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长江下游支流水体中多环芳烃的分布及生态风险评估

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摘要: 长江下游地区是我国一个典型的化学工业园区聚集地, 化工园区企业生产过程中产生和排放的多环芳烃通过大气沉降、地表径流等方式进入支流水体, 并最终汇入长江。本研究选择了典型的支流水体, 开展了多环芳烃的分布特征、源解析和生态风险评估研究。结果表明多环芳烃单体以低环为主, 总浓度为 37.27 ~ 285.88 ng·L⁻¹, 平均值为 78.31 ng·L⁻¹。PAHs 单体浓度范围 0 ~ 61.35 ng·L⁻¹, 检出率最低单体为苯并[k]荧蒽和苯并[a]芘, 其检出率均为 75%。苯并[a]芘是毒性当量因子最大的 PAHs, 其浓度范围为 0 ~ 11.08 ng·L⁻¹。根据我国《生活饮用水水源水质标准》(CJ 3020-1993) 规定, 饮用水中苯并[a]芘的限值为 10 ng·L⁻¹, 其中研究区域内无锡市的一个水样(S12)中浓度超出了标准限值, 长江下游支流水体的 PAHs 浓度总体处于低至中等的污染水平。根据比值法和主成分分析的源解析结果, 水体中多环芳烃主要受化工排放、汽车尾气的影响, 还有部分来自燃煤。生态风险评估结果显示, 水体的生态风险处于中等水平, 从长期的环境暴露角度出发, 应当考虑采取相应地控制措施, 防止进一步污染。研究结果可为长江下游支流水环境中多环芳烃风险评估以及化工园区的污染控制提供参考。

关键词: 多环芳烃(PAHs); 长江; 水体; 生态风险评估; 来源; 分布

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Distribution, Sources, and Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Tributary Waters of the Lower Reaches of the Yangtze River, China

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Abstract: The lower reaches of the Yangtze River are a typical gathering place of chemical industrial parks in China. Polycyclic aromatic hydrocarbons (PAHs) emitted in the production process of chemical enterprises enter the tributary water body through atmospheric deposition and surface runoff, and finally merge into the Yangtze River. In this study, the distribution characteristics, source analysis, and ecological risk assessment of PAHs in a series of typical water samples collected in the tributary waters of the Yangtze River were studied. PAH monomers in the samples were mainly low-ring. The total concentration of PAHs was in the range of 37.27 to 285.88 ng·L⁻¹ with a mean value of 78.31 ng·L⁻¹, while the monomer concentration of PAHs ranged from 0 to 61.35 ng·L⁻¹. The lowest detection rate was benzo [k] fluoranthene and benzo [a] pyrene at 75%. As a toxic PAH monomer, the concentration of benzo [a] pyrene ranged from 0 to 11.08 ng·L⁻¹. According to "Water Quality Standards for Drinking Water Sources (CJ 3020-1993)" of China, the concentration of benzo [a] pyrene in a water sample (S12) located near Wuxi City exceeded the limit of drinking water standards (10 ng·L⁻¹). Compared with the total concentration of PAHs in rivers in some typical regions of the world, the concentration of PAHs in this study was generally at low to moderate levels. According to the source analysis results of the ratio method and principal component analysis, the concentration of PAHs in water was mainly affected by fossil combustion, automobile exhaust, and chemical emissions. To assess the potential ecosystem risk of PAHs in the investigated area, the risk quotient (RQ) was used. In addition to the DBA monomer, the relative quantities (RQs) (replication) of the remaining monomers were greater than 1, and the RQ (MPCs) values in all the monomers were less than 1, indicating that the ecological risk of water samples was at a medium level. From the perspective of long-term environmental exposure, appropriate control measures should be considered to prevent further pollution. The results can provide reference for PAH risk assessment and pollution control of chemical industrial parks in the lower reaches of the Yangtze River.

Key words: polycyclic aromatic hydrocarbons (PAHs); Yangtze River; water; risk assessment; source; distribution

多环芳烃 (polycyclic aromatic hydrocarbons, PAHs) 是一类环境中普遍存在的持久性有机污染物 (POPs), 由于其致癌和诱变特性, 已经引起了广泛的关注^[1]。根据性质和分子量的不同可将 PAHs 分为两类, 即含 2 ~ 3 环的低分子量 (低环) PAHs

