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Distribution of Polycyclic Aromatic Hydrocarbons (PAH) in Natuna Coastal Waters

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Abstract: Surface seawater samples collected in Natuna coastal waters were analyzed for 17 parent polycyclic aromatic hydrocarbons (PAHs) to get insight their presence for their toxic and carcinogenic impacts. The study was aimed to collect some PAHs preliminary data for baseline data as Natuna coastal waters are susceptible from this contamination possibly arisen from oil spills, shipping activities and mariculture industries. The samples were collected from 10 selected stations along the survey location. The results showed that total PAH concentrations at the sampling sites ranged <0.02-5.84 µg/L. A higher concentration was found in the northwest of Sedanau Islands with PAH compound dominated by acenaphthene at 4.5 µg/L. The value is still acceptable for aquatic resources in seawater. Wind and tidal profiles in the location were also presented in the study to get insights on the PAH migration which varied depending on the direction and speed of each profile. It can be concluded that the PAH profile in Natuna coastal water is still low and feasible for aquatic resources and marine environment.

Key words: PAH, hydrocarbon, Natuna coastal waters.

Introduction

Natuna Islands, containing 272 islands as one of the districts in Riau Islands Province, are located in the Natuna Sea between Peninsula Malaysia to the west and Borneo to the east. Natuna Sea is in the section of the South China Sea making the Natuna waters one of the busiest international shipping lanes where mostly tankers and cargo liners pass through on a daily basis. Regarding its seabed resources, Natuna has oil and gas fields, one of which is called Natuna Sea Block Area. These circumstances could make Natuna Sea and its adjacent area prone to contaminations, such as heavy metals and persistent organic pollutants (POPs), resulting from oil spills, shipping activities, and industries. The contaminations could potentially impact marine resources and coastal ecosystems.

Polycyclic aromatic hydrocarbons (PAHs) are one of POPs groups consisting of two or more rings of benzene (aromatic), containing no heteroatoms. PAHs are mainly derived from anthropogenic sources resulting from incomplete combustion of fossil fuels, several industry processes, and biomass or through petroleum transportations and processes (Law et al., 1997; Bouloubassi et al., 2006). PAH compounds enter into the seawater through direct discharges, river discharges and continental run-off, and atmospheric interaction (dry-wet deposition, water-air gas exchanges) (Bouloubassi

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et al., 2006). Law and Biscaya (1994) reported that in the water column most PAH tend to absorb particles and will deposit in the sediments. PAH degradation in sediments is generally slow, particularly for those with higher molecular weights (Readman et al., 1982) and when the underlying sediments are anaerobic (Meador et al., 1995).

Physical and chemical characteristics of PAHs vary with their molecular weight; as a result they differ in the behaviour, distribution in the environment, and their effects on ecosystems. The lower molecular weight polycyclic aromatic hydrocarbons, for instance, have marked acute toxicity to aquatic organisms, whereas higher molecular weight PAHs are carcinogenic to marine and human life (Neff, 1979; Witt, 1995). For these impacts, the presence of PAH compounds in seawater is of concern and has to be controlled. Falahudin et al. (2012) reported that aqueous solubility, vapour pressure, and partition coefficient of octanol-water and organic carbon-water are important factors affecting PAH environmental behaviour. Some PAH compounds can form naturally in minerals, such as coronene and pyrelene (Redmann et al., 2002); however, inputs resulting from natural processes are considerably low compared to those from anthropogenic activities. The present study was aimed to collect some preliminary data for PAHs in Natuna seawater for baseline data which will be useful as comparison data when oil spill contamination occur or anthropogenic activities potentially resulting in PAH compounds in the future.

Materials and Methods

The survey was carried out in one of regional marine conservation areas (namely Conservation Area I or known as KKLD I) in Natuna Regency, Riau Islands Province during November 22 to 25, 2012 (Figure 1). The conservation area I is an area highly intended for sustainable marine aquaculture (mariculture) activities. Ten PAH sampling stations were determined as shown in Figure 1 and Table 1; PAH samples were taken from surface water (ca. 1-3 metre deep).

