

Concurrent Extraction and Analysis of Atmospheric Particulate Matter-bound PBDEs, PAHs, Nitrated PAHs, and OPEs

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ABSTRACT

This study aimed to develop and validate a robust method for the simultaneous extraction of polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs (N-PAHs), and organophosphate esters (OPEs) bound to atmospheric particulate matter. These compounds are widely distributed pollutants known to have detrimental effects on both human health and the environment. The concurrent microwave extraction took a total of 40 minutes and utilized n-hexane:acetone:dichloromethane (2:2:1 v/v). After a series of cleanup and fractionation steps involving silica gel and alumina columns, PBDEs were analyzed using high-resolution gas chromatography-high-resolution mass spectrometry (HRGC-HRMS), while PAHs, N-PAHs, and OPEs were analyzed using GC-MS/MS. The detected values of the SRM samples (n = 4) were all within 30%, except for 3 N-PAH congeners. The recovery rates for the spiked concentrations (n = 5) were 82.2% ± 8.7%–122% ± 4.4% for PBDEs, 84.2% ± 9.9%–115% ± 17.4% for PAHs, 83.2% ± 2.2%–111% ± 2.5% for N-PAHs, and 93.9% ± 5.3%–111% ± 10.7% for OPEs. These results support the robustness and reliability of the method. The developed method was then applied to real atmospheric PM samples collected from five locations in and around an industrial park in Taiwan during the winter months. Atmospheric PM concentrations ranged from 39.1 to 68.9 μg m⁻³, with PM-bound OPEs having the highest concentrations (432–2815 pg m⁻³), followed by PAHs (503–1774 pg m⁻³), N-PAHs (39.1–277 pg m⁻³), and PBDEs (5.07–13.6 pg m⁻³). This method provides a reliable and fast approach to extracting and analyzing multiple compounds from a single atmospheric PM sample. The research contributes significantly to the ongoing efforts to address the critical issue of air pollution.


Keywords: GC-MS/MS, HRGC-HRMS, Microwave extraction, Simultaneous extraction

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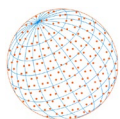
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1 INTRODUCTION

Atmospheric particulate matter (PM), composed of tiny airborne particles, plays a crucial role in environmental and public health concerns (Manullang *et al.*, 2023). Elevated levels of atmospheric PM have been linked to compromised air quality, leading to adverse health effects (Yadav *et al.*, 2020; Lin *et al.*, 2022). These particles constitute a complex mixture of organic and inorganic compounds with various sources, including industrial emissions. Among the organic compounds associated with particulate matter, polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs (N-PAHs), and organophosphate esters (OPEs) are of particular interest due to their detrimental effects on human health and the environment (Doherty *et al.*, 2019; He *et al.*, 2021; Lao *et al.*, 2022; Akinpelumi *et al.*, 2023; Gomes *et al.*, 2023).



PAHs, derived from incomplete combustion and pyrolysis of organic matter and unburnt petroleum products, are of great concern due to their potential carcinogenic and mutagenic properties (Cheruiyot *et al.*, 2015). These compounds are primarily generated by anthropogenic activities, such as traffic, domestic heating, biomass burning, and industrial processes (Lara *et al.*, 2022). It is worth noting that, despite being well-studied, the full spectrum of PAH derivatives, e.g., N-PAHs, and their carcinogenic properties remain an area of active investigation. In the atmosphere, N-PAHs can form from the photo-oxidation reactions of PAHs (Lee *et al.*, 2022). They can also be formed during combustion processes (Lee *et al.*, 2022). These compounds, characterized by their higher molecular weights and lower vapor pressures, have an elevated tendency to adsorb onto particulate matter compared to their parent PAH compound (Lara *et al.*, 2022). Studies have shown that N-PAHs may pose even higher health risks compared to their parent PAHs, due to their direct mutagenic potency (Zhang *et al.*, 2022). However, these compounds are often underrepresented in air quality monitoring networks.

Polybrominated diphenyl ethers (PBDEs) are widely known as flame retardants and have a history of use in consumer goods (Abbasi *et al.*, 2015). Despite the phase-out of certain formulations, ongoing emissions persist due to the presence of in-use products containing these chemicals (Abbasi *et al.*, 2019). Additionally, these compounds have been shown to form in combustion sources (Altarawneh *et al.*, 2020; Yang *et al.*, 2022). PBDE flame retardants have been replaced by alternative flame retardants, particularly organophosphate esters (OPEs), which have also become increasingly prevalent in the environment (Kung *et al.*, 2022). These compounds have been detected in various environmental samples and even in human biota, raising concerns about their environmental impact and potential health risks (Kung *et al.*, 2022).

As these organic compounds are present in atmospheric PM, the challenges of monitoring their concentrations, variations, and potential effects on public health and the environment have become more evident. Furthermore, quantifying these compounds in trace amounts (ng m^{-3} and pg m^{-3}) within a complex environmental matrix such as atmospheric PM is a demanding endeavor, necessitating the development of reliable, sensitive, and selective analytical methods.

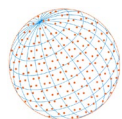
The techniques widely used for solid extraction of semi-volatile and non-volatile compounds include Soxhlet, sonication, pressurized liquid extraction, and microwave extraction. Pressurized liquid extraction and microwave extraction improve on the more traditional extraction techniques, i.e., Soxhlet and sonification by using automation, reducing the amount of solvent used, and quickening the extraction process. Clark *et al.* (2015) extracted eight groups of compounds, including PAHs, pesticides, and flame retardants, from atmospheric particulate matter using a pressurized liquid extraction technique, achieving acceptable recoveries. Microwave extraction is faster, reducing the extraction times from hours to minutes. It is also more energy efficient, selective, and uses minimal solvent (Nieto *et al.*, 2008). Therefore, microwave extraction is a better technique if green analytical chemistry concepts and extraction time are considered. The technique has been used to simultaneously extract PAHs, organic acids, pesticides, phthalates, and PCBs (Alvarez-Avilés *et al.*, 2007), and PAHs, N-PAHs, and oxygenated PAHs in atmospheric particles (Lara *et al.*, 2022).

The primary objectives of this study were to develop and validate a robust method for simultaneous extraction of PAHs, OPEs, NPAHs, and PBDEs from a single PM sample. Furthermore, we aimed to apply this method to samples collected from and around an industrial park during winter. The accuracy and reliability of our methods were evaluated using Standard Reference Materials (SRMs) and employing quality control measures with deuterated and isotopically labeled standards. Actual atmospheric samples were collected from five locations in and around an industrial park in Taiwan in November and January and analyzed for the four organic contaminants. By addressing these objectives, we aim to establish a reliable and fast extraction method and contribute valuable data to the fields of environmental analysis while also providing insights that may guide future research in air quality management and pollution control.

