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大气中硝基多环芳烃的污染特征和环境行为研究综述*

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摘要 环境空气中的硝基多环芳烃 (nitrated polycyclic aromatic hydrocarbons, NPAHs) 因致癌和致突变属性受到人们的广泛关注. 本文总结了国内外关于环境空气中 NPAHs 的组成特征、时空分布、粒径分布、气固分配、来源和毒性效应的研究. 我国城市地区大气环境中的 NPAHs 浓度常高于农村地区; 受生物质燃烧和机动车排放的影响, 9-硝基蒽对城市地区 NPAHs 浓度的贡献占比最高. 尽管 NPAHs 在夏季存在二次源, 不利的气象条件和升高的一次排放导致我国大气中 NPAHs 的峰值常出现在秋、冬季节. NPAHs 因蒸气压较低主要分布在颗粒物中, 而颗粒态 NPAHs 主要分布在亚微米级颗粒物中 ($D_p < 1 \mu\text{m}$). 低分子量 NPAHs (例如, 1N-NAP 和 2N-NAP) 可随着温度变化经蒸发、冷凝过程迁移至粗颗粒物 ($D_p > 2.5 \mu\text{m}$). 根据考虑不同气固分配机制模型的气固分配系数模拟结果, 吸附作用在 NPAHs 的气固分配过程中不应被忽略. NPAHs 的来源包括化石和生物质燃料的不完全燃烧, 以及母体 PAHs 在大气中的二次反应过程. 相关性分析和特征比值常用于推断 NPAHs 的主要来源, 但无法量化 NPAHs 的源贡献分布. 根据环境空气中 NPAHs 的毒性风险评估结果, 颗粒物中 NPAHs 对所有 PAHs 衍生物致突变性和致癌性的贡献比其质量占比高数倍, 并且因毒性累积效应对成年人具有更高的致癌风险. 为进一步了解 NPAHs 的环境行为, 合理评估其健康效应, 有必要在将来的研究中完善 NPAHs 的排放信息, 厘清 NPAHs 在环境中的迁移转化过程.

关键词 硝基多环芳烃, 时空分布, 气固分配, 源解析, 毒性.

Review on pollution characteristics and environmental behaviors of nitrated polycyclic aromatic hydrocarbons in ambient air

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Abstract Ambient nitrated polycyclic aromatic hydrocarbons (NPAHs) have been investigated intensively due to their carcinogenic and mutagenic properties. In this work, studies in chemical composition, spatial and temporal distributions, particle size distributions, gas-particle partitioning, sources, and toxic effects of NPAHs were summarized. The concentrations of ambient NPAHs in urban areas were usually higher than those in rural areas. Due to the influences of biomass

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burning and motor vehicle emissions, 9-nitroanthracene had the highest contributions to ambient NPAHs in urban areas. Although NPAHs have secondary sources in summer, their peak concentrations often appear in fall and winter because of adverse meteorological conditions and elevated primary emissions. NPAHs mainly exist in the particle phase owing to their low vapor pressures, and particulate NPAHs were primarily enriched in submicron particles ($D_p < 1 \mu\text{m}$). Low molecular weight NPAHs (such as 1N-NAP and 2N-NAP) can shift toward coarse particles ($D_p > 2.5 \mu\text{m}$) through evaporation and condensation processes with varied temperatures. According to the modeling results of gas-particle partitioning coefficients considering different mechanisms, the adsorption of NPAHs on PM surfaces should not be neglected in the gas-particle partitioning process. Incomplete combustion of fossil and biomass fuels and secondary reactions of parent PAHs are the main sources of NPAHs in the atmosphere. Correlation analysis and diagnostic ratios were typical methods used to indicate the main sources of NPAHs, but they were unable to determine the contribution distributions of NPAH sources. According to the toxicity risk assessment of ambient NPAHs, the contributions of NPAHs in particulate matter to the mutagenicity and carcinogenicity of all PAH derivatives were several times higher than their mass fractions. Due to the cumulative effect of toxicity, NPAHs had a higher carcinogenic risk in adults. To further understand the environmental behaviors and health effects of NPAHs, it is necessary to improve their source inventories and clarify the migration and transformation processes of NPAHs in the environment.

Keywords nitrated polycyclic aromatic hydrocarbons, spatial and temporal distributions, gas-particle partitioning, source apportionment, toxicity.

硝基多环芳烃(nitrated polycyclic aromatic hydrocarbons, NPAHs)由多环芳烃(polycyclic aromatic hydrocarbons, PAHs)的硝基取代而形成,是大气中的一类重要有机污染物.毒理学研究表明 NPAHs 比母体 PAHs 具有更直接的致癌和致突变作用^[1-2].另外,大气颗粒物中的 NPAHs 是棕碳的重要组分,可通过吸收太阳辐射改变地球热平衡,从而影响天气和气候^[3].

颗粒物中的多环芳烃类化合物由于其致癌和致突变性受到广泛关注^[4].大气中已检测到的多环芳烃及其衍生物约 500 余种.目前关于大气环境中母体 PAHs 的浓度水平、迁移转化和健康效应已有较多研究,并且有很多国家和国际组织对环境中的 PAHs 实施监控^[5-7].然而,具有更高潜在毒性的 NPAHs 尚未被纳入监管范围^[8-10].NPAHs 和 PAHs 均可来自化石燃料的不完全燃烧过程,NPAHs 还能产生自有 NO_x 参与的光化学反应^[11].表 1 给出了环境空气中常见的 NPAHs 及其理化性质,由美国环保局(U.S. EPA)化学品毒性(toxicity estimation software tool, TEST)和理化性质评估软件(estimation program interface, EPI)计算获得^[12-13].如表 1 所示,常见 NPAHs 的饱和蒸气压值(p_L°)普遍高于 10^{-14} atm,可同时以气态和颗粒态形式存在,正辛醇-空气分配系数(K_{OA})、正辛醇-水分配系数(K_{OW})和沸点随分子量(MW)增大而增大,而它们的水溶性则随分子量增大而降低.

表 1 环境空气中常见 NPAHs 的物理化学性质(25 °C)

Table 1 Physicochemical properties (25 °C) of typical NPAHs in ambient air

化合物 Compounds	缩写 Abbreviation	CAS	分子量/ ($\text{g}\cdot\text{mol}^{-1}$) Molecular weight	蒸气压/Pa Vapour pressure	$\lg K_{OA}$	$\lg K_{OW}$	水溶性/($\text{mg}\cdot\text{L}^{-1}$) Water solubility	沸点/°C Boiling point
1-硝基萘 (1-Nitronaphthalene)	1N-NAP	86-57-7	173	4.49×10^{-2}	7.33	2.99	38.1	294
2-硝基萘 (2-Nitronaphthalene)	2N-NAP	581-89-5	173	3.96×10^{-2}	7.31	3.24	44.5	303
2-硝基联苯 (2-Nitrobiphenyl)	2N-BIP	86-00-0	199	9.35×10^{-3}	7.75	3.57	13.2	321

续表 1

化合物 Compounds	缩写 Abbreviation	CAS	分子质量/ (g·mol ⁻¹) Molecular weight	蒸气压/Pa Vapour pressure	lg K _{OA}	lg K _{OW}	水溶性/(mg·L ⁻¹) Water solubility	沸点/°C Boiling point
3-硝基联苯 (3-Nitrobiphenyl)	3N-BIP	2113-58-8	199	3.49 × 10 ⁻³	8.05	3.87	8.06	318
5-硝基茈 (5-Nitroacenaphthene)	5N-ACE	602-87-9	199	5.81 × 10 ⁻³	8.19	3.85	12.9	321
2-硝基茈 (2-Nitrofluorene)	2N-FLU	607-57-8	211	1.37 × 10 ⁻⁴	7.94	3.37	1.51	325
3-硝基茈 (3-Nitrofluorene)	3N-FLU	5397-37-5	211	7.77 × 10 ⁻⁵	NA	NA	0.62	321
3-硝基菲 (3-Nitrophenanthrene)	3N-PHE	17024-19-0	223	6.75 × 10 ⁻⁵	9.24	4.16	1.03	375
9-硝基菲 (9-Nitrophenanthrene)	9N-PHE	954-46-1	223	2.25 × 10 ⁻⁴	9.24	4.16	1.78	371
9-硝基蒽 (9-Nitroanthracene)	9N-ANT	602-60-8	223	4.88 × 10 ⁻⁴	9.86	4.78	1.31	384
2-硝基荧蒽 (2-Nitrofluoranthene)	2N-FLT	13177-29-2	247	1.32 × 10 ⁻⁶	8.52	4.29	0.057	428
3-硝基荧蒽 (3-Nitrofluoranthene)	3N-FLT	892-21-7	247	7.64 × 10 ⁻⁷	10.6	4.75	0.11	422
1-硝基苊 (1-Nitropyrene)	1N-PYR	5522-43-0	247	6.32 × 10 ⁻⁷	10.9	5.06	0.028	455
2-硝基苊 (2-Nitropyrene)	2N-PYR	789-07-1	247	2.60 × 10 ⁻⁷	10.6	4.75	0.022	454
2,7-二硝基茈 (2,7-Dinitrofluorene)	2,7N-FLU	5405-53-8	256	1.37 × 10 ⁻⁶	10.3	3.35	1.01	346
6-硝基蒽 (6-Nitrochrysene)	6N-CHR	7496-02-8	273	1.01 × 10 ⁻⁶	11.4	5.34	0.015	455
7-硝基苯并[a]蒽 (7-Nitrobenz[a]anthracene)	7N-BaA	20268-51-3	273	2.89 × 10 ⁻⁷	11.4	5.34	0.11	488
1,3-二硝基苊 (1,3-Dinitropyrene)	1,3-DNP	75321-20-9	292	2.41 × 10 ⁻⁸	12.8	4.57	0.017	465
1,6-二硝基苊 (1,6-Dinitropyrene)	1,6-DNP	42397-64-8	292	2.97 × 10 ⁻⁸	12.8	4.57	0.020	467
1,8-二硝基苊 (1,8-Dinitropyrene)	1,8-DNP	42397-65-9	292	4.20 × 10 ⁻⁸	12.8	4.57	0.010	459
6-硝基苯并[a]苊 (6-Nitrobenzo[a]pyrene)	6N-BaP	63041-90-7	297	5.88 × 10 ⁻⁹	12.8	5.93	0.00092	517

目前关于大气 NPAHs 的研究主要集中在基于受体点位采样的化学表征,而有关 NPAHs 环境行为的研究仍非常有限. 本文根据国内已有研究探讨大气中 NPAHs 的化学组成和时空分布特征,并同国外部分国家地区的结果进行对比. 针对 NPAHs 在大气中的环境行为,我们基于有限的研究对 NPAHs 在粒径分布、气固分配、来源和毒性方面具有代表性的特点进行论述,为研究大气环境中 NPAHs 的环境行为和健康风险提供参考.