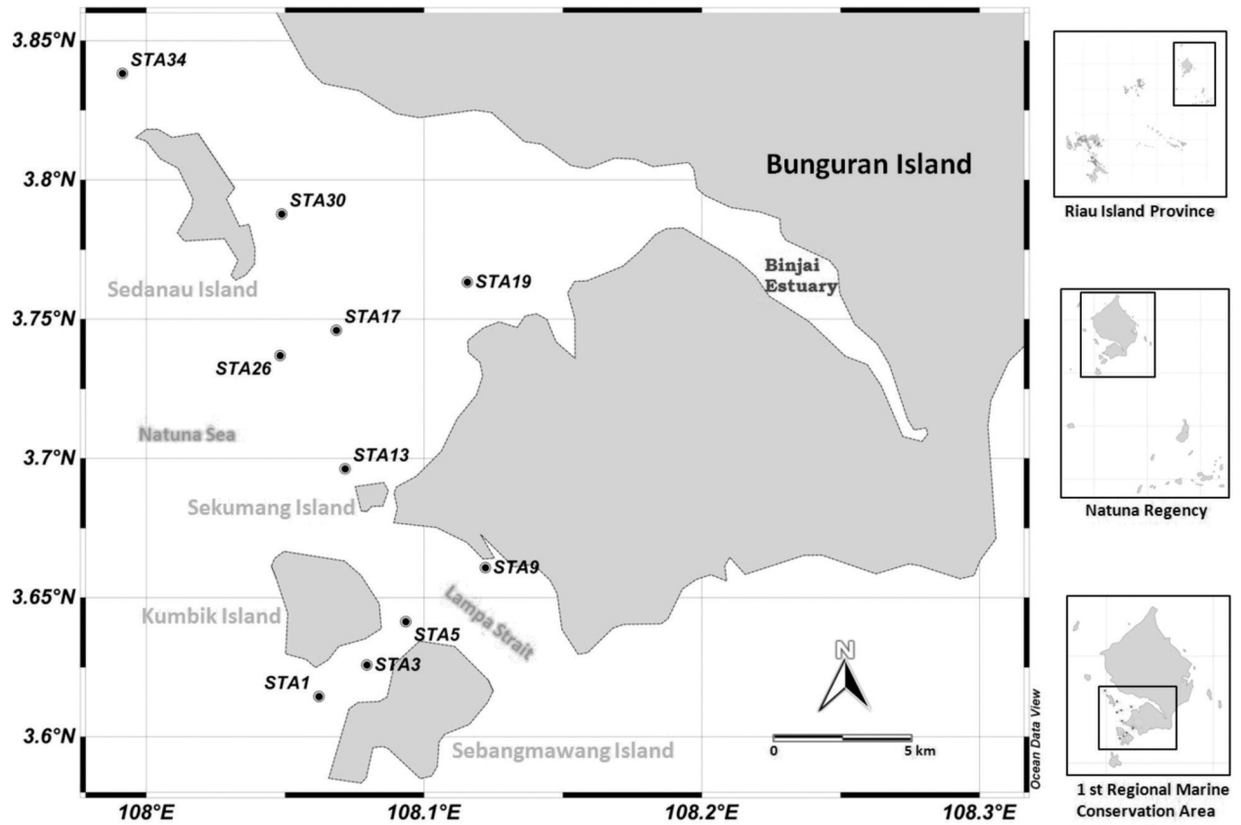

Figure 1: Distribution of PAH sampling stations in Natuna coastal waters, Natuna District, Riau Islands Province. (*Note:* The nomenclature of the sampling stations was based on water quality survey with 34 sampling points.)

Table 1: Sampling stations of PAH in Natuna coastal waters

Name of station	*Position*		*Depth (m)*
	Longitude (E)	*Latitude (N)*	
Station 1	108.0621442	3.61450734	12.0
Station 3	108.0793605	3.62581047	20.9
Station 5	108.0934451	3.64137133	25.0
Station 9	108.1220421	3.66072935	29.0
Station 13	108.0715631	3.69622754	22.2
Station 17	108.0684138	3.74600607	15.0
Station 19	108.1156141	3.76329399	11.1
Station 26	108.0481667	3.73696667	25.7
Station 30	108.0487667	3.78775000	9.0
Station 34	107.9913800	3.83824655	13.0

Seawater samples were taken using Nansen water sampler at approximately 1-3 m deep, stored in dark bottles and kept cold during transport to laboratory for analysis.