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(LMW PAHs)和含 4~6 环的高分子量(高环)PAHs(HMW PAHs),前者易挥发,具有急性毒性作用,对水生生物有一定的毒性;而后者中某一些具有强致癌、致突变性.环境中的 PAHs 污染来源可分为自然来源和人为来源,自然来源指 PAHs 可以通过自然过程排放,如森林火灾、火山活动和生物的内源合成等过程,而环境中大多数 PAHs 由人为来源排放,包括化石燃料(即煤和石油等)和其他有机材料(如木材)的不完全燃烧^[2]、某些化学工业的排放等^[3]. PAHs 通过大气干湿沉降、地表径流、工业废水和生活污水等途径进入环境,并迁移到不同环境介质中^[4-7].长江下游流经江苏和上海,该地区经济发达,分布着大量化学工业园区,是我国一个典型的化学工业园区聚集地.化学工业生产和人群活动产生和排放的 PAHs 通过大气沉降、地表径流等方式进入支流水体,并最终汇入长江,可能会对下游地区生态环境产生影响^[8-11].然而目前相关研究还很不足,有必要对该区域 PAHs 的分布及生态风险进行研究.本文研究了长江下游地区典型支流水体中 PAHs 的分布特征,采用比值法和主成分分析法(PCA)分析其潜在来源,并采用风险熵数法对水体开展生态风险评估,以期为长江下游支流水体中 PAHs 风险评估以及化工园区的污染控制提供参考.

1 材料与方法

1.1 化学标准品与主要试剂

19 种 PAHs 混合标准样品:萘(naphthalene, Nap)、2-甲基萘(2-methylnaphthalene, 2-Methylnap)、苊(acenaphthene, Ace)、苊烯(acenaphthylene, Any)、芴(flourene, Fl)、菲(phenanthrene, Phe)、蒽(anthracene, Ant)、荧蒽(flouanthene, Flu)、芘(pyrene, Pyr)、苯并[a]蒽[benzo(a)anthracene, BaA]、䝑(chrysene, Chr)、苯并[b]荧蒽[benzo(b)fluoranthene, BbF]、苯并[k]荧蒽[benzo(k)fluoranthene, BkF]、苯并[e]芘[benzo(e)pyrene, BeP]、苯并[a]芘[benzo(a)pyrene, BaP]、芘(perylene, Pery)、茚并[1,2,3-c,d]芘[indeno(1,2,3-cd)pyrene, IcdP]、二苯并[a,h]蒽[dibenz(ah)anthracene, DBA]和苯并[g,h,i]芘[Benzo(ghi)perylene, BghiP];14 种替代标准样品:氘代萘(D8-naphthalene, D8-Nap)、氘代 2-甲基萘(D10-2-methylnaphthalene, D10-2-2-Methylnap)、氘代苊烯(D8-acenaphthylene, D8-Acy)、氘代菲(D10-phenanthrene, D10-Phe)、氘代荧蒽(D10-flouanthene, D10-Flu)、氘代苯并[a]蒽[D12-benzo

(a)anthracene, D12-BaA]、氘代䝑(D12-chrysene, D12-Chr)、氘代苯并[b]荧蒽[D12-benzo(b)fluoranthene, D12-BbF]、氘代苯并[k]荧蒽[D12-benzo(k)fluoranthene, D12-BkF]、氘代苯并[a]芘[D12-benzo(a)pyrene, D12-BaP]、氘代芘(D12-perylene, D12-Pery)、氘代茚并[1,2,3-c,d]芘[D12-indeno(1,2,3-cd)pyrene, D12-IcdP]、氘代二苯并[a,h]蒽[D14-dibenz(ah)anthracene, D14-DBA]和氘代苯并[g,h,i]芘[D12-benzo(ghi)perylene, D12-BghiP];3 种内标化合物:氘代苊(D10-acenaphthene, D10-Ace)、氘代芘(D10-pyrene, D10-Pyr)和氘代苯并[e]芘[D12-benzo(e)pyrene, D12-BeP]均购于美国 Wellington 公司.农残级的正己烷、丙酮、二氯甲烷均购于美国 J. T. Baker 公司.

1.2 样品采集

根据长江下游(江苏省和上海市)的典型化工园区及长江主要支流水体的分布特征,参考江苏省控断面,确定了研究区域的采样点,研究化工园区排放对长江下游的潜在环境影响.2019 年 6 月,在长江下游主要支流水体共采集了 12 个水样.其中南通市 3 个采样点,分别为: S1、S3 和 S5;苏州市 2 个采样点,分别为 S2 和 S4;无锡市 3 个采样点,分别为: S6、S7 和 S12;泰州为采样点 S8;镇江为采样点 S9;扬州为采样点 S10;南京市为采样点 S11.采样点具体分布如图 1 所示.水体采集参考《水质 湖泊和水库采样技术指导》(GB/T 14581-93)和《水质采样方案设计技术规定》(GB 12997-91),采用 DN-100 型不锈钢采水器(容积为 2 L;直径 20 cm,高 20 cm)采集表层水体(水下约 25 cm).样品储存于棕色玻璃瓶中,加入 5 mL 甲醇后放入冰箱内冷藏保存.

