based on its consistent usage as an antifouling biocide at the selected major ports in Peninsular Malaysia, with no additional source. Irgarol 1051 is a notable alternative in tributyltin-free vessel coating paints and has been used widely since the usage of tributyltin coating was banned owing to its severe impact toward the marine ecosystem (Konstantinou and Albanis 2004; Ali et al. 2015; Gallucci et al. 2015). Additionally, the consistent pattern of Irgarol 1051 in the seawater samples indicated that the accumulation of Irgarol 1051 compound correlated with its half-life cycle. According to Dafforn et al. (2011) and Gallucci et al. (2015), since the half-life of Irgarol 1051 in the seawater is between 100 and 350 days, it does not easily degrade in a short period of time. In the present study, the gap left between the sampling periods was approximately 2 months apart, i.e., 60 days. The Irgarol 1051 compound that was introduced in November 2011 did not completely degrade in the seawater; however, the continuous usage of Irgarol 1051 for boats and vessel coating activities was introducing additional Irgarol 1051 into the water column. Therefore, the concentration of Irgarol 1051 constantly accumulates over time, which explains the increasing trend of Irgarol 1051 in the collected seawater at the major ports in Peninsular Malaysia.

Meanwhile, diuron is less persistent in the seawater than is Irgarol 1051 (Thomas et al. 2002), a finding that may justify the vague distribution of diuron recorded throughout the study period. As can be seen in Fig. 2, the average concentrations of diuron recorded in Kemaman Port and Pasir Gudang Port were slightly lower than those recorded in Klang ports (Klang North Port, Klang South Port, and Klang West Port). The random distribution of diuron in the collected seawater samples is deemed to be affected by the usage of antifouling paints containing this booster biocide at the ports as well as the continuous usage of diuron in agricultural activities. A similar finding was found by Omar and Aris (2018), wherein the possible sources of organic pollutants found within the Klang Port region were the high industrial and agricultural activities surrounding it.

On-site observation during sampling activities found that Kemaman Port is largely surrounded by urbanization and industrial activities; Pasir Gudang Port is located within the vicinity of high industrial and urban activities, whereas Klang ports are predominantly enclosed by high industrial, agricultural, and urbanization activities. According to Rameli and Jaafar (2014), a large area of southwest Selangor, which includes Carey Island, Morib, and Tanjong Sepat, is dominantly being occupied by a palm oil plantation. Therefore, this activity is counted as a non-point source of diuron, which has been contaminating the water column of Klang ports since diuron is being actively used as a herbicide in agricultural activities (Ali et al. 2014), besides its continuous usage as an antifouling paint biocide in the shipping sector (Ansanelli et al. 2017; Hanapiah et al. 2017).

The variation of Irgarol 1051 and diuron throughout the present study was further investigated using DA. DA was applied on the raw dataset for both biocides using standard, stepwise forward, and stepwise backward methods. The spatial variation of Irgarol 1051 using the standard-mode DFA (refer to Table 1 in the supplementary file) shows an accuracy of 50% with one discriminant variable, whereas the accuracy of Irgarol 1051 spatial variation using stepwise forward-mode DFA is similar to that using stepwise backward-mode DFA, which is 42.86%, with one discriminant variable. The only significant discriminant variable for all DA modes is the sampling period of November 2011, which explains why the variation of Irgarol 1051 was significant between sampling areas during November 2011. The spatial distribution of Irgarol 1051 during the November 2011 sampling period shows a significant variation compared to that during the January 2012 and April 2012 sampling periods (Fig. 3).

As shown in Table 2 in the supplementary file, the accuracy of Irgarol 1051 temporal classification using standard-mode DFA is 93.33% (five discriminant variables), whereas the accuracy of temporal classification for stepwise forward-mode DFA is similar to that for stepwise backward-mode DFA, which is 80% (three discriminant variables). Klang North Port, Klang South Port, and Pasir Gudang Johor Port were found to be the discriminant variables using the stepwise forward and stepwise backward DA methods. According to DA temporal variation, Klang North Port, Klang South Port, and Pasir Gudang Johor Port showed a high variation of Irgarol 1051 than did Kemaman and Klang West Port (Fig. 4).

