atmosphere

Supplementary Materials:

Main Emission Sources and Health Risks of Polycyclic Aromatic Hydrocarbons and Nitro-Polycyclic Aromatic Hydrocarbons at Three Typical Sites in Hanoi

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Table S1. Pretreatment and instrumental analysis of PAHs and NPAHs.

To analyze the PAHs and NPAHs, each filter was cut into small pieces and placed in flasks. Internal standards (pyrene-d_{10} (Pyr-d_{10}), benzo[*a*]pyrene-d_{12} (BaP-d_{12})) were added to the filter. Then, dichloromethane was added to each flask for extracting. After ultrasonic extraction twice (once for 15 min at room temperature), the solution was then filtered through filter paper (Advantec, Toyo No. 6, Toyo Roshi Kaisha, Ltd., Tokyo, Japan) into a conical flask. The solution was concentrated with a rotary evaporator after adding dimethyl sulfoxide (100 μL). Then, ethanol was added to make the residue up to 1 mL. Finally, the solution was filtered through a 0.45 μm membrane filter (HLC-DISK13, Kanto Chemical CO., Inc., Tokyo, Japan) into an injection vial. A high-performance liquid chromatography (HPLC) system (Shimadzu Inc., Kyoto, Japan) with a fluorescence detector (RF-20Axs, Shimadzu Inc., Kyoto, Japan) was used to analyze ten PAHs and six NPAHs. The analyte first through a reducer column (NPpak-RS, 4.0 i.d. × 10 mm, JASCO Co., Tokyo, Japan) with acetate (pH 5.5)/ethanol (95%) buffer and ascorbic acid to reduce NPAHs to their amino PAHs. Two reversed-phase column (Inertsil ODS-P, 4.6 i.d. × 250 mm, GL Sci., Inc., Tokyo, Japan) were used as the analytical columns. A mixture of imidazole buffer (pH 7.6) and acetonitrile was used as the mobile phase with a flow rate of 1.0 mL min^{-1} under a gradient concentration. For fluorescence detection, a two-detection channel on a single run was performed. The time program for the fluorescence detector was set at the optimum excitation (Ex) and emission (Em) wavelengths for PAHs as follows: ch1: 0 – 45.0 min, Ex/Em = 513/283 nm (2-NFR); 45.0 – 51.0 min, Ex/Em =437/273 nm (2-NP and 6-NC); 51.0 – 60.0 min, Ex/Em =513/283 nm (6-NBaP); 60.0 – 80.0 min, Ex/Em = 378/288 nm (BeP); 80.0 -100 min, Ex/Em = 482/294 nm (IDP); ch2: 0 - 46.0 min, Ex/Em = 430/360 nm (1-

NP); 46.0 – 50.0 min, Ex/Em = 475/300 nm (7-NBaA); 50.0 – 54.0 min, Ex/Em = 433/280 nm (FR); 54.0 – 56.0 min, Ex/Em = 392/331 nm (Pyr-d_{10} and PyR); 56.0 – 58.8 min, Ex/Em = 407/267 nm (BaA); 58.8 – 61.0 min, Ex/Em = 381/265 nm (Chr); 61.0 – 66.0 min, Ex/Em = 420/295 nm (BbF, BkF); 66.0 – 100 min, Ex/Em = 407/267 nm (BaP-d_{12}, BaP and BgPe).

Table S1. The toxic equivalent factor (TEF) of PAHs and NPAHs.

PAHs and NPAHs	TEF	Reference
FR	0.001	[1]
Pyr	0.001	[1]
BaA	0.1	[2]
Chr	0.01	[2]
BbF	0.1	[2]
BkF	0.1	[2]
BaP	1	[2]
BeP	0.002	[2]
BgPe	0.01	[1]
IDP	0.1	[2]
2-NFR	0.01	[1]
1-NP	0.1	[1]
6-NC	10	[1]

Table S2. Parameters of incremental lifetime cancer risks (ILCRs).

Exposure parameters	Unit	Male	Female	Reference
Body weight (BW)	Kg	61.2	54.0	[3]
Ingestion rate (IR_{ing})	mg/day	100	100	
Exposure frequency (EF)	day^{-1}	365	365	
surface factor (SL)	mg/cm^2	0.07	0.07	[4]
absorption factor (ABS)	day^{-1}	0.13	0.13	
Inhalation rate (IR_{Inh})	m^3/day	19.3	16.2	
Surface area (SA)	cm^2/day	5,700	5,700	
Exposure duration (ED)	years	65	65	[5]
Average life span (AT)	days	25550	25550	
Particle emission factor (PEF)	m^3/kg	1.36×10^9	1.36×10^9	
Lifetime (LT)	years	75	80	[6]
Absorption factor (AF)	mg/cm^2	0.07	0.07	[7]

Table S3. Average PAHs concentration (ng/m^3) at three sites in Hanoi during the sampling periods.