2 METHODS

2.1 Chemicals

All reagents, materials, and analytical standards were purchased from commercially available



vendors. The deuterated standards for OPEs (TEP-d15, TCPP-d18, TCEP-d12, TBOEP-d27, TDCIP-d15, and TPhP-d15), PAHs (Acp-d10, Phe-d10, Chr-d12, and Per-d12), and N-PAHs (1-NitroNap-d7 and 9-NitroAnt-d9), and the isotopically-labeled PBDE standards ($^{13}\text{C}_{12}$ -PBDE 28, $^{13}\text{C}_{12}$ -PBDE 47, $^{13}\text{C}_{12}$ -PBDE 99, $^{13}\text{C}_{12}$ -PBDE 154, $^{13}\text{C}_{12}$ -PBDE 153, $^{13}\text{C}_{12}$ -PBDE 183, $^{13}\text{C}_{12}$ -PBDE 197, $^{13}\text{C}_{12}$ -PBDE 207, and $^{13}\text{C}_{12}$ -PBDE 209) were purchased from AccuStandard. TBP-d27 and 6-NitroChr-d11 were purchased from Chiron, while 1-NitroPyr-d9 was purchased from TCI, and 1-NitroNap-d7 from TORONTO. The reagents including hexane, acetone, and dichloromethane were bought from Merck, and the glass fiber filters from ADVANTEC. Helium gas was purchased from a local vendor.

2.2 Standard Reference Materials (SRMs)

The accuracy and precision of the extraction and analytical method were evaluated using Standard Reference Materials (SRMs). SRM 2585 “Organic Contaminants in House Dust” was used for the analysis of PBDEs, PAHs, and OPEs, while SRM 2975 “Diesel Particulate Matter” was used for the analysis of N-PAHs. 100 mg of SRM 2585 and 10 mg of SRM 2975 were measured and extracted via microwave extraction, as shown in Fig. 1 and described in Section 2.4. After extraction and cleanup, gas chromatography and triple quadrupole tandem mass (Agilent 7000D) (GC-MS/MS) were used for the analysis of PAHs, N-PAHs, and OPEs and high-resolution gas chromatography (6890N) and high-resolution mass spectrometry (Micromass AutoSpec-Ultima) (HRGC-HRMS) for PBDE analysis. Identification of congeners was performed using the retention time (± 0.05 min) and the ions and their ratios ($\pm 20\%$). The quantification of the congeners was carried out using

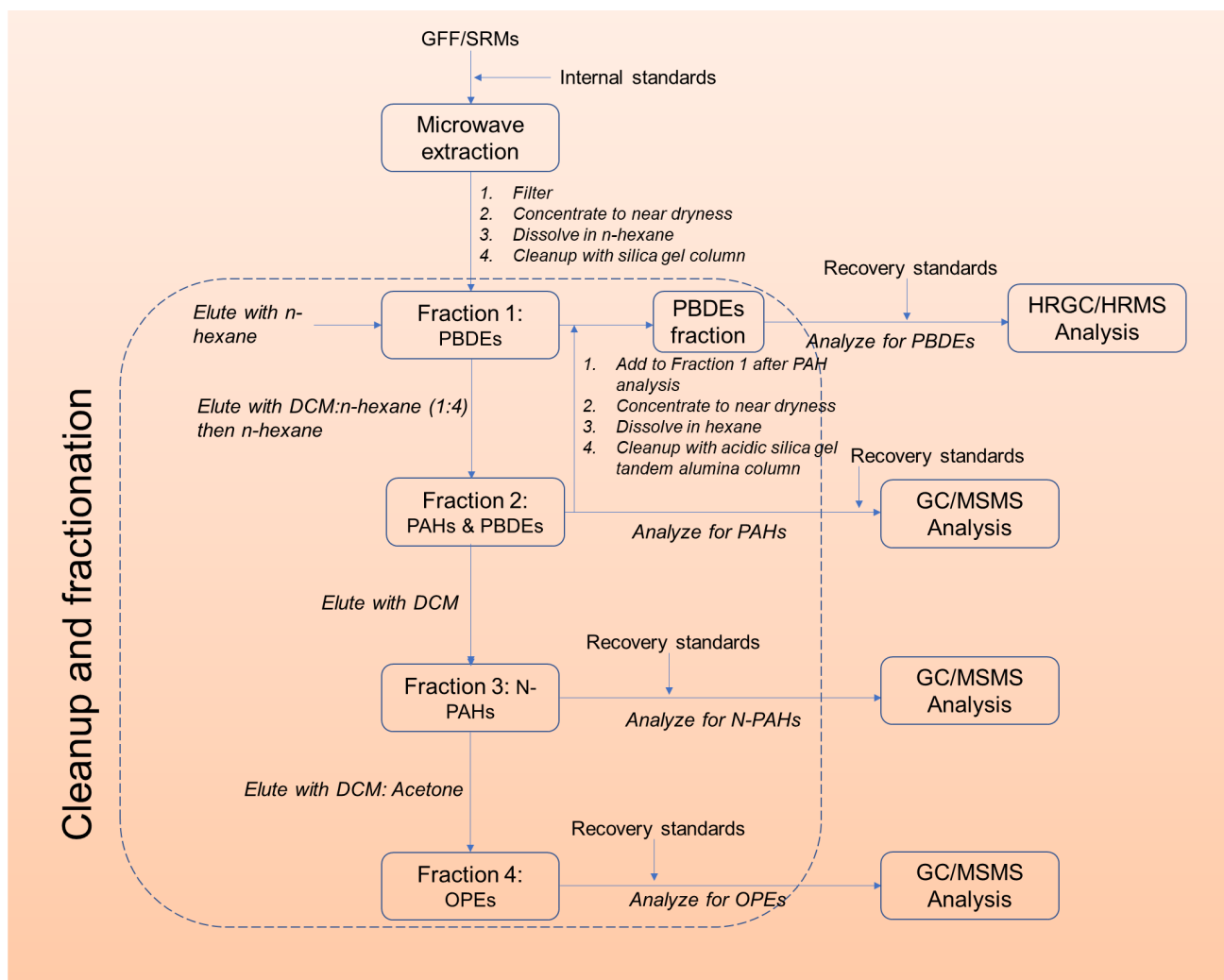
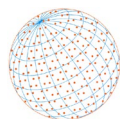


Fig. 1. The flow chart of the sample cleanup process.

**Table 1.** Relative time (RT), ion pairs, quantitation standards, and HRGC/HRMS QC/QA analysis parameters for the detection of PM-bound PBDEs.