The spatial variation of diuron using standard-mode DFA (refer to Table 3 in the supplementary file) shows an accuracy of 50% with no discriminant variable, which means there is no significant spatial distribution of diuron throughout the present sampling period.

As shown in Table 4 in the supplementary file, the accuracy of diuron temporal classification using standard-mode DFA is 58.33% (one discriminant variable), whereas the accuracy of diuron temporal classification for stepwise forward-mode DFA is similar to that for stepwise backward-mode DFA, which is 54.17% (one discriminant variable). DA temporal variation of diuron shows that the Kemaman sampling area is the only discriminant variable where the diuron distribution was highly varied during the present sampling periods (Fig. 5).

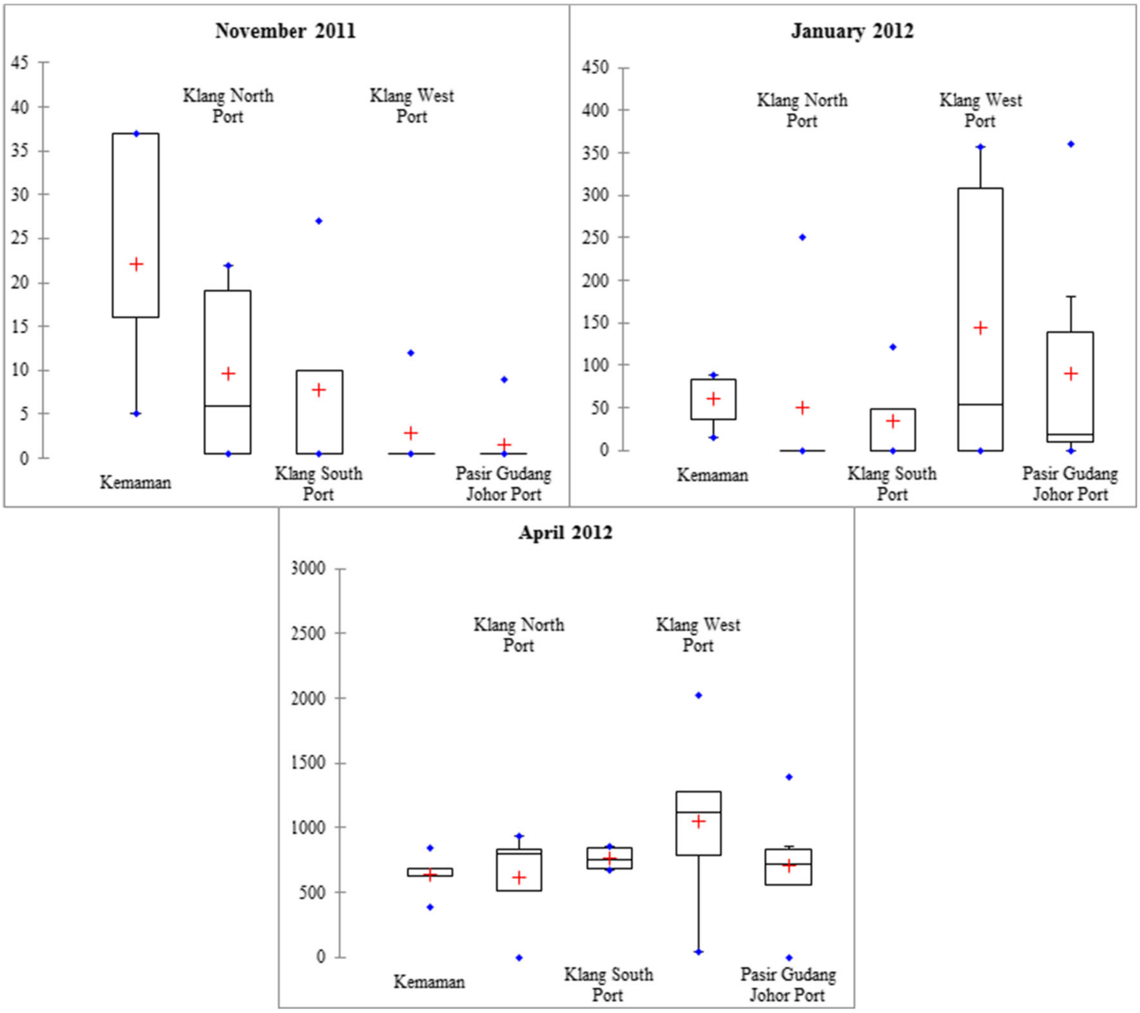


Fig. 3 Box and whisker plots of Irgarol 1051 spatial distribution throughout all sampling periods

Risk assessments of pollutants in the environment have been widely applied to indicate the extent of contamination of various types of organic pollutants in the ecosystem, particularly in the aquatic compartment. The estimation of ecological risks for pesticides and other types of organic pollutants in the Malaysian coastal waters has been described by several studies, and it was observed that the risks are categorized into negligible, low, medium, and high. For the record, in the Klang estuary, pesticides such as