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Occurrence and distribution of Polycyclic aromatic hydrocarbons (PAHs) in seawater, sediments and corals from Hainan Island, China

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ABSTRACT

The levels of 16 US EPA priority polycyclic aromatic hydrocarbons (PAHs) were investigated in corals, ambient seawater and sediments of Hainan Island, China, using gas chromatography - mass spectrometry (GC-MS). The total PAHs (ΣPAHs) concentrations ranged from 273.79 to 407.82 ng/L in seawater. Besides, the concentrations of ΣPAHs in corals 333.88–727.03 ng/g dw) were markedly ($P < 0.05$) higher than ambient sediments 67.29–196.99 ng/g dw), demonstrating the bioaccumulation ability of PAHs by corals. The highest concentration of ΣPAHs was detected at site S2 in *Pavona decussate*, which also bore the highest ΣPAHs levels in both seawater and sediments. The massive corals were more enriched with PAHs than the branching corals. Although 2 and 3-ring PAHs were predominant and accounted for 69.27–80.46% of the ΣPAHs in corals and ambient environment, the levels of high molecular weight (HMW) PAHs (4–6 ring) in corals also demonstrated their potential dangers for corals and organisms around coral reefs. Biota-sediment accumulation factor (BSAF) refers to an index of the pollutant absorbed by aquatic organisms from the surrounding sediments. The poor correlation between log BSAF and log K_{ow} (hydrophobicity) indicated that PAHs in corals maybe not bioaccumulate from the ambient sediments but through pathways like absorbing from seawater, symbiosis, and feeding. Based on our data, long-term ecological monitoring in typical coral reef ecosystems combined with ecotoxicological tests of PAHs on corals is necessary to determine the impacts of PAHs on coral reefs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous contaminants in the marine environment. LMW (Low molecular weight) PAHs (2–3 ring) are highly bio- and photo-degradable while HMW (High molecular weight) PAHs (4–6 ring) are more resistant to degradation (Friedman et al., 2014). It has been known for many years that the teratogenic, carcinogenic and mutational toxic characteristics of PAHs can impose serious harm to organisms (Hawliczek et al., 2012). Moreover, since the United States Environmental Protection Agency (US EPA) has listed 16 PAHs as priority control pollutants (Keith and Telliard, 1979), they have received special concerns (Botsou and Hatzianestis, 2012). PAHs can be introduced into the marine environment via various routes, such as atmospheric deposition, oil leakage and combustion activities, and they are distributed throughout the seawater, sediments and organisms (Hong et al., 2016; Tongo et al., 2017a).

Coral reefs are the most diverse and productive ecosystem in the marine. They provide critical ecosystem services including facilitating the marine nitrogen cycle and optimizing the marine environment. Organisms in coral reef ecosystems have evolved over millions of years, which has resulted in the ability to resist environmental disturbance to some degree (Pait et al., 2009; Dam et al., 2011). However, coral reefs worldwide have suffered and continue to face catastrophic declines, demonstrating that environmental pressures have exceeded the reefs' tolerance thresholds, gaining the attention of researchers all over the world (Dam et al., 2012; Tanaka et al., 2015).

China occupies 2.57% of the global coral reefs area, the eighth highest in the world in terms of national reef area. The Sanya coral reef regions are located in the tropical region of the southernmost part of Hainan Island with rich and varied coral reef resources. In last decades, industrial, fishing and tourist activities have put pressure on the health of local coral reefs. Anthropogenic activities have been regarded as a considerable factor in declining coral reef health, especially in the dry

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season when undiluted discharged industrial and domestic seawater may induce severe contamination in the marine environment. In the past, PAHs investigations have been performed on Hainan Island focusing on the seawater and sediments (Li et al., 2015a, 2015b). A redistribution of the contaminants could occur at any time in the marine environment (e.g. within seawater, sediments and organisms) (Zheng et al., 2016). PAHs can cause damage to corals at different levels (Martínez et al., 2007). Previous studies have provided that the ΣPAHs concentrations detected in corals were in a tendency of increasing with time globally (Readman et al., 1996; Thomas and Li, 2000; Pait et al., 2009; Sabourin et al., 2013). Furthermore, the study of (Ko et al., 2014) indicated the bioaccumulation of PAHs by corals for the ΣPAHs concentrations in corals were higher than ambient sediments. There is a lack of research on the occurrence of PAHs in the coral reef ecosystem overall, it is important to conduct the preliminary survey by PAHs contaminants in corals, ambient seawater and sediments here.

