

Short Communication

Bioaccumulation of PAHs in *Padina boryana* Alga Collected from a Contaminated Site on the Red Sea, Saudi Arabia

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Abstract

We used the brown alga *Padina boryanawas* to determine polyromantic hydrocarbons (PAHs) bioaccumulation at a Jeddah City seashore. We also measured PAHs in the coastal water and in algal tissues using gas chromatography mass spectrometry (GC-MS).

Acenaphthene (Ace) and dibenzo(a,h)anthracene (dB(a,h)An) were the main PAHs in sea water (50.02 and 46.18 ng l⁻¹, respectively) and in algal tissues (64.67 and 72.45ng g⁻¹, respectively), respectively. The ratios of low molecular weight/high molecular weight hydrocarbons (1.76-1.44), fluoranthene/pyrene (1.57-1.52), and phenanthrene/anthracene (0.86-0.67) in seawater and algal tissues indicated the origin of PAHs to be mainly pyrogenic.

The high concentrations of PAHs in algal tissues demonstrated the utility of using *Padina boryana* as a biomonitor of PAH contamination and bioavailability in the coastal waters.

Keywords: Polycyclic aromatic hydrocarbons, *Padina boryana*, bioaccumulation

Introduction

Living organisms are good accumulators of environmental pollutants and they have been used as bioindicators [1-3]. Sinaei and Mashinchian [4] reported that marine environments are heavily polluted with polycyclic aromatic hydrocarbon (PAH) compounds. PAHs are a group of environmental contaminants formed during the incomplete combustion of organic materials such as coal, fossil fuel, and wood, as well as from forest fires, volcanic activity, and petroleum seeps [5-7].

Seashores that are close to large cities are known to have high concentrations of organic matter such as PAHs due to industrial, aquacultural, and urban activities.

PAHs are of special concern in the marine environment due to their widespread distribution and to the mutagenic and carcinogenic properties of their homologues, among other cytotoxic properties [8-9]. They can be diffused through membranes of marine organisms and accumulate in their tissues, posing a threat to the food chain [10-11]. However, information related to the role of algae in PAH bioconcentration and metabolism are widely scattered in spite of hydrophobic chemicals entering the food-chain by bioconcentration from water into the algae, and algae are capable of accumulating and metabolizing PAHs after

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their bioconcentration [12]. Algae can accumulate PAHs rather than synthesize them [13].

In Saudi Arabia, wastewater is disposed of in the sea; moreover, seashores are stressed by oil pollution and other fossil fuels [3]. In addition, there is a lack of awareness and interest regarding biomonitoring in spite of increasing rates of industrialization and urbanization, as well as an increasing number of motor vehicles [1].

Due to rapid expansion and increasing population and improper management in Jeddah, raw sewage is dumped into the sea, causing serious environmental problems [14]. However, there is scant data about PAH pollution in Jeddah – especially for marine environments.

This study was undertaken to fill the above-mentioned gap of knowledge aimed at investigating the levels of PAHs in the brown alga *Padina boryana* and water samples collected from the Jeddah seashore, and to assess the bioaccumulation of PAHs by brown algae.

Materials and Methods

Sampling and Analysis

Coastal seawater (1,000 ml) was collected in acid-washed amber glass bottles fitted with Teflon screw caps from three different locations. To remove suspended matter, samples were filtered through binder-free glass fiber filters (Whatman GF/C). Filtered samples were stored in pre-cleaned (with deionized water) glass bottles at 4°C prior to PAH analysis [15]. A mixture of 100 ml n-hexane and dichloromethane (1:1 v/v) was added to 800 ml water samples and shaken vigorously for 5 min. The water-phase was drained into a 1-L beaker. The organic phase was carefully poured into a glass funnel containing 20 g of anhydrous Na₂SO₄. The water phase was poured back into the separatory funnel for extraction with 50 ml of the same solvent mixture. The extract was concentrated to 2 ml under a gentle stream of nitrogen using a rotary evaporator and then analyzed by GC-MS [11]. The U.S. Environmental Protection Agency (EPA) PAH standard (16 PAHs) was used for identification [16].

Algae (*Padina boryana*) were collected in plastic bags containing seawater and transported immediately to the laboratory for analysis. Algae were dried at 60°C for 48 h and the dry weight was determined. They were extracted in a Soxhlet-apparatus and analyzed using GC-MS [10].

