DOI:10.7524/j.issn.0254-6108.2018121903
孙俊玲, 张庆华, 李英明.北京市冬季大气细颗粒物中二噁英的污染特征[J].环境化学,2019,38(9):1982-1989.
SUN Junling, ZHANG Qinghua, LI Yingming. Profiles of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in atmospheric fine particulate matter of Beijing in winter[J].Environmental Chemistry,2019,38(9):1982-1989.

北京市冬季大气细颗粒物中二噁英的污染特征*

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摘 要 为了解北京市大气细颗粒物($PM_{2.5}$)中二噁英(PCDD/Fs)的污染特征,利用中流量大气颗粒物采样器,在北京市 3 个功能区 5 个采样点(两个市区点、两个工业区点和一个背景点),同步连续采集了大气细颗粒物 $PM_{2.5}$样品.参照 US EPA 1613B 标准方法,应用高分辨率气相色谱/高分辨率质谱(HRGC/HRMS),分析了 $PM_{2.5}$中 17 种 PCDD/Fs 的浓度水平和区域分布特征,并对 PCDD/Fs 的污染来源做了初步探讨.结果表明,5 个采样点 $PM_{2.5}$的日均质量浓度范围 102—146 μg·m^{-3},平均日均值 119 μg·m^{-3},超出国家二级标准(75 μg·m^{-3})59%,污染较重.在空间分布上,$PM_{2.5}$的日均浓度表现为工业区大于背景点大于市区的特征.所有采样点 17 种 PCDD/Fs 的总浓度范围∑PCDD/Fs 是 1.60—4.09 pg·m^{-3},平均值 3.23 pg·m^{-3},PCDD/Fs 总毒性当量∑TEQ 范围是 140.54—275.69 fg I-TEQ·m^{-3},平均值 233.18 fg I-TEQ·m^{-3}.与国内外其他城市相比,北京市大气 $PM_{2.5}$中 PCDD/Fs 污染处于相当或略高水平.OCDD、OCDF 和 1,2,3,4,7,8-HpCDF 是 PCDD/Fs 的主要组成成分,分别占总浓度∑PCDD/Fs 的 10%、19%和 24%.对于总毒性当量∑TEQ 贡献最大的是 2,3,4,7,8-PeCDF,占总毒性当量的 48.3%,∑PCDDs/∑PCDFs 比值范围为 0.19—0.23,平均值 0.22,属于典型的"热源" 特征.在浓度变化上, PCDDs 呈现为随氯取代个数的增加而增加,除 OCDF 外, PCDFs 的各单体浓度也随着取代氯原子个数的增加而增大.在区域分布上,PCDD/Fs 浓度表现为工业区高于市区,市区大于背景点,充分体现了局地源的特点.采样期间工业热过程(化石燃料燃烧、电弧炉、烧结和冶炼等)、机动车排放和固体垃圾焚烧是北京冬季大气 $PM_{2.5}$中 PCDD/Fs 和 $PM_{2.5}$污染水平的主要影响因素.

关键词 $PM_{2.5}$, 二噁英(PCDD/Fs), 高分辨率气相色谱/高分辨率质谱(HRGC/HRMS), 北京大气.

Profiles of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in atmospheric fine particulate matter of Beijing in winter

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Abstract: Atmospheric $PM_{2.5}$ samples were collected concurrently with middle-volume active sampler at five contrasting sites (two urban sites, two industrial sites, and a background site) to investigate the level and distribution of PCDD/Fs in air of Beijing. The concentrations and spatial distributions of 17 PCDD/F congeners were analyzed with isotope dilution high resolution gas chromatography/high resolution mass spectrometry (HRGS/HRMS) based on US EPA 1613B method. The results

