




Article

Method Development for Low-Concentration PAHs Analysis in Seawater to Evaluate the Impact of Ship Scrubber Washwater Effluents

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Abstract: A naval ship's exhaust gas scrubber may discharge polycyclic aromatic hydrocarbons (PAHs) into seawater. Due to the high lipophilicity and low water solubility of PAHs, their concentrations in seawater are extremely low, making them difficult to detect or accurately determine. To accurately assess the impact of scrubber washwater effluent on the PAHs concentration of seawater, appropriate analysis methods must be established. In this study, a large-volume pre-concentration water sampler was used onboard to concentrate PAHs in surface seawater (100 L) from four sites offshore of southern Taiwan. The quantitative and qualitative analysis of dissolved PAHs in seawater and quality control samples were implemented using a GC/MS system with the aid of internal and surrogate standards. Results showed that the field and equipment blank samples of quality control samples were lower than twice the detection limit. The detection limit of individual PAHs is between 0.001 (naphthalene, NA) and 0.014 ng/L (dibenzo[a,h]anthracene, DBA), which meets the requirements for evaluating PAHs in seawater (that is, less than the maximum permissible concentrations (MPCs)). The concentration of total PAHs (TPAHs) in the four seawater samples ranged from 2.297 to 4.001 ng/L and had an average concentration of 3.056 ± 0.727 ng/L. The concentrations of 16 PAHs were determined in each seawater sample, indicating that the analytical method in this study is suitable for the determination of low-concentration PAHs in seawater. Phenanthrene (PHE) is the most dominant compound in seawater samples accounting for $59.6 \pm 12.6\%$ of TPAHs, followed by fluorine (FL) accounting for $8.5 \pm 3.7\%$. The contribution of high-ring PAHs to TPAHs is not high (0.5–9.2%), but the observed concentrations can cause a higher risk to aquatic organisms than low-ring PAHs. The diagnostic ratio showed that the sources of PAHs in the seawater collected offshore of southern Taiwan may include mixed sources such as petrogenic, petroleum combustion, and biomass combustion. The results can be used for regular monitoring, which contributes to pollution prevention and management of the marine environment.

Keywords: seawater; polycyclic aromatic hydrocarbons (PAHs); maximum permissible concentrations (MPCs); pre-concentration system



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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a kind of persistent organic pollutants which are ubiquitous in the marine environment. They are toxic, mutagenic, carcinogenic, and bioaccumulative [1,2]. Therefore, the US Environmental Protection Agency (US EPA) has identified 16 PAHs as priority environmental pollutants. The PAHs in the marine environment

are mainly imported by human activities and can be divided into petrogenic and pyrogenic sources [3–5]. PAHs of petrogenic sources are mainly low-ring PAHs (LPAHs), which are mainly derived from petroleum, including the input of crude oil and its refined products. On the other hand, PAHs of pyrogenic sources are mainly medium-ring (MPAHs) and high-ring (HPAHs) PAHs. They are mainly produced by incomplete combustion of organic substances [3,5] and enter the marine environment through atmospheric transport and deposition [4,6]. The high lipophilicity and low water solubility of PAHs make them easy to adsorb on organic matter and/or accumulate in the biota after entering the water environment [7]. Although most PAHs may be deposited on the seafloor and stored in sediments, some still exist in the seawater column. In addition, the deposited PAHs may be reintroduced into the water body due to the biological disturbance process or the submarine ocean currents and be reused by the organisms [8]. PAHs in a seawater column can be directly accumulated in marine organisms through the gills or skin and cause potential hazards. PAHs dissolved in seawater are more bioavailable than PAHs in the form of a composite, adsorbant, or particles [9]. Therefore, understanding the concentration of dissolved PAHs in seawater and their potential ecological risks are crucial for marine ecosystems research due to their potential harm even at lower concentrations [7,10].

To reduce air pollution caused by ships burning high-sulfur fuel oil and for improvement of air quality, a new regulation on the upper limit of sulfur content in marine fuel oils in January 2020 was implemented by the International Maritime Organization (IMO). This rule states that ships should use fuel oil with sulfur contents of less than 0.5% by weight, seek for alternative fuels, or install an exhaust gas cleaning system (EGCS) called scrubbers. According to the forecast of the International Energy Agency [11], to comply with this new regulation, about 37% of ships will use low-sulfur fuels, about 40% will use alternative fuels, and about 22% will choose to install scrubbers and continue to use high-sulfur fuels by 2024 [11]. However, the sulfur, particulate matter, and other contaminants (including carcinogens such as PAHs and heavy metals) removed by scrubbers from the ship's exhaust gases are eventually discharged to the sea in the form of scrubbing water [12–14]. This may cause non-biodegradable contaminants (such as PAHs) in the washwater which can accumulate in the marine environment and food web, causing biological hazards [13–15]. Moreover, Thor et al. [14] have shown that washwater from the marine scrubber system is highly toxic to zooplanktonic organisms.

At present, it is inappropriate for IMO to use the fluorescence signal characteristics of a single compound phenanthrene as an indicator of all PAHs [12]. Therefore, the Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) provided IMO with a report on EGCS; the “Report of the GESAMP task team on exhaust gas cleaning systems”. The report suggests that a maximum permissible concentration (MPC) [10] should be used as the scientific basis for assessing the hazards of PAHs to the environment, ecology, and environmental quality. However, the MPC of the dissolved phase in seawater is very low, especially for PAHs with higher ring numbers, such as dibenzo[a,h]anthracene (DBA), whose MPC value is 0.014 ng/L. Due to the limitation of the instruments, the detection limits using general traditional liquid-liquid extraction or relatively low concentration factor may be higher than the MPC value. Therefore, it should be a feasible way to collect large-volume water samples, increase the concentration factor, and prepare samples with higher PAH concentrations for quantitative and qualitative analysis [16–18].

In this study, a pre-concentration water sampler was used to collect surface seawaters (100 L) from four different sites offshore southern Taiwan, and quantitatively and qualitatively analysis of the dissolved-phase PAHs in the seawater samples was carried out. In addition, relevant quality control was implemented to confirm that it has not been contaminated during the sampling process, and the accuracy as well as recovery rate of the analytical method were determined. The concentration, composition, and source of PAHs in seawater offshore of southern Taiwan were also discussed. The results of this research

can be used for routine monitoring and evaluation of PAHs in seawater, and contribute to the management and prevention of PAHs pollution in the marine environment.