1 硝基多环芳烃的组成特征和时空分布 (Chemical composition and spatial-temporal distributions of NPAHs)

表 2 列出了国内外不同地区大气环境中 NPAHs 的浓度和主要成分. NPAHs 的总浓度范围为 22.0—5480 pg·m⁻³, 比母体 PAHs (3.00—580 ng·m⁻³) 低 1—2 个数量级^[14-31]. 9-硝基蒽、1-硝基萘、2-硝基萘、2-硝基荧蒽和 3-硝基荧蒽是环境空气中检测出的 NPAHs 的主要成分, 占比高达 46.2%—94.1%^[14-17,21,25-26,29]. 9-硝基蒽是我国城市大气中浓度最高的 NPAHs (76.0—1089 pg·m⁻³, 29.0%—64.1%), 依次为 2+3-硝基荧蒽 (123—430 pg·m⁻³, 14.7%—24.3%)、2-硝基萘 (30.0—297 pg·m⁻³, 10.5%—30.5%) 和 1-硝基萘 (19.0—283 pg·m⁻³, 6.59%—20.1%)^[14,17,21]. 9-硝基蒽主要来自生物质燃烧和机动车尾气的直接排放^[31]; 3-硝基荧蒽常用于指示柴油机动车排放^[26,31]; 1-硝基萘和 2-硝基萘主要通过萘和 OH· 的气相反应生成^[32]; 2-硝基荧蒽在白天和夜间分别来自 OH· 和 NO₃· 引起的气相反应 (荧蒽+NO₂)^[19]. 该组成特征表明尽管我国在机动车尾气控制上已取得较大的进展和明显的效果, 但一次排放及相关仍是城市大气中 NPAHs 的主要来源.

表 2 国内外不同地区 NPAHs 浓度比较
Table 2 Comparisons of NPAHs concentrations in different cities of China and foreign countries

地点 Location	采样时间 Sampling period	采样点特征 Site description	类型 Sample type	种类 Species No.	平均浓度/($\text{pg}\cdot\text{m}^{-3}$) Average concentration	主要组分/(占比) Major compounds
中国北方						
哈尔滨 ^[23]	2017.6—2018.5	城区	PM _{2.5}	16	5480	9N-ANT, 3N-PHE, 9N-PHE
大连 ^[7]	2010.4—2011.3	城区	气相+PM ₁₀	12	468	9N-ANT (27.1), 2+3N-FLT (21.4), IN-NAP (16.0), 2N-NAP (15.4)
	2010.4—2011.3	农田	气相+PM ₁₀	12	314	6N-BaP (26.1), 2N-NAP (23.9), IN-NAP (17.8), 2+3N-FLT (14.3)
北京 ^[7]	2010.4—2011.3	城区	气相+PM ₁₀	12	1397	9N-ANT (36.9), 2+3N-FLT (20.7), 2N-NAP (15.1), IN-NAP (12.7)
北京 ^[15]	2012.3—2013.3	城区	PM _{2.5}	15	1730	9N-ANT (51.6), 2N-FLT (23.9)
北京 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	1400	9N-ANT (59.2), 2N-NAP (16.6), IN-NAP (7.43)
兰州 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	1100	9N-ANT (41.1), 2N-NAP (22.2), IN-NAP (11.2)
武威 ^[7]	2010.4—2011.3	城区	气相+PM ₁₀	12	828	9N-ANT (44.1), 6N-BaP (12.0), 2+3N-FLT (11.8)
	2010.4—2011.3	乡村	气相+PM ₁₀	12	614	9N-ANT (45.4), 6N-BaP (13.7), 2+3N-FLT (10.3)
	2010.4—2011.3	农田	气相+PM ₁₀	12	555	9N-ANT (47.9), 2+3N-FLT (13.0), 6N-BaP (8.65)
银川 ^[7]	2010.4—2011.3	城区	气相+PM ₁₀	12	968	9N-ANT (46.3), 2+3N-FLT (14.7), 2N-NAP (11.9), IN-NAP (11.2)
	2010.4—2011.3	乡村	气相+PM ₁₀	12	956	9N-ANT (44.4), 2+3N-FLT (17.9), 2N-NAP (11.3), IN-NAP (10.9)
	2010.4—2011.3	农田	气相+PM ₁₀	12	1015	9N-ANT (44.9), 2+3N-FLT (19.0), 2N-NAP (10.5), IN-NAP (10.0)
济南 ^[20]	2014.12—2015.1	城区	气相+TSP	16	2800	IN-NAP + 2N-NAP + 3N-BIP + 9N-ANT + 2+3N-FLT (> 90%)
济南 ^[23]	2016.3—2016.12	城区	PM _{2.5}	16	1880	2+3N-FLT (24.5), 9N-ANT (18.5), 2N-PYR (11.6), 6N-BaP (8.40)
	2016.3—2016.12	郊区	PM _{2.5}	16	1570	2+3N-FLT (17.4), 2N-PYR (10.1), 9N-ANT (9.55), 6N-BaP (9.24)
砭矶岛 ^[20]	2014.12	岛屿	气相+TSP	16	770	IN-NAP + 2N-NAP + 3N-BIP + 9N-ANT + 2+3N-FLT (> 90%)
泰山 ^[20]	2014.11	山地	气相+TSP	16	270	IN-NAP + 2N-NAP + 3N-BIP + 9N-ANT + 2+3N-FLT (> 90%)
德州 ^[17]	2010.4—2011.3	城区	气相+PM ₁₀	12	1768	9N-ANT (47.9), 2+3N-FLT (24.3), 2N-NAP (11.3), IN-NAP (10.6)
	2010.4—2011.3	乡村	气相+PM ₁₀	12	1447	9N-ANT (46.4), 2+3N-FLT (18.8), 7N-BaA (9.33), IN-NAP (8.57)
	2010.4—2011.3	农田	气相+PM ₁₀	12	1516	9N-ANT (45.8), 2+3N-FLT (21.2), 7N-BaA (8.84), 2N-NAP (8.05)
烟台 ^[17]	2010.4—2011.3	城区	气相+PM ₁₀	12	760	9N-ANT (33.7), 2+3N-FLT (16.2), 2N-NAP (14.9), IN-NAP (14.1)
	2010.4—2011.3	乡村	气相+PM ₁₀	12	926	9N-ANT (43.3), 2+3N-FLT (15.1), 2N-NAP (11.3), IN-NAP (9.29)
	2010.4—2011.3	农田	气相+PM ₁₀	12	641	9N-ANT (25.0), 2N-NAP (19.2), 2+3N-FLT (18.9), IN-NAP (16.1)
太原 ^[17]	2010.4—2011.3	城区	气相+PM ₁₀	12	2056	9N-ANT (35.0), 2+3N-FLT (18.6), 2N-NAP (14.2), IN-NAP (13.8)
	2010.4—2011.3	乡村	气相+PM ₁₀	12	1239	9N-ANT (29.0), 2+3N-FLT (16.9), 2N-NAP (13.7), 6N-BaP (13.7)
	2010.4—2011.3	农田	气相+PM ₁₀	12	1429	9N-ANT (32.2), 2+3N-FLT (20.2), IN-NAP (14.5), 2N-NAP (14.4)
太原 ^[24]	2013.1	城区	PM _{2.5}	3	446	IN-PYR (69.3), 9N-ANT (26.5), 2N-FLU (4.26)
太原 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	1700	9N-ANT (64.1), 2N-NAP (14.5), IN-NAP (6.59)
新乡 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	1200	9N-ANT (58.8), 2N-NAP (18.6), IN-NAP (8.25)

续表 2

地点 Location	采样时间 Sampling period	采样点特征 Site description	类型 Sample type	种类 Species No.	平均浓度/($\text{pg}\cdot\text{m}^{-3}$) Average concentration	主要组分% (占比) Major compounds
中国南方						
广州 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	1600	9N-ANT (58.9), 2N-NAP (18.6), 1N-NAP (7.81)
成都 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	730	9N-ANT (33.8), 2N-NAP (30.5), 1N-NAP (13.6)
重庆 ^[9]	2016.4—2017.1	城区	气相+TSP	27	1650	2N-NAP (13.9), 2N-FLT (13.3), 5N-ACE (12.7)
上海 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	680	2N-NAP (31.5), 9N-ANT (29.4), 1N-NAP (14.0)
南京 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	680	9N-ANT (36.3), 2N-NAP (30.1), 1N-NAP (13.4)
武汉 ^[4]	2013.10—2014.8	城区	PM _{2.5}	12	570	9N-ANT (49.6), 2N-NAP (21.6), 1N-NAP (9.65)
昆明 ^[21]	2014.3—2015.2	城区	气相+PM ₁₀	7	344	9N-ANT (44.8), 2N-NAP (23.5), 1N-NAP (20.1)
绵阳 ^[21]	2014.3—2015.2	城区	气相+PM ₁₀	7	164	9N-ANT (46.3), 2N-NAP (18.3), 1N-NAP (17.7)
珠三角 ^[6]	2010.11—2010.12	乡村	气相+TSP	29	4143	2N-FLT (38.5), 9N-ANT (19.8), 7N-BaA (12.7)
国外地区						
墨西哥合众国墨西哥城 ^[25]	2006.3—2007.2	城区	PM _{2.5}	8	152	9N-ANT (30.1), 2N-FLT (27.6)
巴西贝洛奥里宗特 ^[18]	2017.5—2018.4	城区	气相+PM _{2.5}	4	1830	9N-ANT, 3N-FLT, 1N-PYR
法国马赛 ^[26]	2004.6	城区	气相+PM ₁₀	17	710	1N-NAP (29.3), 2N-NAP (16.9), 9N-ANT (15.1), 2+3N-FLT (12.7)
	2004.6	郊区	气相+PM ₁₀	17	350	1N-NAP (50.3), 2N-NAP (23.7), 9N-ANT (8.00), 2+3N-FLT (6.86)
	2004.6	乡村	气相+PM ₁₀	17	30	1N-NAP (33.3), 2N-NAP (30.0), 2+3N-FLT (10.0), 9N-ANT (6.67)
法国巴黎 ^[28]	2009.7	郊区	PM ₁₀	18	30	2+3N-FLT (53.3), 9N-ANT (23.3)
	2010.9	道路	PM ₁₀	18	171	1N-PYR (42.7), 9N-ANT (17.0), 2+3N-FLT (9.36)
卢旺达 ^[27]	2017.5	城区	PM _{2.5}	7	190	9N-ANT (48.9), 2N-PYR+2N-FLT (44.2), 1,8-DNP (11.6)
	2017.6	城区	PM _{2.5}	7	428	9N-ANT (56.8), 2N-PYR+2N-FLT (36.2), 7N-BaA (14.0)
	2017.5	道路	PM _{2.5}	7	661	2N-PYR+2N-FLT (41.9), 9N-ANT (32.4), 1,8-DNP (24.1)
	2017.6	道路	PM _{2.5}	7	1129	9N-ANT (46.3), 2N-PYR+2N-FLT (33.2), 1,8-DNP (12.5)
	2017.5	乡村	PM _{2.5}	7	155	2N-PYR+2N-FLT (54.8), 9N-ANT (38.1)
日本金泽 ^[28]	1989—1996	城区	TSP	4	699	1N-PYR (98.7)
	1989—1996	城区	TSP	4	222	1N-PYR (99.1)
	1989—1996	郊区	TSP	4	22	1N-PYR (100)
越南胡志明 ^[30]	2005.1—2006.3	城区	TSP	2	173	2N-FLT (95.4), 1N-PYR (4.62)
	2005.1—2006.3	城区	TSP	2	199	2N-FLT (95.5), 1N-PYR (4.52)
	2005.1—2006.3	道路	TSP	2	264	2N-FLT (72.3), 1N-PYR (27.7)
丹麦哥本哈根 ^[31]	1996春冬	道路	TSP	5	340	1N-PYR (37.4), 2N-FLT (26.8), 9N-ANT (18.5), 3N-FLT (11.5)
	1998.2—1999.2	乡村	TSP	5	160	2N-FLT (37.5), 3N-FLT (20.0), 9N-ANT (18.8), 1N-PYR (18.8)