2018 年 12 月 19 日收稿(Received: December 19, 2018).
* 国家自然科学基金(91743206, 21777186,41676183)资助.
Supported by National Nature Science Foundation of China (91743206, 21777186,41676183).
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showed that $PM_{2.5}$ concentrations for different districts were in the range of 102—146 $\mu g \cdot m^{-3}$ with mean value of 119 $\mu g \cdot m^{-3}$, which was 59% higher than the second class daily average standards (75 $\mu g \cdot m^{-3}$). The $\sum_{17}$PCDD/Fs concentrations ranged 1.60—4.09 $pg \cdot m^{-3}$ with an average concentration of 3.23 $pg \cdot m^{-3}$. The TEQs varied from 140.54 to 275.69 fg I-TEQ$\cdot m^{-3}$ with an average value of 233.18 fg I-TEQ$\cdot m^{-3}$. For individual PCDD/Fs, 1,2,3,4,6,7,8-HpCDF showed higher concentrations than other congeners and accounted for 24% of $\sum_{17}$PCDD/Fs, followed by OCDF (19%) and OCDD(10%). The 2,3,4,7,8-PeCDF was the largest contributor to $\sum$TEQ, which accounted for 48.3% of $\sum$TEQ, the ratio of $\sum$PCDDs/$\sum$PCDFs varied from 0.19—0.23 with an average value of 0.22, which was classified as thermal source pollution profiles. Both the PCDDs and the PCDFs (except OCDF) concentrations increased with the increasing levels of chlorination. For spatial distribution, the highest PCDD/Fs concentration in $PM_{2.5}$ was observed in industrial sites followed by urban sites and background site. The major factors affecting $PM_{2.5}$ and PCDD/Fs levels were industrial thermal process, vehicle emissions and solid waste incinerators during sampling.

Keywords: $PM_{2.5}$, PCDD/Fs, HRGC/HRMS, Beijing air.

二噁英(PCDD/Fs)是《斯德哥尔摩公约》首批严格控制的 12 种持久性有机污染物(POPs)之一,具有半挥发性和高毒性,在环境中能够稳定存在,在生物的脂肪中累积,并且能在环境中远距离传输和扩散. PCDD/Fs 的毒性与氯取代个数及取代位置密切相关,17 种 2,3,7,8-PCDD/Fs 对人类健康和生态系统危害尤为严重,引起了全社会的广泛关注[1-2], PCDD/Fs 主要随空气扩散远实现远距离迁移,$PM_{2.5}$作为大气的重要组成,对二噁英在区域或全球分布起着重要作用,研究[3-4]表明,PCDD/Fs 主要富集在 $D_P < 2.1$ μm 的颗粒物上,文献[5]报道大气 PCDD/Fs 80%集中在粒径小于 1.35 μm 的大气颗粒物上,所以大气环境中尤其是 $PM_{2.5}$中 PCDD/Fs 对人体危害最大[6],在一定程度上能够反映某一地区大气 PCDD/Fs 的污染状况.近年来科研人员陆续对大气环境中 PCDD/Fs 污染进行了一些研究,但是这些研究主要集中在对 TSP 和气相中 PCDD/Fs 的污染状况进行表征,对于 $PM_{2.5}$中 PCDD/Fs 的研究较少.北京作为我国的首都,工业和机动车发展非常快, PCDD/Fs 排放难以避免.因此,在北京地区开展大气环境中,尤其大气细颗粒物中二噁英类的污染研究意义重大.

本研究通过分析北京市大气细颗粒物 $PM_{2.5}$中 17 种 2,3,7,8-PCDD/Fs 浓度水平和分布特征,初步掌握了该地区大气 PCDD/Fs 的污染状况,虽然采样时间较早,目前北京地区工业结构也发生了较大变化,但由于大气中的二噁英等持久性有机污染物(POPs)含量极低、分析流程和精度要求高、检测成本昂贵等因素,北京地区环境中尤其是大气环境中二噁英的研究数据极少,该研究结果对于现在的科研工作者能够起到很好的借鉴作用,另外政府部门也可以根据其他监测数据与本监测结果之间的变化趋势来评价近年来所制定污染治理措施的成效,并以此为依据有针对性实时调整污染治理措施和产业结构,使其更加合理有效.