2. Materials and Methods

2.1. Chemicals and Materials

Standards of 16 PAHs (including acenaphthene (ACE), acenaphthylene (ACY), anthracene (AN), benzo[a]anthracene (BaA), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[g,h,i]perylene (BP), benzo[k]fluoranthene (BkF), chrysene (CH), DBA, fluoranthene (FLU), fluorine (FL), indeno[1,2,3-cd]pyrene (IP), naphthalene (NA), phenanthrene (PHE), and pyrene (PY)) in a 1000 mg/L mixture solution were obtained from AccuStandard Chem. Co. (New Haven, CT, USA). Internal standard (IS) solutions (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12) at 2000 mg/L and surrogate standard (SS) solutions (2-fluorobiphenyl and 4-terphenyl-d14) at 1000 mg/L were purchased from AccuStandard Chem. Co. (New Haven, CT, USA). PAH working standard, IS mixture solutions and SS mixture solutions are appropriately diluted with HPLC grade *n*-hexane and prepared daily before analysis. The IS and SS were used for sample quantification and procedural recovery analysis. In this study, all solvents and reagents used were chromatographic (HPLC) grade. The glasswares used were rinsed with *n*-hexane (HPLC grade, Duksan Co., Gyeonggi Province, South Korea) before drying in an oven. Glass fiber filter (GFF: Whatman GF/D, 142 mm id, 3 µm pore size, Cytiva, Buckinghamshire, United Kingdom and Advantec GC-50, 142 mm id, 0.5 µm pore size, Advantec Co., Tokyo, Japan) and polyurethane foam (PUF: Tisch TE1010, 63.5 mm id, 75 mm height, density 0.022 g/cm³, Tisch Environmental Inc., OH, USA) were Soxhlet pre-extracted with acetone: *n*-hexane (1:1) for 24 h before sample collection to ensure that there were no organic contaminant. All other materials used were pre-washed with ultrapure water (>18.2 MΩ·cm) (Purity-SP; Lotun Technic CO., LTD., Taipei, Taiwan) and acetone (HPLC grade, Duksan Co., Gyeonggi Province, South Korea).

2.2. Sample Collection

In order to accurately measure the low concentrations of PAHs in seawater, large-volume water samples were collected and pre-concentrated on site. Field sampling was carried out from R/V (New Ocean Researcher 3, NOR3-0018) from 9 to 10 August 2020. The surface water from four sampling sites (T1–T4) within 12 nautical miles offshore southern Taiwan were collected (Figure 1). Surface seawater temperature and salinity were measured at all sites, using a SCTD Sea–Bird SBE 21 SeaCAT Thermosalinograph.

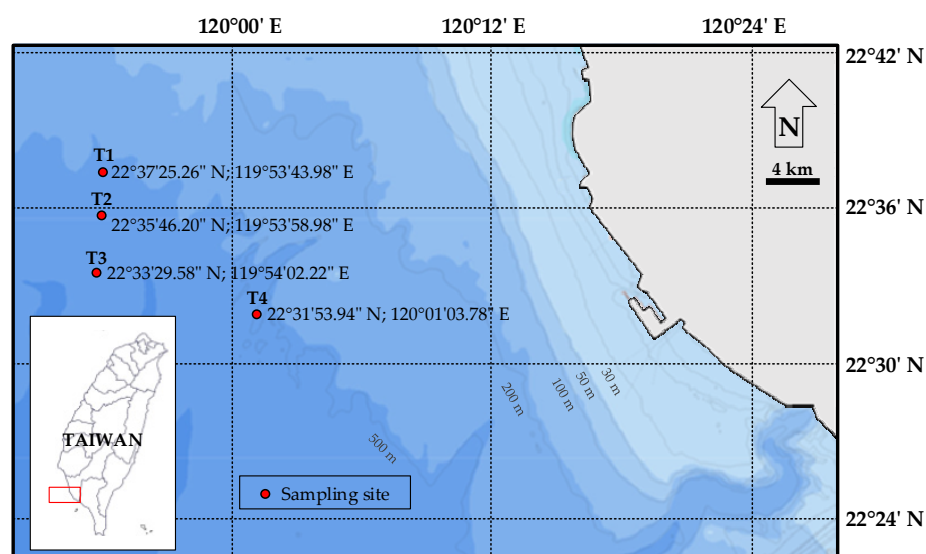


Figure 1. Map of the study area and sampling sites.

About 115 L of seawater was collected by a stainless steel pump and stored in a polished stainless steel airtight container. The 100 L of seawater samples collected in each site were concentrated onboard using a pre-concentration water sampler (Machine Shop, Model G23-027III, Fortelice International Co., Ltd., New Taipei, Taiwan). The pre-concentration water sampler system consists of stainless steel, glass fiber filter case, foam holder, water pump, pressure control switch, liquid level sensor, buffer tank, flow meter and computer controller [19]. The seawater sample passes through the coarse GFF (3 µm pore size), the fine GFF (0.5 µm pore size), and the two PUFs connected in series at a flow rate of about 1 L/min and then discharged. The particles in the seawater are removed by GFF, and the PAHs in the dissolved phase are adsorbed and captured by PUF. All PUF samples were wrapped in aluminum foil paper, placed in a sealed glass jar, and temporarily stored in the refrigerator until they were brought back to the laboratory for further processing. At the sampling site, equipment blank samples, field blank samples, and duplicate samples were prepared respectively. Equipment blank: After each seawater sample was concentrated, 5 L of deionized water was filtered as the equipment blank sample to confirm whether the sampling equipment is contaminated. Field blank: A set of PUF were placed into the sampler without sampling treatments. The PUF were taken out after 100 minutes and placed back into a sealed glass bottle as field blank sample. Duplicate samples: Duplicate (2 × 115 L) samples were collected at T1, T2, and T4 sites for repeated analysis to confirm the precision of the sampling and analytical methods.