1.3 样品的前处理与测定

水样中的 PAHs 依据《海水中 16 种多环芳烃的测定气相色谱-质谱法》(GB/T 26411-2010)的方法,采用液液萃取法提取,取 1 L 水样转移至分液漏斗,加入 14 种 PAHs 的替代标准样品后,用 100 mL 的二氯甲烷振荡萃取 3 min,重复 3 次.经无水硫酸钠过滤后,将所有有机相收集经旋转蒸发器浓缩至 2 mL.将样品转移至活化硅胶柱净化,再经旋转蒸发仪和氮吹定容至 1 mL,加入 PAHs 内标化合物进行 GC-MS 分析.

样品采用 Agilent 6890-5975 GC/MS 气质联用仪分析,色谱柱为 DB-5MS 型,规格为 30 m × 0.25 mm × 0.25 μm,载气为高纯度氦气,采用不分流进样,进样量为 1 μL,色谱柱的升温程序为:初始温度为 50℃,以 20℃·min⁻¹的速度升至 150℃,保持 2 min;再以 12℃·min⁻¹的速度升至 290℃,保持



图1 长江下游支流采样示意

Fig. 1 Sampling of the tributaries of the lower Yangtze River

7 min. 进样口温度 250℃, 载气流量 1 mL·min⁻¹. 离子源为 EI 源, 选择离子扫描 (SIM) 模式进行定量分析.

1.4 质量控制与质量保证

水样 19 种 PAHs 的方法检出限范围为 0.5 ~ 0.99 ng·L⁻¹, 测试样品中加入 2 个现场空白和 2 个加标空白用于确定背景污染和人为影响情况, 小于检出限 (not detected, ND) 的数据按 0 计算. 空白加标和 PAHs 替代物的回收率在 70% ~ 130% 之间, 符合标准方法中质控要求.

2 结果与讨论

2.1 PAHs 含量特征

表 1 显示了长江下游支流水体中 PAHs 浓度的最大值、最小值、平均值和中位值. 水体中 \sum PAHs 浓度范围为 37.27 ~ 285.88 ng·L⁻¹, 平均值为 78.31 (±88.97) ng·L⁻¹, 中位值为 51.10 ng·L⁻¹. PAHs 单体浓度范围 0 ~ 61.35 ng·L⁻¹, 浓度最高的单体为苯并[e]芘, 浓度为 61.35 ng·L⁻¹; 浓度较低的单体为苯并[k]荧蒽、苯并[a]芘、芘、茚并[1,2,3-c,

表1 长江下游支流水体中 PAHs 单体浓度

Table 1 PAHs monomer concentration in the tributary waters of the lower reaches of the Yangtze River

PAHs 单体	检出率/%	浓度/ng·L ⁻¹		
		范围	平均值	中位值
萘	100.00	10.72 ~ 29.52	15.99 (±5.09)	14.81
2-甲基萘	100.00	5.67 ~ 13.18	9.02 (±2.67)	8.54
苊	100.00	0.55 ~ 1.81	0.85 (±0.33)	0.75
苊烯	100.00	0.39 ~ 5.58	1.58 (±1.51)	1.10
芴	100.00	1.45 ~ 5.85	2.44 (±1.20)	2.11
菲	100.00	4.19 ~ 27.12	9.34 (±6.49)	7.00
蒽	100.00	0.27 ~ 3.90	0.99 (±1.02)	0.62
荧蒽	100.00	1.21 ~ 33.12	5.94 (±8.78)	3.82
芘	100.00	1.18 ~ 30.23	6.71 (±8.38)	4.39
苯并[b]荧蒽	100.00	0.76 ~ 28.24	3.14 (±7.91)	0.82
苯并[k]荧蒽	83.30	ND* ~ 18.63	3.60 (±6.14)	1.06
苯并[e]芘	100.00	0.05 ~ 61.35	7.74 (±17.01)	2.56
苯并[a]芘	75.00	ND ~ 14.58	1.69 (±4.11)	0.35
芘	91.70	ND ~ 12.66	1.77 (±3.55)	0.39
茚并[1,2,3-c,d]芘	75.00	ND ~ 11.08	1.34 (±3.12)	0.27
二苯并[a,h]蒽	100.00	0.06 ~ 6.14	1.46 (±1.97)	0.69
苯并[g,h,i]芘	100.00	0.05 ~ 13.67	1.82 (±3.80)	0.60
苯并[b]荧蒽	83.30	ND ~ 2.33	0.32 (±0.66)	0.03
苯并[k]荧蒽	91.70	ND ~ 15.45	2.57 (±4.24)	1.19
\sum PAHs	—	37.27 ~ 285.88	78.31 (±88.97)	51.10

d] 芘、苯并[b]荧蒹和苯并[k]荧蒹,在部分样品低于检出限.检出率最低单体为苯并[k]荧蒹和苯并[a]芘,其检出率均为75%.