The limit of detection was 5 ng l⁻¹ for water and 5 ng g⁻¹ for algae [10]. The EPA PAH standard (16 PAHs) was used for identification. Accordingly, the total PAHs describe $\sum 16$ PAHs = naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fl), phenanthrene (Ph), anthracene (An), fluoranthene (F), pyrene (Pyr), benzo(a)anthracene (B(a)An), chrysene (Cry), benzo(b)fluoranthene (B(b)F), benzo(k)fluoranthene (B(k)F), benzo(a)pyrene (B(a)Pyr), indeno(1,2,3cd)pyrene (I(c,d)Pyr), dibenzo(a,h)anthracene (dB(a,h)An), and dibenzo(g,h,i)perylene (dB(g,h,i)P).

Statistical Analyses

The data obtained were analyzed statistically using Statistical Package for the Social Sciences (SPSS 15) software. The independent sample t test was applied to determine the significant difference between the samples at $p < 0.05$.

Results and Discussion

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the marine environment, occurring at their highest environmental concentrations around urban centers. While they can occur naturally, the highest concentrations are mainly from human activities, and the primary sources are combustion products and petroleum. Moreover, Jeddah has the main harbor in the kingdom and could present a source of pollution.

Table 1 shows the concentrations of the 16 detected PAHs in surface water and algal tissue and the ratios of low molecular weight to high molecular weight (LMW / HMW) PAH and some selective descriptive congener ratios.

The minimum concentration recorded was related to B(k)F, whose mean values were 2.57 (ng L⁻¹) and 4.41 (ng g⁻¹) for water and algae samples, respectively. On the other hand, the highest concentration was related to dB(h,h,i)P, whose mean values were 46.18 (ng L⁻¹) and 72.45 (ng g⁻¹) for the same samples, respectively. The mean values of PAH concentrations in water samples and in algae tissues were 298.32 ng L⁻¹ and 482.11 ng g⁻¹, respectively.

Algae tissues had significantly ($p < 0.05$) higher concentrations of total PAHs (summation of 16 PAHs) than the seawater (Table 1). It is most likely that the large presence of lipids in algae tissues could be the main reason for the observed differences in PAHs.

LMW PAHs represent 63.8 and 59% of the total PAH in water samples and in algal tissues, respectively, while HMW PAHs present 36.2% and 41% in the same samples, respectively (Table 1).

Some PAH ratios were calculated to characterize PAH mixture and possible sources, including LMW PAHs/HMW PAHs, F/Pyr and Phen/An (Table 1). The ratios of LMW/HMW were higher than 1.0, which indicated the dominance of LMW PAHs, suggesting petrogenic- and petroleum-related compounds as the main PAH sources [16].

The presence of LMW PAHs in algal tissue could be due to the higher bioavailability of LMW PAHs in the coastal waters ($r = 0.79$, data not shown). This could be due to LMW PAHs in the coastal waters being more susceptible to microbial degradation and volatilization and dissolution into the water column [17], thus becoming more bioavailable. Consequently, living tissues were more enriched with LMW PAHs in relation to their environments. The present finding agreed with the results of Isobe et al. [18], who found LMW/HMW ratios > 1.0 in

Table 1. Concentrations of the 16 congeners of PAHs in seawater and algae tissues ($n = 5 \pm SE$) and the ratios of concentrations of LMW/HMW = sum of the lower molecular weight PAHs versus sum of the higher molecular weight PAHs; F/Pyr = fluoranthene versus pyrene; Ph/An = phenanthrene versus anthracene.

Congener	Water (ng l ⁻¹)	Alga (ng g ⁻¹)
Nap	33.45±4.24	51.03±5.18
Acy	29.45±2.67	41.18±6.25
Ace	50.02±6.36	64.67±5.18
Fl	15.56±4.43	33.12±6.28
Ph	28.56±5.27	37.92±4.56
An	33.34±6.58	56.33±5.12
F	7.34±0.67	13.56±2.56
Pyr	4.67±0.67	8.91±1.35
B(a)An	5.43±2.45	13.56±3.16
Cry	6.04±0.23	10.46±0.94
B(b)F	5.67±0.67	11.35±2.10
B(k)F	2.57±0.56	4.41 ±0.92
B(a)Pyr	7.24±1.12	12.78±2.18
I(c,d)Pyr	18.93±2.46	44.37±7.29
dB(a,h)An	3.87±0.87	6.01±1.04
dB(h,h,i)P	46.18±7.67	72.45±11.46
LMW PAHs	190.38 (36%)	284.25(41%)
HMW PAHs	107.94 (64%)	197.86 (59%)
ΣPAHs	298.32	482.11
Ratios		
LMW PAHs/HMW PAHs	1.76	1.44
F/Pyr	1.57	1.52
Phen/An	0.86	0.67

many Asian countries. Skarpheðinsdóttir et al. [19] also reported that blue mussels collected close to ports had relatively higher levels of LMW PAHs. Baumard et al. [20] found that the blue mussels sampled in the western Baltic Sea were enriched in LMW PAHs. Thus, the presence of higher LMW PAHs in marine biota is due to their ability to be selectively uptaken [16].