2.3. Sample Pretreatment and Analysis

All PUF samples (including 4 seawater samples, 3 replicate samples, 3 field, and 5 equipment blanks) were freeze-dried and extracted by Soxhlet extraction method for PAHs. PUF were placed into the Soxhlet extraction device and extracted with 250 mL acetone: *n*-hexane (1:1) for 24 h. A 100 ng SS were added before extraction. After the extraction was completed, samples were let to stand at room temperature. Extracts were concentrated to near dryness with a vacuum rotary evaporator, and anhydrous sodium sulfate was added to remove water. A glass dropper was used to transfer the extracts to a sample bottles and blown with nitrogen to concentrate to 0.2 mL. A 100 ng IS was added, and 16 PAHs were qualitatively and quantitatively analyzed by GC/MS.

A GC/MS system (Agilent 7890B GC/5977A MS; Agilent Technologies, Santa Clara, CA, USA) was used to analyze the PAH compounds. The GC/MS system and operating conditions for PAHs analysis are listed in Table 1, and the selected ion mass program used for quantification is detailed in Table 2. Figure 2 shows the selected quantification ion chromatogram of the T4 seawater sample in this study, indicating that 16 PAHs can be clearly separated. The identity of PAHs in the samples were confirmed by the retention time and the relative intensities of confirmation ions of the PAHs standards. The internal standard calibration method was used to quantify the 16 PAHs. In the laboratory, this study carried out calibration standards, laboratory blanks, control standards, repeated analyses and quantification of detection limits to ensure the accuracy and precision of the PAHs analysis process.

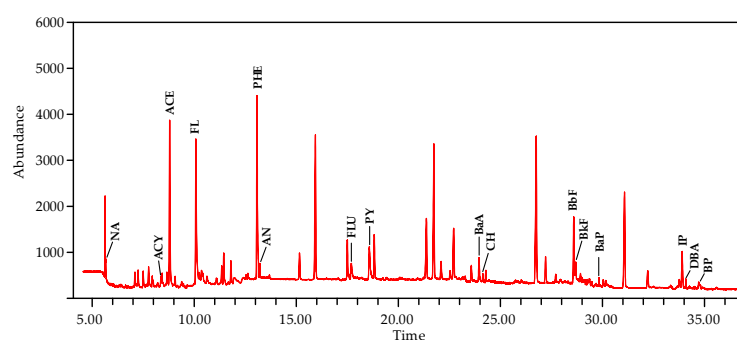


Figure 2. GC/MS selected quantification ion chromatograms of 16 PAHs in the T4 seawater sample. The definitions of compound abbreviations see Table 2.

Table 1. The GC/MS system and operating conditions for PAHs analysis.

Instrument Parameter	Condition Setting
Autosampler	Agilent 7693A
Injection volume	1 µL
Gas chromatography (GC)	Agilent 7890B
Carrier gas	Helium ($\geq 99.999\%$)
Injection mode	Splitless
Column	HP-5MS (30 m, 0.25 mm, 0.25 µm)
Column flow rate	1 mL/min
Temperature of inlet	300 °C
Oven temperature program	40 °C (hold for 1 min), 120 °C (35 °C/min), 160 °C (10 °C/min), 300 °C (5 °C/min, hold for 10 min)
Mass selective detector (MSD)	Agilent 5977A
Temperature of ion source	230 °C
Temperature of quadrupole	150 °C
Temperature of transfer line	280 °C
Electronic energy	70 eV
Ionization mode	Electron ionization (EI)
Type of mass scan	Selective ion monitoring (SIM) (see Table 2)

Table 2. Selected ion monitoring of individual PAH in the GC/MS system.

Compounds	Ring	Retention Time (min)	Quantitative Ion (m/z)	Time Window (min)	Selected Ions (m/z)
Naphthalene-d ₈ (IS1)	2	5.653	136	4.00–8.00	127, 128, 129, 136, 172
Naphthalene (NA)	2	5.676	128		
2-Fluorobiphenyl (SS1)	2	7.372	172		
Acenaphthylene (ACY)	3	8.363	152	8.00–11.00	151, 152, 153, 154, 164, 165, 166, 167
Acenaphthene-d ₁₀ (IS2)	3	8.713	164		
Acenaphthene (ACE)	3	8.782	154		
Fluorene (FL)	3	10.077	166		
Phenanthrene-d ₁₀ (IS3)	3	12.986	188	11.00–19.00	101, 176, 178, 179, 188, 200, 202, 203
Phenanthrene (PHE)	3	13.062	178		
Anthracene (AN)	3	13.221	178		
Fluoranthene (FLU)	4	17.702	202		
Pyrene (PY)	4	18.582	202		
4-Terphenyl-d ₁₄ (SS2)	4	19.733	244	19.00–27.00	226, 228, 229, 240, 244
Benzo[a]anthracene (BaA)	4	23.978	228		
Chrysene-d ₁₂ (IS4)	4	24.043	240		
Chrysene (CH)	4	24.155	228		
Benzo[b]fluoranthene (BbF)	5	28.612	252	27.00–45.29	125, 138, 139, 252, 253, 264, 276, 277
Benzo[k]fluoranthene (BkF)	5	28.723	252		
Benzo[a]pyrene (BaP)	5	29.833	252		
Perylene-d ₁₂ (IS5)	5	30.072	264		
Indeno[1,2,3-c,d]pyrene (IP)	6	33.919	276		
Dibenz[a,h]anthracene (DBA)	5	34.094	278		
Benzo[g,h,i]perylene (BP)	6	34.719	276		

2.4. Analytical Characteristics

The response factors based on the five-point (10, 50, 100, 200, and 500 µg/L) calibration curve for individual PAHs showed an acceptable coefficient of variation (CV) of 4.4 to 16.3%. The results of the laboratory blank samples were always below the detection limit. The individual PAHs recovery in check standards ranged from $94 \pm 4.5\%$ to $117 \pm 6.1\%$ ($n = 3$) and the relative percent differences of repeated analysis ranged from $2.8 \pm 7.7\%$ to $9.8 \pm 5.0\%$ ($n = 5$) for all of the target analyses (Table 3). The recoveries of SS were $63.1 \pm 16.1\%$ for 2-fluorobiphenyl and $78 \pm 19.6\%$ for 4-terphenyl-d₁₄ with seawater

samples ($n = 16$). The method detection limit (MDL) was estimated based on the triple standard deviation of the repeated ($n = 7$) analysis of 16 PAHs ($10 \mu\text{g/L}$) and the amount of sample extracted. The detection limits were 0.001 (NA)–0.014 (DBA) ng/L for individual PAHs. All PAHs blew the 2x MDL detected in any of the field blank sample and equipment blank samples. The relative percent differences of sample duplicates ranged from 4.0% to 25.7% for 16 PAHs and 2 SS (Table 3).