1　材料与方法(Materials and methods)

1.1　样品采集

根据城市功能区划特点,2008 年 1 月,在北京市设置 5 个采样点,海淀区 (A 地质大学东门、B 地质大学测试楼顶), 位于成府路与学院路交叉口南,人口密集,交通繁忙,石景山区 (C 首钢焦化、D 高井电厂) 典型工业区, 主要是以煤为燃料的发电、钢铁冶炼、炼焦等工业企业,昌平区(E 十三陵)背景点,远离市区,车流量和人口密度相对较小, 植被较密集的村庄[7],能很好地代表区域背景点的污染状况,采样点分布见图 1.

样品采集应用中流量大气颗粒物采样器,各采样点分别同步采集 8 d(约 900 m^3),采样间隔 24 h,共采集 40 个 $PM_{2.5}$样品.采样滤膜为玻璃纤维滤膜(GFF_S),直径 9 cm, 采样器流量:77.59 $L \cdot min^{-1}$.样品采集参照 US EPA 标准方法 T0-9A 进行,使用前 GFF_S在马弗炉 450 ℃焙烧 12 h,用电子天平准确称量

采样前后 GFF_S得到 $PM_{2.5}$质量浓度[7],然后铝箔密封冷冻保存.

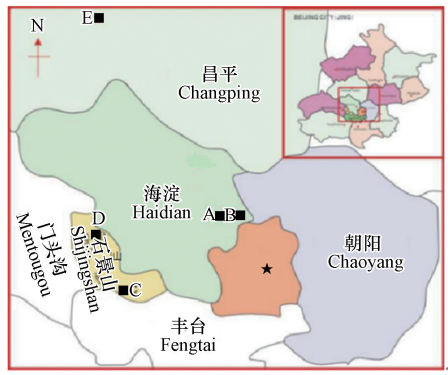

图 1 北京大气 $PM_{2.5}$采样点分布图

Fig.1 Location of sampling sites in Beijing

1.2 样品处理

严格按照 US EPA 1613B 的前处理方法,提取前 GFF_S上添加含 15 种$^{13}C_{12}$标记的 PCDD/Fs 净化内标($^{13}C_{12}$-2,3,7,8-TCDD、$^{13}C_{12}$-1,2,3,7,8,9-HxCDF、$^{13}C_{12}$-1,2,3,6,7,8-HxCDD、$^{13}C_{12}$-2,3,4,6,7,8-HxCDF、$^{13}C_{12}$-OCDD、$^{13}C_{12}$-1,2,3,7,8-PeCDF、$^{13}C_{12}$-1,2,3,4,7,8-HxCDD、$^{13}C_{12}$-2,3,7,8-TCDF、$^{13}C_{12}$-2,3,4,7,8-PeCDF、$^{13}C_{12}$-1,2,3,4,7,8-HxCDF、$^{13}C_{12}$-1,2,3,7,8-PeCDD 、$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF、$^{13}C_{12}$-1,2,3,6,7,8-HxCDF、$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD、$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF),用加速溶剂提取(Dionex, ASE300)对剪碎的 GFF_S样品进行抽提,溶剂正己烷和二氯甲烷的比例是 1:1,抽提的温度和压力分别为 100 ℃和 1500 PSI,抽提液经旋转蒸发浓缩至 2 mL, 经过 4 g 碱性硅胶柱、8 g 酸性硅胶柱和 1 g 弗罗里土柱进行净化,最后样品经氮吹浓缩,移至事先加入 20 μL 壬烷(做稳定剂)的进样小瓶,在样品溶液中加入$^{13}C_{12}$标记的 PCDD/Fs 进样内标($^{13}C_{12}$-1,2,3,4-TCDD 和$^{13}C_{12}$-1,2,3,7,8,9-HxCDD),涡轮混匀用 HRGC/HRMS 进行测定,具体前处理流程详见参考文献[8].

