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经济快速发展区场地污染特征、源-汇关系与管控对策专辑

我国经济快速发展区工业VOCs排放特征及管控对策 孟博文,李永波,孟晶,李倩倩,史斌,周喜斌,李金灵,苏贵金



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Environmental Science

近20年中国表层土壤中多环芳烃时空分布特征及源 解析

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摘要: 随着中国经济社会的快速发展,表层土壤多环芳烃(polycyclic aromatic hydrocarbons, PAHs)污染问题受到了全社会的高 度关注. 本研究通过搜集 2000~2020 年间有关我国表层土壤 PAHs 污染的相关研究,并对筛选得到的 166 篇文献采样数据综 合运用统计学、空间插值分析和污染物特征比值源解析方法,定量分析了我国表层土壤 PAHs 污染水平、时间变化特征、空间 分布特征以及来源特征. 结果表明,我国表层土壤普遍存在人为因素的 PAHs 污染,其含量中位值为 675.70 μg·kg-1,总体情 况良好但部分采样点位污染情况较为严重,单体含量中荧蒽(Fla)和芘(Pvr)含量较高,而苊烯(Acv)和二氢苊(Ace)含量较 低;调查时段中,表层土壤 PAHs 含量数据大体稳定在 313. 10~1 070. 45 μg·kg-1的中度污染水平范围内,其年度变化受石油 生产与消费的影响相对较小,且不存在明显波动;统计学以及空间插值结果表明,我国表层土壤 PAHs 污染存在明显区域特 征,地区含量从西北、华北、华东、东北、西南和中南依次递减,多数省份的 PAHs 污染水平处于"中度污染"或"轻度污染";源 解析结果表明,我国大部分地区表层土壤 PAHs 污染来源于石油、生物质和煤等化石燃料的高温燃烧,但黑龙江以及新疆、西 藏等西北地区主要表现为石油源污染. 本研究对我国土壤环境管理和 PAHs 污染治理工作开展有一定参考价值.

关键词:表层土壤; 多环芳烃(PAHs); 污染水平; 时空分布; 源解析

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Polycyclic Aromatic Hydrocarbons in Surface Soil of China (2000-2020): Temporal and Spatial Distribution, Influencing Factors

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Abstract: With the rapid development of China's economy and society, the polycyclic aromatic hydrocarbon (PAH) pollution of surface soil has attracted increasing attention. Based on a systematic review, this study identified 166 relevant papers (published from 2000 to 2020) dealing with the contamination of 16 PAHs in the surface soil of China and summarized the pollution level, temporal, and spatial distribution influencing factors of PAHs with statistics, spatial interpolation analysis, and source analysis methods. The results showed that the surface soil of China has been polluted by human-caused PAHs, with a median concentration of 675.70 μg·kg⁻¹. Although the overall condition is good, some sampling points have been seriously polluted. Among the monomers of PAHs, the concentrations of fluoranthene (Fla) and pyrene (Pyr) are high, while acenaphthylene (Acy) and acenaphthene (Ace) are relatively low. During the survey period, the concentration data of surface soil PAHs are generally within the moderate pollution levels of 313. 10-1070. 45 µg·kg⁻¹, while the annual changes of PAHs do not show obvious fluctuations and are less affected by oil production and consumption. Statistics and spatial interpolation results show that PAH pollution in the surface soil of China has regional characteristics, where the concentration decreases in order from northwest, north, east, northeast, southwest, and south-central China. The pollution level in most provinces is "contaminated" or "weakly contaminated." From the source analysis results, PAH pollution in surface soils in most areas of China comes from the high-temperature combustion of fossil fuels such as petroleum, biomass, and coal. Heilongjiang and some northwestern regions (e.g., Xinjiang and Tibet) were mainly represented by oil source pollution. Such results could provide a reference for soil environmental management and PAH pollution control in China.