苯并[a]芘是毒性当量因子最大的 PAHs,其浓度范围为 $0 \sim 11.08 \text{ ng}\cdot\text{L}^{-1}$. 根据我国《生活饮用水水源水质标准》(CJ 3020-1993)规定,饮用水中苯并[a]芘的限值为 $10 \text{ ng}\cdot\text{L}^{-1}$,其中研究区域内无锡市的一个水样(S12)中浓度超出了标准限值,在 Cai 等^[12]和 Zhu 等^[13]的研究中也发现无锡市附近的土壤样品中 PAHs 浓度较高,应引起足够重视.

PAHs 的环数分布见图 2,其中 2、3、4、5 和 6 环 PAHs 分别占 \sum PAHs 的 $43.4\% (\pm 16.2\%)$ 、 $22.4\% (\pm 7.2\%)$ 、 $18.5\% (\pm 9.8\%)$ 、 11.8%

($\pm 10.3\%$)和 $3.9\% (\pm 3.3\%)$. 水体中以低环 PAHs 为主,2 环和 3 环的 PAHs 占比较高,2~3 环 PAHs 共占 \sum PAHs 的 $65.8\% (\pm 21.2\%)$,高环占比相对较低,4~6 环 PAHs 共占 \sum PAHs 的 $34.2\% (\pm 21.2\%)$. 这可能与 PAHs 的物化性质以及来源有关,影响 PAHs 在水、土等介质之间质量分配的主要因素为 PAHs 的辛醇-水分配系数(K_{ow}). 高环的 PAHs 分子量较大,具有较大的 K_{ow} 值,较低的水溶性($< 0.01 \text{ mg}\cdot\text{L}^{-1}$),有亲脂疏水性,易吸附在土壤有机质中而难于迁移^[14];而低环 PAHs 分子量较低($MW < 210$),具有较小的辛醇-水分配系数值($K_{ow} < 5$),更易存在于水体中,导致水体中低环 PAHs 相对较高.

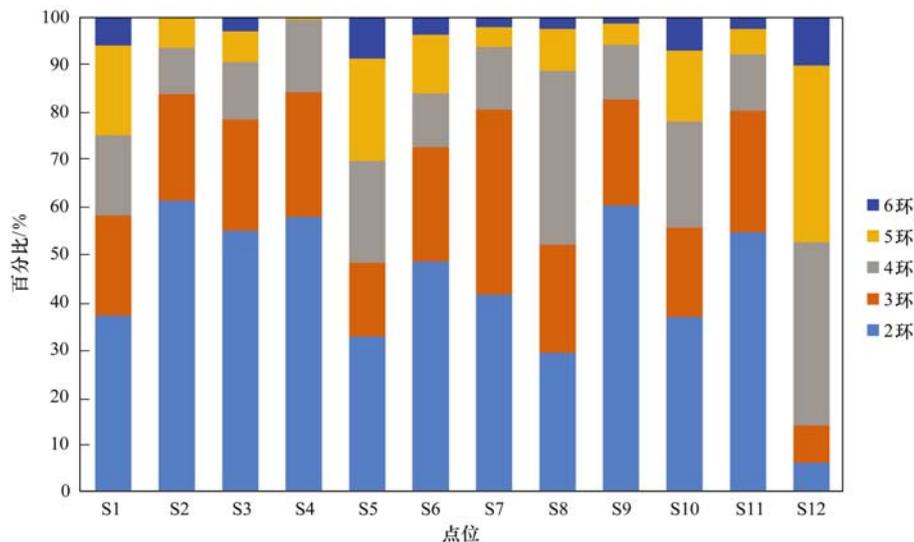


图 2 长江下游支流中 PAHs 的环数分布

Fig. 2 Compositional patterns of PAHs by ring size in the lower reaches of the Yangtze River