	RT (min)	Ions (m/z) 1 st and 2 nd	Quantitation standard	SRM 2585			Reproducibility and linearity			
				Reported (ng g ⁻¹)	Detected (ng g ⁻¹) (N = 4)	Error (%)	n = 5 (%)	LOD S/N > 3 (pg)	Ranges (ppb)	RSD (%)
PBDE 28	5.39	405.8026, 407.8006	¹³ C ₁₂ -PBDE 28	46.9 ± 4.40	38 ± 2	19.0	87.6 ± 5.3	0.31	1–400	< 30
PBDE 47	7.44	483.7131, 485.7111	¹³ C ₁₂ -PBDE 47	497 ± 46	428 ± 38	13.9	92.4 ± 10.5	0.62	1–400	< 30
PBDE 100	9.37	563.6217, 565.6197	¹³ C ₁₂ -PBDE 99	145 ± 11	114 ± 9	21.4	82.2 ± 8.7	2.17	1–400	< 30
PBDE 99	9.92	563.6217, 565.6197	¹³ C ₁₂ -PBDE 99	892 ± 53	758 ± 55	15.0	–	–	–	–
PBDE 154	11.42	481.6975, 483.6955	¹³ C ₁₂ -PBDE 154	83.5 ± 2.0	69 ± 2	17.4	92.4 ± 8.8	2.61	2–800	< 30
PBDE 153	12.14	481.6975, 483.6955	¹³ C ₁₂ -PBDE 153	119 ± 1	106 ± 3	10.9	88.2 ± 5.6	2.98	2–800	< 30
PBDE 183	14.11	561.6060, 563.6040	¹³ C ₁₂ -PBDE 183	43.0 ± 3.5	37 ± 2	14.0	89.8 ± 6.9	4.49	2–800	< 30
PBDE 197	16.26	639.5165, 641.5145	¹³ C ₁₂ -PBDE 197	–	25 ± 1	–	95.7 ± 4.6	2.90	2–800	< 30
PBDE 203	16.51	639.5165, 641.5145	¹³ C ₁₂ -PBDE 197	36.7 ± 6.4	32 ± 2	12.8	91.7 ± 8.9	1.78	2–800	< 30
PBDE 196	16.62	639.5165, 641.5145	¹³ C ₁₂ -PBDE 197	–	51 ± 6	–	100 ± 11.2	2.89	2–800	< 30
PBDE 208	17.76	719.4250, 721.4230	¹³ C ₁₂ -PBDE 207	–	91 ± 5	–	122 ± 4.4	3.70	5–2000	< 30
PBDE 207	17.86	719.4250, 721.4230	¹³ C ₁₂ -PBDE 207	–	256 ± 10	–	–	6.43	5–2000	< 30
PBDE 206	18.12	719.4250, 721.4230	¹³ C ₁₂ -PBDE 207	271 ± 42	333 ± 44	18.6	–	1.38	5–2000	< 30
PBDE 209	19.20	797.3355, 799.3335	¹³ C ₁₂ -PBDE 209	2510 ± 190	2172 ± 119	13.5	–	4.26	5–2000	< 30

5–7 point external calibration curves which contain known amounts of internal and surrogate standards spiked before extraction. The detected concentrations were compared to the reported certified, reference, and informational values of both SRMs, as shown in Table 1 and Table 2.

2.3 Sampling of Atmospheric Total Particulate Matter (PM)

Atmospheric particulate matter (PM) was collected from five designated locations (A1–A5) surrounding Liuying Technology Industrial Park in Tainan, Taiwan, during two periods in winter (24–26 November 2021 and 5–7 January 2022), as shown in Table 3. The primary industries within the industrial park include, electrical and electronic equipment, machinery manufacturing, and metal manufacturing. Sites A1 and A2 were situated in residential areas, whereas A3 and A4 were located within an elementary school and junior high school, respectively. Site A5 was specifically located within the industrial park. Additionally, meteorological parameters including, temperature, relative humidity, wind speed, and wind direction, during sampling were collected. The sampling followed the U.S. EPA, 40 CFR Appendix B to Part 50 – Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). The PM samples were collected continuously at a flow rate of 1.1 m³ min⁻¹ to 1.7 m³ min⁻¹ for 24 hours on a glass fiber filter (20 cm × 25 cm) using a high-volume air sampler. Prior to sampling, the glass fiber filters were pretreated by rolling them into clean microwave tubes and adding 10 mL of n-hexane, 10 mL of acetone, and 5 mL of dichloromethane, and extracting them at 120°C for 30 min. After sampling,

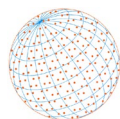


Table 2. Relative time (RT), precursor and product ion pairs, quantitation standards, and GC-MS/MS QC/QA analysis parameters for the detection of PM-bound PAHs, N-PAHs, and OPEs.