本文分析了 17 种 2,3,7,8-PCDD/Fs (2,3,7,8-TCDF、1,2,3,7,8-PeCDF、2,3,4,7,8-PeCDF、1,2,3,6,7,8-HxCDD、1,2,3,4,7,8-HxCDF、1,2,3,6,7,8-HxCDF、1,2,3,7,8,9-HxCDD、2,3,4,6,7,8-HxCDF、1,2,3,4,7,8-HxCDD、1,2,3,7,8,9-HxCDF、1,2,3,7,8-PeCDD、1,2,3,4,6,7,8-HpCDF、1,2,3,4,7,8,9-HpCDF、OCDF、2,3,7,8-TCDD、1,2,3,4,6,7,8-HpCDD、OCDD),所有溶剂为农残级.

1.3 样品测定

PCDD/Fs 的测定采用 HRGS/HRMS 技术,色谱和质谱分别是 Agilent 6890 和 AutoSpec Ultima, Waters.质谱电离方式是电子轰击(EI),采集方式为选择离子检测模式(SIR); 分辨率 $R \geq 10000$, 源温 270 ℃,电子能量 35 eV, 载气(He)流速为 1.2 mL·min^{-1}.色谱柱为 DB-5MS(0.25 mm ID×0.25 μm film, 柱长 60 m). 无分流进样, 进样量为 1 μL.气相色谱柱程序升温: 150 ℃ (3 min) —230 ℃ (18 min, 20 ℃·min^{-1}),230—235 ℃(10 min, 5 ℃·min^{-1}), 235—320 ℃(3 min, 4 ℃·min^{-1}).

1.4 质量控制和质量保证

实验分析过程中同步进行了采样点现场空白和实验室空白样品分析,结果显示,空白样品中 PCDD/Fs 几乎没有检出.大气颗粒物样品中除$^{13}C_{12}$-OCDD 平均回收率为 43%(26%—58%)外,其他$^{13}C_{12}$标记净化内标为 60%—90%,实际样品中 PCDD/Fs 的检测限为 0.0034—0.0307 pg·m^{-3},符合 US EPA 1613B 的要求.

2 结果与讨论(Results and discussion)

2.1 $PM_{2.5}$中 PCDD/Fs 的浓度水平

表 1 给出了各采样点 $PM_{2.5}$中 PCDD/Fs 的浓度和毒性当量(TEQ)以及 $PM_{2.5}$的质量浓度,结果表明,5 个样点 17 种单体的总浓度∑PCDD/Fs 范围是 1.60—4.09 pg·m^{-3},平均值 3.23 pg·m^{-3}, 总毒性当

量∑TEQ 范围为 140.54—275.69 fg I-TEQ·m^{-3},平均值 233.18 fg I-TEQ·m^{-3}. Xu 等[9]和 Qin 等[10]的研究表明,90%以上的 PCDD/Fs 主要富集在细颗粒物上,而且比较其它季节,由于各种燃烧(如取暖等)增强和逆温等不利于扩散的气象条件增加,冬季 PCDD/Fs 更容易吸附在颗粒相上[10-11],因此,尽管不同的研究之间的研究介质不尽相同,但是有关大气环境中的 PCDD/Fs 研究结果之间仍然可以进行比较.与国内外其他文献报道相比,北京大气 $PM_{2.5}$中∑PCDD/Fs 的浓度水平低于上海(497.1 fg I-TEQ·m^{-3})[12]、苏州(∑TEQ 81—1220 fg I-TEQ·m^{-3}, 平均值 320 fg I-TEQ·m^{-3})[13], 与大连(平均 235 fg I-TEQ·m^{-3})[10]以及北京大气中 PCDD/Fs(平均值 268 fg I-TEQ·m^{-3})[14]研究结果相当,略高于美国 (16 fg-TEQ·m^{-3})[15]、西班牙(平均值 140 fg I-TEQ·m^{-3})[16]、韩国 (平均值 28 fg I-TEQ·m^{-3})[17]、希腊 (42-73 fg I-TEQ·m^{-3})[18]、葡萄牙(145 fg I-TEQ·m^{-3})[19]、成都 (66.5 fg-TEQ·m^{-3})[20],但仍然低于日本大气的控制标准(0.6 pg TEQ·m^{-3})[14].