2.2 PAHs 空间分布

各采样点的 \sum PAHs 空间分布状况如图 3 所示. 水体中 \sum PAHs 总体分布范围在 $37.27 \sim 285.88 \text{ ng}\cdot\text{L}^{-1}$,除采样点 S7、S8 以及 S12 浓度较高外,其他采样点浓度较低且水平相近. 最高值出现在 S12,浓度值为 $285.88 \text{ ng}\cdot\text{L}^{-1}$,以高环 PAHs 为主,占总浓度的 88.11%,主要贡献来源于荧蒹和苯并(b)荧蒹两种化合物. 调研发现该工业园区以精细化工、冶金为主,可能含有较多的高环 PAHs. S7 和 S8 分别为长江在泰州和无锡的入境断面,其浓度分别为 $102.65 \text{ ng}\cdot\text{L}^{-1}$ 和 $104.53 \text{ ng}\cdot\text{L}^{-1}$. S7 和 S8 位于工业园区密集区域河段,其主要贡献来源于萘、二甲基萘和菲这 3 种化合物,以低环 PAHs 为主. 说明水体中 PAHs 空间分布可能受到化工园区污染物排放的影响.

2.3 长江下游支流水体与其他典型地区 PAHs 污染水平比较

表 2 汇总了全球部分典型地区河水中的 PAHs 总浓度,比较而言长江下游支流水体的 PAHs 处于低至中等水平. PAHs 的总浓度与 Liu 等^[27]在上海城市河网($46.53 \sim 221.54 \text{ ng}\cdot\text{L}^{-1}$)、Aziz 等^[25]在苏安河($61 \sim 207 \text{ ng}\cdot\text{L}^{-1}$)以及 Wang 等^[26]在黄河三角洲($64.8 \sim 334.6 \text{ ng}\cdot\text{L}^{-1}$)的研究相差不大,略高于三峡水库^[15]($13.8 \sim 97.2 \text{ ng}\cdot\text{L}^{-1}$)、晋江^[16]($42.02 \sim 63.00 \text{ ng}\cdot\text{L}^{-1}$)、三峡水库支流^[29]($1.92 \sim 40.33 \text{ ng}\cdot\text{L}^{-1}$)、易北河,埃姆斯河,威悉河^[22]($13 \sim 140 \text{ ng}\cdot\text{L}^{-1}$)和莫斯科河^[24]($50.6 \sim 120.1 \text{ ng}\cdot\text{L}^{-1}$),显著低于大辽河口及邻近地区^[17]($71.12 \sim 4255.43 \text{ ng}\cdot\text{L}^{-1}$)、鳌江^[18]($909.9 \sim 1519.8 \text{ ng}\cdot\text{L}^{-1}$)、黄河(河南河段)^[19]($144.3 \sim 2360 \text{ ng}\cdot\text{L}^{-1}$)、钱塘江^[21]($70.3 \sim 1844.4 \text{ ng}\cdot\text{L}^{-1}$)和考卡河^[23]($52.1 \sim 12$,

图3 长江下游支流水体中 \sum PAHs 浓度Fig. 3 Concentration of \sum PAHs in the tributaries of the lower reaches of the Yangtze River表2 其他典型地区河水中的 \sum PAHs 总浓度Table 2 Comparison of concentrations of \sum PAHs in water with other areas

地点	采样年份	PAHs 单体数量	PAHs 浓度范围 (均值)/ng·L ⁻¹	国家	文献
长江下游支流	2019	19	37.27 ~ 285.88	中国	本研究
三峡水库	2008	16	13.8 ~ 97.2 (30.11)	中国	[15]
晋江	2011	16	42.02 ~ 63.00 (53.23)	中国	[16]
大辽河口及邻近地区	2013	16	71.12 ~ 4255.43 (748.76)	中国	[17]
鳌江	—	15	909.9 ~ 1519.8	中国	[18]
黄河(河南河段)	2005 ~ 2006	16	144.3 ~ 2360 (662)	中国	[19]
淮河(上游)	2013	15	79.79 ~ 421.07 (140.37)	中国	[20]
钱塘江	2005	15	70.3 ~ 1844.4 (283.3)	中国	[21]
下萨克森州的易北河, 埃姆斯河, 威悉河	2009 ~ 2012	16	13 ~ 140	德国	[22]
考卡河	2010 ~ 2011	12	52.1 ~ 12,888.2 (2344.5)	哥伦比亚	[23]
莫斯科河	2013	15	50.6 ~ 120.1	俄罗斯	[24]
苏安河	2013	17	61 ~ 207 (134.4)	巴基斯坦	[25]
黄河三角洲	2007	16	64.8 ~ 334.6 (121.3)	中国	[26]
上海城市河网	2015	16	46.53 ~ 221.54 (112.92)	中国	[27]
三峡水库支流	2015	16	1.92 ~ 40.33 (14.72)	中国	[28]
长三角地区	2010	16	12.9 ~ 638.1 (201.1)	中国	[29]