Key words: surface soil; polycyclic aromatic hydrocarbons (PAHs); pollution level; temporal and spatial distribution; source analysis

随着中国经济社会的快速发展,工业化和城市 化进程的进一步加快,土壤污染问题受到了全社会

的高度关注[1]. 土壤作为环境中最重要的"汇"之 一,承载了来自车辆排放、生物质燃烧、煤炭燃烧、石

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油残渣和大气交换等不同来源的多环芳烃 (polycyclic aromatic hydrocarbons, PAHs)^[2], 其 PAHs 污染情况以及来源分析受到了国内外相关学 者的广泛研究. 刘瑞民等[3] 基于地统计学的因子克 立格方法展开研究,结果表明天津地区土壤中 PAHs 污染在小空间尺度上主要是各种燃烧源和汽车尾 气,在大空间尺度上主要是区域性的大气沉降所造 成的. 而在全国尺度上, 曹云者等[4] 从点、面源和地 区角度对我国主要地区表层土壤多环芳烃总量进行 了讨论,指出我国表层土壤 PAHs 含量处于较低水 平,其组成以高环 PAHs 为主,但不占绝对优势; 邓 绍坡等[5] 利用特征比值法分析我国表层土壤中 PAHs 来源,结果表明煤燃烧是我国 PAHs 的主要来 源,尤其是我国北方地区;尚庆彬等[6]运用 ArcGIS 空间插值技术、地理探测器模型和统计学方法分析 了我国表层土壤 PAHs 含量、空间分布、主要来源及 成因,结果表明我国各地表土 PAHs 平均含量的空 间分布具有明显的区域特征. 我国土壤中 PAHs 含 量以及来源解析的空间大尺度研究多为定性或半定 量研究,且鲜见对我国土壤中 PAHs 含量年度变化 的研究报道.

在上述研究基础上,本研究通过对 2000 ~ 2020 年间发表的 166 篇中国不同地区表层(0 ~ 20 cm) 土壤 PAHs 的采样数据进行统计分析,分析我国表层土壤 PAHs 污染水平和 \sum_{16} PAHs 年度变化特征及影响因素,使用空间插值方法分析 \sum_{16} PAHs 空间分布特征,并从污染物特征比值角度对插值结果进行来源解析,获取表层土壤 PAHs 含量时空分布特征信息,以期为我国土壤环境管理和 PAHs 污染治理工作提供科学依据.

1 材料与方法

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1.1 数据收集与统计

于2020年4月,在中国知网(CNKI)、斯普林格期刊数据库(Springer)、爱思唯尔期刊数据库(Elsevier)和Web of Science等全文数据库中,使用"中国"、"多环芳烃"和"PAHs"作为检索关键词,检索2000~2020年间发表的有关我国不同地区表层土壤中PAHs的相关研究.舍去检索结果中未给出采样时间、空间点位和PAHs单体及总量含量采样数据信息的文献,最终筛选出166篇有效文献用于后续分析过程.所涉及的PAHs单体为美国环保局(USEPA)列出的优先控制污染物名单中的16种多环芳烃:萘(Nap)、苊烯(Acy)、二氢苊(Ace)、芴(Flu)、菲(Phe)、蒽(Ant)、荧蒽(Fla)、芘(Pyr)、苯

本研究使用的国内生产总值、民用汽车拥有量、能源生产总量、原煤生产总量、原油生产总量、能源消费总量、煤炭消费总量和石油消费总量数据均来自国家统计局年度数据(https://data. stats. gov. cn/easyquery. htm? cn = C01),选取的时间段为 2000~2018 年. 使用的全国政区图编辑自自然资源部标准地图网站(http://bzdt. ch. mnr. gov. cn/),原审图号为 GS(2019)1697 号,底图无修改.

1.2 数据处理

对 16 种多环芳烃及 \sum_{16} PAHs 的含量数据进行对数正态分布的 Shapiro-Wilk 检验,结果显示其显著度均小于 0.05,不服从正态分布,因此本研究采用多环芳烃含量的中位值来表征其平均水平^[7]. 对文献地块的位置信息,若仅给出经纬度范围或者所有经纬度坐标,则选取所描述范围的中心点经纬度作为代表.

数据统计分析及作图分别采用 IBM SPSS Statistics 26 和 Origin 2021b 完成,地统计学分析及作图则采用 ArcGIS 10.6 完成.

1.3 普通克里金空间插值

克里金插值法(Kriging)又称为空间局部估计, 是建立在变异函数理论及结构分析基础上,在有限 区域内对区域化变量进行线性无偏最优估计的一种 方法^[8]. 总的公式为:

$$Z_v^x(x) = \sum_{i=1}^n \lambda_i Z(x_i)$$

式中, x_i 为研究区内任一点的位置; λ_i 为权重系数,表示各个已知样品值对克里金估计量 $Z_v^x(x)$ 的贡献.