Table 3. Quality assurance and quality control for PAHs analysis in this study.

PAHs ^a	Response Factor (RF) ($n = 5$)		Check Standard ($n = 3$) R ^b (%)	Repeat Analysis ($n = 5$) RPD ^b (%)	Duplicate Sample ($n = 3$) RPD ^b (%)	Detection Limits (ng/L)	Field Blank ($n = 3$) (ng/L)	Equipment Blank ($n = 5$) (ng/L)
	Average \pm SD ^a	CV ^b (%)						
NA	1.01 ± 0.16	15.7	94 ± 4.5	5.3 ± 5.1	15.5 ± 3.0	0.001	0.001 ± 0.001	0.001 ± 0.000
ACY	0.75 ± 0.08	10.2	101 ± 2.9	3.7 ± 3.2	17.0 ± 5.2	0.001	0.001 ± 0.001	0.001 ± 0.000
ACE	0.46 ± 0.05	12.0	106 ± 1.3	7.2 ± 5.1	15.8 ± 4.2	0.006	0.003 ± 0.001	0.004 ± 0.002
FL	0.58 ± 0.07	11.5	100 ± 7.9	4.1 ± 8.4	11.4 ± 3.2	0.002	0.003 ± 0.001	0.002 ± 0.001
PHE	0.74 ± 0.08	11.0	110 ± 3.3	2.8 ± 5.8	13.5 ± 3.4	0.004	0.002 ± 0.001	0.003 ± 0.001
AN	0.87 ± 0.12	13.3	106 ± 4.1	4.1 ± 4.2	7.5 ± 3.8	0.009	0.002 ± 0.002	0.002 ± 0.003
FLU	0.97 ± 0.14	14.4	101 ± 12.0	5.4 ± 8.2	12.7 ± 5.4	0.007	0.002 ± 0.002	0.003 ± 0.002
PY	1.01 ± 0.17	16.3	107 ± 10.0	6.1 ± 7.1	14.1 ± 10.6	0.012	0.002 ± 0.001	0.005 ± 0.004
BaA	0.69 ± 0.06	8.5	108 ± 5.6	9.8 ± 5.0	9.8 ± 4.5	0.013	0.004 ± 0.002	0.007 ± 0.004
CH	0.90 ± 0.08	9.0	102 ± 8.3	2.1 ± 7.5	14.5 ± 4.6	0.013	0.002 ± 0.001	0.009 ± 0.004
BbF	0.69 ± 0.07	9.9	110 ± 5.8	6.2 ± 9.0	12.5 ± 4.4	0.011	0.003 ± 0.001	0.013 ± 0.004
BkF	1.01 ± 0.10	8.9	106 ± 5.8	4.4 ± 6.0	12.9 ± 3.7	0.011	0.002 ± 0.001	0.004 ± 0.004
BaP	0.77 ± 0.03	4.4	117 ± 6.1	2.8 ± 7.7	16.4 ± 7.8	0.015	0.004 ± 0.002	0.008 ± 0.005
IP	0.77 ± 0.08	10.7	103 ± 1.4	3.2 ± 3.4	14.8 ± 6.7	0.011	0.004 ± 0.001	0.010 ± 0.004
DBA	0.83 ± 0.12	13.9	102 ± 0.8	6.1 ± 6.1	15.8 ± 5.9	0.014	0.004 ± 0.002	0.008 ± 0.005
BP	0.95 ± 0.11	11.6	109 ± 5.3	7.5 ± 4.6	14.5 ± 5.0	0.009	0.002 ± 0.001	0.004 ± 0.003
SS1	1.22 ± 0.08	1.6	103 ± 5.4	6.1 ± 3.1	8.3 ± 0.5	-	-	-
SS2	1.40 ± 0.06	9.2	103 ± 2.4	3.7 ± 6.5	9.1 ± 2.5	-	-	-

^a See Table 2 for the definitions of compound abbreviations; ^b SD: standard deviation; CV: coefficient of variation; R: recoveries of check standard; RPD: relative percent differences.

3. Results and Discussion

3.1. PAHs Concentrations in the Surface Seawater

The water depth of the four seawater sampling points in this study were between 587 and 852 m, and the surface seawater temperature and salinity ranged between 30.4 and 30.6 °C and between 33.9 and 34.0 psu, respectively (Table 4). There were no significant differences in temperature and salinity between the four areas, indicating that the hydrological conditions are similar. The concentration of total PAHs (TPAHs) in the dissolved phase of seawater at the four sampling points ranged from 2.297 to 4.001 ng/L , with an average concentration of $3.056 \pm 0.727 \text{ ng/L}$. The concentrations of 16 individual PAHs in each seawater sample were determined, indicating the suitability of the method used in the measurement of low PAHs concentrations in seawater. The composition and source of PAHs in seawater and their biological and physicochemical effects in the environment can be further explored.