表 1　$PM_{2.5}$浓度((μg·m^{-3})、$PM_{2.5}$中二噁英的 TEQ(fg I-TEQ·m^{-3})和浓度 (pg·m^{-3})

Table 1　The levels and TEQ of PCDD/Fs for sites in $PM_{2.5}$ in Beijing (pg·m^{-3})

		A	C	B	E	D	Average
浓度 Concentration	$PM_{2.5}$	102	146	102	122	123	119
	∑PCDFs	2.72	3.01	2.82	1.34	3.38	2.66
	∑PCDDs	0.58	0.70	0.62	0.25	0.71	0.57
	∑PCDD/Fs	3.30	3.72	3.44	1.60	4.09	3.23
	∑PCDDs/∑PCDFs	0.21	0.23	0.22	0.19	0.21	0.22
TEQ	$I\text{-}TEQ_{PCDF}$	214.19	232.23	219.25	131.44	251.68	209.78
	$I\text{-}TEQ_{PCDD}$	30.56	22.14	31.31	9.11	24.01	23.42
	∑I-TEQ	244.75	254.37	250.56	140.54	275.69	233.18

目前中国已经步入城市化和工业化中后期,正在面临更为严重的环境问题,由于 PCDD/Fs 强毒性和强致癌性,有必要做进一步研究,并逐步开展污染防治工作.

2.2　$PM_{2.5}$中 PCDD/Fs 同系物分布

表 1 显示,北京市大气 $PM_{2.5}$中 PCDF 浓度和毒性当量对总 PCDD/Fs 贡献率分别为 82.4%和 89.96%,不同采样点∑PCDDs/∑PCDFs 比值范围是 0.19—0.23,平均值 0.22,与 Qin 等[10]的报道(∑PCDDs/∑PCDFs 范围 0.2—0.6)近似.先前的研究[21]表明,大气中 PCDDs 与 PCDFs 的比值从不到 0.5到大于 2,并据此将 PCDD/Fs 分为"汇"和"源" 两类, 当 PCDF 浓度大于 PCDD 时为"源",当 PCDF 浓度小于 PCDD 时为"汇".北京大气 $PM_{2.5}$中 PCDFs,明显高于 PCDDs 显著,属于典型的"热源"特征[22],比如工业生产和人类活动等各种燃烧过程.

影响大气颗粒物中 PCDD/Fs 单体组成和分布因素较多,包括气候条件和污染释放源等.不同采样点大气 $PM_{2.5}$中 PCDD/Fs 各单体浓度(图 2) 组成模式基本相同,OCDD、OCDF 和 1,2,3,4,6,7,8-HpCDF 对总∑PCDD/Fs 浓度的贡献率最大,分别是 10%、19%和 24%,同样的大气 PCDD/Fs 单体组成模式在其他文献[23]中也有报道,然而 Cleverly 等[24]对美国乡村和偏远地区大气的研究结果(PCDD/Fs 中丰度最大的是 1,2,3,4,6,7,8-HpCDD 和 OCDD,而 OCDF 和 1,2,3,4,6,7,8-HpCDF 分别仅占 2%—6%和 1.9%—2.7%),Lohmann 等[25]对英国和爱尔兰大气研究结果(PCDD/Fs 中以 OCDD 为主)与北京大气 $PM_{2.5}$中 PCDD/Fs 单体组成存在差异, 原因可能是污染释放源和控制因素等不同导致.与同系物浓度分布不同,北京大气 $PM_{2.5}$中 17 种 PCDD/Fs 对于毒性当量贡献最大的是 2,3,4,7,8-PeCDF,贡献率为 48.3%(图 3),与其他研究结果[10,26]一致,其他主要单体是 2,3,4,6,7,8-HxCDF、1,2,3,4,7,8-HxCDF、1,2,3,6,7,8-HxCDF,分别占 9.8%、9.1%、7.5%,与 Li 等[14]对北京大气的研究类似.