本研究使用普通克里金插值法进行空间插值. 普通克里金法属于线性平稳地统计学范畴,是对区域化变量的线性估计,认为区域化变量的期望值是未知的,通过确定待插点周围采样点的权重来求取待插点的近似值^[9]. 在插值过程中,选择插值的变量类型为半变异函数,插值模型为指数函数.

1.4 PAHs 源解析方法

环境中 PAHs 主要来源于自然源和人为源. 特征比值法是利用各种污染源的机制和特性不同,生成的污染物组成和含量存在不同程度的差别来识别污染物的来源^[10]. 通常可以根据环数的分布特征作初步的来源分析^[11], 2、3 环多环芳烃(low molecular weight PAHs, LMW PAHs)相对分子质量

低,主要来自石油类产品的泄漏,当其含量占比超过50%时代表了石油源;3~4环多环芳烃(middle molecular weight PAHs,MMW PAHs)和5~6环多环芳烃(high molecular weight PAHs,HMW PAHs)相对分子质量高,主要来源于化石燃料燃烧、燃煤和生物质燃烧,当3环以上多环芳烃含量占比超过50%时代表了燃烧源.也可采用 InP/(InP+BgP)、BaA/(BaA+Chr)等异构体比值进行源解析^[12],若 InP/(InP+BgP)值小于0.2意味着石油输入,大于0.5则来自于煤和生物燃烧,介于0.2与0.5之间为石油燃烧源^[13];若 BaA/(BaA+Chr)值小于0.2意味

着石化来源,大于 0.35 意味着燃烧源,而介于 0.2 与 0.35 之间为石化和燃烧混合来源[14].

2 结果与讨论

2.1 我国表层土壤 PAHs 污染水平

调查的 166 篇文献分布于 27 个省级行政区,研究区域集中于我国东部地区,特别是珠三角、长三角、京津冀以及东三省这些经济或者工业发达地区. 如表 1 所示,共涉及 234 个污染地块, 9 284个采样点位,基本能代表我国多数地区表层土壤 PAHs 污染情况.

表 1 我国表层土壤 PAHs 污染调查文献信息分布1)

Table 1 Distribution of PAHs in China's surface soils based on literature

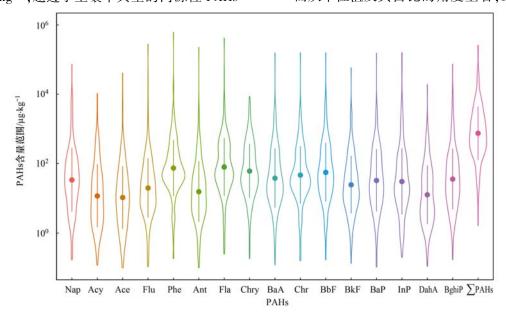
地区	省级行政区划及文献计数	文献总数	地块总数	样点总数
华北	北京市(11)、天津市(8)、河北省(4)、山西省(6)和内蒙古自治区(0)	29	31	2 103
东北	辽宁省(12)、吉林省(2)和黑龙江省(8)	22	35	1 420
华东	上海市(10)、江苏省(16)、浙江省(9)、安徽省(2)、福建省(10)、江西省(1)和山东省(10)	58	88	2 977
中南	河南省(4)、湖北省(4)、湖南省(1)、广东省(21)、广西壮族自治区(1)和海南省(0)	31	43	2 045
西南	重庆市(3)、四川省(0)、贵州省(7)、云南省(1)和西藏自治区(2)	13	13	492
西北	陕西省(4)、甘肃省(4)、青海省(0)、宁夏回族自治区(1)和新疆维吾尔自治区(4)	13	24	247
合计	a li ia l'V	166	234	9 284

1)括号内数据为对应省级行政区划的相关文献计数;不包括中国香港、澳门和台湾地区

从 16 种多环芳烃及 \sum_{16} PAHs 的含量分布来看,我国表土 \sum_{16} PAHs 含量从未检出到6 100 000 μ g·kg⁻¹,平均值为30 530.51 μ g·kg⁻¹,标准差为399 049.83 μ g·kg⁻¹,变异系数(CV)为13.07,属于强变异关系,数据离散度高,上下四分位值分别为252.52 μ g·kg⁻¹和2 500.00 μ g·kg⁻¹,中位值为675.70 μ g·kg⁻¹,超过了土壤中典型的内源性 PAHs

范围(1~10 μg·kg⁻¹)^[15],说明我国表层土壤均受到了人为因素的影响,且部分点位受 PAHs 影响较为严重. 如图 1 所示,不同 PAHs 单体的 25%~75%区间分布在 1.15~288.30 μg·kg⁻¹范围内,其中Phe 和 Fla 含量的中位值最高,分别为 62.1 μg·kg⁻¹和 60.6 μg·kg⁻¹;而 Acy 和 Ace 含量的中位值最低,分别为 6.57 μg·kg⁻¹和 6.98 μg·kg⁻¹.