Verbruggen [10] derived 16 PAH maximum allowable concentrations (MPCs) for the ecosystem. This MPCs value were derived using ecotoxicology and environmental chemistry data, and represents the potential risk of the substance to the ecosystem. It is recognized as a scientific reference for evaluating PAH's harm to the ecology and environmental quality [20]. In addition, generally negligible concentrations (NCs) can be defined as one percent of MPCs ($\text{MPC}/100$) [21]. Therefore, the NCs value of 16 PAHs are calculated based on MPCs. The comparison of dissolved phase PAHs with NCs and MPCs at four sites is shown in Figure 3. The concentrations of NA, ACY, ACE, FL, PHE, AN, FLU, PY, BkF, and BaP in the dissolved phases of seawater at each site were lower than NCs, which means that the risk of adverse effects on aquatic organisms is negligible. The concentrations of CH and BbF in one water sample were higher than NCs value but lower than MPCs value, while BaA, IP and BP in four water samples were higher than NCs value but also

lower than MPCs value. These results indicate that the risk of adverse effects on aquatic organisms is acceptable. The DBA concentration of three water samples were between the NCs value and the MPCs value, and one water sample was higher than the MPCs value, which represents the risk of possible negative effects on aquatic organisms [21,22]. It is worth noting that although five-ring (DBA) and six-ring (IP and BP) PAHs contribute little to TPAHs (0.5–9.2%), the observed concentration was higher than that of NCs in a higher proportion than low-ring PAHs (Figure 3). High-ring PAHs are generally more hydrophobic, with a higher Kow value ($\log Kow = 6.13\text{--}6.91$) and lower water solubility ($<1\text{ }\mu\text{g/L}$), so the dissolved phase concentration in water is extremely low. Some studies may fail to measure the concentration of some high-ring PAH due to the small sampling volume and low concentration factor, and ignore their influence [23–25]. However, the results of this study indicate that the potential pollution source and ecological impact of the dissolved phase high-ring PAHs in seawater require further attention. High-ring PAHs are generally more toxic and may be mainly caused by traffic emissions and burning of fossil fuels [26].

Table 4. Concentrations of dissolved polycyclic aromatic hydrocarbons in seawater collected offshore of southern Taiwan.

Item	MDL ^a	MPCs ^b	T1	T2	T3	T4
Water depth (m)	–	–	683	626	852	587
Water temp (°C)	–	–	30.4	30.5	30.6	30.5
Salinity (psu)	–	–	34.0	34.0	34.0	33.9
PAHs (ng/L)						
Naphthalene (NA)	0.001	2000	0.030	0.037	0.043	0.092
Acenaphthylene (ACY)	0.001	130	0.012	0.013	0.017	0.022
Acenaphthene (ACE)	0.006	380	0.026	0.016	0.019	0.406
Fluorene (FL)	0.002	300	0.137	0.179	0.235	0.552
Phenanthrene (PHE)	0.004	1100	1.215	1.624	2.208	2.169
Anthracene (AN)	0.009	100	0.135	0.098	0.134	0.160
Fluoranthene (FLU)	0.007	120	0.087	0.078	0.120	0.014
Pyrene (PY)	0.012	23	0.130	0.102	0.167	0.048
Benzo[a]anthracene (BaA)	0.013	1.2	0.058	0.016	0.028	0.021
Chrysene (CH)	0.013	7	0.114	0.017	0.029	0.021
Benzo[b]fluoranthene (BbF)	0.011	17	0.094	0.018	0.033	0.221
Benzo[k]fluoranthene (BkF)	0.011	17	0.078	0.012	0.014	0.033
Benzo[a]pyrene (BaP)	0.015	10	0.094	0.020	0.029	0.025
Indeno[1,2,3-c,d]pyrene (IP)	0.011	0.27	0.202	0.016	0.026	0.148
Dibenz[a,h]anthracene (DBA)	0.014	0.14	0.253	0.040	0.065	0.046
Benzo[g,h,i]perylene (BP)	0.009	0.82	0.075	0.012	0.020	0.025
Total PAHs (sum of 16 PAHs)	–	–	2.740	2.297	3.187	4.001

^a MDL: method detection limit; ^b MPCs: maximum allowable concentrations.

Comparing the concentrations of dissolved PAHs in surface seawater reported in different regions of the world (Table 5), the concentration of dissolved PAHs in the offshore southern Taiwan ($3.06 \pm 0.73\text{ ng/L}$) is slightly higher than that of the Southern Ocean ($2.3 \pm 0.52\text{ ng/L}$), Indian Ocean ($2.7 \pm 1.0\text{ ng/L}$) [17], Atlantic Ocean (1.4 ng/L), and North Pacific Ocean (1.3 ng/L) [18]. It is slightly lower than the adjacent seas such as the South China Sea (4.7 ng/L) [23] and the south eastern Japan Sea ($6.0 \pm 1.8\text{ ng/L}$) [27]. However, it is lower than the Gulf of Mexico ($35.5 \pm 9.0\text{ ng/L}$) [28], the Xiamen coast, China (62 ng/L) [29], the Hainan Island coast, China ($104 \pm 38\text{ ng/L}$) [30], and the Taiwan Strait ($62 \pm 8.3\text{ ng/L}$) [31]. The distribution of PAHs concentrations in seawater in different regions of the world shows that nearshore seas with anthropogenic influence are higher than the adjacent sea and oceanic areas. The concentrations of dissolved PAHs in seawater are gradually diluted and diffused into the offshore and far seas with the input of land and coastal anthropogenic activities [32–34].

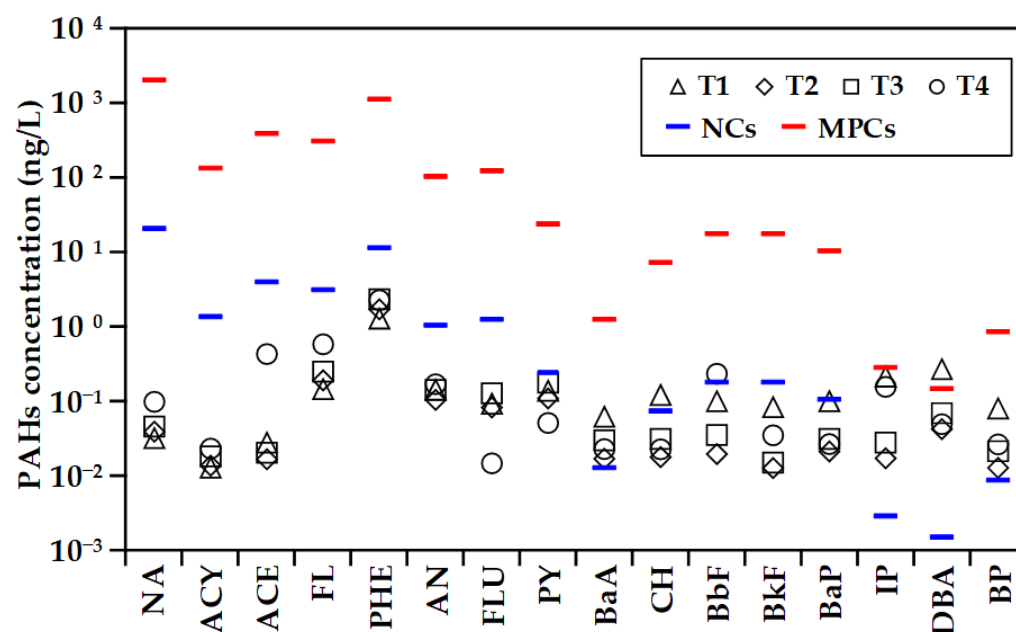


Figure 3. Comparison of PAHs measured in seawater with NCs (negligible concentrations) and MPCs (maximum permissible concentrations).

