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Distribution and Source of PAHs in Surface Sediments of Canon River Mouth, Taiwan

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Abstract**—**Surface sediment samples were collected from the Canon River mouth, Taiwan and analyzed for polycyclic aromatic hydrocarbons (PAHs). Total PAHs concentrations varied from 337 to 1,252 ng/g dry weight, with a mean concentration of 827 ng/g dry weight. The spatial distribution of PAHs reveals that the PAHs concentration is relatively high in the river mouth region, and gradually diminishes toward the harbor region. Diagnostic ratios showed that the possible source of PAHs in the Canon River mouth could be petroleum combustion. The toxic equivalent concentrations (TEQ^{carc}) of PAHs varied from 47 to 112 ng TEQ/g dry weight. Higher total TEQcarc values were found in the river mouth region. As compared with the US Sediment Quality Guidelines (SQGs), the observed levels of PAHs at Canon River mouth were lower than the effects range low (ERL), and would probably not exert adverse biological effects.

Keywords**—**PAHs, sediment, river mouth, sediment quality guidelines (SQGs), toxic equivalent (TEQ^{carc})

I. INTRODUCTION

THE Canon River is approximately 5 km long, and drains a catchment of less than 11.3 km^2. The river flow through the downtown area of Kaohsiung City and finally discharged into Kaohsiung Harbor (Fig. 1). Kaohsiung City is the largest industrial city in Taiwan with 1.5 million residents. During earlier years, the lack of sanitary sewer system causes un-treated raw wastewater to be discharged directed into adjacent water bodies that leads to serious deterioration of river water quality. Although in recent years, Kaohsiung City actively promotes the construction of wastewater collection and treatment systems, in 2009, the wastewater system only serves 56% of the city in 2009. Additionally, regions along Canon River have dense population with prosperous business and industrial establishments. The major pollution source includes domestic wastewater discharges, industrial wastewater discharges (e.g. tanneries, paint and dye, chemical production, metal processing, electronic and foundry), municipal surface runoff, and transportation pollution. All the pollutants will eventually be transported to the river mouth to deposit and accumulate in the bottom sediment.

Polycyclic aromatic hydrocarbons (PAHs) are included in the European Union and US EPA priority pollutant lists because PAHs represent the largest group of compounds that are mutagenic, carcinogenic, and teratogenic [1,2]. They could also pose potential threat to the marine environment. The major sources of PAHs could be both natural and anthropogenic. For examples, the terrestrial deposit of coals, atmospheric input from incomplete combustion (wood burning, forest fire, fossil fuel, and coke oven), oil leaks or spills, and exhaust emission from vehicles are the major sources PAHs in environments [3]. The effect of PAHs is usually widespread and permanent in environmental media, and thus, PAHs can be eventually deposited and persist in bed sediment (as a sink) in the aquatic system. This occurs because most PAHs, with their high hydrophobicity, sorb strongly to the organic in sediment, and are resistant to bacterial degradation in an anoxic environment. Under favorable environmental conditions, PAHs may be released to the water as a continuing source and threaten the aquatic marine ecosystem through bioaccumulation in food chains.

The objectives of this study were to: (a) examine the spatial distribution, composition, and relative pollution levels of PAHs in the sediments of Canon River mouth, (b) identify possible sources of PAHs, and (c) evaluate the potential toxicological and biological impacts on humans and the environment.