PAHs were analyzed in a laboratory as follows. The water samples were extracted at a neutral pH with methylene chloride and concentrated until 1 ml. A 2- to 5-µL aliquot of extraction was injected into a gas chromatography (GC) using the solvent flush technique and compounds containing PAHs in the GC effluent were detected by a flame ionization detector (EPA Methods 8001). The laboratory analysis was carried out at Aquatic Productivity and Marine Environment Laboratory (ProLing), Bogor Agricultural University (IPB), Bogor. As additional data, indirect measurements (secondary data) of wind speed and direction, and (tidal) surface currents were also taken into account in the present study.

Results and Discussion

Polycyclic aromatic hydrocarbons dissolved in seawater in the study area are presented in Figure 2. Figure 2 shows that total PAH contents in seawater in the sampling sites ranged from undetected (< 0.02) to 5.84 µg/L. PAH concentrations in seawater of around Sebangmawang Island and Lampa Strait (stations 1, 3, 5 and 9) were significantly low and below detection limit. A similar condition was also found in the stations among Sedanau, Sekumang and Bunguran waters (stations 17, 26 and 30). The highest PAH content (5.84 µg/L) was found in northwest of Sedanau Island waters. Ministry of Environment of Indonesia (MEI) in 2004 has set a standard value that an acceptable PAH concentration in seawater is 3 µg/L (0.003 mg/L). Compared to this value, the PAH concentration of the Natuna Sea, and around Sebangmawang Island and Lampa Strait was still in an acceptable level, whereas the PAH content in the northwest Sedanau Islands waters exceeded.

It was described previously that the study area in the present paper is an area set regionally as conservation area for sustainable marine aquaculture activities and business (known as KKLD I Area). It is therefore expected that marine aquaculture activities, particularly using floating net cage system, open international economic networks through which marine transportation such as cargo and shipping activities could occur. The exceeded value obtained in surface water of station 34 could possibly be attributed to the incomplete combustion and oil spill of fossil fuel discharged from ships and vessels in these areas.

Meanwhile, the relatively high PAH level in surface water of station 19 could be more likely influenced by run-off and/or contributed from transport activities running in estuaries/rivers (one of which is Binjai estuary) located adjacent to station 19. In this study field, there are several rivers flowing to the narrow bay across Sedanau Islands where Binjai river is the biggest one. The estuary is used as ferry port for Bunguran Island and Sedanau Island connection. As there are regular transportation, oil discharge or incomplete combustion resulted from the boats could possibly contribute to the high PAH level of the surface water in the station. Similarly, the high level of PAHs in station 13 is influenced by the activities in Binjai estuary where PAH contamination is possibly distributed through water current running to the station. Interestingly, the high values in these two stations are still below MEI PAH standard value.

Total PAH concentration presented in the study describes 17 PAH compounds which are categorized as the pollutant priority. They are naphthalene (Naph), 2-methylnaphthalene, 2-chloronaphthalene, acenaphthene (Ace), flurene (FI), phenanthrene (Phe), anthracene (Ant), fluoranthrene (Flu), pyrene (Pyr), chrysene (Chr), benz(a)anthracene (BaA), perylene, benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), indeno(1,2,3-cd)pyrene (InP), dibenzo(ah) anthracene (DBahA), and benzo(ghi)perylene (BghiP). Individual PAH concentrations at the study sites (particularly stations 1, 3, 5, 9, 26 and 30) were generally low and undetected (the figure is not given for their low and safe values). Of ten sampling sites, three stations (sta 13, 19 and 34) showed relatively high individual PAH concentrations as given in Figure 3. The distribution of individual PAH compounds varies