Table 5. Comparing the concentrations of dissolved PAHs in surface seawater reported in different regions of the world.

Locations	No. of PAHs	Sample Volume (L)	Total PAHs (ng/L)	Reference
Pacific Ocean	21	200	4.0 ± 1.4	[17]
Southern Ocean	21	200	2.3 ± 0.52	
Indian Ocean	21	200	2.7 ± 1.0	
East Asia	15	45–181	3.0–3.7 (3.3)	[18]
North Pacific	15	120–166	1.0–1.6 (1.3)	
Arctic Ocean	15	49–142	0.82–2.1 (1.4)	
Northwestern Pacific Ocean	15	60–100	5.5–15.6 (9.4)	[35]
East China Sea	16	3	380–4000	[36]
Northern South China Sea	15	4	0.98–13 (4.7)	[23]
South eastern Japan Sea	13	3	3.7–10 (6.0 ± 1.8)	[27]
East and South China Seas	15	765–1080	30.4–120.3 (66 ± 32)	[16]
Taiwan Strait	15	8	53–79 (62 ± 8.3)	[31]
Gulf of Mexico	43	20	24.2–58 (35.5 ± 9.0)	[28]
Xiamen coast, China	13	4	18–250 (62)	[29]
Hainan Island coast, China	15	12–18	28–207 (104 ± 38)	[30]
Kaohsiung Harbor and adjacent areas, Taiwan	15	1	1.25–9.39 (3.85 ± 2.43)	[24]
Kenting coast, Taiwan	22	40	0.9–8.0 (2.17 ± 1.19)	[37]
Offshore southern Taiwan	16	100	2.30–4.00 (3.06 ± 0.73)	This study

3.2. Composition Patterns of PAHs

In this study, PHE was the most dominant PAHs in the surface water collected offshore of southern Taiwan, accounting for about $59.6 \pm 12.6\%$ of TPAHs, followed by FL, accounting for about $8.5 \pm 3.7\%$ of TPAHs, and the remaining 14 types of PAHs accounting for about 0.5–4.3% of TPAHs. These results are consistent with that in the coastal areas of Taiwan [24,37], southeastern Japan Sea [27], Bransfield Strait, Antarctica [38], Arctic fjords [7], Pacific Ocean, the Indian Ocean, and the Southern Ocean [17]. Szatylowicz and Skoczko [5] pointed out that the PHE of soot from burning coal and wood accounts for 55–67% of the total low-ring PAHs. In addition, unburned coal also contains high PHE, accounting for 44–69% of the TPAHs [39]. Coal is the most commonly used energy source

in industries such as steel plants, power plants, etc. The PAHs generated during the coal combustion process can be transported through atmospheric, wet and dry deposition, and surface runoff into the coast and ocean. Thor et al. [14] showed that PHE (5690 ng/L) is the most dominant component in the washwater of marine open-loop scrubbers, which accounts for about 35.5% of TPAHs, followed by NA (4790 ng/L), which accounts for about 29.9%. The concentration of PHE and NA in washwater is about 5000 and 1000 times that of background seawater. Moreover, it is known that a predominance of low-ring PAHs was observed in urban wastewater where PHE, NA, FLU, and PY are usually the most abundant compounds [40]. Based on the above, it seems not surprising that PHE is the most important PAH compound in seawater. According to the structure of PAHs, 16 PAHs can be divided into two-, three-, four-, five-, and six-ring PAHs. The composition percentage of two- to six-ring PAHs in the dissolved phase of seawater offshore southern Taiwan is shown in Figure 4. The dissolved phase of PAHs is dominated by three-ring PAHs, which account for about 55.7–84.0% of TPAHs, with an average of $76.1 \pm 13.6\%$ (Figure 4). The average composition percentages of two-, four-, five-, and six-ring PAHs were $1.6 \pm 0.5\%$, $9.2 \pm 4.9\%$, $8.8 \pm 7.0\%$, and $4.3 \pm 4.1\%$, respectively. The lowest percentage of two-ring PAH in seawater may be due to its high volatility and bioavailability. The medium- and high-ring PAHs (four- to six-ring) may be easily combined with particles and deposited on the seafloor due to their relatively high hydrophobicity and low water solubility [7]. The advantages of three-ring PAH reflect the presence of combustion products from low-temperature pyrolysis processes and/or petroleum sources [41,42]. PAHs in most seawaters are also mainly composed of three-ring PAH, such as southeastern Japan Sea [27], Northern South China Sea [23], and East China Sea [36]. Petroleum sources and coal/wood burning sources of PAHs may be the main contributors to 3-ring PAH [17].