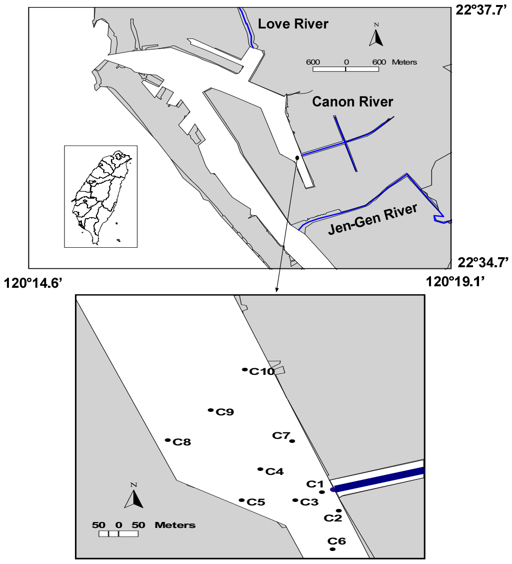

Fig. 1 Map of the study area and sampling locations

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TABLE I
PAHs CONCENTRATION (NG/G DRY WEIGHT) AND SELECTED MOLECULAR RATIOS IN SEDIMENTS OF CANON RIVER MOUTH

Site	NA	ACE	AC	FL	PH	AN	FLU	PY	BaA	CH	BbF	BkF	BaP	IP	DBA	BP
C1	46	7.5	7.7	20	71	22	108	136	59	62	101	27	61	57	16	104
C2	69	18	20	51	157	38	231	274	77	102	99	25	47	25	3.5	16
C3	63	12	14	38	130	30	163	201	88	89	123	34	73	45	13	8.0
C4	16	2.9	2.9	7.1	24	8.6	34	48	24	21	42	13	29	24	8.2	33
C5	35	7.3	6.0	19	55	20	80	101	51	44	84	23	51	36	11	40
C6	43	10	13	26	96	32	131	167	64	62	102	25	56	44	14	61
C7	37	10	8.6	20	72	26	96	136	57	50	95	26	56	46	7.8	62
C8	30	14	11	17	69	26	115	156	68	62	110	31	66	43	14	47
C9	30	7.0	5.9	13	47	18	58	79	44	36	77	21	48	41	13	47
C10	29	8.3	7.9	19	64	21	90	128	60	52	98	28	63	46	9.1	59
ERL[a]	160	44	16	19	240	85.3	600	665	261	384	–	–	430	–	63.4	–
ERM[a]	2100	640	500	540	1500	1100	5100	2600	1600	2800	–	–	1600	–	260	–

Site	ΣPAHs	ΣLPAHs	ΣHPAHs	$\frac{\Sigma LPAHs}{\Sigma HPAHs}$	$\frac{PH}{AN}$	$\frac{AN}{(PH+AN)}$	$\frac{FLU}{PY}$	$\frac{FLU}{(FLU+PY)}$	ΣCPAHs	TEQ^{carc}
C1	905	173	732	0.24	3.3	0.23	0.80	0.44	384	99
C2	1252	352	900	0.39	4.1	0.20	0.84	0.46	379	71
C3	1123	287	836	0.34	4.4	0.18	0.81	0.45	463	112
C4	337	61	276	0.22	2.8	0.26	0.71	0.42	162	47
C5	663	142	521	0.27	2.8	0.26	0.79	0.44	301	79
C6	945	220	725	0.30	3.0	0.25	0.79	0.44	366	92
C7	806	174	632	0.27	2.8	0.26	0.71	0.41	338	84
C8	877	167	710	0.23	2.7	0.27	0.74	0.43	393	102
C9	585	121	464	0.26	2.6	0.28	0.74	0.43	280	77
C10	781	149	632	0.24	3.0	0.25	0.70	0.41	354	92
ERL[a]	4022	552	1700	–	–	–	–	–	–	–
ERM[a]	44,792	3160	9600	–	–	–	–	–	–	–

a ERL and ERM refers to the effects range low and median [23].

II. MATERIALS AND METHODS

Surface sediment samples were collected at 10 stations near Canon River mouth (Fig. 1) with Ekman Dredge Grab aboard a fishing boat. Immediately after collection, the samples were scooped into glass bottles, which have been pre-washed with *n*-hexane and kept in an icebox, and then transported to the laboratory for analysis. In the laboratory, the samples were freeze-dried for 72 h, ground to pass through an 0.5 mm sieve and fully homogenized [4]. The dried sediments were placed at -20°C in pre-washed with n-hexane amber glass bottles covered with solvent-rinsed aluminum foil until further processing and analysis. The particle size, water content, and organic matter content (OM) in sediment of the study are listed elsewhere [4].