chlorpyrifos have been classified as having a high risk (Wee and Aris 2017), whereas other organic pollutants such as pharmaceutically active compounds are classified as low risk (Omar et al. 2019). However, no previous studies have reported on the ecological risk of Irgarol 1051 and diuron in the aquatic environment of the Malaysian coastal waters, and thus, the present assessment will be the first to report on the risk of these biocides. As chemicals that are widely being used for marine applications as well as in the agriculture sector, Irgarol 1051 and diuron should be given specific attention owing to their toxicity toward marine organisms in the aquatic food web.

Several toxicological studies have indicated that both biocides are the major threat to non-target organisms, such as coral reefs and fishes, as well as other aquatic life. A study by Ali et al. (2015) reported the toxicological evaluation of Irgarol 1051 on Asian seabass, *Lates calcarifer*, and found that this substance was toxic and reduced the fatty acid composition of the fish at the low level of concentration. Both compounds also showed toxic effects on marine microalgae species such as *Tisochrysis lutea*, *Skeletonema marinoi*, and *Tetraselmis suecica* Dupraz et al. (2018). Another study by Park et al. (2016a) reported that exposure to Irgarol 1051 and diuron have potential hazardous effect on Pacific oyster, *Crassostrea gigas*, whereas Park et al. (2016b) observed

