

## **DISTRIBUTION AND SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS IN AQUATIC SEDIMENT FROM CAN GIO COASTAL WETLAND, HOCHIMINH CITY**

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### **ABSTRACT**

The distribution of fifteen polycyclic aromatic hydrocarbons (PAHs) indicated from USEPA as priority pollutants was studied in surface sediments (0 - 20 cm) of coastal wetland area of Can Gio district, Hochiminh City. PAHs were recovered from the sediments by solvent extraction and then analyzed by means of high performance liquid chromatography system. Total concentrations of the  $\Sigma$ PAHs in the range 5 – 38 ng/g dw were detected, and a distinct spatial trend was observed. The contents of Nap, Ace, Flu, Phe and dBA were below detection limit. Diagnostic ratios such as benzo[a]anthracene/chrysene and fluoranthene/pyrene were achieved to evaluate the emission sources of PAHs. These ratios indicated an anthropogenic source (pyrolysis) of PAHs for sediments. Furthermore PAHs were associated mainly with fine particle sediments. Although the PAHs contents were below Vietnamese standard but potential risk to ecosystem needs further study since the high percentages of carcinogenic PAHs.

*Keywords:* polycyclic aromatic hydrocarbons, sediment, coastal wetland, pollution.

### **1. INTRODUCTION**

Polycyclic aromatic hydrocarbons (PAHs) are aromatic hydrocarbons with two or more fused benzene rings with natural as well as anthropogenic sources. Due to their ubiquitous occurrence, recalcitrance, bioaccumulation potential and carcinogenic activity, the PAHs have gathered significant environmental concern. Unlike other pollutants already banned or regulated, PAHs continue to be released into the environment due to widespread formation after fossil fuels use in many countries including Vietnam. The major sources of PAHs are anthropogenic activities as incomplete combustion of fossil fuel, leakage during petroleum recovery, transportation and spills [1]. Due to its hydrophobicity so total concentrations of PAHs ranged from 52.3 to 1,870.6 ng/g dry weight have been found in marine sediments in China [2]. In marine sediments collected from North Vietnam, the total of eight PAHs (phenanthrene, flouranthrene, perylene, benzo[a]anthracene, benzo[a]pyrene, pyrene, triphenylene and benzo[e]pyrene) ranged between 79 - 475  $\mu$ g/kg dw [3]. In the other study, the only three PAHs

have been found (Phenanthrene, Perylene and Pyrene) with the levels from 4.80 to 49.48  $\mu\text{g}/\text{kg dw}$  [4].

Can Gio coastal wetland area located in the Saigon - Dongnai system estuary. Coastal habitats provide ecosystem services essential to people and the environment of Hochiminh City and surrounding area. Numerous PAHs generating activities take place in this area to be precise, without control. In the estuarine area of Saigon - Dongnai river system, over 480,000 $\text{m}^3$  industrial wastewater are discharged daily. In addition, the risks from PAHs released from atmospheric pollutions, domestic wastewaters and shipping as well as oil spill should be also taken into account. Thus, a study aimed at the on the current status of PAHs in Can Gio coastal wetland have been carried out.

## 2. MATERIAL AND METHOD

### 2.1. Sampling

500 g of sediment samples for PAHs analyze have been collected at the low tide period in August and October 2015. The maximum depth of sediment samples were 20 cm. The sample container were pre-cleaned with deionized water, acetone and hexane (EPA 610). Thirteen sampling locations are selected based on monitoring station of Hochiminh City Environmental Protection Agency (HEPA) and divided into 3 zones: inland, estuarine and coastal area (Figure 1).

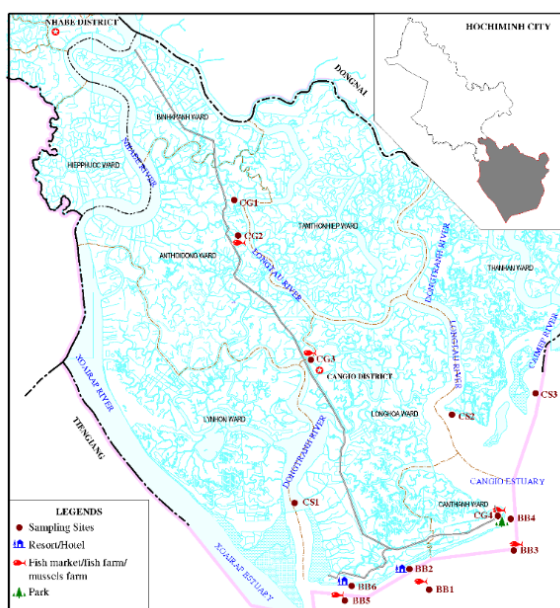


Figure 1. The study area and sampling sites.