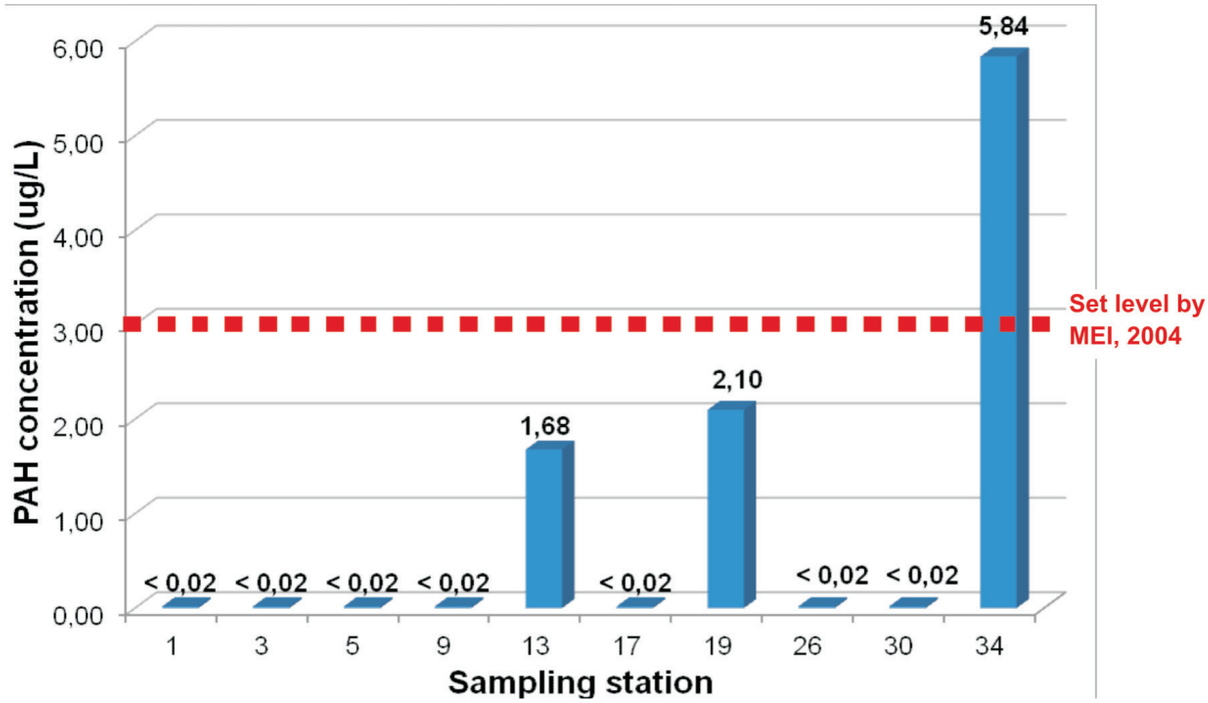

Figure 2: Total PAH concentrations at the location study. Red dash line is a standard value of an acceptable PAH concentration in seawater set by the Ministry of Environment Rep. Indonesia (MEI), 2004.