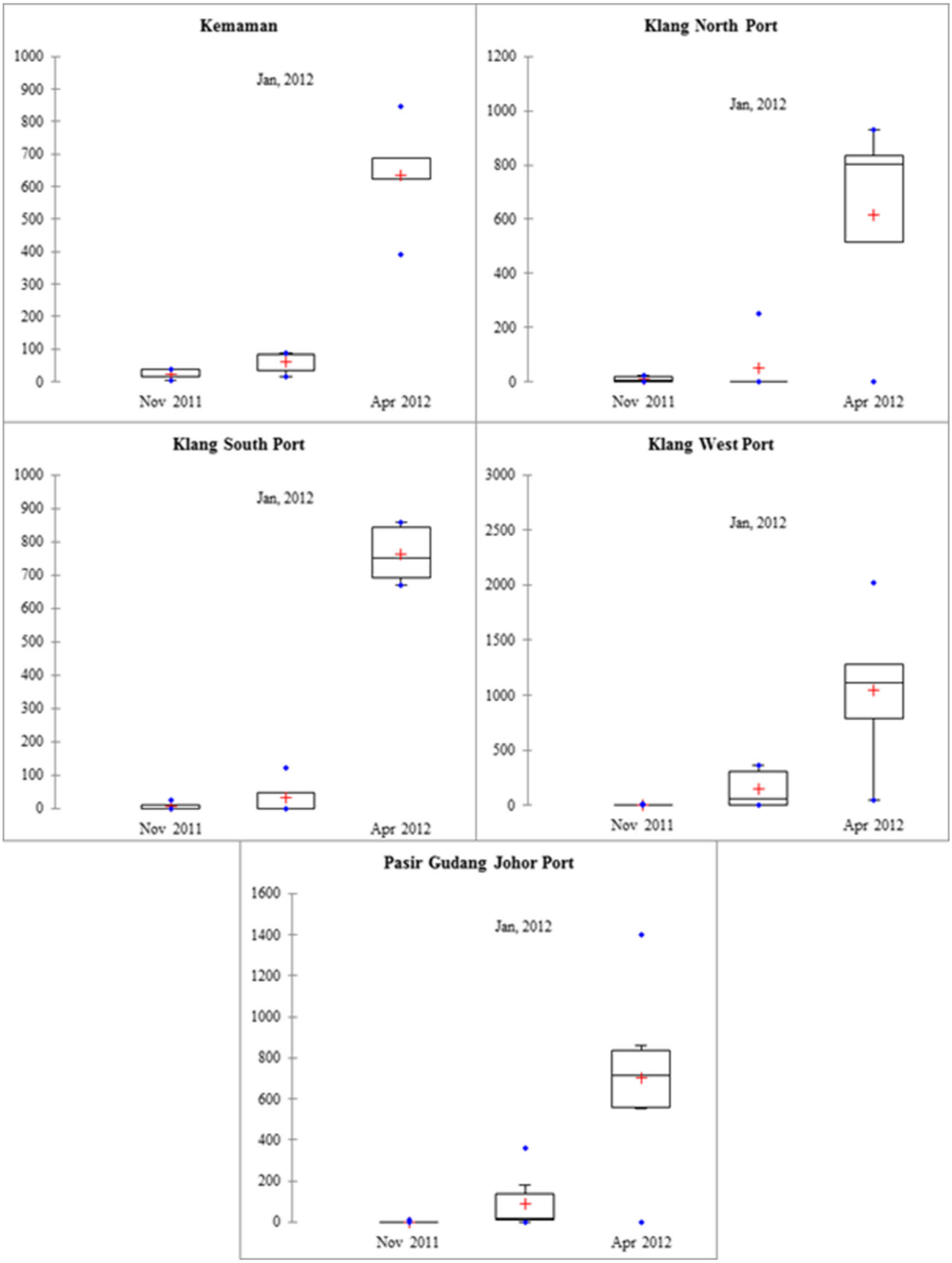


Fig. 4 Box and whisker plots of Irgarol 1051 temporal distribution at all sampling areas

changes in the exoskeleton, molting, and proteolysis metabolism of mud crab, *Macrophthalmus japonicus*, when exposed to Irgarol 1051.

Table 1 shows the ecotoxicity endpoint and RQ of algae, daphnids, and fish for Irgarol 1051 and diuron in the surface water of the selected ports in Peninsular