### 2.2. Analytical methods

The sediment fraction less than 0.075 mm were separated, centrifuged and kept at  $-20\text{ }^{\circ}\text{C}$  in glass bottle until analyze began. 5 g of sediment were ultrasonic extracted with a mixture of acetone and dichloromethane (80:20 v/v). The solution then loaded through silica gel and

aluminum with the ratio 1:1, the washing solution was acetone and dichloromethane. Then, the solution was evaporation with rotary evaporator and transferred to dimethyl sulfoxide solvent.

Fifteen PAHs including Naphthalene (Nap), Acenaphthylene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flt), Pyrene (Pyr), Chryrene (Chr), Benzo(a)anthracene (BaA), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(e)pyrene (BaP), Dibenzo(a,h)anthracene (dBA), Benzo(g,h,i)perylene (BgP) and Indeno(1,2,3-c,d)pyrene (InP) were determined using High performance liquid chromatography system UHPLC-UltiMate® 3000, Dionex (USA).

The accuracy of the analytical method was determined using certificate sample SRM 1941b. The LOD values varied between 0.14 and 0.66 µg/kg; with the exceptions of Phe and Nap (1.8 µg/kg). The analytical results showed that the recovery rate was better than 90 % with the exception of Flu (73 %) [5].

### 3. RESULTS AND DISCUSSION

#### 3.1. PAHs contents in coastal wetland sediment

The concentrations of PAHs in sediment samples of Can Gio coastal wetland were relative low. Eleven of total fifteen PAHs were detected. The concentrations of Nap, Ace, Flu, Phe and dBA were below detection limit. The PAHs contents in sediments collected from site BB4 were also not detected.

The detected PAHs could be divided into 2 groups. Nap, Ace, Flu, Phe and Ant belong to group of low molecular weight PAHs - LPAHs (e.g., 2 to 3 ring group of PAHs), which are significant acute toxicity to aquatic organisms. The other 10 higher molecular weight PAHs (HPAHs), i.e. 4 to 7 ring PAHs (Flt, Pyr, BaA, Chr, BbF, BkF, BaP, BgP, dBA and InP) which are predominantly pyrolytic PAHs. Generally, HPAHs are higher toxicity than those LPAHs do not. In addition, several members of the high molecular weight PAHs have been known to be carcinogenic. Physical and chemical characteristics of PAHs vary with molecular weight. For instance, PAH resistance to oxidation, reduction, and vapourization increases with increasing molecular weight, whereas the aqueous solubility of these compounds decreases. As a result, PAHs differ in their behaviour, distribution in the coastal wetland environment [6].

The contents of LPAHs in the study area were relative low. Only Ant have been detected but with the low concentrations in comparison with other HPAHs (Figure 2). The Ant's contents were similar in inland ( $0.60 \pm 0.17$  ng/g dw) and estuarine area ( $0.57 \pm 0.09$  ng/g dw) and then decreased seaward ( $0.47 \pm 0.2$  ng/g dw). The reason for that because LPAHs was predominantly petroleum PAHs. In addition, LPAHs were less recalcitrant against bio and non-biodegradation. Among LPAHs, Ant had lower solubility 59 µg/L so it may be subject to stronger absorb to sediment particles [6].