而从中位值及其占比的角度上看, Phe、Fla、Pyr



小提琴图外侧框线宽度表示数据的频率分布,长度表示数据范围;中间黑点表示该列数据中数,实线表示该列数据标准差范围

图 1 我国表层土壤 PAHs 单体及 \sum_{16} PAHs 的含量特征

Fig. 1 Content of 16 single PAHs and \sum_{16} PAHs in surface soils of China

和 BbF 的占比较高,均超过总体的 10%,而 Acy、Ace和 DahA 的含量占比较低,这与曹云者等[4]和尚庆彬等[6]的报道结果相一致. 如表 2 所示,就不同环数 PAHs 含量占比而言,4 环 PAHs 占比最高(38.13%),其次为 3 环 PAHs,占比为 23.02%,2 环和 6 环的 PAHs 占比最低,分别为 6.08%和10.51%.而就不同相对分子质量 PAHs 含量占比而言,MMW PAHs 和 HMW PAHs 占比相对较高,分别为 38.13%、32.78%,这可能与其饱和蒸气压较低、水溶性小和辛醇水分配系数 K_{ow} 相对较高、易于吸附在土壤颗粒物上的特性相关,极易在土壤环境中富集[16],而 LMW PAHs 仅占 29.10%,含量相对较小,这可能与其相对分子质量较低、易挥发,且极易被微生物降解有关[17].

表 2 不同单体、环数、相对分子质量 PAHs 的中位数及占比信息 Table 2 Median and percentage of PAHs by rings

	and relative	molecular m	ass	0
划分依据	PAHs	环数	中位数	中位数
	171110	-134	∕µg•kg ⁻¹	占比/%
	Nap	2 环	27. 74	6. 08
	Acy	3 环	6. 57	1. 44
	Ace	3 环	6.98	1.53
6	Flu	3 环	16. 20	3. 55
7	Phe	3 环	62. 1	13. 60
1.6	Ant	3 环	13. 25	2. 90
- B.	Fla	4 环	60.60	13. 27
单体	Pyr	4 环	49. 63	10. 87
74	BaA	4 环	26. 47	5. 80
10 F	Chry	4 环	37. 37	8. 18
	BbF	5 环	46.00	10.08
11	BkF	5 环	18.50	4. 05
	BaP	5 环	29. 50	6. 46
	InP	6 环	21. 20	4. 64
	DahA	5 环	7. 66	1. 68
	BghiP	6 环	26. 80	5. 87
	2 环 PAHs	2 环	27. 74	6. 08
	3 环 PAHs	3 环	105. 10	23.02
环数	4 环 PAHs	4 环	174. 07	38. 13
	5 环 PAHs	5 环	101.66	22. 27
	6 环 PAHs	6 环	48.00	10.51
	LMW PAHs	2、3 环	132. 84	29. 10
相对分子质量	MMW PAHs	4 环	174. 07	38. 13
	HMW PAHs	5、6 环	149.66	32. 78

目前,我国仅在《土壤环境质量 农用地土壤污染风险管控标准(试行)》(GB 15618-2018)中规定了苯并[a]芘(BaP)的农用地土壤污染风险筛选值为 0.55 μg·kg⁻¹,尚未具体制定表土中多环芳烃的污染风险筛选值和管制值标准,在调查的污染地块中仅有 16 个地块(占比 6.83%)的 BaP 单体含量超过了该筛选值标准.参照 Maliszewska-Kordybach 提出的评价标准^[18]:当土壤中 ∑₁₆ PAHs 的含量小于

200 μ g·kg⁻¹为未污染,200~600 μ g·kg⁻¹为轻度污染,600~1000 μ g·kg⁻¹为中度污染,大于1000 μ g·kg⁻¹为重度污染.我国表层土壤中 \sum_{16} PAHs 的含量为中度污染水平,其含量仅低于德国森林,但均高于其它国家及地区的调查研究结果(表 3).