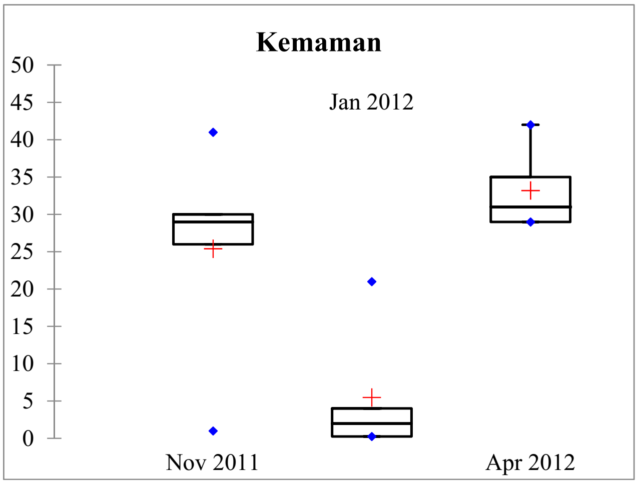


Fig. 5 Box and whisker plots of diuron temporal distribution at Kemaman Port

Malaysia. The calculated RQ for the three test species showed that high risk is posed to algae by both Irgarol 1051 and diuron during the present study, particularly during the April 2012 sampling. On the basis of the maximum concentration from the three sampling periods, the value of RQ is 1.61 and 77.73 for diuron and Irgarol 1051, respectively. Irgarol 1051 was observed to exhibit a higher risk as compared to diuron at the ports of Peninsular Malaysia. Throughout the sampling campaigns that were carried out for a 2- to 3-month interval, the risk of Irgarol 1051 was significantly increased during the April 2012 sampling.

EC50, effective concentration; *LC50*, lethal concentration; *PNEC*, predicted no-effect concentration; *RQ*, risk quotient

As shown by Fig. 6, the RQ for Irgarol 1051 particularly for algae was categorized as high for all sampling points during the April 2012 sampling. By contrast, in the January 2012 and November 2011 sampling periods, only several sampling points indicated a high risk for Irgarol 1051, notably in Klang, and Kemaman Ports. Meanwhile, for diuron, only two sampling points indicated high risk, as shown in Pasir Gudang and Klang Ports during the April 2012 and January 2012 sampling periods, respectively. It was noted that the concentration of diuron at both sampling points during those sampling periods exceeded the maximum level as stipulated in the Malaysian Marine Water Quality Standards (MMWQs), which is regulated at 0.2 μg/L. However, the same comparison cannot be made for Irgarol 1051 because there is no regulation yet for the allowable level of this biocide in the MMWQs. Thus, owing to its high risk, the need for a guideline value for Irgarol 1051 to be included in the MMWQs should be taken into consideration as an effort to protect aquatic and marine life.