HPAHs are dominant in the Can Gio coastal wetland since PAH resistance to oxidation, reduction, and vapourization increases with increasing molecular weight, whereas the aqueous solubility of these compounds decreases (Figure 2). The HPAHs contents showed widely variations and followed a gradient of Pyr ( $3.6 \pm 1.8$  ng/gdw) > BaP ( $3.0 \pm 1.5$  ng/gdw) > Flt ( $2.5 \pm 1.8$  ng/gdw) > Chr ( $1.8 \pm 0.9$  ng/gdw) > BbF ( $1.5 \pm 1.2$  ng/gdw) > BkF ( $0.66 \pm 0.5$  ng/gdw) ~ BaA ( $0.6 \pm 0.6$  ng/gdw). The lowest levels of dBA in study area could be explained that among HPAHs, dBA had highest LogKow (6.86) so it could cause weak sorption ability to sediments [4]. Similar to LPAHs (Ant), spatial variations of HPAHs showed the maximum HPAHs levels

in inland ( $25 \pm 8.4$  ng/g dw) and dilution effect in the estuarine area ( $8.1 \pm 5.3$  ng/g dw). The PAHs in the inland area released from anthropogenic activities such as wastewater containing PAHs. In the estuarine area, the dilution of PAHs have occurred and the PAHs decreased. In the coast, the PAHs increased again since the contributions of shipping ( $16 \pm 9.2$  ng/g dw). However, together with dilution effect so the PAHs in the coast were lower as compared with inland area (Figure 2).

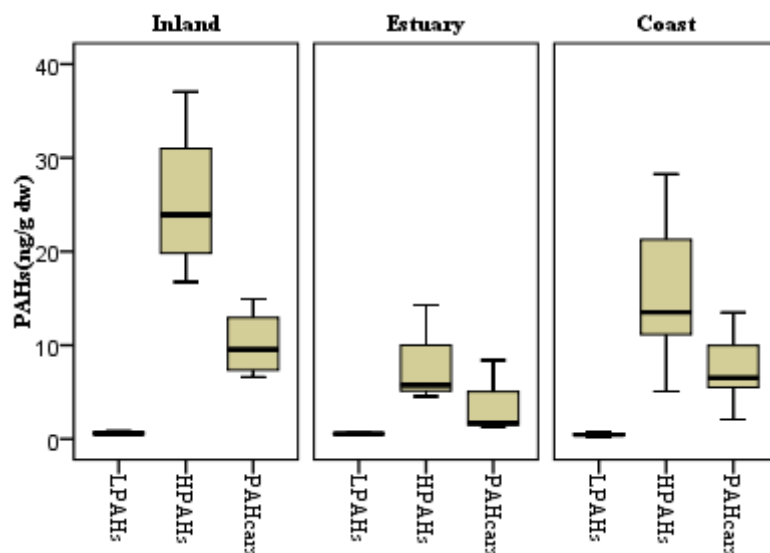


Figure 2. The PAHs pattern in sediments of Can Gio coastal wetland.

In comparison with previous studies in North Vietnam, PAHs in Can Gio coastal wetland showed relative decreased tendency, with the exception of Pyr. Similarly, the contents of  $\Sigma 15\text{PAHs}$ ,  $\Sigma\text{LPAHs}$ ,  $\Sigma\text{HPAHs}$  and  $\Sigma\text{PAHcars}$  in the studied area were lower than Bohai bay, China.

Concentrations of 11 individual PAHs were correlated (Pearson,  $\alpha = 0.01$ ), which is consistent with PAHs originating from similar sources, and the sources were located in close proximity to the sampling locations [5, 7]. Otherwise, PAHs shown significant correlation with fine fractions ( $<0.075 \mu\text{m}$ ) may be subject to strongly absorption of those to clay minerals. However, no significant correlation between PAHs and TOC have been found indicating a insignificant effect of TOCs on PAHs distribution [5].

### 3.2. Sources of PAHs

Anthropogenic PAHs stem mainly from combustion of fossil fuels and spillage of petroleum. The sources of PAHs, whether from fuel combustion (pyrolytic) or from crude oil (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 [2,8]. Generally, the higher percentage of  $\Sigma\text{HPAHs}$  were functional in delineating anthropogenic sources of PAHs (pyrolysis). In addition, the lower LPAHs was related to the insignificant contribution of natural sources (petrogenic). Further, the ratio between  $\text{BaA}/(\text{BaA}+\text{Chr})$  and  $\text{Flt}/(\text{Pyr}+\text{Flt})$  can be also used to distinguish between predominant sources of PAHs between petroleum hydrocarbons and pyrolysis of fuels [2,9]. The ratio of  $\text{BaA}/(\text{BaA}/\text{Chr})$  can be used to

distinguish between predominant sources of PAHs between petroleum hydrocarbons and pyrolysis of fuels. The ratio of Flt/(Pyr+Flt) can be used to further distinguish between types of fuels. In Can Gio coastal wetland, BaA/(BaA+Chr) were greater than 0.35, indicating pyrogenic sources of PAHs (Figure 4). However, some exception could be found, Flt/(Pyr+Flt) ranged from 0.4 to 0.5, indicating of fossil fuel combustion [9]. Therefore, these observed ratios suggest pyrogenic sources of PAHs from vehicular emissions and diesel combustions in vehicles and industrial activities.