Winter	GL (2019)	XT (2021)	DA (2021)
FR	0.79 ± 0.67	0.25 ± 0.12	2.11 ± 1.42
Pyr	0.70 ± 0.54	0.22 ± 0.13	2.37 ± 1.66
BaA	0.48 ± 0.50	0.11 ± 0.09	1.64 ± 1.20
Chr	1.28 ± 1.00	0.26 ± 0.16	2.89 ± 1.85
BbF	1.74 ± 1.36	0.43 ± 0.31	2.00 ± 1.00
BkF	0.79 ± 0.68	0.16 ± 0.12	1.06 ± 0.55
BaP	1.15 ± 1.15	0.25 ± 0.21	2.30 ± 1.36
BeP	1.23 ± 0.92	0.30 ± 0.22	2.63 ± 1.60
BgPe	2.18 ± 1.71	0.62 ± 0.43	3.06 ± 1.40
IDP	1.78 ± 1.48	0.35 ± 0.26	1.98 ± 0.97

PAH	12.1 ± 9.45	2.95 ± 2.04	22.1 ± 12.7
Summer	GL (2020)	XT (2022)	DA (2022)
FR	0.08 ± 0.04	0.11 ± 0.03	0.12 ± 0.04
Pyr	0.09 ± 0.04	0.13 ± 0.04	0.15 ± 0.05
BaA	0.07 ± 0.06	0.07 ± 0.03	0.12 ± 0.04
Chr	0.17 ± 0.13	0.18 ± 0.07	0.24 ± 0.08
BbF	0.23 ± 0.18	0.31 ± 0.13	0.52 ± 0.16
BkF	0.12 ± 0.08	0.12 ± 0.06	0.23 ± 0.06
BaP	0.18 ± 0.15	0.18 ± 0.08	0.39 ± 0.11
BeP	0.24 ± 0.15	0.25 ± 0.12	0.54 ± 0.13
BgPe	0.64 ± 0.34	0.75 ± 0.31	1.24 ± 0.28
IDP	0.38 ± 0.22	0.45 ± 0.18	0.82 ± 0.18
PAH	2.20 ± 1.32	2.55 ± 1.01	4.38 ± 1.07

Table S4. Average NPAHs concentration (pg/m^3) at GL, DA and XT in Hanoi during the sampling periods.

Winter	**GL (2019)**	**XT (2021)**	**DA (2021)**
2-NFR	278 ± 279	32.3 ± 28.1	157 ± 75.7
2-NP	79.8 ± 126	5.47 ± 6.66	60.6 ± 30.5
1-NP	10.2 ± 10.9	N.D.[a]	24.5 ± 19.9
6-NC	5.93 ± 4.56	N.D.	83.3 ± 88.3
7-NBaA	94.7 ± 70.1	11.5 ± 14.0	209 ± 282
6-NBaP	25.4 ± 32.2	N.D.	13.3 ± 19.5
Total NPAHs	494 ± 464	58.0 ± 43.4	548 ± 470
Summer	GL (2020)	XT (2022)	DA (2022)
2-NFR	28.0 ± 16.1	57.2 ± 29.8	56.8 ± 16.4
2-NP	4.76 ± 5.86	13.9 ± 18.0	15.9 ± 5.43
1-NP	1.76 ± 2.07	5.51 ± 4.98	1.70 ± 1.68
6-NC	2.64 ± 2.66	2.98 ± 4.65	11.5 ± 3.17
7-NBaA	14.7 ± 12.0	29.3 ± 34.2	40.1 ± 26.1
6-NBaP	1.48 ± 2.79	6.10 ± 5.55	10.8 ± 2.36
Total NPAHs	55.3 ± 33.5	115 ± 75.6	137 ± 47.0

[a] N.D.: Not Detected

Table S5. The toxic equivalent concentration range (pg/m^3) of PAHs and NPAHs (except 2-NP, 7-NBaA and 6-NBaP).