表 3 不同国家地区表土中 $\sum_{16} PAHs$ 污染水平对比

Table 3 Comparison of \sum_{16} PAHs pollution levels

in surface soils in different countries and regions

			0	
地区	年份	∑ ₁₆ PAHs 含量 /µg⋅kg ⁻¹	污染水平	文献
中国	2020	675. 70	中度污染	本研究
中国香港	2007	140	未污染	[19]
瑞士	2008	163	未污染	[20]
韩国	2003	236	轻度污染	[21]
日本	2007	496	轻度污染	[22]
英国农村	2006	590	轻度污染	[23]
德国森林	2015	1 448	重度污染	[24]

2.2 我国表层土壤 PAHs 时间变化特征

目前我国相关学者对 PAHs 的时间变化特征研究多侧重于年度内含量随季节变化特征. 本研究对近 20 年的时间跨度的我国不同地区、不同类型的表层土壤 \sum_{16} PAHs 进行统计分析,其结果如图 2 所示,我国表层土壤中 \sum_{16} PAHs 含量的 25% ~ 75% 区间于 2000 ~ 2018 年间落在 313.1 ~ 1 070.45 μg·kg⁻¹范围内,随年份变化均值数据大体稳定,属于中度污染水平范围内.

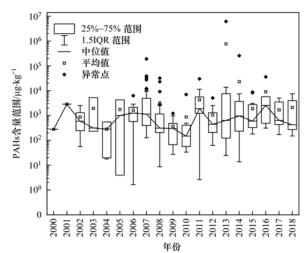


图 2 我国表土 $\sum_{16} PAHs$ 含量年度变化趋势

Fig. 2 Annual Trend of \sum_{16} PAHs concentration in surface soils of China

由于来自不同点位以及不同年度样本之间 $\sum_{16} PAHs$ 含量差异过大,将本研究中得到的 $\sum_{16} PAHs$ 含量年度变化趋势与迄今为止报道的其

 X_1

 X_2

 X_3

 X_4

 X_5

 X_6

它水平进行比较. Jones 等[25]的研究显示,由于工业 化产生的化石燃料燃烧影响,英国耕层土壤 PAHs 含量从 1880~1980 年急剧增长了大约 4 倍(1130 ~1770 μg·kg⁻¹); Honda 等^[22]的研究显示,日本 水稻土中 PAHs 主要来源于化石燃料燃烧,之后由 于燃烧工艺的优化,其平均含量从1959~1969年 的 731 μg·kg⁻¹快速下降,并在 1980~2002 年间 稳定在 236 µg·kg⁻¹的轻度污染水平,且工业化初 期土壤 PAHs 含量急剧升高,随着工业化进程以及 相关环保技术的发展,PAHs 含量开始下降并趋于 稳定. 本研究调查时段正处于我国从工业化中期 向工业化后期发展的重要阶段[26,27],调查时段中 我国表土中 ∑ PAHs 含量及污染水平基本稳定, 与日本等地区工业化中后期相关研究结果相一

致,但污染水平相对世界上其它国家及地区仍 较高.

以年度为控制变量,分析我国表土 ∑ PAHs 含量与我国年度统计中能源、工业部分指标的偏相 关性,结果如表 4 所示. 在选取的统计指标中,表土 ∑ PAHs 含量与原煤生产总量、能源生产总量和 民用汽车拥有量的相关性最好,其绝对值均大于 0.15; 而与原油生产总量及石油消费总量的偏相关 性绝对值小于 0.1,说明我国石油生产量和消费量 变化对我国表土 \sum_{16} PAHs 含量年度变化影响较 小; 其它统计指标的偏相关性均在 0.1 水平,即对 表土 \(\sum_{\text{PAHs}}\) 含量年度变化存在不同程度的影 响,但其相关性均不显著(P>0.05).