	RT (min)	Precursor ions (m/z)	Product ions (m/z)	CE (eV)	Quantitation standard	SRM 2585 and SRM 2975				Reproducibility and linearity			
						Reported	Detected ($\mu\text{g kg}^{-1}$) (N = 4)	Error (%)	n = 5 (%)	MDL (ng)	Linear ranges (ppb)	RSD (%)	
<i>Polycyclic aromatic hydrocarbons (PAHs)</i>													
Nap	6.51	128, 128	102, 127	22, 25	Nap-d8	266 ± 8	191 ± 75.3	28.1	116 ± 12.4	8.76	4–400	< 25	
AcPy	8.01	152, 152	150, 151	40, 40	AcP-d10	–	24.4 ± 6.6	–	96.4 ± 8.00	1.28	4–400	< 25	
AcP	8.17	154, 153	152, 152	40, 40	AcP-d10	–	34.6 ± 30.2	–	106 ± 7.70	0.73	4–400	< 25	
Fl	8.73	166, 166, 166	165, 164, 166	30, 25, 20	AcP-d10	–	43.7 ± 8.2	–	–	–	4–400	< 25	
Phe	10.53	178, 178	178, 176	20, 20	Phe-d10	1920 ± 20	1833 ± 16.8	4.53	115 ± 17.4	4.52	4–400	< 25	
Ant	10.58	178, 178	178, 176	34, 34	Phe-d10	96.0 ± 5.2	77.3 ± 14.6	19.5	99.6 ± 9.60	2.39	4–400	< 25	
Fla	13.88	202, 202	200, 201	50, 30	Phe-d10	4380 ± 100	4701 ± 8.7	6.82	107 ± 13.0	5.86	4–400	< 25	
Pyr	14.73	202, 202	200, 201	45, 30	Phe-d10	3290 ± 30	3557 ± 30.6	7.51	112 ± 13.9	6.04	4–400	< 25	
BaA	18.49	228, 228	228, 226	20, 38	Chr-d12	1160 ± 54	1129 ± 30.9	2.65	112 ± 12.6	4.00	4–400	< 25	
Chr	18.74	228, 228	228, 226	20, 38	Chr-d12	2260 ± 60	2826 ± 94.1	20.0	94.3 ± 7.90	3.34	4–400	< 25	
BbF	21.74	252, 250	250, 248	42, 40	Per-d12	2700 ± 90	2736 ± 148	0.132	104 ± 3.50	4.69	4–400	< 25	
BkF	21.81	252, 250	250, 248	42, 40	Per-d12	1330 ± 70	1084 ± 29.9	18.5	92.0 ± 15.2	5.87	4–400	< 25	
BaP	22.81	252, 250	250, 248	42, 40	Per-d12	1140 ± 10	997 ± 114	12.5	110 ± 8.30	5.43	4–400	< 25	
IcdP	25.66	276, 276	276, 274	20, 42	Per-d12	2080 ± 100	1550 ± 36.0	25.5	92.9 ± 4.40	4.02	4–400	< 25	
DahA	25.72	278, 278	278, 276	20, 38	Per-d12	301 ± 50	388 ± 55.6	22.4	91.2 ± 7.40	4.00	4–400	< 25	
BghiP	26.61	276, 276	276, 274	20, 38	Per-d12	2280 ± 40	2133 ± 87.2	6.44	84.2 ± 9.90	6.15	4–400	< 25	
<i>Nitroated polycyclic aromatic hydrocarbons (N-PAHs)^a</i>													
1-NitroNap	7.46	173.1, 173.1	129.1, 115.1	5, 25	1-NitroNap-d7	44 ± 2	36.1 ± 1.70	18.0	94.0 ± 1.80	0.088	10–400	< 25	
2-NitroNap	7.94	173.1, 173.1	127.1, 115.1	20, 25	1-NitroNap-d7	118 ± 5	115 ± 5.60	2.62	91.9 ± 4.20	0.066	10–400	< 25	
5-NitroAcp	14.64	199.2, 169.1	152.1, 141.1	35, 10	1-NitroPyr-d9	–	–	–	87.3 ± 9.30	0.187	–	–	
2-NitroFl	16.35	211.1, 211.1	165.1, 194.1	15, 5	1-NitroPyr-d9	–	–	–	–	0.324	10–400	< 25	
9-NitroAnt	17.15	223.1, 223.1	165.1, 193.2	30, 10	9-NitroAnt-d9	3070 ± 280	2519 ± 49.8	17.9	95.6 ± 4.80	0.259	10–400	< 25	
9-NitroPhe	18.69	223.1, 223.1	165.1, 139.1	20, 50	1-NitroPyr-d9	466 ± 13	549 ± 37.3	15.1	83.2 ± 2.20	0.400	10–400	< 25	
3-NitroPhe	19.49	223.1, 223.1	165.1, 139.1	20, 50	1-NitroPyr-d9	190 ± 7	132 ± 13.0	30.7	97.3 ± 1.70	0.179	10–400	< 25	
2-NitroFla	25.17	247.1, 247.1	189.2, 201.2	30, 30	1-NitroPyr-d9	231 ± 32	178 ± 9.80	23.1	–	0.198	10–400	< 25	
3-NitroFla	25.60	247.1, 247.1	189.2, 217.2	30, 10	1-NitroPyr-d9	3800 ± 240	3597 ± 18.4	5.34	97.3 ± 3.40	0.107	10–400	< 25	
4-NitroPyr	26.13	247.1, 247.1	189.2, 201.2	25, 30	1-NitroPyr-d9	–	–	–	102 ± 1.50	0.107	10–400	< 25	
1-NitroPyr	27.04	247.1, 247.1	217.2, 189.1	15, 40	1-NitroPyr-d9	35200 ± 2200	53150 ± 4534	33.8	111 ± 2.50	0.444	10–400	< 25	
7-NitroBaA	30.0	273.1, 273.1	215.2, 189.2	35, 50	6-NitroChr-d11	3570 ± 320	5096 ± 313	29.9	103 ± 0.900	0.166	10–400	< 25	
6-NitroChr	31.35	273.1, 273.1	215.2, 189.2	35, 50	6-NitroChr-d11	2450 ± 330	1652 ± 18.2	32.6	85.7 ± 1.80	0.512	10–400	< 25	

^aSRM 2975 was used.

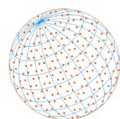


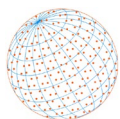
Table 2. (continued).

RT (min)	Precursor ions (m/z)	Product ions (m/z)	CE (eV)	Quantitation standard	SRM 2585 and SRM 2975		Reproducibility and linearity					
					Reported	Detected ($\mu\text{g kg}^{-1}$) (N = 4)	Error (%)	n = 5 (%)	MDL (ng)	Linear ranges (ppb)	RSD (%)	
<i>Organophosphate esters (OPEs)</i>												
TEP	7.69	99, 99, 155	81, 63, 99	25, 40, 6	TEP-d15	-	38.6 ± 5.90	-	103.2 ± 6.80	0.67	5-400	< 30
TIBP	11.64	99, 155	63, 99	27, 6	TBP-d27	-	33.3 ± 0.100	-	105 ± 9.6	1.26	5-400	< 30
TBP	13.47	99, 155	63, 99	27, 6	TBP-d27	276 ± 14	287.3 ± 12.2	3.93	103 ± 4.70	0.75	5-400	< 30
TCPP	16.01	125	99, 81	12, 24	TCPP-d18	1220±350	1164 ± 67.6	4.61	100 ± 4.20	5.59	5-400	< 30
TCEP	16.39	143, 249	117, 125.1	9, 12	TCEP-d12	925±149	876 ± 22.8	5.26	98.0 ± 6.10	5.12	5-400	< 30
TEHP						-	512 ± 39.1	-	102 ± 21.4	7.38		
TBOEP	21.00	199, 113	99.1, 94.7	15, 15	TBOEP-d27	-	97624 ± 6850	-	102 ± 18.4	13.6	20-400	< 30
TDCIP	21.37	209, 191	99, 75	12, 12	TDCIP-d15	-	2164 ± 75.4	-	93.9 ± 5.30	2.09	5-400	< 30
EHDPP	21.79	250, 251, 250	170.1, 175, 94.2	20, 20, 24	TDCIP-d15	-	1025 ± 14.3	-	105 ± 15.9	2.05	5-400	< 30
TPhP	22.68	215, 169	168.1, 115.1	18, 30	TPhP-d15	1190 ± 130	1066 ± 131	10.4	95.3 ± 4.40	3.43	5-400	< 30
TCP	24.61	368	165.1, 196.4, 198.1	36, 33, 36	TPhP-d15	-	693 ± 82.4	-	111 ± 10.7	4.04	10-400	< 30

^a SRM 2975 was used.

Table 3. Coordinates and sampling information of the sampling sites.

Location and description	Longitude	Latitude	Sampling date	Sampling time	Ave. ambient temperature (°C)	Ave. relative humidity (%)	Ave. wind speed (m s ⁻¹)	Ave. wind direction
A1 Residential area	N23°15'41.766"	E120°20'51.543"	2021.11.24-2021.11.25	08:00-08:00	19.8	68.0	1.4	North
A2 Residential area	N23°15'26.553"	E120°22'1.985"	2022.01.05-2022.01.06	08:00-08:00	20.0	89.0	0.6	North Northeast
A3 Elementary school	N23°17'9.798"	E120°21'52.506"	2021.11.26-2021.11.27	13:00-13:00	21.4	73.0	1.7	Northwest
A4 Junior High School	N23°16'48.739"	E120°19'55.033"	2022.01.07-2022.01.08	12:00-12:00	17.0	89.8	0.9	North Northwest
A5 Inside the Industrial Park	N23°17'4.957"	E120°21'4.565"	2021.11.24-2021.11.25	08:00-08:00	20.2	76.8	0.1	West Northwest
			2022.01.05-2022.01.06	08:00-08:00	19.5	84.4	0.2	North Northwest
			2021.11.25-2021.11.26	11:00-11:00	21.8	76.8	1.0	North
			2022.01.06-2022.01.07	10:00-10:00	17.4	84.9	1.4	North Northwest
			2021.11.25-2021.11.26	11:00-11:00	21.1	85.1	1.4	North Northwest
			2022.01.06-2022.01.07	10:00-10:00	17.7	86.4	2.6	North



the filters were covered with aluminum foil and placed in a desiccator. The filters were weighed periodically until a constant weight was attained.