不同国家地区大气中 NPAHs 的组成特征和浓度体现了来源结构和强度的空间差异^[14-31]. 我国城市地区 NPAHs 的环境空气浓度范围为 160—5480 $\text{pg}\cdot\text{m}^{-3}$ ^[15-17,19-24], 远高于墨西哥城(152 $\text{pg}\cdot\text{m}^{-3}$)、马赛(710 $\text{pg}\cdot\text{m}^{-3}$)、卢旺达(190—428 $\text{pg}\cdot\text{m}^{-3}$)和胡志明市(173—199 $\text{pg}\cdot\text{m}^{-3}$)等国外城市^[25-27,30]. 我国北方地区中哈尔滨 NPAHs 的年均浓度最高(5480 $\text{pg}\cdot\text{m}^{-3}$), 其 NPAHs 主要来自燃煤和生物质燃烧, 在取暖期 9-硝基蒽对 NPAHs 的贡献为 38.6%^[22]. 南方地区观测到的 NPAHs 浓度最高值出现在珠三角的冬季(4143 $\text{pg}\cdot\text{m}^{-3}$). 珠三角年均温较高且光照强烈, 由 OH·引起的气相反应是 NPAHs 形成的重要途径, 2-硝基荧蒽在 NPAHs 总浓度中占比最高(38.5%)^[16]. 其余城市相似功能区 NPAHs 浓度的差异均在一个数量级以内(表 2). 我国城市地区的 NPAHs 浓度常高于乡村, 例如济南、太原、银川、德州和武威城区 NPAHs 的浓度(835—2151 $\text{pg}\cdot\text{m}^{-3}$)比乡村(619—1570 $\text{pg}\cdot\text{m}^{-3}$)高 1.01—1.73 倍^[17,23]. 除城区机动车保有量高外, 城市大气中含有更多 NPAHs 的前体物(例如, 母体 PAHs, NO_x)和反应物(OH·和 NO_3 ·自由基)也是重要原因^[17]. 图 1 展示了太原、德州和武威城区和乡村 NPAHs 浓度的月变化特征. 由于家庭采暖排放和大气边界层高度降低, NPAHs 的浓度峰值普遍出现在冬季. 尽管二次反应的增强有利于 NPAHs 的形成, 有利的稀释扩散条件、一次排放减弱以及光解作用增强是 NPAHs 浓度在春、夏季浓度降低的主要原因^[17,33].

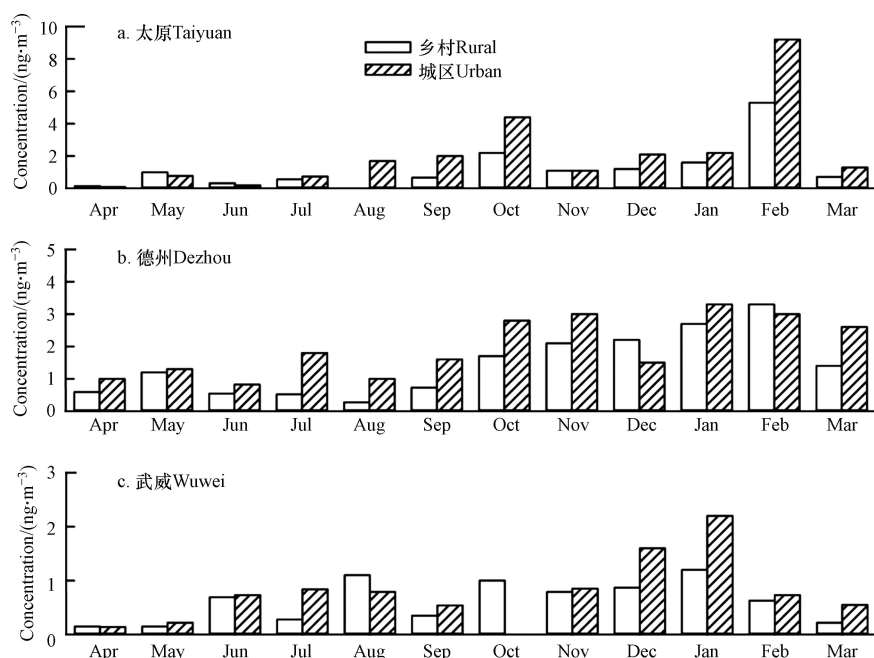


图 1 (a)太原(b)德州和(c)武威城区和乡村 NPAHs 浓度的月变化^[17]

Fig.1 Monthly variations of NPAH concentrations in urban and rural areas of (a) Taiyuan (b) Dezhou and (c) Wuwei^[17]

2 硝基多环芳烃的粒径分布(Size distributions of NPAHs)

NPAHs 的粒径分布决定了其在呼吸系统的传输和沉降行为, 对评价其健康效应至关重要^[34]. 粗颗粒物($D_p > 2.1 \mu\text{m}$)主要沉降在前鼻区和胸膜外区域, 细颗粒物($0.12 < D_p < 2.1 \mu\text{m}$)易伴随呼吸深入肺泡, 超细颗粒物($D_p < 0.12 \mu\text{m}$)在肺泡的沉降效率比细颗粒物更高^[35]. 如图 2 所示, 希腊塞萨洛尼基、法国帕莱索和巴黎大气环境中的 NPAHs 主要富集在亚微米级颗粒物中(PM_1), 粒径分布常呈单峰形态^[36-37], 和日本埼玉市^[35]、法国夏蒙尼山谷和莫列讷河谷^[38]、捷克克拉德诺和俄斯特拉发市^[39]的研究结果相一致. Du 等^[40]的外场观测研究发现山西太谷县大气中 NPAHs 的 24 h 平均浓度为 7.98 $\text{ng}\cdot\text{m}^{-3}$, 分布在 PM_1 中 NPAHs 的浓度约占总浓度的 78%. 在德国美因茨和希腊塞萨洛尼基市, 分布在 $D_p < 0.49 \mu\text{m}$ 颗粒物中的 NPAHs 平均浓度(101—417 $\text{pg}\cdot\text{m}^{-3}$)比分布在 $0.49 < D_p < 0.95 \mu\text{m}$ 的 NPAHs(22.8—222 $\text{pg}\cdot\text{m}^{-3}$)高 1.88—4.43 倍^[36].

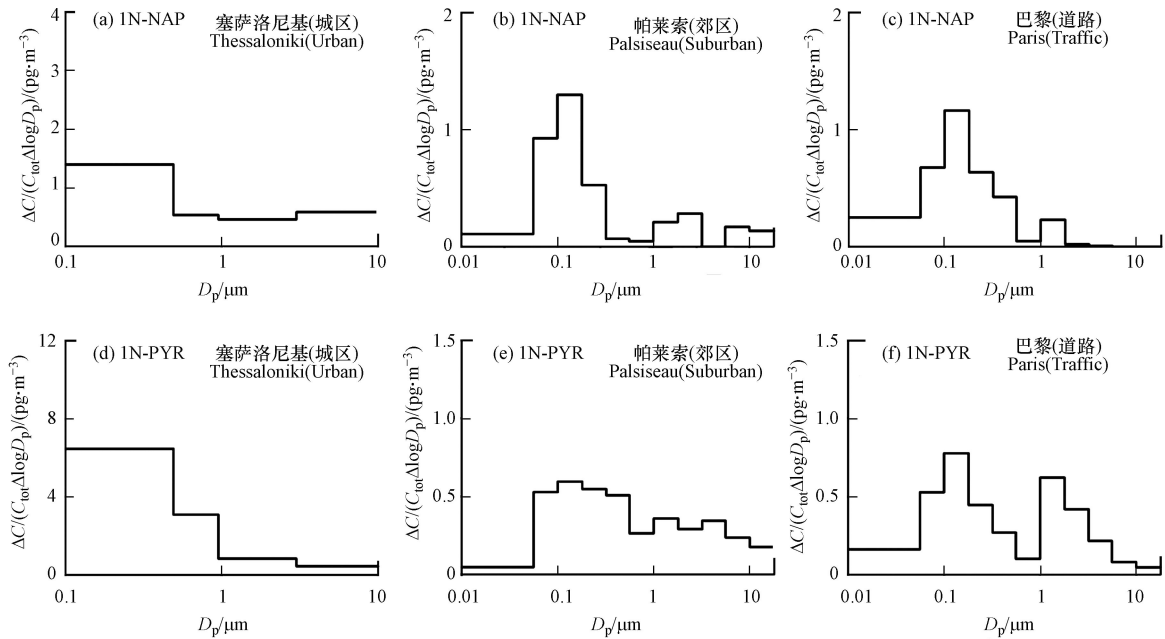


图 2 欧洲典型城市 1N-NAP 和 1N-PYR 的粒径分布^[36-37]

Fig.2 Particle size distributions of 1N-NAP and 1N-PYR in typical European cities^[36-37]

低分子量 NPAHs (例如 1N-NAP 和 2N-NAP) 的饱和蒸气压较高, 可随着气温的变化从细颗粒物上挥发, 再冷凝至粗颗粒物, 导致这些 NPAHs 的粒径分布发生变化^[41-42]. 这是冬季 NPAHs 在粗颗粒物中的浓度占比低于夏季的重要原因^[43]. Shen 等^[44] 发现, 河北农村地区分布在 $D_p > 2.5 \mu\text{m}$ 粗颗粒物中的 1N-NAP 和 2N-NAP 浓度约占其颗粒态总浓度的 20%, 而高分子量 ($MW \geq 223 \text{ g}\cdot\text{mol}^{-1}$) NPAHs 的占比通常低于 10%. 相较于同环数母体 PAHs, NPAHs 的挥发性较弱, 在细粒子中的占比更高. 例如, 法国夏蒙尼山谷和莫列讷河谷约 90% 的 NPAHs 分布在 $D_p < 1.3 \mu\text{m}$ 的细颗粒物上; $D_p < 0.39 \mu\text{m}$ 的颗粒物中含约 63% 的 NPAHs, 而母体 PAHs 所占比例仅为 45%^[38].