北京 $PM_{2.5}$中 PCDD/Fs 单体组成与机动车排放[27]、金属烧结[28]、焚烧垃圾[29]以及煤燃烧排放[30] PCDD/Fs 组成相似.研究发现,1,2,3,4,6,7,8-HpCDF 是无铅汽油/柴油机动车排放以及有害固体废物焚烧释放的重要标志物[11],OCDF、OCDD 是无铅汽油机动车排放和城市固体废物焚烧源标志物[31-33],2,3,4,7,8-PeCDF 主要的释放源为铝二次冶炼、碳钢与钢铁生产过程中电弧炉[31,34],2,3,4,6,7,8-HxCDF 和 1,2,3,4,7,8-HxCDF 主要来自工业燃烧(垃圾焚烧、烧结厂和供暖等)[35-36],1,2,3,6,7,8-

HxCDF 主要来自烧结厂和铝二次冶炼释放[31].因此,冬季北京大气 $PM_{2.5}$ 中 PCDD/Fs 可能主要来源于工业热过程(化石燃料燃烧、电弧炉、烧结和冶炼)、机动车排放和固体垃圾焚烧.

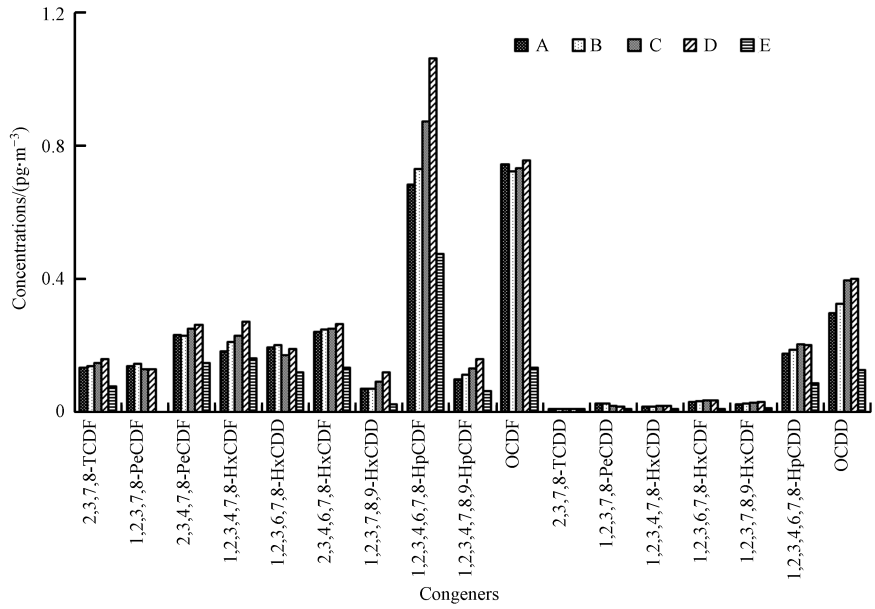

图 2 $PM_{2.5}$ 中 PCDD/Fs 各单体浓度

Fig.2 Congener concentrations of PCDD/Fs in $PM_{2.5}$