2.4 Microwave Extraction, Cleanup, and Fractionation

The glass filter fiber (GFF) and SRM samples were extracted with 10 mL n-hexane, 10 mL acetone, and 5 mL dichloromethane via microwave extraction. Before extraction internal standards of PBDEs, OPEs, PAHs, and N-PAHs were added. The temperature was then ramped up from room temperature to 75°C in 5 min and held for 5 min. Then the temperature was increased to 120°C in 10 minutes and held for 20 min. After the extraction, the extract was filtered and concentrated to near dryness using a stream of pure nitrogen, then reconstituted in n-hexane before cleanup and fractionation.

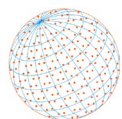
The columns packed with silica gel (4.3 cc × 3) and anhydrous sodium sulfate (2.8 cc × 1) were prewashed sequentially with acetone, dichloromethane, and n-hexane. The sample extract was added to the column with two additional 3 mL n-hexane rinses. Then the column was eluted with two aliquots of 10 mL n-hexane aliquots to obtain the first fraction of PBDEs. The second fraction (PAHs and PBDEs) was eluted with two 10 mL dichloromethane:n-hexane (1:4) and then two additional 5 mL n-hexane aliquots. A third fraction (N-PAHs) was eluted with three aliquots of 10 mL dichloromethane, while a fourth fraction (OPEs) was eluted with two aliquots of 10 mL dichloromethane:acetone (1:2) aliquots. Fractions 2, 3, and 4 were concentrated and analyzed for PAHs, N-PAHs, and OPEs using GC-MS/MS, respectively.

After PAH analysis, the first and second fractions were combined and purified using acidic silica gel: alumina tandem columns. The purification columns, with acidic silica gel (8.6 cc × 1), alumina (12 cc × 1), and anhydrous sodium sulfate (2 cc × 2), were prewashed with 20 mL n-hexane. The extracts were added to the column with three 5 mL n-hexane rinses and then the column was flushed with three additional 10 mL n-hexane aliquots. The extract was discarded, and the acidic silica part was removed. The alumina column was eluted with 10 mL n-hexane, and the extract was retained. Finally, the column was flushed with 25 mL of dichloromethane: n-hexane (1:1), and the extract was collected. Both extracts were concentrated and analyzed for PBDE using HRGC-HRMS.

2.5 Instrumental Analysis

High-resolution gas chromatography and high-resolution mass spectrometry were used to analyze 14 PBDE congeners. A DB-5HT (15 m × 0.25 mm × 0.1 μm) column was utilized for the separation of the congeners. Helium gas, at a flow rate of 1 mL min⁻¹, was used as the carrier gas. The injection temperature was 270°C, with the temperature program as follows: the initial temperature of 100°C was held for 1 min, then ramped up to 180°C at a rate of 20°C min⁻¹, where it was held for 2 min. Subsequently, the temperature was ramped up to 250°C at 8°C min⁻¹ and then further increased to 315°C at 20°C min⁻¹ and held for 4 min. Electron ionization, at a temperature of 250°C, was employed as the ionization source. The resolution power was 10000, and the selected ion monitoring (SIM) mode was adopted for the analysis.

Chemical analysis of 16 PAH, 13 N-PAH, and 11 OPE congeners was carried out using GC-MS/MS. Separation was accomplished using a DB-17MS (30 m × 0.25 mm × 0.25 μm) column. Helium gas was used as the carrier gas with a flow rate set at 1.2 mL min⁻¹, and the injection temperature was maintained at 280°C. For PAH analysis, the temperature program was as follows: initially, the temperature was held at 60°C for 0.5 min, then ramped up to 265°C at a rate of 15°C min⁻¹, followed by a further increase to 305°C at a rate of 5°C min⁻¹ and held at that temperature for 10 min. Electron ionization (EI), at a temperature of 280°C, served as the ionization source, and Multiple Reaction Monitoring (MRM) was employed as the monitoring mode. For N-PAH analysis, the oven temperature was initially held at 120°C for 1 min, then the temperature was raised to 185°C at 30°C min⁻¹. Subsequently, the temperature was further increased at a rate of 8°C min⁻¹ until reaching 310°C, where it was held for 5 minutes. The ionization source and monitoring mode were consistent with the ones chosen for PAH analysis. Finally, the temperature program for OPE analysis was as follows: the temperature was maintained at 45°C for 3 min, then ramped up to 260°C at a rate of 25°C min⁻¹, followed by a further increase to 310°C temperature at a rate of 10°C min⁻¹, where it was held for 8 min. Electron ionization, at a temperature of 250°C, was the ionization source and MRM was used as the monitoring mode.



2.6 Quality Control and Assurance

Five blank GFF samples were spiked with known amounts of target analytes near the mid-point of all calibration curves: PBDE addition concentrations were 20, 40, 100 pg mL^{-1} , PAH concentration was 200 ng mL^{-1} , N-PAH concentration was 200 ng mL^{-1} , and OPE concentration was 200 ng mL^{-1} . Additionally, known amounts of internal standards were spiked prior to extraction and analysis.

In this study, the limit of detection (LOD) for PBDE was defined as the point at which the signal-to-noise ratio exceeded 3. This rigorous criterion ensured the reliable identification of PBDE compounds in our analytical measurements. The method detection limit (MDL), calculated as three times the standard deviation of the instrument's response to the blank, was used to determine the lowest concentrations of PAHs, N-PAHs, and OPEs. The U.S. EPA Definition and Procedure for the Determination of the Method Detection Limit was used to estimate MDLs. In brief, seven sets of pre-cleaned GFF aliquots, used as procedural blanks, were prepared and taken through the analytical method. The MDL was calculated by multiplying the standard deviation of the concentrations measured in each replicated by the student's t-test value for a total of five samples. These well-defined MDL criteria were crucial in ensuring the accuracy and sensitivity of our analytical methods throughout our study.