888.2 ng·L⁻¹)等地。

2.4 PAHs 的污染来源解析

PAHs 的人为来源比较复杂, 主要包括化石燃料的不完全燃烧和化工生产排放等^[30]。为解析长江下游支流水体中 PAHs 的来源, 采用比值法和主成分分析两种方法识别 PAHs 的来源。

2.4.1 比值法

由于同系物的分布与具有相似特征的有机物含碳物质的形成机制密切相关, 可以通过单个 PAHs 化合物的诊断率来确定 PAHs 的来源^[31]。Ant、Phe、Flt 和 Pyr 等具有相对稳定的特征, Ant/(Phe + Ant)、Flt/(Flt + Pyr) 和 BaA/(BaA + Chr)、IP/(IP + BghiP) 的比值被广泛用于 PAHs 来源分析^[32]。水样中 Ant/(Phe + Ant)、BaA/(BaA + Chr)、IP/(IP +

BghiP) 和 Flt/(Flt + Pyr) 的比值见图 4。

由图 4 可以看到, Flt/(Flt + Pyr) 的比值在 0.3 ~ 0.55 之间, 大部分比值均小于 0.5; Ant/(Phe + Ant) 的比值在 0.05 ~ 0.25 之间, 大部分比值小于 0.1; BaA/(BaA + Chr) 的比值在 0 ~ 1.0 之间, 大部分比值大于 0.35; 而 IP/(IP + BghiP) 的比值大部分小于 0.5。通常认为, Ant/(Phe + Ant) 比值小于 0.1 时, 表示 PAHs 主要来自石油源, 大于 0.1 主要为燃烧源; 当 Flt/(Flt + Pyr) 比值小于 0.5 时, 表示其主要来源为石油源, 大于 0.5 为煤和草、木柴等生物燃料的燃烧; 当 BaA/(BaA + Chr) 比值小于 0.2 时, 其主要来源为石油源, 大于 0.35 为燃烧源, 介于 0.2 和 0.35 之间为混合源; 当 IP/(IP + BghiP) 比值小于 0.5 为石油燃烧, 大于 0.5 为生物质或煤的燃

烧^[33,34]. 由图 4(a)~4(c)可知,除 S12、S5 和 S9 外,大部分点位处于燃烧区域内,由此可见,长江下游水体中的 PAHs 主要来源于燃烧.