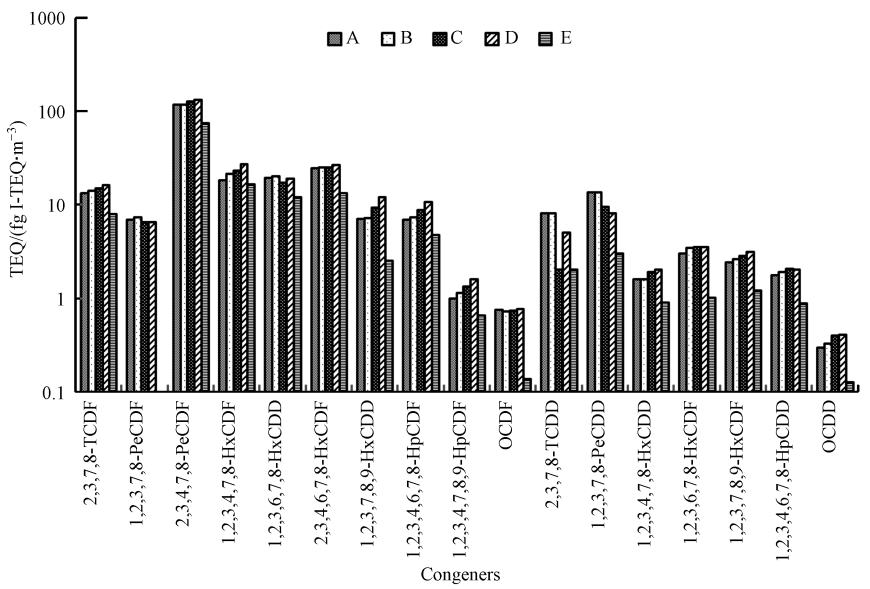

图 3 $PM_{2.5}$ 中 PCDD/Fs 同系物毒性当量

Fig.3 TEQ of PCDD/F congeners in $PM_{2.5}$

不同采样点大气 $PM_{2.5}$ 中 PCDD/Fs 各同族体浓度占比不同,高氯代同族体丰度较大,同族体分布趋势(图 4)总体表现为:除 OCDF 外,PCDDs 和 PCDFs 的浓度随着取代氯原子个数的增加而增大,与 Qin 等[10]对大连冬季大气和 Li[14]等对北京大气的研究结果非常一致.然而,Lee 等[37]的研究却是 PCDFs 的浓度随取代氯原子个数的增加而减少,前人总结了欧美、日本和澳大利亚等城市和地区大气中PCDD/Fs 的研究文献,发现典型城市大气 PCDD/Fs 分布特征也表现为,随着取代氯原子个数的增加,PCDDs 同系物丰度增加,而 PCDFs 同系物丰度降低[38].十三陵做为背景区域,OCDD 的贡献率低于其它功能区,与 OCDD 的贡献率农村大于城市的监测结果[39]不同,污染源和气象条件是大气 PCDD/Fs 的重要控制因素[39],可能不同研究间污染源和气象条件不同,导致了大气 PCDD/Fs 来源不一样,同族体的分布存在

差异,甚至是截然相反的特征.