表 4 表土 $\sum_{16} PAHs$ 含量与部分年度统计指标的偏相关性结果 $^{1)}$

Results of partial correlation between the concentration of \sum_{16} PAHs and annual statistical indicators $\sum_{16} PAHs$ X_1 $\sum_{16} PAHs$ 1.000 0.126 1.000 0.153 0.952 1.000 -0.669 0.839 1.000 0.995 -0.7281.000 -0.608 0.866 0.843 0.728

0.970

0.966

0.115

0.796

0.787

-0.011

 $1)X_1$ 表示国内生产总值(亿元); X_2 表示民用汽车拥有量(万辆); X_3 表示能源生产总量(万吨标准煤); X_4 表示原煤生产总量(万吨标准 煤); X_5 表示原油生产总量(万吨标准煤); X_6 表示能源消费总量(万吨标准煤); X_7 表示煤炭消费总量(万吨标准煤); X_8 表示石油消费总量 (万吨标准煤)

0.959

0.944

- 0. 077

2.3 我国表层土壤 PAHs 空间分布特征

-0.111

-0.076

-0.773

-0.840

0.281

0.898

-0.948

0.316

我国表层土壤中 PAHs 含量在不同地区之间存 在较大差异,不同地区 ∑ PAHs 中位值从大到小 依次为: 西北地区(1815.00 μg·kg⁻¹)、华北地区 (983.44 μg·kg⁻¹、华东地区(912.98 μg·kg⁻¹)、东 北地区(590.50 μg·kg⁻¹)、西南地区(537.60 μg·kg⁻¹)和中南地区(399.18 μg·kg⁻¹). 与张俊叶 等[28]的研究结果相似,均表现为西北和华北地区表 层土壤中 PAHs 含量中位值最高, 而西南和中南地 区中位值最低. 其中, 西北地区统计结果偏高的原因 可能为:①收集到的相关文献中,西北地区点位的地 块类型以工业、道路为主,受工业企业生产加工以及 道路车流的影响,其调查点位含量偏高;②由于"全 球蒸馏效应"的影响,有机污染物通过蒸发、大气运 输向极地地区迁移并沉积[29],而西北地区处于高原 等特殊环境及气候下,其多环芳烃的组成差异和含 量可能受到一定影响,导致相关统计值偏高; ③相 关研究指出土壤 \(\sum_{16} \text{PAHs}\) 含量与石油储量之间存 在正相关关系[28],而西北地区,特别是新疆等地具 有较高石油储量,导致当地本底值偏高,进而影响到 相关点位统计结果.

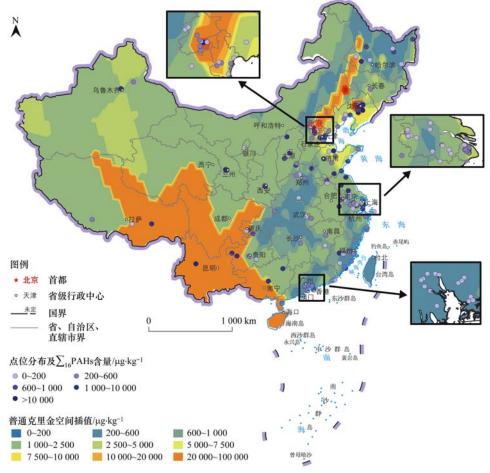
0.989

-0.085

1.000

-0.195

使用 ArcGIS 10.6 地统计模块中的普通 Kriging 插值方法,对收集到234个地块的经纬度信息及 ∑ PAHs 含量进行插值分析,其结果如图 3 所示. 其中,我国西南地区普遍出现较高插值结果,与该地 区中位值统计结果相悖,这可能与该区域收集点位过 少,且已有收集点位多为异常点的原因相关.除此以 外,京津冀地区以及辽宁省也同样出现较高的插值结 果,作为我国的老工业基地,两地历史上均存在大量 排放,且相关研究多围绕这些地区的工业场地或工业 遗留场地进行调查,此外,由于京津冀地区和辽宁省 纬度较高且气温较低,日照辐射[30]、微生物作用[31]等 自然因素导致的 PAHs 降解量较少,导致相关最终含 量插值结果也相对较高. 而我国中南地区以及华东地



改自审图 **图 3 基** Fig. 3 The \sum

改自审图号为 GS(2019)1697 号的标准地图,底图无修改

图 3 基于普通克里金法的我国 $\sum_{16} PAHs$ 空间插值结果

Fig. 3 The \sum_{16} PAHs spatial interpolation result based on ordinary Kriging

区的相关统计以及插值结果相对较低.

对普通 Kriging 插值结果进行栅格化处理,并按省份对应提取对应统计结果. 结果显示,16 个省(51.6%)污染情况为"轻微污染",5 个省(16.1%)污染情况为"中等污染",其余 10 个省份(32.3%)的污染情况为"严重污染",不存在有省份污染情况为"未污染",这说明 PAHs 污染在我国表土中是普遍存在的,但总体情况良好. 且本次插值在西南地区受异常值影响较大,西南地区部分省份实际应处于"中等污染"或者"轻微污染"水平,但西南地区生态地质环境较为脆弱^[32],更应重视对西南地区工矿业企业其生产、运输、存储过程中产生的 PAHs 污染对表层土壤的影响.