This study focused on quantifying PAH concentrations and distribution characteristics in corals, ambient seawater and sediments in the Sanya coral reef regions, and comparing their PAH polluted levels, ring compositions and geographic sources. The main aims of this research were: (1) to provide preliminary data for PAH contamination in the Sanya coral reef regions; (2) to compare the spatial variation of the concentrations and compositions of PAHs in corals, ambient seawater and sediments; (3) to assess the possible sources of PAHs in the Sanya coral reef regions. and (4) determine the rate of bioaccumulation of PAHs in corals;

2. Material and methods

2.1. Study area

Coral samples and ambient samples were collected from three sites of the Sanya coral reef regions, south of Hainan Island (Fig. 1) in March (dry season), 2017. The sampling positions were located using a global positioning system, specific latitude/longitude of the samples along with basic characteristics and information are listed in Table 1; These sampling sites represent the characteristics of the Sanya coral reef regions: Site 1, Luhuitou, was declared a national Coral Reef Natural Reserve in 1990. The reefs in the area experienced declines severely in recent years due to the development of coastal construction and aquaculture (Zhao et al., 2014). Site 2, Phoenix Island, is near a famous hotel and experiences a considerable amount of domestic sewage discharge. Site 3, Wuzhizhou Island, is famous for its sightseeing. Many tourists snorkel and dive in the area, potentially disturbing the coral reefs.

2.2. Field sampling

Coral samples were collected by stainless scissors and ambient sediment samples were collected by shovel, both placed in aluminium containers with ice bags. Only a small fragment (approximately 2 × 2 cm in size) was removed from the coral to minimize the impacts on local coral communities, and samples for one coral specie were taken form three different individuals. Pre-cleaned brown glass bottles were used to collect ambient seawater samples in accordance with the Offshore Marine Areas Monitoring Technical Specifications (HJ422-2008). Seawater and sediment samples were both taken in triplicate at one position. When back to laboratory, seawater samples were stored at 4 °C, sediment and coral samples were stored at − 20 °C. All samples were kept in darkness until analysis.

2.3. Chemicals and solvents

The standards of the sixteen PAHs (purity > 99%) were obtained from AccuStandard (Connecticut, USA). The organic solvents dichloromethane (DCM) and methanol (≥ 99.9%, HPLC grade, Fisher Scientific Company, USA) were used for the processing as well as Ultrapure water (Cascade Lab Water Systems, final resistivity: 18.2 $m\Omega \cdot cm^{-1}$). SPE (solid phase extraction) Solution Classic C18 cartridges (500 mg/6 mL with capacity for 45 μm particle size) were purchased from Simon Aldrich, German. Additionally, all the reagents used in this experiment are of analytical grade.

2.4. Extraction and analysis

2.4.1. Water samples

Detailed procedures of treatment and extraction were performed according to Li et al. (2015a). 10 mL HPLC DCM, 10 mL HPLC methanol and 10 mL ultrapure water were used to activate the SPE Solution Classic C18 cartridge in sequence. A total of 5 mL HPLC methanol was added to 500 mL of the water samples. The samples were blended and then pre-concentrated by the SPE method at a flow rate of 5 mL/min. The cartridge was dried in a vacuum for 15 min after percolation. Then, 12 mL of HPLC DCM was used to elute the PAHs three times. Next,

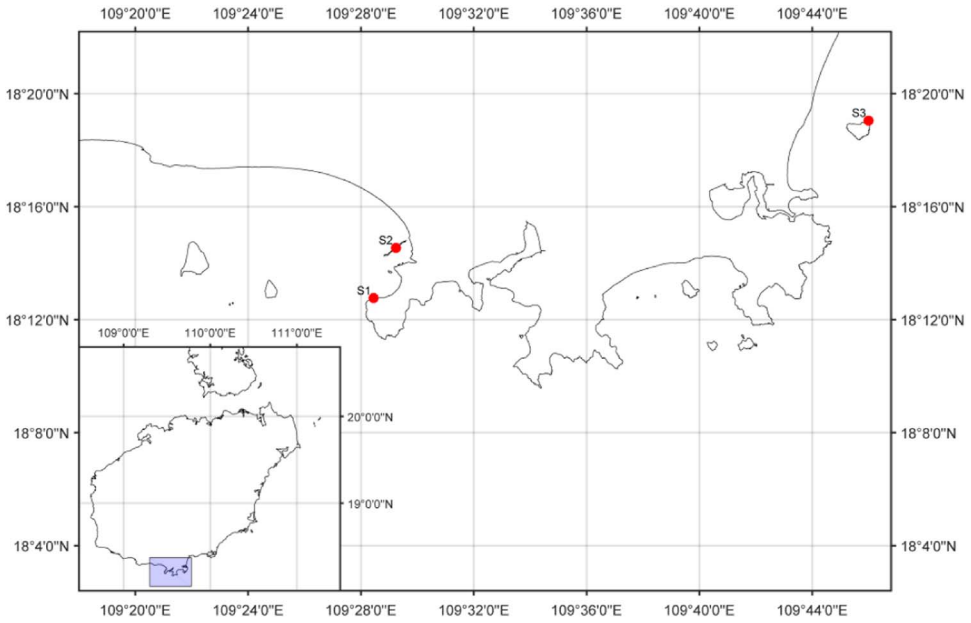

Fig. 1. Study area and sampling sites in the Sanya coral reef regions, China.