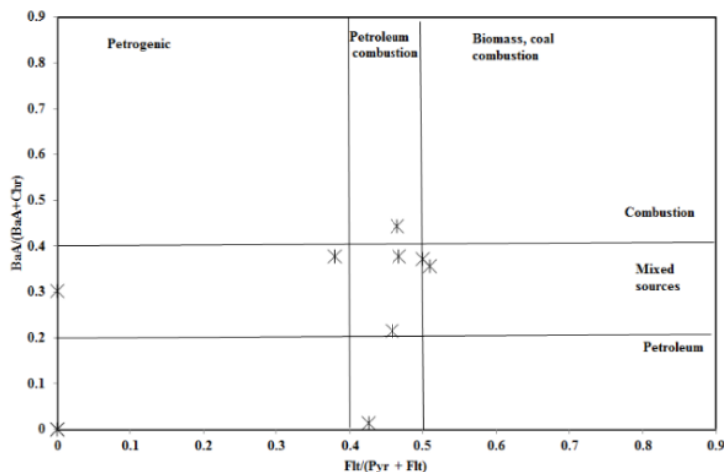


Figure 3. PAH cross plots for the ratios of Flt/(Flt+Pyr) vs. BaA/(BaA+Chr) in sediments of Can Gio coastal wetland.

### 3.3. Risk assessment

In comparison with Vietnamese standard for Sediment Quality (QCVN 43:2012), the PAHs contents in Can Gio coastal wetland were below reference values. However, as showed in Fig.4, the high percentages of carcinogenic PAHs (PAHs cars) including Flu, BaA, BbF, BkF, BaP, dBA and InP) of total 10 detected PAHs have been illustrated.

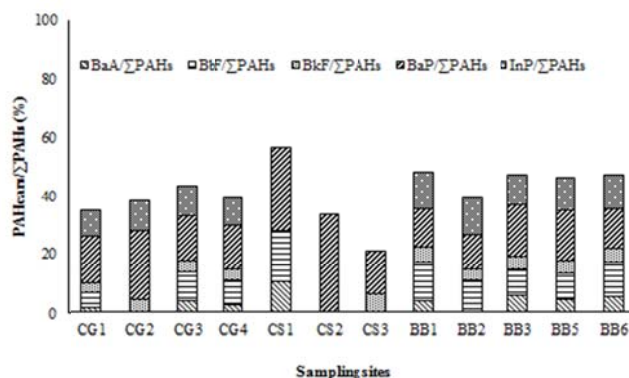


Figure 4. The ratio of PAH cars vs.  $\Sigma$ PAHs in the study area.

Hence, among PAHcars, BaP showed highest concentrations BAP. It is interesting to note that BaP is known to be probably the most carcinogenic PAHs and because it is frequently

formed during anthropogenic sources (pyrolysis processes). Thus, the potential negative effects of PAHs accumulation in sediments of Can Gio coastal wetland could not be negligible and should be further explored.

#### 4. CONCLUSIONS

Present study provided quantitative information in order to evaluate PAH contamination in sediment of Can Gio coastal wetland. A distinct spatial trend in PAH pollution between was observed. The mean  $\Sigma 10$ PAHs concentration averaged  $26 \pm 8.7$ ;  $8.7 \pm 5.4$  and  $16 \pm 9.3$  ng/g for inland, estuarine and coastal zones, respectively. These pollutants tend to be associated mainly with fine-grained particles. The higher the HPAHs/LPAHs ratio have been found indicating the prevalence of pyrolytic (fuel combustion) in the region. Considering some concentration ratios between the different PAHs it was also possible to ascribe to combustion processes the main source of PAHs. The study area can be classified as not heavily polluted with PAHs since the PAHs contents were below Vietnamese standard. The observed concentrations needs to be confirmed by further studies; anyway, the high percentages of carcinogenic PAHs could cause potential risk to ecosystem.

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