Analytical methods for PAHs (i.e., naphthalene (NA), acenaphthylene (ACE), acenaphthene (AC), fluorene (FL), phenantrene (PH), anthracene (AN), fluoranthene (FLU), pyrene (PY), benzo[a]anthracene (BaA), chrysene (CH), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BP)) have been reported in detail previously [4].

Data analysis (e.g., mean, standard deviation, maximum, and minimum concentrations) using statistical methods were performed in this study. To test the relationship between sediment characteristics and PAH concentrations, linear correlation of Pearson technique analysis was used. The following analytical data were taken into account: (a) the amount of each PAH; (b) the sum of 16 PAHs, ΣPAHs; (c) the sum of seven PAHs with low molecular weight (i.e., NA, 2-MP, ACY, ACE, FL, PH, and AN), ΣLPAHs; (d) the sum of 10 PAHs with high molecular weight (i.e., FLU, PY, BaA, CH, BbF, BkF, BaP, DBA, and IP), ΣHPAHs; and (e) the sum of potentially carcinogenic PAHs (i.e., BaA, CH, BbF, BkF, BaP, IP, and DBA), ΣCPAHs.

III. RESULTS AND DISCUSSION

A. Distribution of PAHs

The PAHs concentrations in sediments collected at different sites are given in Table I. The total amount of PAHs (ΣPAHs) varied from 337 to 1,252 ng/g dry weight, with a mean concentration of 827 ng/g dry weight. Concentration distributions of ΣPAHs in Canon River mouth sediment shown in Fig. 2 reveal that the sediment PAHs content is relatively higher near the river mouth, and gradually decreases in the direction toward the harbor. This indicates that the major sources of sediment PAHs came from the polluted urban rivers.

According to the number of aromatic rings, the 16 PAHs were divided into three groups: (a) 2- & 3-ring, (b) 4-ring, and (c) 5- & 6-ring PAHs. The 4- ring and 5- & 6-ring PAHs were predominant in sediments from Canon River mouth, ranging from 37% to 55% and from 17% to 44%, respectively; the percentage compositions are 18–28% for the 2- & 3-ring PAHs. The predominance of high molecular weight PAHs in the sediments of Canon River mouth reflects the presence of significant combustion products from pyrolytic processes and/or pyrolytic sources. The PAHs pollutant level classification was suggested by Baumard et al. [5]: (a) low, 0–100 ng/g; (b) moderate, 100–1000 ng/g; (c) high, 1000–5000 ng/g; and (d) very high, >5000 ng/g. Sediments from Canon

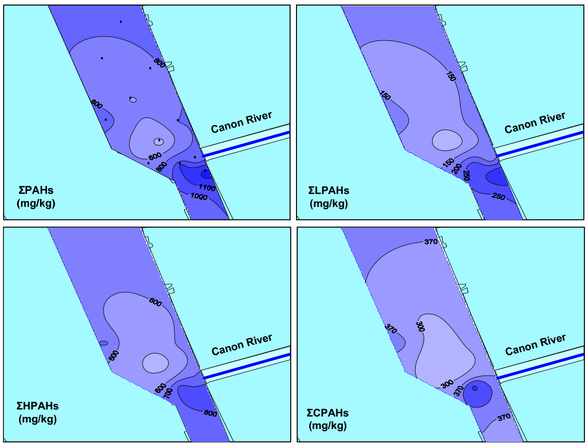

Fig. 2 Distribution of ΣPAHs, ΣLPAHs, ΣHPAHs, and ΣCPAHs contents in surface sediment of Canon River mouth

River mouth can be characterized as moderate to high PAHs pollution. Coefficient of the Pearson correlation between the sediment characteristics and PAHs content were carrying out. The sediment ΣPAHs content is not obviously correlated to either OM or particle size ($p>0.05$) indicating that OM and particle size are not major factors to control the ΣPAHs distribution. The environmental condition of the river mouth in this study region such as discharges of upstream pollutants, and alternation between fresh water and sea water may be very complicated so that very little correlation between the sediment ΣPAHs concentration and other sediment characteristics is observed to exist.