3 硝基多环芳烃的气固分配 (Gas-particle partitioning of NPAHs)

NPAHs 的气固分配影响其传输和化学转化等大气过程^[16]. 研究表明 NPAHs 在气态和颗粒态中的分布主要取决于颗粒态有机物浓度和由温度决定的各 NPAHs 物种的饱和蒸气压^[17,39,45]. 例如, 2 环和 3 环 NPAHs 在气态和颗粒态均有分布, 4 环及以上 NPAHs 由于蒸气压较低主要以颗粒态形式存在^[18-19,46]. Lammel 等^[39] 发现, 捷克夏季 18 种 NPAHs 总浓度在颗粒态中的占比仅为 3%, 而冬季则高达 76%—98%.

气固分配系数常用于参数化大气中有机化合物在气态和颗粒态之间的分布, 可基于观测通过公式 (1) 直接计算^[47-48]:

$$K_p = \frac{F/TSP}{A} \quad (1)$$

式 (1) 中, $K_p (\text{m}^3 \cdot \mu\text{g}^{-1})$ 为气固分配系数, F 和 A 分别是 NPAHs 的颗粒态和气态浓度 ($\text{ng}\cdot\text{m}^{-3}$), TSP 为总悬浮颗粒物浓度 ($\mu\text{g}\cdot\text{m}^{-3}$). 和同环数母体 PAHs 相比, NPAHs 苯环上的硝基增大了物质的分子量和极性, 降低了饱和蒸气压, NPAHs 的 K_p 值高于同环数母体 PAHs^[49].

NPAHs 的气固分配机制主要包括气态分子在颗粒物表面的吸附和颗粒态有机物对气态分子的吸收作用^[50]. 已有研究常根据 NPAHs 的 K_p 值和正辛醇-空气分配系数 (K_{OA})、饱和蒸气压 (p_L°) 之间的线性关系推测其气固分配的主导机制. 中国乡村地区木柴燃烧排放的 NPAHs 的 $\lg K_p$ 和 $\lg K_{OA}$ 的相关系数为 0.92 ($P < 0.05$), 表明气固分配过程主要受吸收作用的影响^[51]. 在吸附和吸收机制主导下, 大气有机化合物 $\lg K_p$ 与 $\lg p_L^\circ$ 线性回归曲线的斜率分别在 < -1 和 > -0.6 范围内^[50,52-53]. 外场观测研究发现 NPAHs 的 $\lg K_p$ vs. $\lg p_L^\circ$ 斜率常位于 -0.54 — -0.32 之间, 进一步说明 NPAHs 的气固分配主要体现为颗

粒态有机物对气态分子的吸收过程^[21,51,54-55].

为探索 NPAHs 的气固分配机制所构建的模型主要包括仅考虑单一分配机制的 Junge-Pankow 吸附模型^[56]、Finizio 吸收模型^[57]、Harner-Bidleman 吸收模型^[58], 同时考虑吸收和吸附过程的 Dachs-Eisenreich 模型^[59] 和多参数线性自由能关系模型 (poly-parameter linear free-energy relationships, pp-LFER)^[60] 等. 其中 Harner-Bidleman 吸收模型和 pp-LFER 模型在近些年被广泛应用. 前者用 K_{OA} 代替 p_L^o 将 K_p 简化为 K_{OA} 的函数, 后者将 K_p 和有机化合物的分子结构、理化性质联系起来, 具体如公式 (2、3) 所示^[58,60]:

$$\lg K_p = \lg K_{OA} + \lg f_{OM} - 11.91 \quad (2)$$

$$\lg K_p = sS + aA + bB + vV + lL + c \quad (3)$$

式(2)中 K_{OA} 和 f_{OM} 分别为正辛醇-空气分配系数和颗粒物中有机质含量(%); 式(3)中 S 、 A 、 B 、 L 和 V 为 Abraham 溶剂化参数, 分别代表极化率/偶极性、溶质氢键酸度、溶质氢键碱度、十六烷-空气分配系数的对数值(无量纲)和 McGowan 摩尔体积($\text{cm}^3 \cdot \text{mol}^{-1}/100$); s 、 a 、 b 、 v 、 l 和 c 为系统参数, 反映了特定环境下各溶剂化参数对 K_p 的贡献率.

同时考虑吸收和吸附过程的参数化模型对 K_p 的模拟结果优于仅考虑单一分配机制的模型. Li 等^[49] 根据中国北部城市和乡村地区的观测数据计算了 10 种 NPAHs 的 K_p 值并基于 3 种模型分别进行模拟, 证明基于 Dachs-Eisenreich 模型获得的 K_p 值和观测值的一致性优于 Junge-Pankow 吸附模型和 Harner-Bidleman 吸收模型的预测结果. Lammel 等^[61] 发现, 基于 pp-LFER 模型计算的 11 种 3—4 环 NPAHs 的 K_p 值和观测值的差异在 1 个数量级之内, 优于 Harner-Bidleman 吸收模型预测. 图 3 比较了 2013—2014 年秋季法国格勒诺布尔市 4 种 NPAHs 的 K_p 观测值和基于 Finizio 吸收模型、pp-LFER 模型的模拟值. 虽然 K_p 的观测值和基于两种模型计算的模拟值相关系数接近, 但基于 pp-LFER 模型的预测值和观测值的散点更接近 1:1 线, 表明采用 Finizio 吸收模型将低估 NPAHs 的 K_p 值.

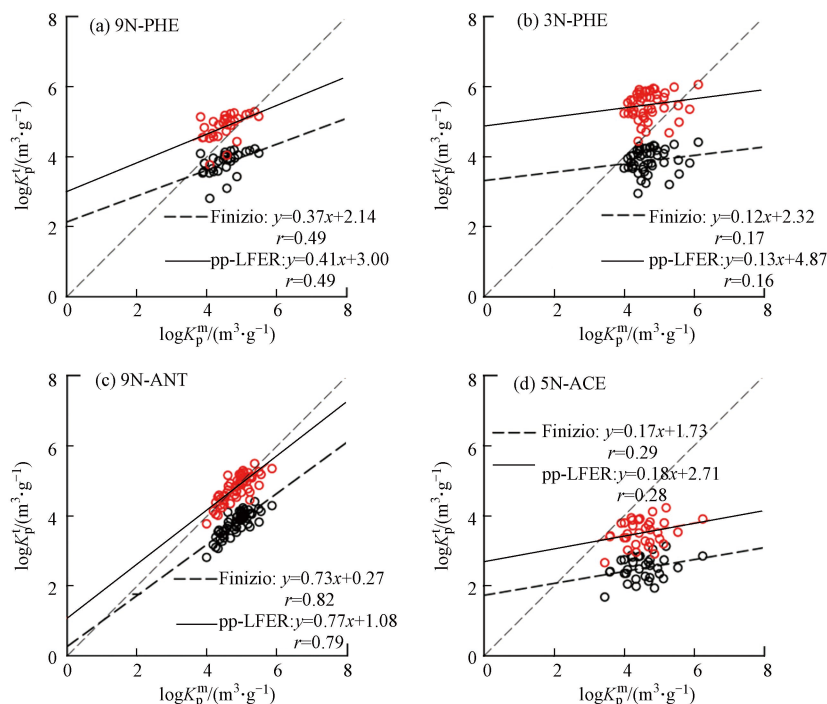


图 3 基于 Finizio 和 pp-LFER 模型计算的 NPAHs 气固分配系数模拟值和观测值的比较(数据引自 Tomaz 等^[45])

Fig.3 Comparisons of predicted gas-particle partitioning coefficients of NPAHs based on Finizio and pp-LFER models and observed values (data obtained from Tomaz et al^[45])

4 硝基多环芳烃的来源(Sources of NPAHs)

4.1 排放因子和二次过程

NPAHs 的一次源主要包括化石和生物质燃料的不完全燃烧^[15]. 为量化不同一次源的贡献和建立

排放源清单,需掌握不同污染源 NPAHs 的排放因子(emission Factors, EFs).表 3 给出了机动车、燃煤和生物质燃烧源相关 NPAHs 的排放因子及组分特征.机动车源的 EFs 通常用单位距离排放的污染物质量表示($\mu\text{g}\cdot\text{km}^{-1}$),排放因子大小及组分特征和机动车类型、运行状况以及尾气处理装置密切相关.基于机动车功率计测试实验和道路观测研究,在汽油机动车排放的颗粒态和气态 NPAHs 中,6-硝基苯并[a]芘(32%—38%)和 1,3-二硝基芘(约 44%)分别占主导地位^[62-63].然而,机动车排放的 NPAHs 主要以气态形式存在,特别是柴油机动车(约 97%).1-硝基芘和 3-硝基菲是柴油车排放 NPAHs 的主要成分,约占 NPAHs 总排放量的 71%—76%,其中 3-硝基菲的排放比 1-硝基芘高 4—6 倍^[64].

表 3 来自机动车、燃煤和生物质燃烧 NPAHs 的排放因子及组分特征

Table 3 Emission factors and chemical compositions of NPAHs from motor vehicles, coal combustions, and biomass burning

燃烧源 Combustion sources	种类 Species No.	类型 Sample Type	排放因子 Emission factors	主要组分/(占比, %) Major compounds
机动车排放 (排放因子, $\mu\text{g}\cdot\text{km}^{-1}$)				
汽油机动车 ^[62]	8	PM _{2.5}	7.57—14.3	6-硝基苯并[a]芘 (32.0)、6-硝基蒽 (20.0)
汽油客运车 ^[63]	9	TSP	7.90	6-硝基苯并[a]芘 (38.4)、3-硝基芘 (15.2)、1,3-二硝基芘 (14.7)
	9	气相	316	1,3-二硝基芘 (44.0)、5-硝基芘 (33.9)
轻型柴油卡车 ^[64]	9	气相+TSP	1124	3-硝基菲 (64.1)、1-硝基芘 (12.1)
中型柴油卡车 ^[64]	9	气相+TSP	842	3-硝基菲 (61.3)、1-硝基芘 (10.1)
重型柴油卡车 ^[64]	9	气相+TSP	1466	3-硝基菲 (58.8)、1-硝基芘 (12.6)
燃煤 (排放因子, $\mu\text{g}\cdot\text{kg}^{-1}$)				
宁夏银川烟煤 ^[65]	23	TSP	4.36	2-硝基芘+2-硝基芘 (66.5)、1-硝基芘 (12.6)
内蒙古东胜烟煤 ^[65]	23	TSP	5.32	6-硝基苯并[a]芘 (77.0)、2-硝基芘 (9.80)
山西大同烟煤 ^[65]	23	TSP	4.14	2-硝基芘+2-硝基芘 (50.7)、1-硝基芘 (22.7)、2-硝基芘 (15.7)
山西大同蜂窝煤 ^[65]	23	TSP	0.32	2-硝基芘 (72.3)
贵州织金无烟煤 ^[65]	23	TSP	3.07	1-硝基芘 (69.4)、6-硝基苯并[a]芘 (15.3)
山西沁源烟煤 ^[66]	26	气相+TSP	1200	2-硝基联苯 (62.9)、5-硝基芘 (10.8)
山西临汾烟煤 ^[66]	26	气相+TSP	440	2-硝基联苯 (22.0)、2-硝基双苯并噻吩 (18.8)
云南宣威烟煤 ^[66]	26	气相+TSP	500	2-硝基双苯并噻吩 (14.6)、2-硝基芘 (9.80)
河南平顶山烟煤 ^[66]	26	气相+TSP	1880	2-硝基联苯 (32.1)、4-硝基联苯 (15.4)
山西晋城无烟煤 ^[66]	26	气相+TSP	140	1-硝基芘 (27.4)、2-硝基芘 (21.6)、2-硝基联苯 (19.3)
山西和顺煤球 ^[67]	9	气相+TSP	640—830	9-硝基芘 (71.1—75.0)、9-硝基菲 (25.0—28.9)
山西和顺煤砖 ^[67]	9	气相+TSP	160—2400	9-硝基芘 (81.3—87.5)、9-硝基菲 (10.0—14.6)
生物质燃烧 (排放因子, $\mu\text{g}\cdot\text{kg}^{-1}$)				
花生壳 ^[65]	23	TSP	100	2-硝基芘+2-硝基芘 (27.0)、1-硝基芘 (25.0)
木头 ^[67]	9	气相+TSP	140—550	9-硝基芘 (33.6—60.0)、9-硝基菲 (30.0—32.7)
灌木 ^[51]	9	气相+TSP	32.2	2-硝基芘 (31.6)、1-硝基芘 (28.4)
木材 ^[67]	9	气相+TSP	8.27	2-硝基芘 (34.5)、1-硝基芘 (31.2)
玉米秸秆 ^[54]	6	气相+TSP	6.50	2-硝基芘 (32.0)、1-硝基芘 (30.0)、9-硝基芘 (22.0)