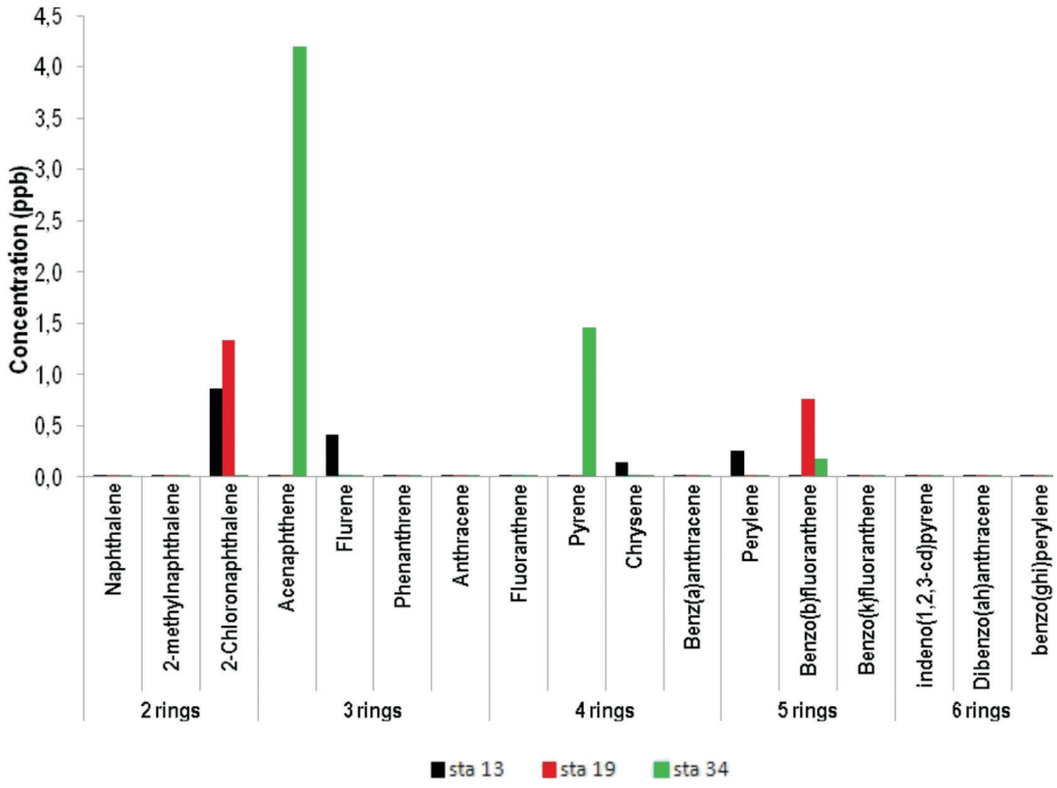

Figure 3: Distribution of PAH compounds (including their benzene ring number) in seawater of Natuna coastal waters.

among these three stations: station 13 is dominated by the presence of 2-chloronapthalene, followed by fluorine, perylene and chysene, respectively; whereas, station 19 is dominated by 2-chloronapthalene and benzo(b)fluoranthene. More interestingly, station 34 showed a significant concentration of acenaphthene. US Environmental Protection Agency has set a standard criterion for human health for the consumption of water and organism contaminated by acenaphthene at a level of 670 µg/L (US-EPA, 2002). Meanwhile, British Columbia Environmental Laboratory (Nagpal, 1993) recommended that the concentration of acenaphthene in seawater should not exceed 6 µg/L. It is apparent that the level of acenaphthene in the present study (4.5 µg/L) is still below the set levels. Other PAH compounds such as pyrene and benzo(b)fluoranthene were also observed in station 34. It, therefore, could be said that high abundance of PAH compounds in seawater was dominated by toxic PAH (2- and 3-rings PAH) but the values are generally considerably feasible.

The distribution and spreading of particulate matters (for instance PAH) in (surface) water could be altered by surface current circulation. The surface current itself is affected by several factors, two of which are wind and tide. Wind condition during survey is given in Figure 4. It is known that wind blows from northeast at dominant speed of 1-4 m/s. It possibly influences the water current running to southwest.

From the current performance as shown in Figure 5, it is observed that the water current generally flows to south due to coastal geometrical topography of the

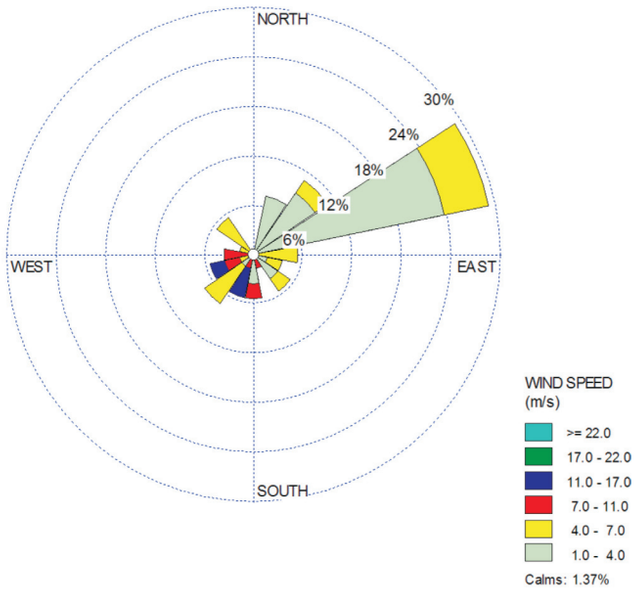

Figure 4: The wind condition in Natuna Islands Regency, Riau Islands Province.