The main anthropogenic PAH sources are spillage of petroleum and fossil fuels [15]. The sources of PAHs, whether from fuel combustion (pyrolytic) or from sediment, could be of pyrogenic sources. The petrogenic contamination may be identified by ratios of individual PAH compounds based on peculiarities in PAH composition and distribution pattern as a function of the emission source. The ratio of phenanthrene to anthracene (Ph/An) and fluoranthene to pyrene (F/Pyr) have been widely used to distinguish petrogenic and pyrogenic

(pyrolytic) sources of PAHs [15]. PAHs of petrogenic origin are generally characterized by Ph/An values >10, whereas combustion processes often result in low Ph/An ratios (<10). For the F/Pyr ratios, values greater than 1 have been used to indicate pyrolytic origins and values less than 1 are attributed to petrogenic sources [15].

In our study, F/Pyr ratios were found to be 1.57 and 1.52 in seawater and in algae tissue, respectively (Table 1). These ratios indicate pyrogenic sources [21]. Moreover, the Ph/An ratios were 0.86 and 0.67 for the same samples, respectively, (Table 1), and they also indicated a pyrogenic origin. It should be noted that pyrolytic PAHs are mainly anthropogenic, which could be due to industrial activities. Since there are many petroleum industries and other industrial activities are available in the city, PAH transport via atmospheric aerosols and particles could be considered as one of the pyrogenic inputs. Our results indicated that PAHs originated mainly from pyrolytic sources, as indicated by LMW/HMW and F/Pyr ratios, and this is in agreement with previous results in Malaysia [16, 21], Iran [15], Iraq [22], and China [23]. An F/Pyr ratio greater than 1 indicates the dominance of the combustion-derived material (i.e., of pyrolytic origin) [24].

Fig. 1 shows that there were significant differences in the concentrations of PAHs in water and algae samples among seasons ($P < 0.01$). The highest concentrations were recorded in summer (301.32 ng l⁻¹) for water and (507.28 ng g⁻¹) for algae tissues, while the lowest concentrations were recorded in spring. Concentrations of PAHs were 101.34 ng l⁻¹ and 235.35 ng g⁻¹ for the same samples, respectively. Such variations could be attributed to such climatic conditions as volatilization and high degradation during the hot season [22, 25-27]. The presence of HMW PAHs (e.g., dB(a,h)An) could indicate that colloidal oil droplets occur in water [24].

The presence of PAHs in marine water combined with other potentially toxic compounds could result in negative effects. The leakage of oils, oily wastes, and mixtures can

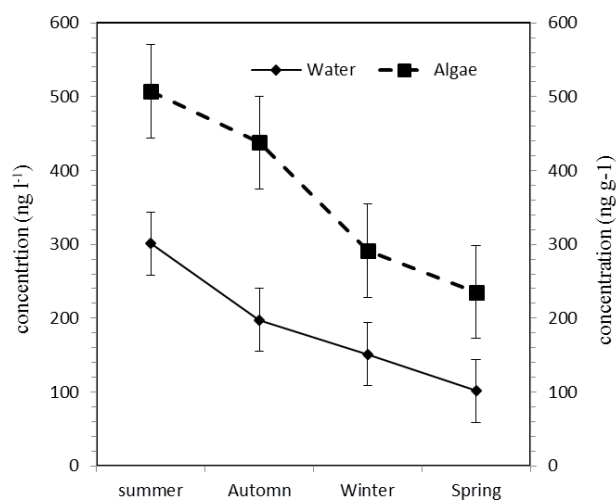


Fig. 1. Comparison of mean PAH concentrations in water and algae tissue samples in different seasons.

directly cause damage to fishery resources, aquatic biota, and coastal habitat. These effects may seriously damage marine and coastal ecology.

Conclusions

The higher concentrations of PAHs that were found in seawater and algae tissues could be due to domestic waste and being near the port. These inputs would pose a threat to the marine ecosystem [16].

Based on ratios of LMW/HMW and F/Pyr, it was found that the main origin could be a pyrogenic source. However, there were significantly ($p < 0.05$) higher concentrations of PAHs in the algal tissues of *Padina boryana* collected from the coastal water. In general, the results also indicated that *P. boryana* was useful for biomonitoring PAH contamination and bioavailability in coastal water.

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