燃煤和生物质燃烧的 EFs 也受诸多因素的影响,例如,燃料性质(堆积密度、大小和潮湿度等)、燃烧设施(炉灶类型等)和燃烧状态(明燃和焖烧)等.即便是同种燃料燃烧的 EFs 和组分特征仍可能存在较大的差异.表 2 中燃煤源产生的气态和颗粒态 NPAHs 的 EFs 范围为 0.16—2.40 $\text{mg}\cdot\text{kg}^{-1}$, NPAHs 的气态排放量比颗粒态高约 2 个数量级. Shen 等^[67]报道了农村家庭煤球、煤砖和木材燃烧产生 NPAHs 的 EFs 分别为 0.64—0.83 $\text{mg}\cdot\text{kg}^{-1}$ 、0.16—2.40 $\text{mg}\cdot\text{kg}^{-1}$ 和 8.27 $\mu\text{g}\cdot\text{kg}^{-1}$, 9-硝基芘在 NPAHs 组分中占据主导地位(0.040—2.10 $\text{mg}\cdot\text{kg}^{-1}$). 生物质燃烧相关 NPAHs 的 EFs 范围为 6.50—550 $\mu\text{g}\cdot\text{kg}^{-1}$ ^[51,54,65,67], 其中 2-硝基芘(31.6%—34.5%)、1-硝基芘(28.4%—31.2%)和 9-硝基芘(22.0%)为常见组分^[51,54,67].

NPAHs的二次生成途径包括母体PAHs和OH·、NO₃·的气相反应,以及颗粒态PAHs和N₂O₅、HNO₃的多相反应.气相反应因速率较快,也因此被认为是大气中NPAHs的主要二次来源^[68].已有研究推测的反应路径为:OH·或NO₃·先和PAHs苯环上的碳原子反应,然后中间产物OH-PAHs或NO₃-PAHs的邻位增加一个硝基,最终失去一个水分子或硝酸分子形成NPAHs^[69].光照强度上升会增加大气活性物质(例如,OH·和NO₃·等)浓度,提高大气反应速率,从而促进NPAHs的生成^[22,70,71].在城市地区,二次源对NPAHs的年均贡献率在10%—47%之间^[22,71],并在夏季因高温和强光照显著上升,例如北京(76%)、上海(84%)、广州(60%)和成都(64%)^[14].

光解是大气中NPAHs降解的主要途径,NPAHs的光解速率比母体PAHs更快^[72].Hayakawa等^[28]将溶于乙腈的1-硝基芘、1,3-二硝基芘、芘和苯并[a]芘溶液分别暴露于254 nm的近紫外光和太阳光直射3h,发现1-硝基芘和1,3-二硝基芘的降解速率比母体PAHs快1—2个数量级.烟雾箱实验证明NPAHs在O₃作用下的非均相氧化是夜间NPAHs的重要降解途径^[73-74],导致NPAHs和O₃的环境空气浓度在夜间通常呈显著负相关^[26,75].实验室研究推断颗粒态NPAHs在光解和O₃非均相氧化作用下的半衰期分别为约1h和约29h^[73].另外,干、湿沉降过程也能从大气中有效去除颗粒态NPAHs^[76-77].

4.2 源解析方法

大气污染物源解析的常用工具包括扩散模型、源排放清单分析和受体模型.扩散模型基于源排放信息、气象条件和化学过程综合模拟污染物的时空分布;源排放清单方法通过调查和统计各种源的排放因子和活动水平估算污染源的贡献率;受体模型根据示踪物浓度信息结合数学统计方法识别源类别并计算贡献率^[78].由于目前尚未建立完善的NPAHs源清单,源排放清单和扩散模型方法的应用受到限制.已有研究采用各种统计手段对NPAHs进行源解析,主要包括相关性分析、特征比值和受体模型法.

4.2.1 相关性分析

NPAHs浓度和大气活性物质(例如,NO_x、OH·和O₃等)浓度和气象条件(例如,温度、辐射照度等)的相关性可用于定性判断二次源的存在.大气活性物质的浓度水平和NPAHs在多地呈显著正相关.例如,法国巴黎市大气中1-硝基萘、2-硝基萘、6-硝基蒽和NO₂、NO、CO浓度的相关系数均超过0.60($P < 0.05$)^[29].但是,NPAHs和NO_x浓度的强相关性可能还和二者间的同源性有关^[26].因此,Lin等^[79]提出根据lg NPAHs和lg NO₂的线性关系区分一次和二次源,二者线性回归曲线斜率在<1和>1情形下分别指示一次排放和二次生成主导.哈尔滨市冬季供暖期大气中NPAHs的浓度和温度、辐射照度的相关性显著($r = 0.35-0.38, P < 0.05$),而母体PAHs的浓度和温度、辐射照度却呈负相关($r = -0.47- -0.47, P < 0.01$)^[22].这是因为供暖期PAHs在环境空气中的浓度升高,其光化学反应促进了NPAHs的形成.

NPAHs浓度和典型源示踪物浓度或人为活动的相关性可用于推断NPAHs的一次源.日本长崎市PAHs、NPAHs浓度和交通量的相关系数分别是0.78和0.82,表明机动车排放是城市大气中NPAHs的重要来源^[80].哈尔滨大气中的9-硝基蒽和1-硝基芘(柴油车排放示踪物)的强相关性说明该地区的9-硝基蒽也主要来源于柴油机动车排放^[22].采用类似方法,法国马赛市空气中的2-硝基芘和6-硝基蒽($r = 0.97-1.00, P < 0.05$)也被认为和柴油机动车排放有关^[26].尽管如此,相关性分析仅能帮助识别某一类排放源的存在,无法对来源贡献进行定量.

4.2.2 特征比值

特征比值法利用不同化学组分浓度的比例关系判断其主导来源.表4列出了NPAHs的典型特征比值、指示源和理论依据.廊坊市白天和夜间的2-硝基芘/1-硝基芘(2N-FLT/1N-PYR)分别为4.36和0.89(<5),因此可判断该地区NPAHs的排放由一次源主导,但白天二次源的贡献增强^[81].2010年上海世博会期间(5—10月)因执行严格的空气质量管控措施,2N-FLT/1N-PYR增大至11—31,说明该时期NPAHs主要来源于二次形成过程^[82].9-硝基蒽/1-硝基芘(9N-ANT/1N-PYR)可作为区分生物质燃烧或机动车排放主导的依据.Ma等^[22]于2017—2018年在哈尔滨市采集了82个PM_{2.5}样品并分析了NPAHs组分,发现几乎所有样品的9N-ANT/1N-PYR值均高于10(平均值为34.6),从而推断生物质燃烧是采样期间颗粒态NPAHs的主要来源.

表 4 用于 NPAHs 来源分析的特征比值
Table 4 Characteristic ratios for NPAHs source analysis

特征比值 Diagnostic ratios	临界点 Critical point	指示源 Sources	理论依据 Rationale	参考文献 Reference
2-硝基荧蒽/1-硝基芘 (2N-FLT/1N-PYR)	<5 >5	一次排放 二次形成	2-硝基荧蒽主要通过荧蒽和NO ₂ 的气相反应生成,白天与夜间分别由OH·和NO ₃ ·引发,而1-硝基芘仅来自一次排放	[8,19,26,81 – 82,84 – 87]
9-硝基蒽/1-硝基芘 (9N-ANT/1N-PYR)	>10 <10	生物质燃烧 机动车排放	9-硝基蒽主要来自生物质燃烧,而1-硝基芘主要来自机动车排放	[14,22,84]
2-硝基荧蒽/2-硝基芘 (2N-FLT/2N-PYR)	~10 ~100	白天由OH·引起的气相反应 夜间由NO ₃ ·引起的气相反应	2-硝基芘仅由OH·引起的气相反应生成,而2-硝基荧蒽可由OH·和NO ₃ ·引起的气相反应生成	[8,14,26,68,84]
ΣNPAHs/ΣPAHs	~10 ⁻⁴ ≈ 0.13	燃煤 柴油机动车排放	高温燃烧产生的PAHs在NO _x 存在时部分被硝化,NPAHs的产量随着温度的升高而增大.柴油机动车燃烧的温度(2700℃)远高于燃煤温度(900℃),会产生更多的NPAHs	[22,83]

2-硝基荧蒽/2-硝基芘(2N-FLT/2N-PYR)可用于区分由OH·和NO₃·引发的NPAHs形成路径.中国北方地区(包括北京、天津、河北、山东、山西和河南)夏、秋季大气中2N-FLT/2N-PYR均值为4.5,由OH·引发的气相反应对NPAHs的贡献高于NO₃·相关的气相反应^[68].在法国夏蒙尼山谷和莫列讷河谷,该比值在夏季(0—80)远高于冬季(0—10)^[8],说明夏季夜间由NO₃·引发的气相反应是该地区NPAHs的主要来源.由于夜间机动车排放的NO会消耗NO₃·,城区和交通干道附近的2N-FLT/2N-PYR值比乡村地区低^[8].另外,NPAHs的排放随燃烧温度而升高.由于柴油车内燃机温度(2700℃)远高于工业煤炉(900℃),柴油车尾气中NPAHs和PAHs的浓度比值(ΣNPAHs/ΣPAHs,0.13)比燃煤(0.0001)高2—3个数量级^[83].因此,可根据环境空气中ΣNPAHs/ΣPAHs的数值区分燃煤和柴油车排放.和相关性分析类似,特征比值仅能帮助定性判断NPAHs主导来源,无法量化源贡献.