Winter	**GL (2019)**	**XT (2021)**	**DA (2021)**
FR	0.79 ± 0.67	0.25 ± 0.12	2.11 ± 1.42
Pyr	0.70 ± 0.54	0.22 ± 0.13	2.37 ± 1.66
BaA	48.4 ± 50.2	11.5 ± 9.39	164 ± 120
Chr	128 ± 9.99	2.61 ± 1.58	28.9 ± 18.5
BbF	174 ± 136	43.2 ± 31.4	200 ± 99.9
BkF	78.9 ± 68.3	15.7 ± 11.8	106 ± 54.8
BaP	1149 ± 1145	247 ± 209	2301 ± 1358
BeP	2.47 ± 1.84	0.60 ± 0.44	5.27 ± 3.20
BgPe	21.8 ± 17.1	6.16 ± 4.32	30.6 ± 14.0
IDP	178 ± 148	35.4 ± 25.7	198 ± 96.9
Total PAHs	1667 ± 1569	363 ± 294	3040 ± 1753

2-NFR	2.78 ± 2.79	0.32 ± 0.28	1.57 ± 0.76
1-NP	1.02 ± 1.09	N.A.[a]	2.45 ± 1.99
6-NC	59.3 ± 45.6	N.A.	833 ± 883
Total NPAHs	63.1 ± 46.2	11.3 ± 31	837 ± 886
Total TEQ	1730 ± 1577	363 ± 319	3877 ± 2548
Summer	GL (2020)	XT (2022)	DA (2022)
FR	0.08 ± 0.04	0.11 ± 0.03	0.69 ± 0.17
Pyr	0.09 ± 0.04	0.13 ± 0.04	0.12 ± 0.03
BaA	6.98 ± 5.97	7.18 ± 2.83	15.3 ± 3.64
Chr	1.70 ± 1.27	1.80 ± 0.74	1.22 ± 0.30
BbF	22.8 ± 17.6	31.1 ± 13.5	23.7 ± 6.39
BkF	11.7 ± 8.08	12.2 ± 5.67	51.6 ± 12.2
BaP	183 ± 145	181 ± 82.1	233 ± 50.1
BeP	0.49 ± 0.31	0.50 ± 0.23	0.78 ± 0.18
BgPe	6.36 ± 3.43	7.46 ± 3.12	5.44 ± 1.12
IDP	38.0 ± 22.0	45.3 ± 18.4	124 ± 25.3
Total PAHs	271 ± 196	287 ± 124	456 ± 115
2-NFR	0.28 ± 0.16	0.57 ± 0.30	0.57 ± 0.17
1-NP	0.18 ± 0.21	0.55 ± 0.50	0.17 ± 0.17
6-NC	26.4 ± 26.6	29.8 ± 46.5	115 ± 32.8
Total NPAHs	26.9 ± 26.8	47.8 ± 34.2	115 ± 31.9
Total TEQ	298 ± 218	318 ± 152	571 ± 111

[a] N.A.: Not Available

References

1. U.S. EPA. 2010 U.S. Environmental Protection Agency (EPA) Decontamination Research and Development Conference; EPA/600/R-11/052; U.S. Environmental Protection Agency: Washington, DC, USA, 2011.
2. Collins, J.F.; Brown, J.P.; Alexeeff, G.V.; Salmon, A.G. Potency equivalency factors for some polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbon derivatives. *Regul. Toxicol. Pharmacol.* **1998**, *28*, 45–54. https://doi.org/10.1006/rtph.1998.1235.
3. NCD Risk Factor Collaboration. Height and body-mass index trajectories of school-aged children and adolescents from 1985 to 2019 in 200 countries and territories: A pooled analysis of 2181 population-based studies with 65 million participants. In Yearbook of Paediatric Endocrinology; Bioscientifica Ltd.: Bristol, UK, 2021. https://doi.org/10.1530/ey.18.13.15.
4. Panis, L.I.; De Geus, B.; Vandenbulcke, G.; Willems, H.; Degraeuwe, B.; Bleux, N.; Mishra, V.; Thomas, I.; Meeusen, R. Exposure to particulate matter in traffic: A comparison of cyclists and car passengers. *Atmos. Environ.* **2010**, *44*, 2263–2270. https://doi.org/10.1016/j.atmosenv.2010.04.028.
5. Zhang, Z.H.; Khlystov, A.; Norford, L.K.; Tan, Z.K.; Balasubramanian, R. Characterization of traffic-related ambient fine particulate matter (PM 2.5) in an Asian city: Environmental and health implications. *Atmos. Environ.* **2017**, *161*, 132–143. https://doi.org/10.1016/j.atmosenv.2017.04.040.
6. The World Bank, Life Expectancy at Birth, Total (Years)—Vietnam. Available online: https://data.worldbank.org/indicator/SP.DYN.LE00.IN?locations=VN (accessed on 9 April 2023).
7. USDOE. The Risk Assessment Information System (RAIS). U.S. Department of Energy's Oak Ridge Operations Office (ORO). 2011. Available online: http://rais.ornl.gov/ (accessed on 9 April 2023).