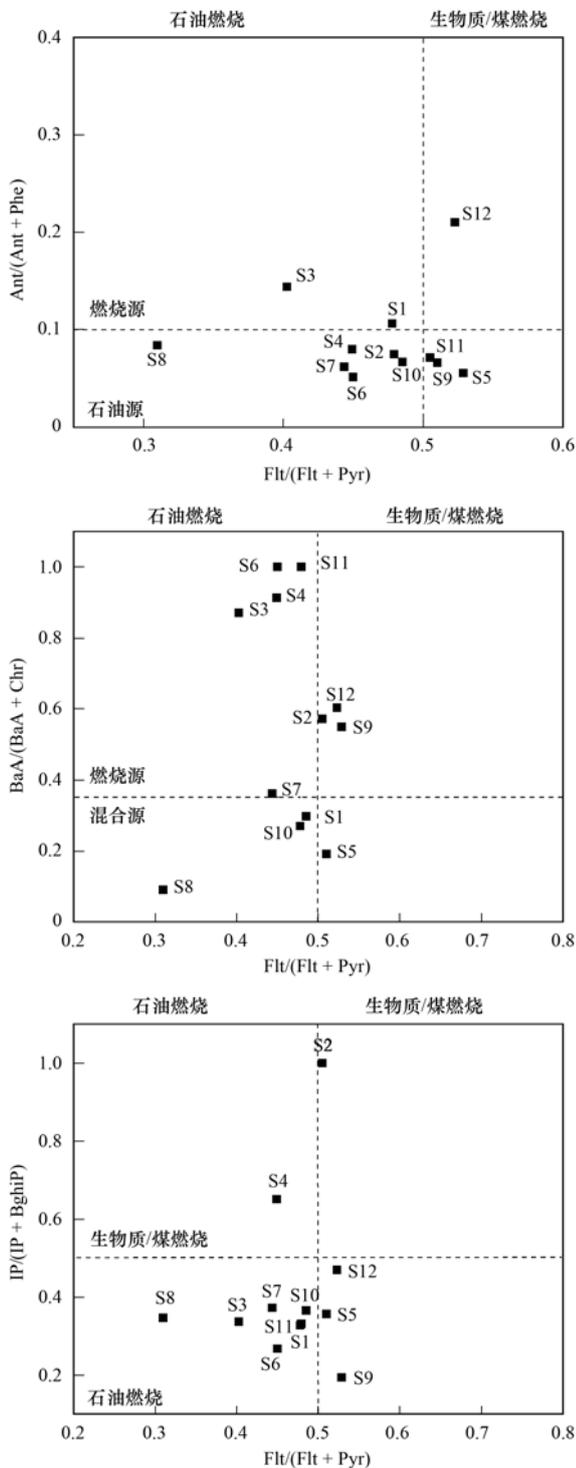


图 4 水中 PAHs 来源的比值法

Fig. 4 Source identification by isomer ratios of PAHs in water

2.4.2 主成分分析法

以 19 种 PAHs 单体作为变量,并参考了已有研究中典型的化工源^[3]和燃烧源^[29]的 PAHs 数据,采用主成分分析法对 PAHs 来源进行解析,结果如图 5 所示. PC1 解释了总方差的 74.8%,该因子包括低分

子量 PAHs (Nap、2-Methyl、Acy、Ace、Ant、Flu 和 Phe). PC2 包含高分子量 PAHs (Flt、Pyr、BaA、Chr、BbF、BkF、BeP、BaP、Pery、IcdP、DBA 和 BghiP). 所有采样点可分为两组,第一组样品共 11 个采样点 (S1~S11),其 PC1 较高而 PC2 相对较低,表明主要受低环 PAHs 影响较多. 但相较于其他 7 个采样点, S8、S5、S10 和 S1 的 PC2 相对较高,表明采样点还受到高环 PAHs 的影响. 第一组样品与燃烧源较为接近,但可能还受到了其他源的影响. 第二组中共 1 个采样点 (S12),该采样点 PC2 较高而 PC1 相对较低,表明主要受高环 PAHs 的影响,采样点与化工源点位非常接近,说明受到了化工排放的影响.

两种方法得出的结论一致:长江下游支流水体中的 PAHs 以燃烧源为主,但是可能还受到了化工排放的影响.

2.5 生态风险评估

本研究只计算美国联邦环保署列入优先控制污染物 16 种 PAHs,采用风险熵值 (RQ) 对调查区 PAHs 潜在生态风险进行评价. 通过比较水中 PAHs 含量与其相应的质量值^[30],计算 RQ 结果如下:

$$RQ = C_{PAHs} / C_{QV}$$

式中, C_{PAHs} 为水样中 PAHs 的浓度, C_{QV} 为水样中 PAHs 的相应质量值. 通常,在计算风险熵时,经常使用水中 PAHs 的可忽略浓度 (NCs) 和最大允许浓度 (MPCs). 因此, $RQ_{(NCs)}$ 和 $RQ_{(MPCs)}$ 定义如下:

$$RQ_{(NCs)} = C_{PAHs} / C_{QV(NCs)}$$

$$RQ_{(MPCs)} = C_{PAHs} / C_{QV(MPCs)}$$

式中, $C_{QV(NCs)}$ 是水中 PAHs 的 NCs 质量值, $C_{QV(MPCs)}$ 是水中 PAHs 的 MPCs 质量值.

此外,上述 RQ 的计算方法只适用于评估 PAHs 的 10 个单体生态系统风险,而其他 6 个 PAHs 单体 (Acy、Ace、Fl、Pyr、BbF 和 DBA) 采用 Cao 等^[35]推荐的 NC 和 MPC 值. 本研究认为 $RQ_{(NCs)} < 1.0$ 表示 PAHs 产生的生态风险可忽略不计,而 $RQ_{(MPCs)} > 1.0$ 则表明 PAHs 的污染严重,须立即采取控制和补救措施. 如果 $RQ_{(NCs)} > 1.0$ 和 $RQ_{(MPCs)} < 1.0$, 这表明 PAHs 污染可列为中等水平,则可能需要采取一些措施控制污染.