4.2.3 受体模型

常用于解析大气污染物的受体模型包括主成分分析(principal component analysis, PCA)、正定矩阵因子分析(positive matrix factorization, PMF)和化学质量平衡法(chemical mass balance, CMB)等.多个国家地区空气中PAHs和NPAHs的PCA分析结果表明机动车排放和生物质燃烧分别是城区和乡村的主要来源^[27,88].由于缺乏本地源成分谱信息,CMB模型较少用于NPAHs的源解析研究.PMF模型是一种具有非负约束的因子分析模型,其运行不需要源排放数据,输出结果中各因子的组成和贡献仅依赖样品数据^[89].已有研究中用于PMF源解析的一次NPAHs示踪物有1-硝基芘和9-硝基蒽,二次源示踪物包括1-硝基萘、2-硝基萘和2-硝基荧蒽.基于PMF源解析结果,Ma等^[22]发现哈尔滨大气中的NPAHs由一次排放主导(非供暖期77%,供暖期81%).北京市交通排放对NPAHs的贡献在供暖期占据主导地位(58%),而在非供暖期二次源的贡献显著上升(64%)^[15].由于和NPAHs有关的化学反应复杂且适用的示踪物较少,需结合相关性分析和特征比值等多种方法来验证受体模型源解析结果的合理性(图4).

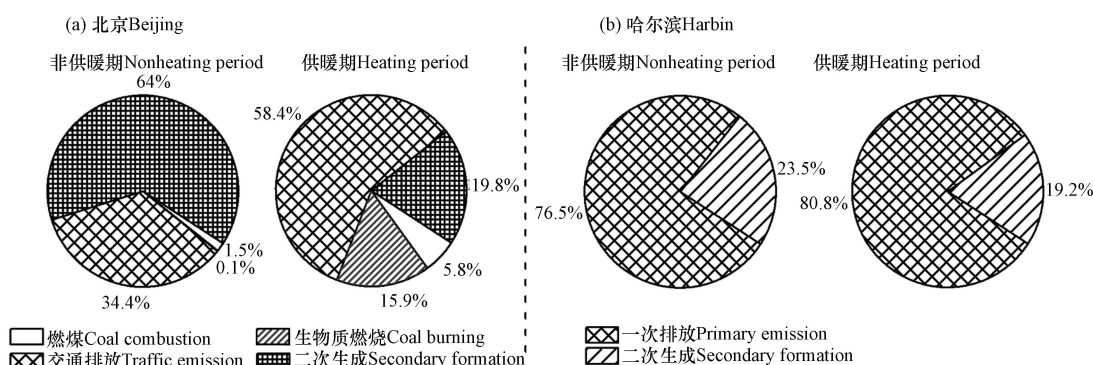


图 4 基于 PMF 模型解析出的(a)北京^[15]和(b)哈尔滨^[22]大气中 NPAHs 的源贡献分布
Fig.4 Source contribution distributions of ambient NPAHs in (a) Beijing^[15] and (b) Harbin^[22] based on PMF modeling

5 硝基多环芳烃的毒性(Toxicity of NPAHs)

尽管 NPAHs 在大气中的浓度比母体 PAHs 低 1—2 个数量级,其致突变性和致癌性比母体 PAHs 高 1—5 个数量级^[1].例如,1,8-二硝基芘的致诱变活性比苯并[a]芘高 3 个数量级^[14]; 50 nmol·L⁻¹ 3-硝基苯并蒽酮对人体肝癌细胞微核形成和 DNA 的损伤效应等同于 50 μmol·L⁻¹ 苯并[a]芘^[90].呼吸道是 NPAHs 进入人体或动物的主要途径,毒理学研究表明当雄性成年鼠暴露于浓度>0.5 mg·m⁻³ 的 1-硝基芘以后,会出现鳞状上皮化生和细胞质改变等不良反应^[91].另外,由于某些特殊职业人群(例如,柴油厂工人)常暴露在 NPAHs 浓度较高的环境中,他们血液和尿液中 NPAHs 的代谢标志物(如氨基蒽)含量明显高于普通人群^[92-93].

NPAHs 对人体健康的潜在风险可通过苯并[a]芘等效毒性当量(benzo[a]pyrene equivalent, BaP_{eq})、总毒性当量(toxic equivalents, ∑TEQ)、终生致癌风险增量(incremental lifetime cancer risk, ILCR)和预期寿命损失(loss of life expectancy, LLE)等指数表征.苯并[a]芘等效毒性当量和终生致癌风险增量的定义式为^[34,40]:

$$C_{\text{BaP}_{\text{eq}}} = C_{\text{NPAHs}} \times \text{TEF}_{\text{NPAHs}} \quad (4)$$

$$\text{ILCR}_{\text{Inhalation}} = \text{CSF}_{\text{Inhalation}} \times \frac{\sum \text{BaP}_{\text{eq}} \times \text{IR}_{\text{Inhalation}} \times \text{EF} \times \text{ED} \times \text{cf}}{\text{BW} \times \text{AT}} \quad (5)$$

式(4)中 $C_{\text{BaP}_{\text{eq}}}$ 为苯并[a]芘等效当量浓度($\text{ng}\cdot\text{m}^{-3}$), C_{NPAHs} 为 NPAHs 的浓度($\text{ng}\cdot\text{m}^{-3}$), $\text{TEF}_{\text{NPAHs}}$ 为相应 NPAHs 的等效毒性因子.式(5)中 $\text{CSF}_{\text{Inhalation}}$ 代表致癌斜率因子($\text{mg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$)⁻¹, $\sum \text{BaP}_{\text{eq}}$ 为苯并[a]芘等效毒性当量总浓度($\text{ng}\cdot\text{m}^{-3}$), $\text{IR}_{\text{Inhalation}}$ 、EF、ED 和 cf 分别代表空气吸入速率($\text{m}^3\cdot\text{d}^{-1}$)、暴露频率($\text{d}\cdot\text{a}^{-1}$)、暴露年限(a)和转换系数($10^{-6} \text{mg}\cdot\text{ng}^{-1}$), BW 和 AT 分别为平均体重(kg)和致癌物的平均寿命(d).

Du 等^[40]根据观测结果,计算得出山西太谷县农村地区 6 种 NPAHs 的 $C_{\text{BaP}_{\text{eq}}}$ 范围为 0.043—48 $\text{ng}\cdot\text{m}^{-3}$,农村居民的 ILCR 平均值为 7.90×10^{-4} ,高于限值 10^{-4} .华北平原大面积的秸秆焚烧是山东泰山环境空气中 NPAHs 的主要来源,NPAHs 相关 ILCR 的最大值(1.81×10^{-9})出现在成人组(30—70 岁),其次是幼儿组(1—6 岁, 5.69×10^{-10}),表明因毒性累积效应 NPAHs 对 30 岁以上的成年人具有更高的致癌风险^[30].NPAHs 对气溶胶毒性的贡献远高于其质量浓度贡献.例如,哈尔滨地区 NPAHs 的环境浓度仅占 $\sum(\text{PAHs}+\text{NPAHs})$ 的 1.54%,但它们对 $\sum\text{TEQ}$ 的贡献则达到 5.88%^[22].西安地区 NPAHs 浓度仅占 $\sum(\text{PAHs}+\text{OPAHs}+\text{NPAHs})$ 的 0.02%,对 $C_{\text{BaP}_{\text{eq}}}$ 的贡献为 0.07%^[86].

6 结论与展望(Conclusion and Prospect)

(1)我国 NPAHs 的大气浓度通常在 $\text{pg}\cdot\text{m}^{-3}$ 级,城市地区的 NPAHs 浓度普遍高于乡村.受机动车排放和生物质燃烧的影响,在城市地区 9-硝基蒽对 NPAHs 浓度的贡献占据主导地位.由于家庭采暖和大气边界层高度降低,浓度峰值通常出现在秋、冬季.NPAHs 的蒸气压比同环数母体 PAHs 低,从而更容易以颗粒态形式存在,并主要分布在亚微米级颗粒物($D_p < 1 \mu\text{m}$)上.仅考虑颗粒态有机物吸收机制的气固分配模型易低估 NPAHs 的气固分配系数.

(2)NPAHs 既可由化石和生物质燃料的不完全燃烧直接排放,也可通过母体 PAHs 和大气氧化物(例如 OH·、NO₃·等)的气相和非均相反应生成.白天的光解作用和夜间在 O₃ 作用下的非均相氧化是环境空气中 NPAHs 的主要降解途径.由于缺乏具有代表性的 NPAHs 源排放数据,已有研究常采用相关性分析、特征比值和受体模型对 NPAHs 的来源进行分析.NPAHs 的致突变性和致癌性比母体 PAHs 高 1—5 个数量级,且因毒性累积效应对 30 岁以上的成年人具有更高的致癌风险.

(3)已有研究仍主要关注 NPAHs 的环境表征(例如,时空差异等),NPAHs 在大气中的迁移转化过程仍不清楚.此外,已有研究往往仅针对单一过程(例如,气固分配,光化学过程)进行模拟和实验研究,较少考虑不同物理化学过程之间的影响.另外,应加快建立全国范围和重点区域的大气排放源清单,识别源指示性较好的 NPAHs 示踪物.这些工作将有助于 NPAHs 的来源和健康效应评估,为污染控制对策的制定提供科学依据.

参考文献 (References)