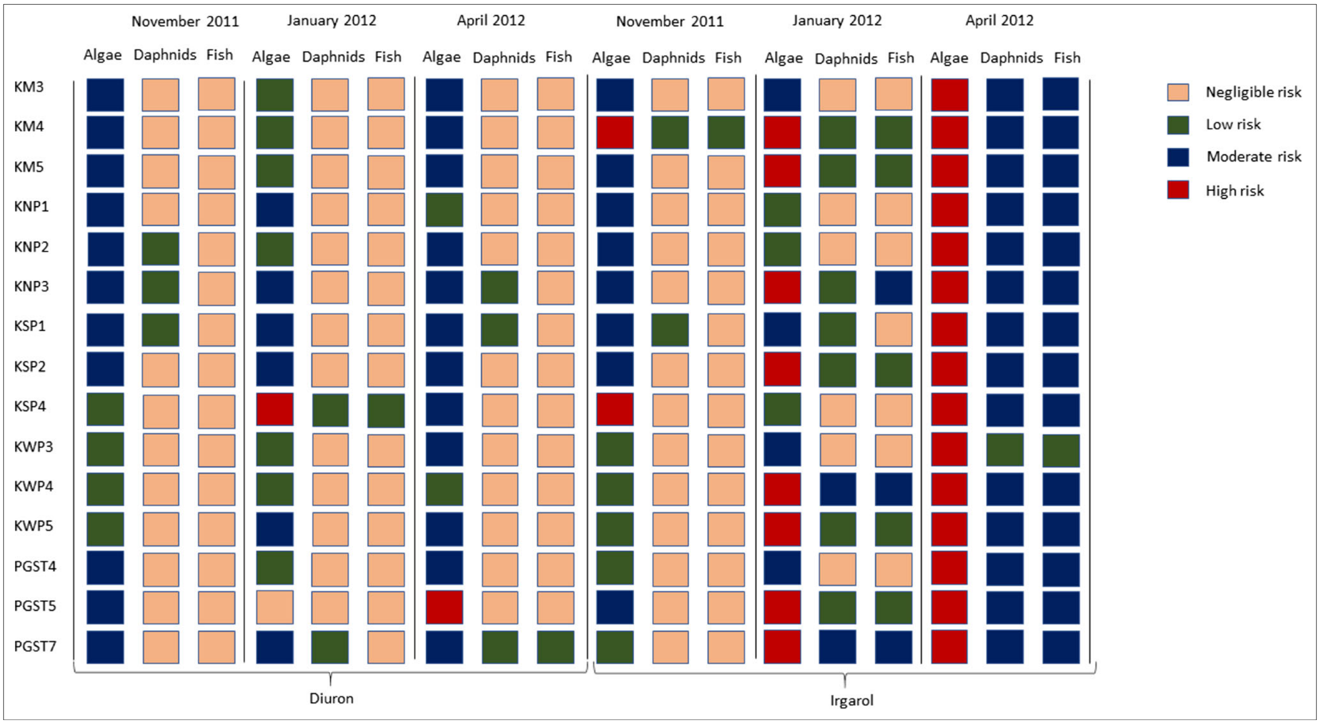
Comparison of worldwide studies on the ecological risk assessment of Irgarol 1051 and diuron showed similar trends of risk classification. As summarized in Table 2, most studies reported a high risk for Irgarol 1051 and diuron in the aquatic ecosystem. A high risk of Irgarol 1051 and diuron was reported in the São Marcos Bay of Brazil Viana et al. (2020), and a similar risk trend was also reported in the Bay of Vilaine, France. Both locations exhibited RQ values greater than 1, with the highest RQ being 100 reported at the Bay of Vilaine (Caquet et al. 2013). Only one study on several river systems in Poland showed an RQ for diuron being less than 1, which was reported at 0.39, indicating a moderate risk to the aquatic ecosystem. This trend of ecological risks suggested that most of the countries having a serious threat with the Irgarol 1051 and diuron contamination, and therefore, they should be considered as priority pollutants that must be continuously monitored.

Conclusion

The present study evaluated the status of biocide contamination in the surface water of major ports across

Table 1 Ecotoxicity endpoints for algae, daphnids, and fish, and RQ assessment for diuron and Irgarol 1051 in surface water of the selected ports in Peninsular Malaysia

Compounds	EC50/LC50 (μg L^{-1})			Assessment factor	PNEC (μg L^{-1})			Concentration (μg L^{-1})	RQ		
	Fish	Daphnids	Algae		Fish	Daphnids	Algae	Maximum	Fish	Daphnids	Algae
Diuron	18,100	5220	177	1000	2.13	3.12	0.26	0.285	0.015	0.052	1.61
Irgarol 1051	2130	3120	26	1000	18.1	5.22	0.177	2.021	0.95	0.65	77.73