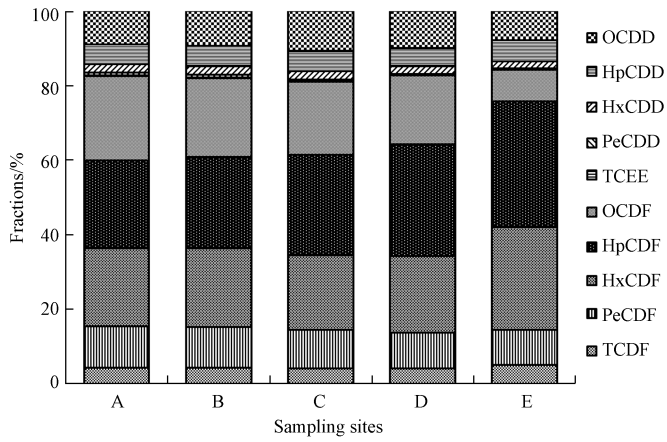

图 4　$PM_{2.5}$中 PCDD/Fs 同族体浓度相对分布

Fig.4　Homologue profiles of PCDD/Fs in $PM_{2.5}$

2.3　$PM_{2.5}$中 PCDD/Fs 的空间分布

大气中 PCDD/Fs 的浓度分布通常表现为工业区>市区>背景点[24,40-41].各种工业热过程[42],如高温炼钢、熔铁、烧结[43-44],以及燃烧和汽车尾气是 PCDD/Fs 的主要污染来源[45-47].北京大气 $PM_{2.5}$中 PCDD/Fs浓度的空间分布与上述文献报道表现出相同特点,即工业区略大于市区,工业区和市区显著大于背景点,PCDD/Fs 的毒性当量空间分布表现出相同趋势,具有局地排放源特征,由于是同步采样,采样期间,各采样点气象条件相似,PCDD/Fs 的浓度空间分布与污染点源有密切关系.所选工业区是燃煤电厂和钢铁生产基地,市区采样点处于交通干道,交通流量大,进一步说明工业生产和汽车尾气是北京市大气 $PM_{2.5}$中 PCDD/Fs 的重要来源. $PM_{2.5}$的质量浓度(表 1)与 PCDD/Fs 浓度的空间分布有所不同,表现为工业区大于背景点大于市区,两者之间没有显著的相关性,说明各种污染源对他们的贡献程度不同,2005 年冬季监测结果同样显示该背景点的 $PM_{2.5}$浓度大于市区[48].化石燃料的不充分燃烧是 $PM_{2.5}$的重要来源,而且燃煤引起的烟尘污染比汽车尾气所引起的污染更为严重[49],冬季采暖季节,背景点的村庄主要依靠燃煤取暖,各家分散供暖的形式导致燃烧极不充分,可能导致 $PM_{2.5}$浓度升高.另外,北京地区冬季常常受西伯利亚干冷气团影响,寒冷干燥,降雨量少,猛烈的西北风携带大量颗粒物而来[50],容易造成沙尘天气,处于北部山区的背景点风力更强,加之冬季植被凋落抵御风沙的能力并不强,还增加了地表裸露范围,另外采样点附近是裸露的农田,致使地面扬尘大量增加,风沙和地面扬尘的共同作用,导致颗粒物浓度升高,但风沙、扬尘不会增加大气 PCDD/Fs 的浓度[51].值得注意的是,北京大气 $PM_{2.5}$日均质量浓度范围 102—146 $\mu g \cdot m^{-3}$,平均日均值 119 $\mu g \cdot m^{-3}$,超过国家二级标准(75 $\mu g \cdot m^{-3}$)59%,污染较重,由于 $PM_{2.5}$粒径较小,可以不受阻挡直接进入肺部,并且不易排出,来源广,对人体健康危害极大,需要持续关注其产生机理并制定应对措施.

3　结论(Conclusion)

(1) 采样期间北京市大气 $PM_{2.5}$中∑PCDD/Fs 范围 1.60—4.09 $pg \cdot m^{-3}$,平均值 3.23 $pg \cdot m^{-3}$,总毒性当量∑TEQ 范围为 140.54—275.69 fg I-TEQ$\cdot m^{-3}$,平均值 233.18 fg I-TEQ$\cdot m^{-3}$.低于日本大气的控制标准(0.6 pg TEQ$\cdot m^{-3}$). 空间分布趋势表现为工业区略大于市区,工业区和市区显著大于背景点,初步研究认为,采样期间北京大气 $PM_{2.5}$中 PCDD/Fs 主要来自化工业热处理过程和人类活动.

(2) OCDD、OCDF 和 1,2,3,4,6,7,8-HpCDF 是 PCDD/Fs 的主要组成成分, 对毒性当量贡献最大的是 2,3,4,7,8-PeCDF, 其他依次是 2,3,4,6,7,8-HxCDF、1,2,3,4,7,8-HxCDF、1,2,3,6,7,8-HxCDF. 除 OCDF 外,PCDDs 和 PCDFs 的浓度随着取代氯原子个数的增加而增大.

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