- [1] NASSAR H F, TANG N, KAMEDA T, et al. Atmospheric concentrations of polycyclic aromatic hydrocarbons and selected nitrated derivatives in Greater Cairo, Egypt [J]. *Atmospheric Environment*, 2011, 45(39): 7352-7359.
- [2] TOKIWA H, OHNISHI Y, ROSENKRANZ H S. Mutagenicity and carcinogenicity of nitroarenes and their sources in the environment [J]. *CRC Critical Reviews in Toxicology*, 1986, 17(1): 23-58.
- [3] 关东杰, 沈振兴, 陈庆彩. 棕碳气溶胶的生成机制研究进展 [J]. *环境化学*, 2020, 39(10): 2812-2822.
GUAN D J, SHEN Z X, CHEN Q C. Formation and elimination of brown carbon aerosol: A review [J]. *Environmental Chemistry*, 2020, 39(10): 2812-2822(in Chinese).
- [4] GUO L Q, LIU Z Q, LI P H, et al. Association between mitochondrial DNA methylation and internal exposure to polycyclic aromatic hydrocarbons (PAHs), nitrated-PAHs (NPAHs) and oxygenated-PAHs (OPAHs) in young adults from Tianjin, China [J]. *Ecotoxicology and Environmental Safety*, 2022, 241: 113799.
- [5] BOSTRÖM C E, GERDE P, HANBERG A, et al. Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air [J]. *Environmental Health Perspectives*, 2002, 110(Suppl 3): 451-488.
- [6] CHEN Y, HO K F, HO S S H, et al. Gaseous and particulate polycyclic aromatic hydrocarbons (PAHs) emissions from commercial restaurants in Hong Kong [J]. *Journal of Environmental Monitoring*, 2007, 9(12): 1402-1409.
- [7] RAVINDRA K, SOKHI R, van GRIEKEN R. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation [J]. *Atmospheric Environment*, 2008, 42(13): 2895-2921.
- [8] ALBINET A, LEOZ-GARZIANDIA E, BUDZINSKI H, et al. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys [J]. *Atmospheric Environment*, 2008, 42(1): 43-54.
- [9] BOLTON J L, TRUSH M A, PENNING T M, et al. Role of quinones in toxicology [J]. *Chemical Research in Toxicology*, 2000, 13(3): 135-160.
- [10] LUNDSTEDT S, WHITE P A, LEMIEUX C L, et al. Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites [J]. *Ambio*, 2007, 36(6): 475-485.
- [11] WILSON N K, MCCURDY T R, CHUANG J C. Concentrations and phase distributions of nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air [J]. *Atmospheric Environment*, 1995, 29(19): 2575-2584.
- [12] TEBES-STEVENSON C, PATEL J M, KOOPMANS M, et al. Demonstration of a consensus approach for the calculation of physicochemical properties required for environmental fate assessments [J]. *Chemosphere*, 2018, 194: 94-106.
- [13] CARD M L, GOMEZ-ALVAREZ V, LEE W, et al. History of EPI Suite™ and future perspectives on chemical property estimation in US Toxic Substances Control Act new chemical risk assessments [J]. *Environmental Science-Processes & Impacts*, 2017, 19: 203-212.
- [14] LIU D, LIN T, SYED J H, et al. Concentration, source identification, and exposure risk assessment of PM_{2.5}-bound parent PAHs and nitro-PAHs in atmosphere from typical Chinese Cities [J]. *Scientific Reports*, 2017, 7: 10398.
- [15] LIN Y, MA Y Q, QIU X H, et al. Sources, transformation, and health implications of polycyclic aromatic hydrocarbons (PAHs) and their nitrated, hydroxylated, and oxygenated derivatives in fine particulate matter (PM_{2.5}) in Beijing [J]. *Journal of Geophysical Research Atmospheres*, 2015, 120(14): 7219-7228.
- [16] HUANG B, LIU M, BI X H, et al. Phase distribution, sources and risk assessment of PAHs, NPAHs and OPAHs in a rural site of Pearl River Delta region, China [J]. *Atmospheric Pollution Research*, 2014, 5(2): 210-218.
- [17] LI W, WANG C, SHEN H Z, et al. Concentrations and origins of nitro-polycyclic aromatic hydrocarbons and oxy-polycyclic aromatic hydrocarbons in ambient air in urban and rural areas in Northern China [J]. *Environmental Pollution*, 2015, 197: 156-164.
- [18] dos SANTOS R R, CARDEAL Z D L, MENEZES H C. Phase distribution of polycyclic aromatic hydrocarbons and their oxygenated and nitrated derivatives in the ambient air of a Brazilian urban area [J]. *Chemosphere*, 2020, 250: 126223.
- [19] HU H L, TIAN M, ZHANG L M, et al. Sources and gas-particle partitioning of atmospheric parent, oxygenated, and nitrated polycyclic aromatic hydrocarbons in a humid city in southwest China [J]. *Atmospheric Environment*, 2019, 206: 1-10.
- [20] ZHANG J M, YANG L X, MELLOUKI A, et al. Atmospheric PAHs, NPAHs, and OPAHs at an urban, mountainous, and marine sites in Northern China: Molecular composition, sources, and ageing [J]. *Atmospheric Environment*, 2018, 173: 256-264.
- [21] ZHUO S J, DU W, SHEN G F, et al. Urban air pollution and health risks of parent and nitrated polycyclic aromatic hydrocarbons in two megacities, southwest China [J]. *Atmospheric Environment*, 2017, 166: 441-453.
- [22] MA L X, LI B, LIU Y P, et al. Characterization, sources and risk assessment of PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) in Harbin, a cold city in Northern China [J]. *Journal of Cleaner Production*, 2020, 264: 121673.
- [23] LI J S, YANG L X, GAO Y, et al. Seasonal variations of NPAHs and OPAHs in PM_{2.5} at heavily polluted urban and suburban sites in North China: Concentrations, molecular compositions, cancer risk assessments and sources [J]. *Ecotoxicology and Environmental Safety*, 2019, 178: 58-65.
- [24] LI R J, KOU X J, GENG H, et al. Pollution characteristics of ambient PM_{2.5}-bound PAHs and NPAHs in a typical winter time period in Taiyuan [J]. *Chinese Chemical Letters*, 2014, 25(5): 663-666.

- [25] VALLE-HERNÁNDEZ B L, MUGICA-ÁLVAREZ V, SALINAS-TALAVERA E, et al. Temporal variation of nitro-polycyclic aromatic hydrocarbons in PM₁₀ and PM_{2.5} collected in Northern Mexico City [J]. *Science of the Total Environment*, 2010, 408(22): 5429-5438.
- [26] ALBINET A, LEOZ-GARZIANDIA E, BUDZINSKI H, et al. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources [J]. *Science of the Total Environment*, 2007, 384(1/2/3): 280-292.
- [27] KALISA E, NAGATO E G, BIZURU E, et al. Characterization and risk assessment of atmospheric PM_{2.5} and PM₁₀ particulate-bound PAHs and NPAHs in Rwanda, central-east Africa [J]. *Environmental Science & Technology*, 2018, 52(21): 12179-12187.
- [28] HAYAKAWA K, TANG N, AKUTSU K, et al. Comparison of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in airborne particulates collected in downtown and suburban Kanazawa, Japan [J]. *Atmospheric Environment*, 2002, 36(35): 5535-5541.
- [29] RINGUET J, ALBINET A, LEOZ-GARZIANDIA E, et al. Diurnal/nocturnal concentrations and sources of particulate-bound PAHs, OPAHs and NPAHs at traffic and suburban sites in the region of Paris (France) [J]. *Science of the Total Environment*, 2012, 437: 297-305.
- [30] HIEN T T, THANH L T, KAMEDA T, et al. Nitro-polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons in particulate matter in an urban area of a tropical region: Ho Chi Minh City, Vietnam [J]. *Atmospheric Environment*, 2007, 41(36): 7715-7725.
- [31] FEILBERG A, B POULSEN M W, NIELSEN T, et al. Occurrence and sources of particulate nitro-polycyclic aromatic hydrocarbons in ambient air in Denmark [J]. *Atmospheric Environment*, 2001, 35(2): 353-366.
- [32] WEI S L, HUANG B, LIU M, et al. Characterization of PM_{2.5}-bound nitrated and oxygenated PAHs in two industrial sites of South China [J]. *Atmospheric Research*, 2012, 109/110: 76-83.
- [33] DEGRENDELE C, KANDUČ T, KOČMAN D, et al. NPAHs and OPAHs in the atmosphere of two central European Cities: Seasonality, urban-to-background gradients, cancer risks and gas-to-particle partitioning [J]. *Science of the Total Environment*, 2021, 793: 148528.
- [34] GAO Y, YANG L X, CHEN J M, et al. Nitro and oxy-PAHs bounded in PM_{2.5} and PM_{1.0} under different weather conditions at Mount Tai in Eastern China: Sources, long-distance transport, and cancer risk assessment [J]. *Science of the Total Environment*, 2018, 622/623: 1400-1407.
- [35] KAWANAKA Y, MATSUMOTO E, WANG N, et al. Contribution of nitrated polycyclic aromatic hydrocarbons to the mutagenicity of ultrafine particles in the roadside atmosphere [J]. *Atmospheric Environment*, 2008, 42(32): 7423-7428.
- [36] KITANOVSKI Z, SHAHPOURY P, SAMARA C, et al. Composition and mass size distribution of nitrated and oxygenated aromatic compounds in ambient particulate matter from southern and central Europe - implications for the origin [J]. *Atmospheric Chemistry and Physics*, 2020, 20(4): 2471-2487.
- [37] RINGUET J, LEOZ-GARZIANDIA E, BUDZINSKI H, et al. Particle size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons (NPAHs and OPAHs) on traffic and suburban sites of a European megacity: Paris (France) [J]. *Atmospheric Chemistry and Physics*, 2012, 12(18): 8877-8887.
- [38] ALBINET A, LEOZ-GARZIANDIA E, BUDZINSKI H, et al. Nitrated and oxygenated derivatives of polycyclic aromatic hydrocarbons in the ambient air of two French alpine valleys Part 2: Particle size distribution [J]. *Atmospheric Environment*, 2008, 42(1): 55-64.
- [39] LAMMEL G, KITANOVSKI Z, KUKUČKA P, et al. Oxygenated and nitrated polycyclic aromatic hydrocarbons in ambient air-levels, phase partitioning, mass size distributions, and inhalation bioaccessibility [J]. *Environmental Science & Technology*, 2020, 54(5): 2615-2625.
- [40] DU W, CHEN Y C, SHEN G F, et al. Winter air pollution by and inhalation exposure to nitrated and oxygenated PAHs in rural Shanxi, North China [J]. *Atmospheric Environment*, 2018, 187: 210-217.
- [41] ALLEN J O, DOOKERAN N M, SMITH K A, et al. Measurement of polycyclic aromatic hydrocarbons associated with size-segregated atmospheric aerosols in Massachusetts [J]. *Environmental Science & Technology*, 1996, 30(3): 1023-1031.
- [42] VENKATARAMAN C, THOMAS S, KULKARNI P. Size distributions of polycyclic aromatic hydrocarbons—Gas/particle partitioning to urban aerosols [J]. *Journal of Aerosol Science*, 1999, 30(6): 759-770.
- [43] TIAN M, LIANG B, ZHANG L M, et al. Measurement of size-segregated airborne particulate bound polycyclic aromatic compounds and assessment of their human health impacts - A case study in a megacity of southwest China [J]. *Chemosphere*, 2021, 284: 131339.
- [44] SHEN G F, CHEN Y C, DU W, et al. Exposure and size distribution of nitrated and oxygenated polycyclic aromatic hydrocarbons among the population using different household fuels [J]. *Environmental Pollution*, 2016, 216: 935-942.
- [45] TOMAZ S, SHAHPOURY P, JAFFREZO J L, et al. One-year study of polycyclic aromatic compounds at an urban site in Grenoble (France): Seasonal variations, gas/particle partitioning and cancer risk estimation [J]. *Science of the Total Environment*, 2016, 565: 1071-1083.