2.4 我国表层土壤 PAHs 来源解析

从 PAHs 相对丰度来看,我国表土 PAHs 污染来源可分为 5 个聚类,如图 4 所示,其中表现为燃烧源的聚类 1 和聚类 5 的 LMW PAHs 占比相对偏低(分别为 10%~30% 和 0~10%),所涉及的调查文献多体现为煤及生物质的燃烧影响,与于国光等^[33]对薪

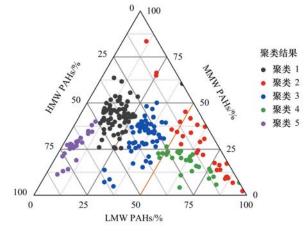


图 4 我国表土 $\sum_{16} PAHs$ 组分的含量分布

Fig. 4 Distribution of \sum_{16} PAHs in surface soils of China

柴燃烧源和燃煤源的 PAHs 成分谱中 3、4 环多环芳 烃含量较高的研究结论相吻合,而同样表现为燃烧源的聚类 3 的 LMW PAHs 占比则相对较高,所涉及的调查文献多体现为石油燃烧、道路机动车排放的影响,也与刘定超等[34]对石油燃烧过程中释放的

PAHs 均以低环芳烃为主的结论相吻合;而聚类 2 和聚类 4 则表现为石油源,其范围 HMW PAHs 占比分别为 0~10% 及 10%~30%.调查文献所涉及的地块中,判定为燃烧源的地块占比 75%,而判定为石油源的地块占比 25%,且主要分布在黑龙江以及新疆、西藏等西北地区.初步可认为我国主要 PAHs 来源于燃烧源,即主要由于石油和煤等化石燃料的高温燃烧造成我国 PAHs 污染.

而 InP/(InP + BghiP) 与 BaA/(BaA + Chry)的 K-Means 聚类结果(如图 5) 同样印证了燃烧源是我国表土 PAHs 污染来源的结论,除聚类 3 的主体及聚类中心落在 InP/(InP + BghiP) < 0.2 范围内,主要表现为石油燃烧外,其他聚类解析结果均表现为燃烧源,这其中聚类 2 主要表现为混合源,以油类燃烧为主,而聚类 1 和聚类 4 则表现为以生物质、煤炭为代表的化石燃料燃烧.

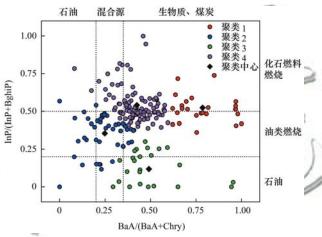


图 5 我国表土中 BaA/(BaA + Chry)和 InP/(InP + BghiP)比值分布

Fig. 5 Plot of PAHs between BaA/(BaA + Chry) and $InP/(InP + BghiP) \ in \ surface \ soils \ of \ China$

综合来看,我国 PAHs 来源分布较为分散,但以生物质、煤炭和油类燃烧源为主要来源,除此以外,在我国主要产油区如黑龙江省、新疆维吾尔自治区,统计数据显示其表土中 PAHs 污染主要来自于石油源污染.

3 结论

- (1)PAHs 污染在我国表层土壤普遍存在,其含量中位值为 675.70 μg·kg⁻¹,污染水平与其它国家及地区相比较高. PAHs 单体含量中 Fla 和 Pyr 含量较高,而 Acy 和 Ace 含量较低.
- (2)我国表层土壤 PAHs 污染存在明显区域特征,地区含量从西北、华北、华东、东北、西南、中南依次递减.除北京和辽宁省外,多数省份的 PAHs 污染水平处于"中度污染"或"轻度污染".

- (3)2000 ~2018 年间,我国表土中 \sum_{16} PAHs 含量及污染水平基本稳定在 313. 10 ~1 070. 45 $\mu g \cdot k g^{-1}$ 范围内,其变动受我国石油生产和消费影响较小.
- (4)不同源解析的结果均表明我国表土 PAHs 主要来源于石油、生物质和煤等化石燃料的高温燃 烧,但黑龙江省以及新疆、西藏等西北地区则以石油 源污染为主.

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