3 RESULTS AND DISCUSSION

3.1 Reproducibility Studies and SRM

In this section, we present the method validation and reproducibility studies for the detection of atmospheric PM-bound PBDEs, PAHs, N-PAHs, and OPEs. Commercially available standard reference materials, SRM2585 and SRM2975, were employed for method validation. SRM2585 was used for PBDEs, PAHs, and OPEs validation, while SRM2975 was used for NPAHs. Four SRM samples were processed according to our procedures, and the results were compared to the reported values to assess the accuracy and precision of the methods. Table 1 summarizes the relative time, ion pairs, quantitation standards, and QC/QA analysis parameters for the detection of PM-bound PBDEs, while Table 2 provides similar parameters for PM-bound PAHs, N-PAHs, and OPEs. Notably, the detected values for PBDE, PAH, and OPE congeners were below 30% of the reported values, indicating the accuracy and precision of the methodology (Tables 1 and 2). However, for 3-NitroPhe, 1-NitroPyr, and 6-NitroChr, the recovery rates were slightly above 30%. These findings suggest that our technique is generally reliable and accurate for majority of the target compounds.

To assess the reproducibility of our method, five replicates for each analyte were analyzed as presented in Section 2.6. The recovery rates for the spiked concentrations were $82.2\% \pm 8.7\%$ – $122\% \pm 4.4\%$ for PBDEs, $84.2\% \pm 9.9\%$ – $115\% \pm 17.4\%$ for PAHs, $83.2\% \pm 2.2\%$ – $111\% \pm 2.5\%$ for N-PAHs, and $93.9\% \pm 5.3\%$ – $111\% \pm 10.7\%$ for OPEs. These results indicate the robustness and consistency of our analytical procedures. Additionally, standards listed in Table S2 were spiked prior to microwave extraction, cleanup, and analysis. The recovery rates for PBDEs were $48.2\% \pm 8.7\%$ – $83.5\% \pm 28.1\%$, PAHs were $33.7\% \pm 10.8\%$ – $64.4\% \pm 15.1\%$, NPAHs were $49.6\% \pm 15.6\%$ – $97.2\% \pm 31.0\%$, and that for OPEs were $57.6\% \pm 15.5\%$ – $85.9\% \pm 27.0\%$. The recovery rates meet the acceptance criteria for PBDEs 25%–150% (U.S. EPA, 2010) and 30%–150% for PAHs, N-PAHs, and OPEs.

3.2 Estimated Limit of Detection and Method Detection Limit

The limit of detection (LOD) and method detection limits (MDLs) for the target compounds are presented in Tables 1 and 2. The LOD for PBDEs ranged from 0.31–6.43 pg, highlighting the discernable differences in detectability among various PBDE congeners. The variability may stem from differences in molecular structures and chemical properties among the congeners. Notably, higher brominated PBDEs had higher LODs. The extremely low LODs achieved by the HRGC/HRMS instill confidence in analyzing very low PBDE concentrations. The MDL for PAHs, N-PAHs, and OPEs ranged from 0.73–6.15 ng, 0.066–0.512 ng, and 0.67–13.6 ng, respectively. While PAHs and OPEs were measured in nanograms, N-PAHs were in the sub-nanogram range, which signifies the higher sensitivity required for N-PAH analysis due to their relatively low concentrations in the environment. The MDLs in this study were much lower compared to previous studies that used GC-MS (Clark *et al.*, 2015), which is attributed to the high sensitivity of GC-MS/MS.

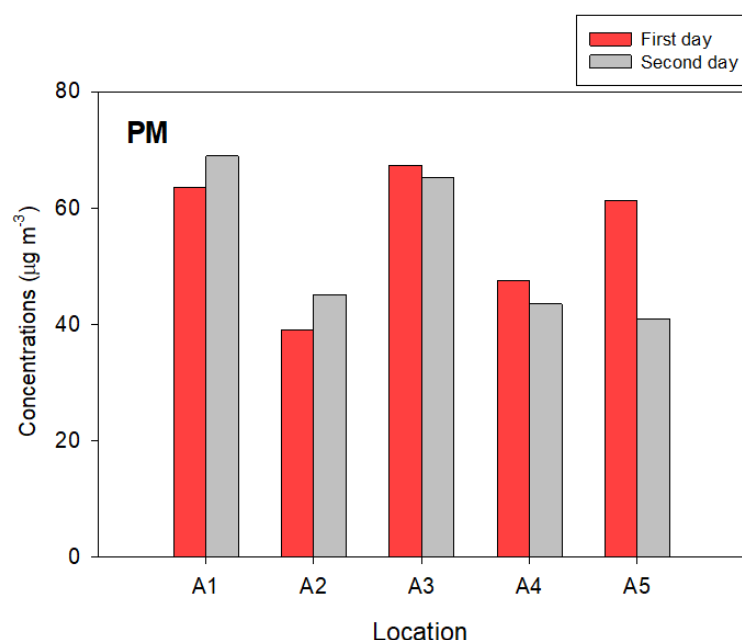
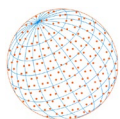


Fig. 2. Atmospheric PM concentrations in the different sampling sites on the first and second days.

3.3 Analysis of Actual Atmospheric PM Samples

The developed extraction and analysis methods were tested on real atmospheric PM samples collected in and around an industrial park in Tainan, Taiwan. Fig. 2 shows the concentrations from the five locations in and around the industrial park. The concentrations in the first day of sampling were in the order of: A3 ($67.4 \mu\text{g m}^{-3}$) > A1 ($63.5 \mu\text{g m}^{-3}$) > A5 ($61.4 \mu\text{g m}^{-3}$) > A4 ($47.6 \mu\text{g m}^{-3}$) > A2 ($39.1 \mu\text{g m}^{-3}$), while in the second day of sampling they were: A1 ($68.9 \mu\text{g m}^{-3}$) > A3 ($65.2 \mu\text{g m}^{-3}$) > A2 ($45.1 \mu\text{g m}^{-3}$) > A4 ($43.5 \mu\text{g m}^{-3}$) > A5 ($41.0 \mu\text{g m}^{-3}$). The concentrations in A1 and A2 were higher in the second than the first day, while the concentrations in A3 to A5 were higher in the first than the second day. Atmospheric PM originates from a variety of sources, including vehicle emissions, cooking activities, construction work, wind-blown dust, tire wear, and the formation of secondary organic aerosols through the oxidation of volatile organic compounds in the atmosphere (Mukherjee and Agrawal, 2017; Hopke *et al.*, 2020; Le *et al.*, 2023).

3.4 Atmospheric Total PM-bound PBDE, PAHs, N-PAHs, and OPEs

The mass concentrations of PM-bound compounds during the two sampling periods are shown in Fig. 3. On average, OPEs ($432\text{--}2815 \text{ pg m}^{-3}$, mean = 1088 pg m^{-3}) had the highest concentrations followed by PAHs ($503\text{--}1774 \text{ pg m}^{-3}$, mean = 1075 pg m^{-3}), N-PAHs ($39.1\text{--}277 \text{ pg m}^{-3}$, mean = 125 pg m^{-3}), and finally PBDEs ($5.07\text{--}13.6 \text{ pg m}^{-3}$, mean = 9.19 pg m^{-3}). Clark *et al.* (2015) also found OPEs bound to atmospheric particulate matter were in higher concentrations than PAHs and PBDEs. In a review of OPEs in the atmosphere, Kung *et al.* (2022) concluded that OPEs tend to partition mostly in the particulate phase. In addition, OPEs are prevalent compounds in the environment and are considered high production value chemicals by the Organization of Economic Co-operation and Development (OECD) (Kung *et al.*, 2022).