B. Sources of PAHs in Canon River mouth

PAH isomeric ratios have been used to identify different sources that contribute PAHs to environmental samples [5-7]. The predominant sources of PAHs in estuarine/marine sediments originate from pyrolytic (combustion) or petrogenic (fossil fuel) related activities [8-9]. Characterized by predominance of parent compounds with four or more aromatic rings, pyrolytic PAHs are derived during combustion. In contrast, petrogenic PAHs (from petroleum and its products) contain only two or three aromatic ring compounds. Therefore, a ratio of low (2- & 3-ring) to high (4- to 6-ring) PAHs has been used to identify pyrogenic (<1) and petrogenic (>1) sources of PAHs in sediments [7,10]. In all Canon River mouth stations, ΣLPAHs/ΣHPAHs ratios were <1 (Table I), indicating they originated from pyrogenic sources.

Other isomeric ratios have been used to assess the pyrogenic or petrogenic sources of PAHs in sediments: (a) PH/AN [11,12] or alternatively, AN/(PH + AN) ratio [2,5,6,8]; (b) FLU/PY [12]; and (c) FLU/(FLU + PY) [12]. The PH is thermodynamically more stable and its prevalence over AN indicates that the sediment PAHs were mainly from petrogenesis activities. Indeed, petroleum product usually exhibits a quite high PH/AN ratio. Therefore, if the PH/AN ratio is higher than 10 (or AN/(PH + AN) > 0.1), it reveals that the sediment is mainly contaminated by petrogenic inputs. Moreover, if the PH/AN ratio is less than 15 (or AN/(PH + AN) < 0.1), it typically reveals that the PAH source is from pyrolytic activities [2,5]. As showed in Table I, the ratios of PH/AN and AN/(PH + AN) at all stations were lower than 10 and higher than 0.1, respectively, this implies that the PAH source could be combustion activities.

The FLU/PY and FLU/(FLU + PY) ratios are also useful indicators in evaluating the attribution of PAH pollution in sediment [13-14]. Baumard et al. [5] concluded that the source of contamination is mainly from pyrolytic sources if the ratio of FLU/PY is higher than 1. Their results also revealed that petrogenic discharges would cause the increase in PAH in sediments if the ratio of FLU/PY is less than 1 [6]. In this study, the ratios of FLU/PY at all stations were lower than 1 (Table I), this indicates that the main PAH source was combustion activities. Moreover, when FLU/(FLU + PY) is higher than 0.5, biomass combustion (grass, wood, or coal combustion) would cause the increase in PAHs in sediments [2,6,7]. However, if the ratio of FLU/(FLU + PY) is between 0.4 and 0.5, PAHs are mainly from combustion of petroleum; if the ratio is less than 0.4, typical petroleum contamination is usually the cause of PAHs in sediments [2,6,7]. As showed in Table I, the ratios of FLU/(FLU + PY) at all stations were between 0.4 and 0.5, indicating they originated from petroleum combustion.

With the evaluation of both PH/AN and FLU/PY ratios, misleading estimate of PAHs sources can be prevented [6,13,14]. Fig. 3 shows the distribution AN/(PH + AN) and FLU/(FLU + PY) ratios in all sediment samples. Ratios of FLU/(FLU + PY) in sediment of all sediment samples ranged between 0.4 and 0.5; ratios of AN/(PH + AN) in sediment of all sediment samples were higher than 0.1. This indicates that petroleum combustion could be a possible source of PAHs.