- [46] WU S P, YANG B Y, WANG X H, et al. Diurnal variation of nitrated polycyclic aromatic hydrocarbons in PM₁₀ at a roadside site in Xiamen, China [J]. *Journal of Environmental Sciences*, 2012, 24(10): 1767-1776.
- [47] PANKOW J F. Common γ -intercept and single compound regressions of gas-particle partitioning data vs 1/T [J]. *Atmospheric Environment. Part A. General Topics*, 1991, 25(10): 2229-2239.
- [48] YAMASAKI H, KUWATA K, MIYAMOTO H. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons [J]. *Environmental Science & Technology*, 1982, 16(4): 189-194.
- [49] LI W, SHEN G F, YUAN C Y, et al. The gas/particle partitioning of nitro- and oxy-polycyclic aromatic hydrocarbons in the atmosphere of Northern China [J]. *Atmospheric Research*, 2016, 172/173: 66-73.
- [50] GOSS K U, SCHWARZENBACH R P. Gas/solid and gas/liquid partitioning of organic compounds: Critical evaluation of the interpretation of equilibrium constants [J]. *Environmental Science & Technology*, 1998, 32(14): 2025-2032.
- [51] SHEN G F, TAO S, WEI S Y, et al. Emissions of parent, nitro, and oxygenated polycyclic aromatic hydrocarbons from residential wood combustion in rural China [J]. *Environmental Science & Technology*, 2012, 46(15): 8123-8130.
- [52] LOHMANN R, LAMMEL G. Adsorptive and absorptive contributions to the gas-particle partitioning of polycyclic aromatic hydrocarbons: State of knowledge and recommended parametrization for modeling [J]. *Environmental Science & Technology*, 2004, 38(14): 3793-3803.
- [53] SHEN G F, WANG W, YANG Y F, et al. Emissions of PAHs from indoor crop residue burning in a typical rural stove: Emission factors, size distributions, and gas-particle partitioning [J]. *Environmental Science & Technology*, 2011, 45(4): 1206-1212.
- [54] SHEN G F, XUE M, WEI S Y, et al. Emissions of parent, nitrated, and oxygenated polycyclic aromatic hydrocarbons from indoor corn straw burning in normal and controlled combustion conditions [J]. *Journal of Environmental Sciences*, 2013, 25(10): 2072-2080.
- [55] WEI C, HAN Y M, BANDOWE B A M, et al. Occurrence, gas/particle partitioning and carcinogenic risk of polycyclic aromatic hydrocarbons and their oxygen and nitrogen containing derivatives in Xi'an, central China [J]. *Science of the Total Environment*, 2015, 505: 814-822.
- [56] PANKOW J F. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere [J]. *Atmospheric Environment (1967)*, 1987, 21(11): 2275-2283.
- [57] FINIZIO A, MACKAY D, BIDLLEMAN T, et al. Octanol-air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols [J]. *Atmospheric Environment*, 1997, 31(15): 2289-2296.
- [58] HARNER T, BIDLLEMAN T F. Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air [J]. *Environmental Science & Technology*, 1998, 32(10): 1494-1502.
- [59] DACHS J, EISENREICH S J. Adsorption onto aerosol soot carbon dominates gas-particle partitioning of polycyclic aromatic hydrocarbons [J]. *Environmental Science & Technology*, 2000, 34(17): 3690-3697.
- [60] ABRAHAM M H. Scales of solute hydrogen-bonding: Their construction and application to physicochemical and biochemical processes [J]. *Chemical Society Reviews*, 1993, 22(2): 73-83.
- [61] LAMMEL G, MULDER M D, SHAHPOURY P, et al. Nitro-polycyclic aromatic hydrocarbons - gas-particle partitioning, mass size distribution, and formation along transport in marine and continental background air [J]. *Atmospheric Chemistry and Physics*, 2017, 17(10): 6257-6270.
- [62] ZHAO T, YANG L X, HUANG Q, et al. PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) and nitrated-PAHs (NPAHs) emitted by gasoline vehicles: Characterization and health risk assessment [J]. *Science of the Total Environment*, 2020, 727: 138631.
- [63] HAO X W, ZHANG X, CAO X Y, et al. Characterization and carcinogenic risk assessment of polycyclic aromatic and nitro-polycyclic aromatic hydrocarbons in exhaust emission from gasoline passenger cars using on-road measurements in Beijing, China [J]. *Science of the Total Environment*, 2018, 645: 347-355.
- [64] CAO X Y, HAO X W, SHEN X B, et al. Emission characteristics of polycyclic aromatic hydrocarbons and nitro-polycyclic aromatic hydrocarbons from diesel trucks based on on-road measurements [J]. *Atmospheric Environment*, 2017, 148: 190-196.
- [65] YANG X Y, LIU S J, XU Y S, et al. Emission factors of polycyclic and nitro-polycyclic aromatic hydrocarbons from residential combustion of coal and crop residue pellets [J]. *Environmental Pollution*, 2017, 231: 1265-1273.
- [66] HUANG W, HUANG B, BI X H, et al. Emission of PAHs, NPAHs and OPAHs from residential honeycomb coal briquette combustion [J]. *Energy & Fuels*, 2014, 28(1): 636-642.
- [67] SHEN G F, TAO S, WEI S Y, et al. Field measurement of emission factors of PM, EC, OC, parent, nitro-, and oxy- polycyclic aromatic hydrocarbons for residential briquette, coal cake, and wood in rural Shanxi, China [J]. *Environmental Science & Technology*, 2013, 47(6): 2998-3005.
- [68] LIN Y, QIU X H, MA Y Q, et al. Concentrations and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) in the atmosphere of North China, and the transformation from PAHs to NPAHs [J]. *Environmental Pollution*, 2015, 196: 164-170.
- [69] ZHANG Q Z, GAO R, XU F, et al. Role of water molecule in the gas-phase formation process of nitrated polycyclic aromatic

- hydrocarbons in the atmosphere: A computational study [J]. *Environmental Science & Technology*, 2014, 48(9): 5051-5057.
- [70] AREY J, ATKINSON R, ZIELINSKA B, et al. Diurnal concentrations of volatile polycyclic aromatic hydrocarbons and nitroarenes during a photochemical air pollution episode in Glendora, *California* [J]. *Environmental Science & Technology*, 1989, 23(3): 321-327.
- [71] ZHUO S J, DU W, SHEN G F, et al. Estimating relative contributions of primary and secondary sources of ambient nitrated and oxygenated polycyclic aromatic hydrocarbons [J]. *Atmospheric Environment*, 2017, 159: 126-134.
- [72] FEILBERG A, NIELSEN T. Photodegradation of nitro-PAHs in viscous organic media used as models of organic aerosols [J]. *Environmental Science & Technology*, 2001, 35(1): 108-113.
- [73] FAN Z, KAMENS R, ZHANG J B, et al. Ozone-nitrogen dioxide-NPAH heterogeneous soot particle reactions and modeling NPAH in the atmosphere [J]. *Environmental Science & Technology*, 1996, 30: 2821-2827.
- [74] FAN Z H, KAMENS R M, JIANXIN H U, et al. Photostability of nitro-polycyclic aromatic hydrocarbons on combustion soot particles in sunlight [J]. *Environmental Science and Technology*, 1996, 30(4): 1358-1364.
- [75] BAMFORD H A, BAKER J E. Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region [J]. *Atmospheric Environment*, 2003, 37(15): 2077-2091.
- [76] TERRY B. Atmospheric processes: Wet and dry deposition of organic compounds are controlled by their vapor - particle partitioning [J]. *Environmental Science and Technology*, 1988, 22(4): 361-367.
- [77] TANG N, SUZUKI G, MORISAKI H, et al. Atmospheric behaviors of particulate-bound polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Beijing, China from 2004 to 2010 [J]. *Atmospheric Environment*, 2017, 152: 354-361.
- [78] 郑玫, 张延君, 闫才青, 等. 中国PM_{2.5}来源解析方法综述 [J]. *北京大学学报(自然科学版)*, 2014, 50(6): 1141-1154.
ZHENG M, ZHANG Y J, YAN C Q, et al. Review of PM_{2.5} source apportionment methods in China [J]. *Acta Scientiarum Naturalium Universitatis Pekinensis*, 2014, 50(6): 1141-1154 (in Chinese).
- [79] LIN Y, QIU X H, MA Y Q, et al. A novel approach for apportionment between primary and secondary sources of airborne nitrated polycyclic aromatic hydrocarbons (NPAHs) [J]. *Atmospheric Environment*, 2016, 138: 108-113.
- [80] WADA M, KIDO H, KISHIKAWA N, et al. Assessment of air pollution in Nagasaki City: Determination of polycyclic aromatic hydrocarbons and their nitrated derivatives, and some metals [J]. *Environmental Pollution*, 2001, 115(1): 139-147.
- [81] ZHAO J B, ZHANG J, SUN L N, et al. Characterization of PM_{2.5}-bound nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air of Langfang during periods with and without traffic restriction [J]. *Atmospheric Research*, 2018, 213: 302-308.
- [82] WANG W, JING L, ZHAN J, et al. Nitrated polycyclic aromatic hydrocarbon pollution during the Shanghai World Expo 2010 [J]. *Atmospheric Environment*, 2014, 89: 242-248.
- [83] TANG N, HATTORI T, TAGA R N, et al. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries [J]. *Atmospheric Environment*, 2005, 39(32): 5817-5826.
- [84] ZHANG J M, YANG L X, LEDOUX F, et al. PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) in rural and suburban areas in Shandong and Henan Provinces during the 2016 Chinese New Year's holiday [J]. *Environmental Pollution*, 2019, 250: 782-791.
- [85] MA Y Q, CHENG Y B, QIU X H, et al. A quantitative assessment of source contributions to fine particulate matter (PM_{2.5})-bound polycyclic aromatic hydrocarbons (PAHs) and their nitrated and hydroxylated derivatives in Hong kong [J]. *Environmental Pollution*, 2016, 219: 742-749.
- [86] WANG J Z, XU H M, GUINOT B, et al. Concentrations, sources and health effects of parent, oxygenated- and nitrated- polycyclic aromatic hydrocarbons (PAHs) in middle-school air in Xi'an, China [J]. *Atmospheric Research*, 2017, 192: 1-10.
- [87] YADAV I C, DEVI N L, SINGH V K, et al. Concentrations, sources and health risk of nitrated- and oxygenated-polycyclic aromatic hydrocarbon in urban indoor air and dust from four cities of Nepal [J]. *Science of the Total Environment*, 2018, 643: 1013-1023.
- [88] KALISA E, NAGATO E, BIZURU E, et al. Pollution characteristics and risk assessment of ambient PM_{2.5}-bound PAHs and NPAHs in typical Japanese and New Zealand Cities and rural sites [J]. *Atmospheric Pollution Research*, 2019, 10(5): 1396-1403.
- [89] PAATERO P, TAPPER U. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values [J]. *Environmetrics*, 1994, 5(2): 111-126.
- [90] LAMY E, KASSIE F, GMINSKI R, et al. 3-Nitrobenzanthrone (3-NBA) induced micronucleus formation and DNA damage in human hepatoma (HepG2) cells [J]. *Toxicology Letters*, 2004, 146(2): 103-109.
- [91] SCHEEPERS P T, MARTENS M H, VELDERS D D, et al. 1-Nitropyrene as a marker for the mutagenicity of diesel exhaust-derived particulate matter in workplace atmospheres [J]. *Environmental and Molecular Mutagenesis*, 1995, 25(2): 134-147.
- [92] SCHEEPERS P T J, MARTENS M H J, KIMMEL J P F, et al. Determination of inhalation exposure to 1-nitropyrene in workplace atmospheres and urban dwellings [J]. *Polycyclic Aromatic Compounds*, 1999, 17(1/2/3/4): 267-275.
- [93] SCHEEPERS P T J, MICKA V, MUZYKA V, et al. Exposure to dust and particle-associated 1-nitropyrene of drivers of diesel-powered equipment in underground mining [J]. *The Annals of Occupational Hygiene*, 2003, 47(5): 379-388.