	Diuron									Irgarol								
	November 2011			January 2012			April 2012			November 2011			January 2012			April 2012		
	Algae	Daphnids	Fish	Algae	Daphnids	Fish	Algae	Daphnids	Fish	Algae	Daphnids	Fish	Algae	Daphnids	Fish	Algae	Daphnids	Fish
KM3	🟦	🟧	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟦	🟧	🟧	🟦	🟧	🟧	🟥	🟦	🟦
KM4	🟦	🟧	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟥	🟩	🟩	🟥	🟩	🟩	🟥	🟦	🟦
KM5	🟦	🟧	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟦	🟧	🟧	🟥	🟩	🟩	🟥	🟦	🟦
KNP1	🟦	🟧	🟧	🟦	🟧	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟩	🟧	🟧	🟥	🟦	🟦
KNP2	🟦	🟩	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟦	🟧	🟧	🟩	🟧	🟧	🟥	🟦	🟦
KNP3	🟦	🟩	🟧	🟦	🟧	🟧	🟦	🟩	🟧	🟦	🟧	🟧	🟥	🟩	🟦	🟥	🟦	🟦
KSP1	🟦	🟩	🟧	🟦	🟧	🟧	🟦	🟩	🟧	🟦	🟩	🟧	🟦	🟩	🟧	🟥	🟦	🟦
KSP2	🟦	🟧	🟧	🟦	🟧	🟧	🟦	🟧	🟧	🟦	🟧	🟧	🟥	🟩	🟩	🟥	🟦	🟦
KSP4	🟩	🟧	🟧	🟥	🟩	🟩	🟦	🟧	🟧	🟥	🟧	🟧	🟩	🟧	🟧	🟥	🟦	🟦
KWP3	🟩	🟧	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟥	🟩	🟩
KWP4	🟩	🟧	🟧	🟩	🟧	🟧	🟩	🟧	🟧	🟩	🟧	🟧	🟥	🟦	🟦	🟥	🟦	🟦
KWP5	🟩	🟧	🟧	🟦	🟧	🟧	🟦	🟧	🟧	🟩	🟧	🟧	🟥	🟩	🟩	🟥	🟦	🟦
PGST4	🟦	🟧	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟩	🟧	🟧	🟦	🟧	🟧	🟥	🟦	🟦
PGST5	🟦	🟧	🟧	🟧	🟧	🟧	🟥	🟧	🟧	🟦	🟧	🟧	🟥	🟩	🟩	🟥	🟦	🟦
PGST7	🟦	🟧	🟧	🟦	🟩	🟧	🟦	🟩	🟩	🟩	🟧	🟧	🟥	🟦	🟦	🟥	🟦	🟦

🟧 Negligible risk
🟩 Low risk
🟦 Moderate risk
🟥 High risk

Fig. 6 Risk assessment of Irgarol 1051 1051 and diuron from the selected ports of Peninsular Malaysia. Note: KM, Kemaman Port; KNP, Klang North Port; KSP, Klang South Port; KWP, Klang West Port; PGST, Pasir Gudang Pasir Gudang Johor Port

Peninsular Malaysia. The ecological risk assessment was carried out using the deterministic approach, based on the RQ method. Ecological risk estimation for the two commonly used biocides, Irgarol 1051 and diuron, in the selected ports of Peninsular Malaysia revealed that more attention should be given to monitoring these contaminants in various marine or ship-related activities across Malaysia. As evidenced by the present study, the occurrence and presence of Irgarol 1051 should be of concern owing to its relatively higher risk as compared to diuron. Even though in several sampling points, the level of diuron exceeded the allowable limit of MMWQs and showed high risk in some locations, overall, it can be regarded as safe on the basis of the present assessment. This risk assessment evaluation is an important step for the preliminary risk screening of organic pollutants that can provide a basis for an environmental management plan that can be useful for

Table 2 Comparison of biocides (Irgarol 1051 and diuron) in the surface water of the selected ports in Peninsular Malaysia relative to other countries

Location/country	Method	Diuron			Irgarol 1051			Reference
		LOD (ng L^{-1})	Concentration$_{max}$ (μg L^{-1})	RQ	LOD (ng L^{-1})	Concentration$_{max}$ (μg L^{-1})	RQ	
São Marcos Bay/Brazil	SPE-LC-MS/MS	0.8	0.022	14.7	1.4	0.089	37	Viana et al. (2020)
Bay of Vilaine/Brittany, France	SPE-LC-MS/MS	50	0.268	5	20	0.186	100	Caquet et al. (2013)
River in southern Poland/Poland	SPE-GC-MS/MS	2.5	0.077	0.39	—	—	—	Durak et al. (2021)
Kemaman, Klang, and Pasir Gudang Ports/Malaysia	SPE-GC-MS/MS	0.5	0.285	1.61	1.0	2.021	77.73	This study

relevant authorities such as environmental legislators and policymakers. This study will also provide information on risk prioritization, which will set direction toward the protection and sustainability of marine ecosystem from harmful contaminants.

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