For the spatial variation, only PAHs had a similar trend as PM, i.e., higher PM concentrations lead to higher PAH concentrations and vice versa. The toxic PAH concentrations (Fig. S1) also had a similar spatial concentration trend as PM, with concentrations ranging from $18\text{--}294 \text{ pg BaP-TEQ m}^{-3}$ (mean = $120 \text{ pg BaP-TEQ m}^{-3}$).

3.4.1 Congener profiles

The congener profiles for the four target compounds are shown in Fig. S2. For PBDEs, the highly brominated congener, BDE 209, was the main congener followed by BDE 206 and 207 for all locations and periods. Several studies have also reported the predominance of BDE 209 in the

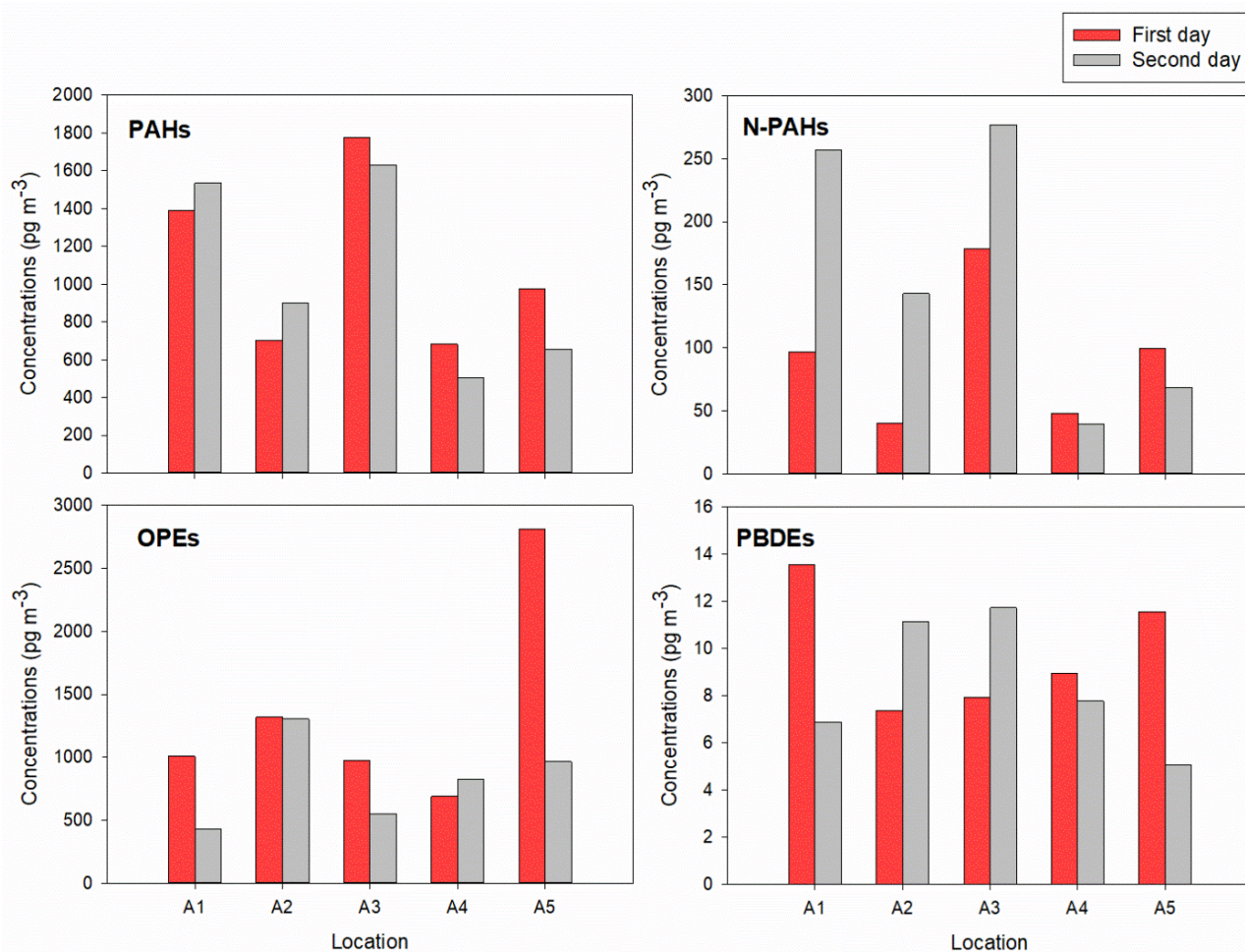
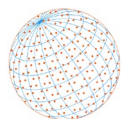


Fig. 3. Atmospheric PM-bound PAH, N-PAH, PBDE, and OPE concentrations in the different sampling sites on the first and second days.

particle phase and total concentrations (gas + particle phases) (Yang *et al.*, 2013; Qiao *et al.*, 2020; Su *et al.*, 2022). BDE 209 is the main ingredient in deca-PBDE flame retardants (Li *et al.*, 2023) but has also been reported to form during the combustion of municipal waste (Lin *et al.*, 2014; Yang *et al.*, 2022) and recycling of electrical and electronic wastes (Zennegg *et al.*, 2014). High-molecular-weight PAHs (> 4 rings) were predominant for all locations and periods, accounting for 88.9%–93.9% of the total PAHs. The main congeners were BghiP, IcdP, BbF, BaP, Fla, and Pyr. High-molecular-weight PAHs usually partition in the particulate phase due to their hydrophobicity (Cheruiyot *et al.*, 2015). Furthermore, the sampling was carried out during winter when temperatures were relatively low, enhancing the partitioning of the PAHs on the particulate phase (He *et al.*, 2014). These results are similar to other studies on atmospheric PM-bound PAHs (He *et al.*, 2014; Clark *et al.*, 2015; Shen *et al.*, 2019). For N-PAHs, 2-NitroFla was the main congener for all locations and periods, contributing to 34.5%–81.6%, followed by 7-NitroBaA (2.69%–38.1%) and 1-NitroPyr (6.34%–18.1%). 9-NitroAnt was only present on the first day, accounting for 8.36%–17.7%. TCPP was the main OPE congener in A1 to A4. TCPP has been also reported as the main congener bound to particulate matter (Clark *et al.*, 2015). Aromatic OPEs (TCP, and TPhP) and long-chain alkyl TEHP were also predominant. TiBP and TBEP were found in locations A4 and A5.