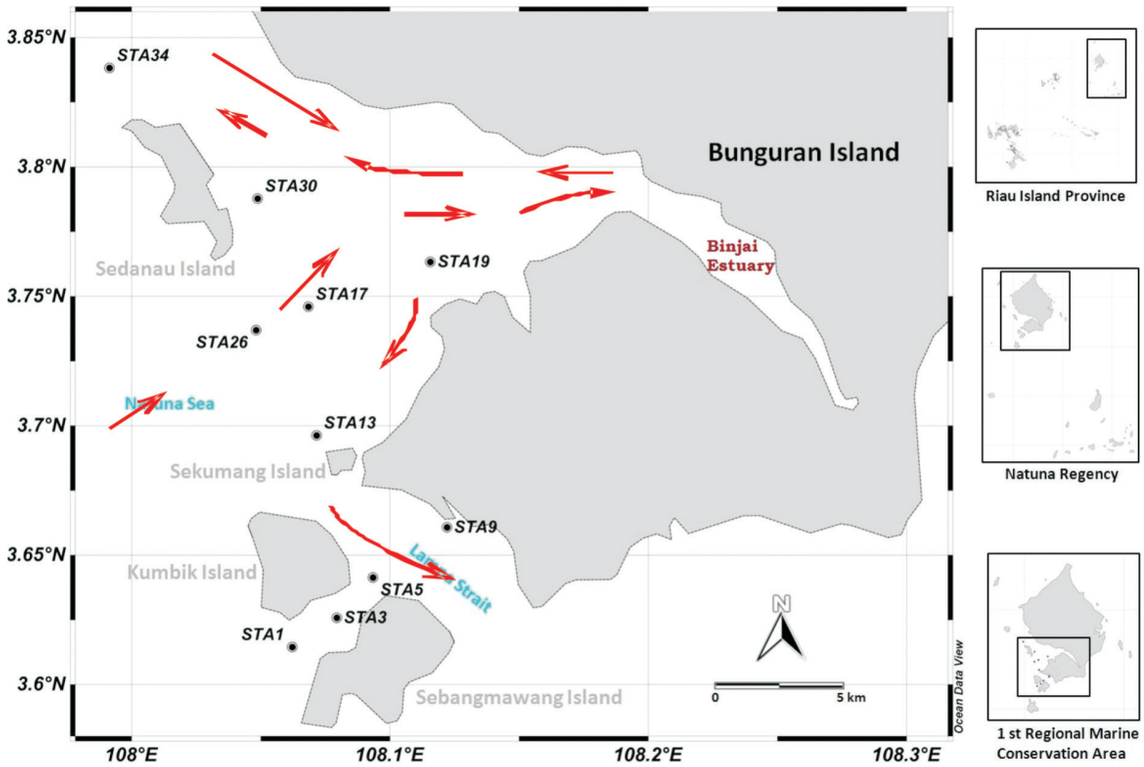

Figure 5: Surface current pattern in Natuna coastal waters observed during survey.

islands (CRITC, 2005) and also to the northwest due to wind condition. In estuary, the water current plays as the main driving force affecting the water movement and thus, contributing to a longer residence time of water in this area.

The present study is in an agreement with a previous study by Ren et al. (2010) that PAH compounds might migrate from the release source to the ocean through wind, stream and oceanic (tidal) surface current circulation. The migration could even be far removed from the original point.

Natuna Sea region is in a relatively pristine condition, in particular when compared to Timor Sea region (Falahudin et al., 2012; Li et al., 2010). Total PAH concentrations in seawater of Timor Sea in the study by Falahudin et al. (2012) were significantly high (54.46-213.70 µg/L) exceeding the acceptable level set by MEI. The high content of PAH was attributed to petroleum, petroleum combustion and organic material combustion. As explained previously, the presence of PAH compounds in high concentration and long exposure can cause adverse effects to marine life biota. In 2000, an incident in which 7000 tonnes of crude oil was spilled from a tanker occured in Natuna Sea and prompt actions by spraying chemical dispersant were carried out. The spill was closer to Singapore strait than the present study; however, it can spread over by the influence of water current and tide and could possibly be still and sedimentated in long terms. Nevertheless, the present study showed that the condition of Natuna coastal waters is in a good condition, in terms of PAH content. The data obtained in the present study can be used as baseline data in monitoring PAH condition in future.

Conclusions

Though the sampling points did not cover the whole area of Natuna Sea/Regency, this study has provided information to date for PAH in seawater around Natuna coastal waters. It is concluded that polycyclic aromatic hydrocarbons in Natuna coastal water is present but the values are still considerably accepted. There is high concentration of several PAHs (dominantly 2-3 benzene rings) observed at some sampling points; however the values are still feasible for marine ecosystem. As polycyclic aromatic hydrocarbons are persistent contaminants and potentially harm both marine resources and human health, further study is needed to determine their environmental distribution and behaviour.

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