C. Sediment potential toxicity and biological effects based on PAHs

The assessment of sediment toxicity in this study was performed based on the total concentration of potentially carcinogenic PAHs (i.e., BaA, CH, BbF, BkF, BaP, IP, and DA), ΣCPAHs [2,15,16]. The ΣCPAHs concentration varied

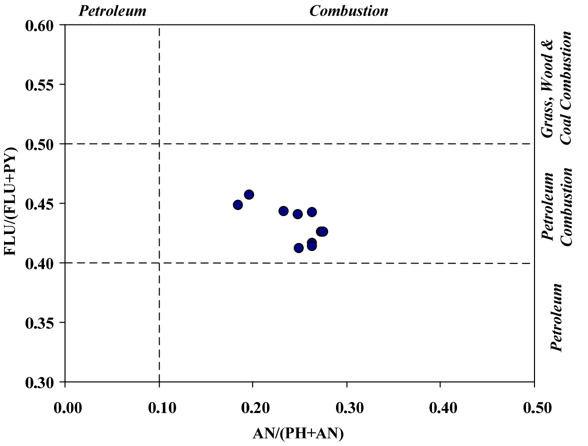

Fig. 3 Cross plots for the ratios of FLU/(PY+FLU) vs. AN/(AN+PH)

from 162 to 463 ng/g dry weight, with a mean concentration of 342 ng/g dry weight (Table I). The ΣCPAHs accounted for 30% to 48% of ΣPAHs in sediments of Canon River mouth.

The potential toxicity of sediment was evaluated using the total toxic benzo[a]pyrene equivalent (TEQ^{carc}) [2,15,16]. The TEQcarc for all CPAHs was calculated using the following equation: $TEQ^{carc} = [\Sigma C_i \times TEF_i^{carc}]$, where Ci is the carcinogenic PAHs concentration (ng/g dry weight); TEF_i^{carc} (toxic equivalency factors) is the toxic factor of carcinogenic PAHs relative to benzo[a]pyrene (BaP). Among all known potentially carcinogenic PAHs, benzo[a]pyrene is the only PAH for which toxicological data are sufficient for derivation of a carcinogenic potency factor [17]. According to US EPA [18], TEFs for BaA, CH, BbF, BkF, BaP, IP, and DBA are 0.1, 0.001, 0.1, 0.01, 1, 0.1, and 1, respectively.

In this study, the total TEQ^{carc} values of sediment samples varied from 47 to 112 ng TEQ/g dry weight, with the mean value of 86 ng TEQ/g dry weight. The higher total TEQ^{carc} values were found at Station C3 near the river mouth. Among different CPAHs, contribution to the total TEQ^{carc} decreased in the following order: BaP (64.3%), DA (12.8%), BbF (10.9%), BaA (6.9%), IP (4.7%), BkF (0.30%), and CH (0.07%).

A widely used sediment toxicity screening guideline of the US National Oceanic and Atmospheric Administration provides two target values to estimate potential biological effects: effects range low (ERL) and effect range median (ERM) [19]. The guideline was developed by comparing various sediment toxicity responses of marine organisms or communities with observed PAHs concentrations in sediments. These two values delineate three concentration ranges for each particular chemical. When the concentration is below the ERL, it indicates that the biological effect is rare. If concentration equals to or greater than the ERL but below the ERM, it indicates that a biological effect would occur occasionally. Concentrations at or above the ERM indicate that a negative biological effect would frequently occur. Table I shows the measured concentrations of PAHs in comparison with the ERM and ERL values. The PAHs, ΣHPAHs, ΣPAHs, and individual PAH at all sediment samples were below the ERL. This indicates that biological effects would rarely occur.

IV. CONCLUSIONS

PAHs were detected in sediment samples collected from Canon River mouth. The results reveal that the PAHs contained in the sediment at Canon River mouth belong to moderate to high pollution category. The PAHs concentration is relatively high in the river mouth region, and gradually diminishes toward the harbor region. The possible source of PAHs in the Canon River mouth could be petroleum combustion. Results from this study suggest that these polluted urban rivers played important roles in the leaching of PAHs into the environments.

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