3.4.2 Emission sources based on diagnostic ratios

The PAH diagnostic ratios were calculated and used to assess the sources and origin of PAH contamination in the atmosphere (Fig. 4). The $\sum\text{LMW}/\sum\text{HMW}$ and $\text{COMB}/\sum\text{PAHs}$ for all the locations and periods were < 1 and ~1, respectively, indicating that combustion was the PAH source

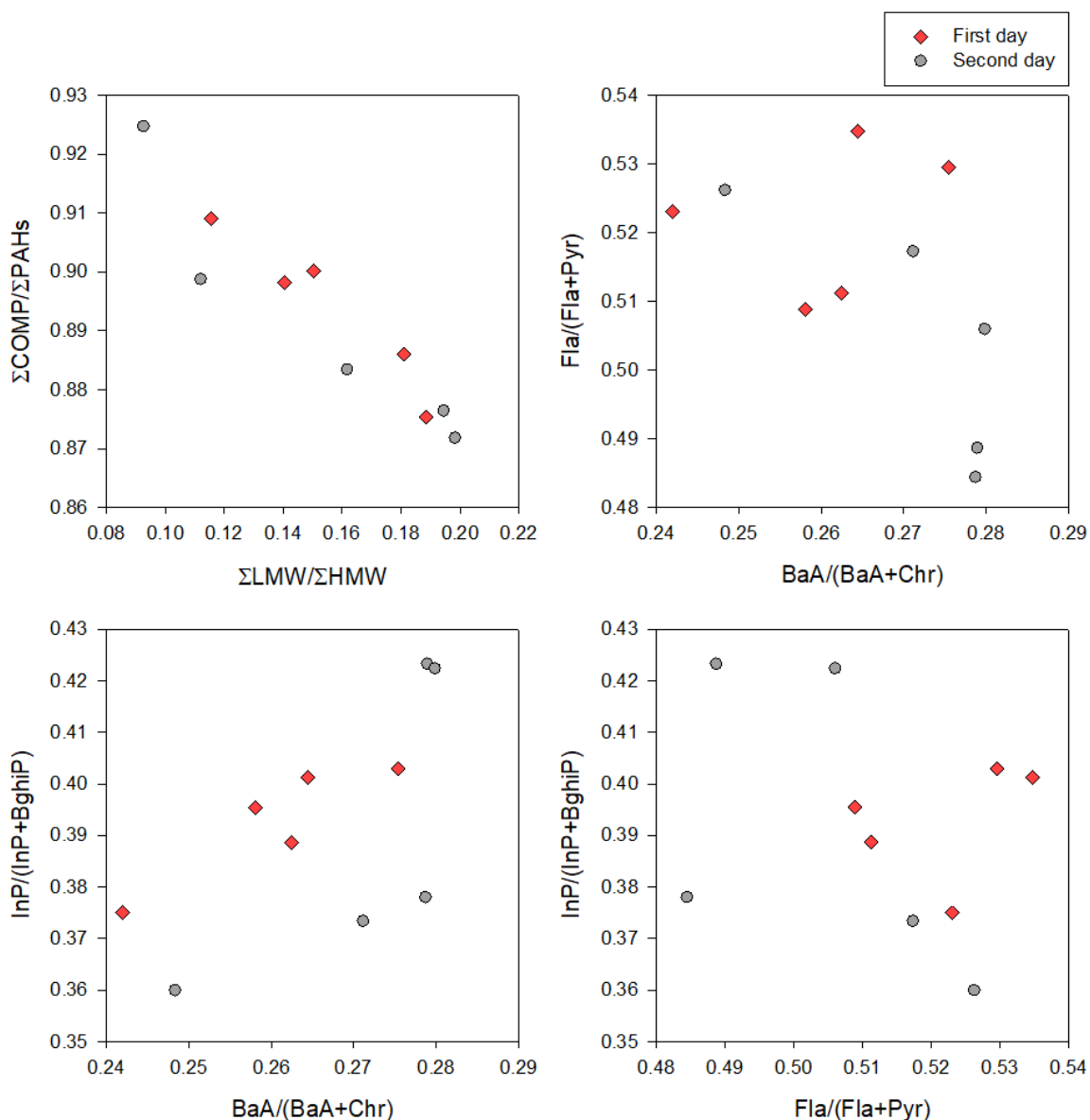
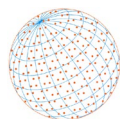
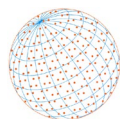


Fig. 4. Diagnostic ratios for the atmospheric PM-bound PAHs for the first and second days.

(Tobiszewski and Namieśnik, 2012; Kozak *et al.*, 2017). The Fla/(Fla+Pyr), BaA/(BaA+Chr), and InP/(InP+BghiP) values were within 0.4–0.5, 0.2–0.35, and 0.2–0.5, respectively, suggesting that petroleum combustion was the probable source of PAHs (Tobiszewski and Namieśnik, 2012; Jiao *et al.*, 2017; Kozak *et al.*, 2017). Furthermore, the BaP/(Chr+BaP) values for all the locations and periods were > 0.35, suggesting that the PAHs originated from vehicular emissions (Tobiszewski and Namieśnik, 2012). For all locations and periods, except for the second sampling days in A1 and A3, the Fla/(Fla+Pyr) values were > 0.5, indicating the PAH source came from diesel combustion. Therefore, we can conclude that the PM-bound PAHs might have originated from vehicular emissions.

4 CONCLUSIONS

This study provides a reliable method for simultaneous extraction and analysis of atmospheric PM-bound PBDEs, PAHs, N-PAHs, and OPEs. The validation process included the use of standard reference materials (SRMs), which demonstrated the accuracy and precision of the analytical



techniques employed. The results indicated that the majority of target compounds exhibited excellent recovery rates (within 30%), with minor deviations observed for specific congeners. Overall, these findings affirm the reliability and accuracy of the developed methodology for the analysis of the selected compounds. Additionally, the reproducibility of the method was assessed through replicates, consistently yielding robust results and reinforcing the reliability of the analytical procedures. The recovery rates for the four compounds ranged from $82.2\% \pm 8.7\%$ to $115\% \pm 17.4\%$. The practical application of the method was demonstrated by analyzing actual atmospheric PM samples collected in and around an industrial park in Tainan, Taiwan. The results highlighted the spatial variation of PM-bound compounds, with some evidence suggesting a potential pollution source in the vicinity of the industrial park. The congener profiles of the target compounds revealed important insights into their distribution and partitioning in atmospheric PM. High-molecular-weight PAHs, BDE 209, and TCPP were the main congeners. Finally, diagnostic ratios of PAHs were used to assess the likely sources of PAH contamination in the atmosphere, with the results suggesting combustion, petroleum combustion, and vehicular emissions as the primary sources of PM-bound PAHs.

ACKNOWLEDGMENTS

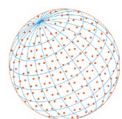
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SUPPLEMENTARY MATERIAL

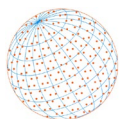
Supplementary material for this article can be found in the online version at <https://doi.org/10.4209/aaqr.230262>

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