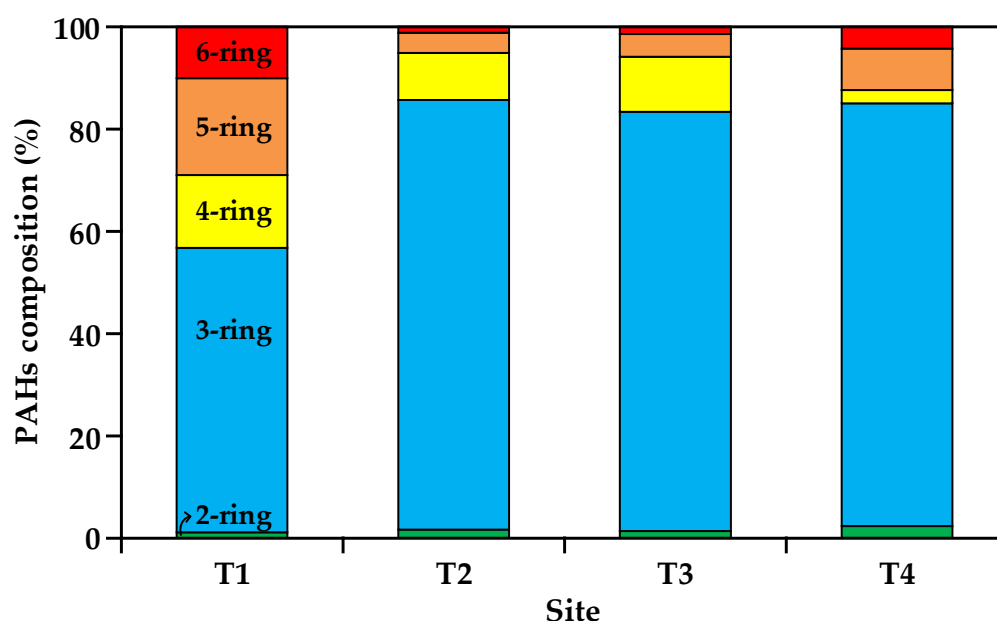


Figure 4. Distribution of composition percentage of two- to six-ring PAHs.

3.3. Identification of PAHs Sources

This study used the diagnostic ratio to assess the potential source of PAHs. The $AN/(AN + PHE)$, $FLU/(FLU + PY)$, $BaA/(BaA + CH)$, and $IP/(IP + BP)$ were used to evaluate the potential sources of PAHs in seawater based on their calculated ratio [26]. When $AN/(AN + PHE) < 0.1$, it is regarded as the petrogenic source, while > 0.1 represents the pyrogenic source + [43]. $FLU/(FLU + PY) < 0.4$ means petroleum source, $FLU/(FLU + PY)$ between 0.4 and 0.5 means petroleum combustion (including traffic emissions and burning crude oil), $FLU/(FLU + PY) > 0.5$ means grass, wood, and coal combustion. The ratio of $BaA/(BaA + CH) < 0.2$ is the source of petroleum, between 0.2 and 0.35 is the mixed

source of petroleum and combustion, and >0.35 is the source of combustion. When the pollution source is combustion plants and coal, its $IP/(IP + BP)$ is greater than 0.5. If it is the combustion products of gasoline, diesel, kerosene, etc., the ratio of $IP/(IP + BP)$ is between 0.2 and 0.5, and $IP/(IP + BP) < 0.2$, the pollution source may be petroleum.

The $AN/(AN + PHE)$ ratios of four seawater samples (T1–T4) in the offshore waters of southern Taiwan ranged from 0.06 to 0.10, indicating that PAH may come from petroleum sources (Figure 5). The $FLU/(FLU + PY)$ ratios of the four seawater samples were 0.40, 0.43, 0.42, and 0.22, respectively. Except for the oil source at the T4 station, the other three stations belonged to the oil burning sources (Figure 5A). The $BaA/(BaA + CH)$ ratios of the four (T1–T4) seawater samples were 0.34, 0.49, 0.49, and 0.50, respectively. Except for the T1 station which is a mixture of oil and combustion sources, the other three stations belong to combustion sources (Figure 5B). The ratio of $IP/(IP + BP)$ ranged between 0.57 and 0.86, indicating that PAHs may come from the combustion source of liquid fuels (Figure 5C). In summary, the PAHs source of the four seawater samples include petroleum, combustion petroleum, and combustion biomass sources. This may be due to the mixing of PAHs generated by human activities on land and nearshores, including ship traffic, untreated and/or treated wastewater, river input, and atmospheric deposition, distributed through ocean currents and the atmosphere, resulting in a mixture of PAHs sources. It would be interesting to know the contribution of each possible source, but it is not easy to obtain. However, based on the PAHs concentration in ship scrubber washwater reported by Thor et al. [14], the ratios of $AN/(AN + PHE)$, $FLU/(FLU + PY)$, $BaA/(BaA + CH)$ and $IP/(IP + BP)$ are calculated to be 0.02, 0.50, 0.45, and 0.26. Among them, the ratio of $IP/(IP + BP)$ shows that the washed PAHs is mainly from combustion petroleum, which corresponds to the actual situation, that is, ships combustion heavy oil. This result indicates that $IP/(IP + BP)$ may be a suitable indicator for the contribution of seawater PAHs from washwater. In addition, the diagnostic ratio of the washwater also needs to be established in the future, which is of great help in evaluating the impact of the discharges on the PAHs concentration of seawater.

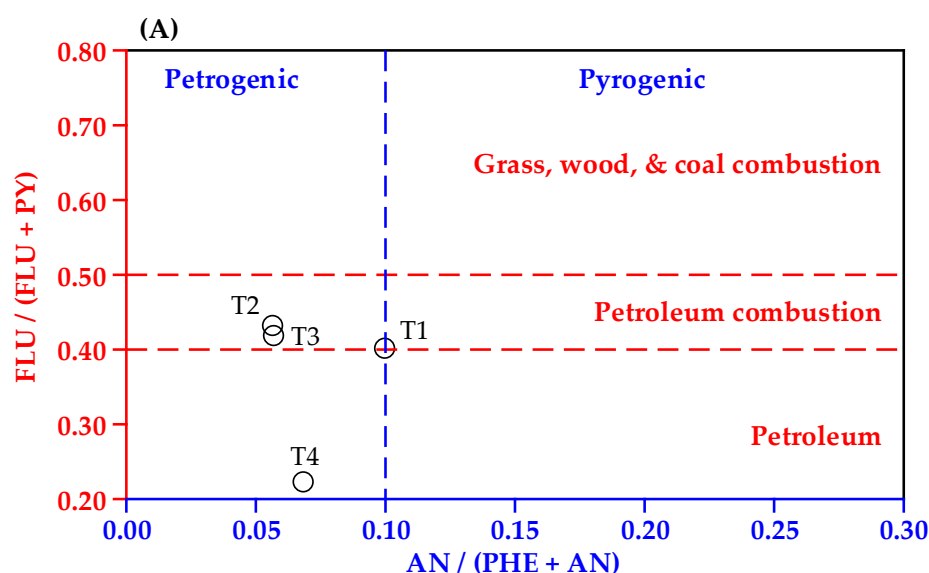


Figure 5. Cont.