16 种 PAHs 的风险熵值结果如表 3 所示,除 DBA 单体外,其余单体 $RQ_{(NCs)}$ 均大于 1,而所有单体的 $RQ_{(MPCs)}$ 值均低于 1,其中 BbF 单体的 $RQ_{(NCs)}$ 值最高,其 $RQ_{(NCs)}$ 值为 77.43, $RQ_{(MPCs)}$ 值为 0.77, 单体 BaA 的 $RQ_{(NCs)}$ 值也较高,其 $RQ_{(NCs)}$ 值为 31.37, $RQ_{(MPCs)}$ 值为 0.31, 风险熵值均处于中等偏高的水平,表明这些单体会对长江下游水体造成一定的危害,且水体中 PAHs 造成生态风险处于中等

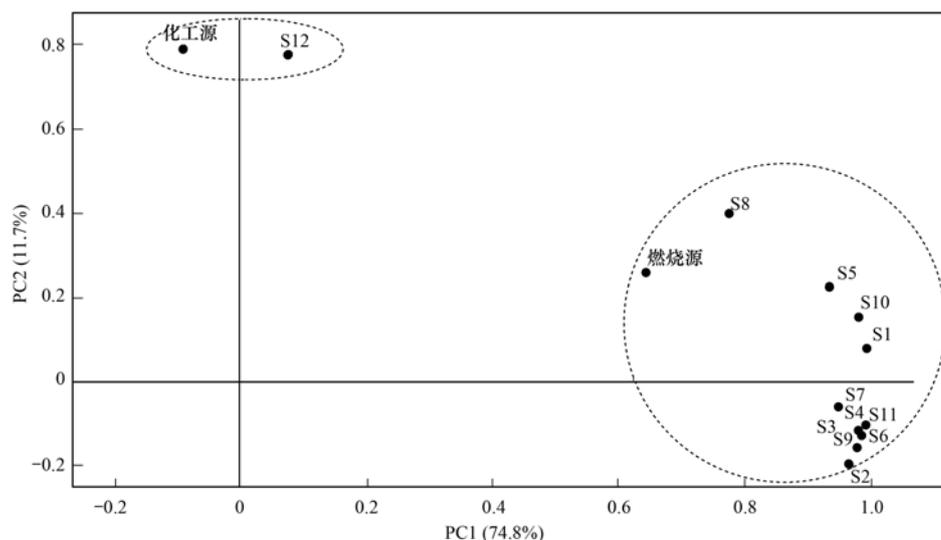


图5 长江下游支流水体中 PAHs 的主成分

Fig. 5 Main components of PAHs in tributaries of the lower reaches of the Yangtze River

表3 长江下游支流水体中 PAHs 的风险熵值

Table 3 Risk assessment of PAHs in tributaries of the lower reaches of the Yangtze River

项目	NCs	MPCs	平均浓度 /ng·L ⁻¹	RQ _(NCs)	RQ _(MPCs)
Nap	12.0	1 200	15.99	1.33	0.01
Any	0.7	70	0.85	1.21	0.01
Ace	0.7	70	1.58	2.26	0.02
Flu	0.7	70	2.44	3.48	0.03
Phe	3.0	300	9.34	3.11	0.03
Ant	0.7	70	0.99	1.41	0.01
Flt	3.0	300	5.94	1.98	0.02
Pyr	0.7	70	6.71	9.59	0.10
BaA	0.1	10	3.14	31.37	0.31
Chr	3.4	340	3.60	1.06	0.01
BbF	0.1	10	7.74	77.43	0.77
BkF	0.4	40	1.69	4.22	0.04
BaP	0.5	50	1.34	2.68	0.03
IcdP	0.4	40	1.82	4.54	0.05
DBA	0.5	50	0.32	0.65	0.01
Bghip	0.3	30	2.57	8.58	0.09
∑ PAHs	27.2	2 720	66.06	2.43	0.02

水平,从长期的环境暴露角度出发,可以考虑采取相应地控制措施,防止 PAHs 的进一步污染。

3 结论

(1)在长江中下游支流收集的水样中不同程度检测到了 PAHs, ∑ PAHs 浓度范围为 37.27 ~ 285.88 ng·L⁻¹ (均值为 78.31 ng·L⁻¹),无锡采样水体中多环芳烃含量最高污染最严重,其浓度为 285.88 ng·L⁻¹. PAHs 单体中 2 环、3 环和 4 环检出率较高,5~6 环检出率相对较低。

(2)通过比值法和主成分分析均得出长江下游支流水体中受低环 PAHs 影响较多,以燃烧源为主;

少量在化工园区附近的采样点高环 PAHs 比例较高,说明水体中 PAHs 空间分布受到工业园区污染物排放的强烈影响。

(3)生态风险评估结果显示,在长江中下游支流水体中未发现生态系统风险,除 DBA 单体外,其余单体 RQ_(NCs) 均大于 1,而所有单体的 RQ_(MPCs) 值均低于 1,但其 PAHs 造成污染可列为中等水平,从长期的环境暴露角度出发,可以考虑采取相应地控制措施,防止 PAHs 的进一步污染。

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