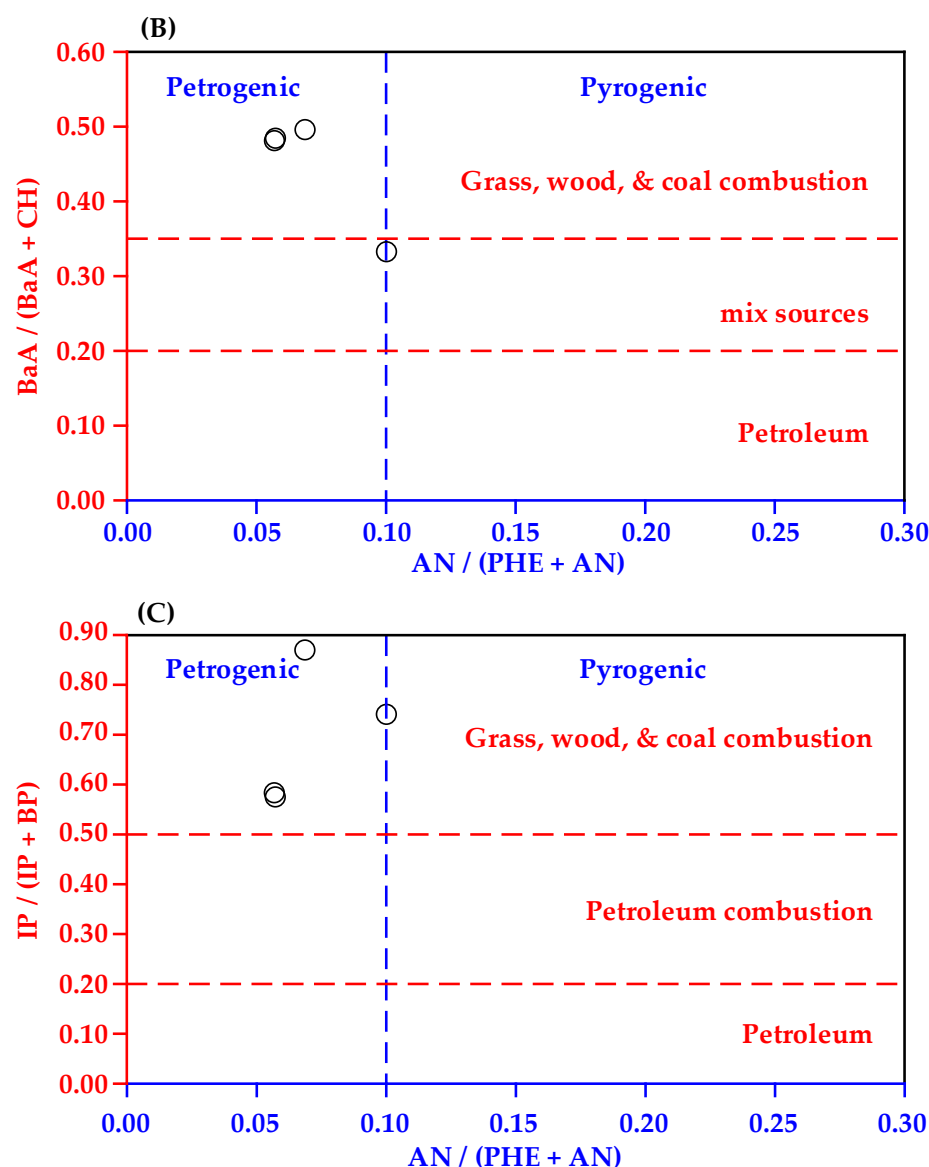


Figure 5. Diagnostic ratios of PAHs and possible sources in surface seawater collected offshore of southern Taiwan. $AN/(PHE + AN)$ vs (A) $FLU/(FLU + PY)$, (B) $BaA/(BaA + CH)$, and (C) $IP/(IP + BP)$.

4. Conclusions

This study developed an on-site large-volume pre-concentration method for the determination of low-concentration PAH in seawater. The detection limits were 0.001 (NA)–0.014 (DBA) ng/L for individual PAHs. The field blank, equipment blank, and laboratory blank samples were all below the two times value of the detection limit, indicating that the sampling and analysis process were not significantly contaminated. The concentrations of 16 PAHs were measured in surface seawaters collected from the offshore, which means that the method in this study is suitable for the measurement of low-concentration PAHs in seawater. Although the large-volume pre-concentration method takes time (about 1.7 h per sample) to concentrate the water sample, it can detect low-concentration PAHs in seawater, especially PAHs with high ring numbers that are often ignored. The concentration of dissolved phase TPAHs in surface seawater samples collected offshore of southern Taiwan ranged from 2.297 to 4.001 ng/L, with an average of 3.056 ± 0.727 ng/L. The concentration of TPAHs in the offshore waters of southern Taiwan is higher than that of adjacent seas and oceanic areas, but lower than that of coastal waters. Among the 16 PAHs, PHE is the most important compound ($59.6 \pm 12.6\%$ of TPAHs), followed by FL ($8.5 \pm 3.7\%$ of TPAHs). Although the concentration of high-ring PAHs in seawater is relatively lower than that

of low-ring PAHs, the observed concentration of high-ring PAHs poses a higher risk to aquatic organisms than low-ring PAHs. Diagnostic ratio shows that the sources of PAHs in offshore seawater is a mixture of multiple sources. The IP/(IP + BP) may be a suitable indicator for the contribution of seawater PAHs from ship scrubber wastewater. In addition, the diagnostic ratio of the wastewater also needs to be established in the future. The results of this study can be used to establish a baseline of the PAHs concentration in seawater, including ports and coastal waters. The method is conducive to assess the impacts of wastewater discharged from scrubbers on the marine ecological and environmental health.

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