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五种典型环境内分泌干扰物赋存及风险评估的研究进展*

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摘 要 内分泌干扰物(EDCs)作为一类新型持久性有机污染物,进入生物体后将干扰机体内分泌系统,引起多种疾病.本文对5种典型EDCs,包括双酚类(bisphenol, BPs)、多溴联苯醚类(poly brominated diphenyl ethers, PBDEs)、烷基酚类(alkyl phenols, APs)、邻苯二甲酸酯类(phthalic acid esters, PAEs)和有机磷酸酯类(organophosphate esters, OPEs),的应用、分布和风险评估研究进行了总结概述,总的来说,EDCs在全球范围内应用广泛,易脱落到环境中引发环境效应,在土壤、水体和空气等多种环境介质中广泛分布,且在城市化水平和工业化水平较高的地区分布尤为广泛.从风险熵法和危害指数法两个方面进行总结发现,典型EDCs对生态系统,特别是水生生态系统存在一定的风险.最后,从环境健康出发,对现阶段EDCs研究进行了展望.

关键词 内分泌干扰物, 分类和应用, 分布, 风险评估.

Occurrence and risk assessment of five typical environmental endocrine disruptors

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Abstract: As a new class of persistent organic pollutants, endocrine disruptors (EDCs) can interfere with the endocrine system of organisms, and cause a variety of diseases. This study provided an overview of the application, distribution and risk assessment of five typical EDCs, including bisphenol (BPs), poly brominated diphenyl ethers (PBDEs), alkyl phenols (APs), phthalic acid esters (PAEs) and organophosphate esters (OPEs). The wide application of EDCs in the world, which were easy to release from the product, were frequently detected in inorganic environments, such as soil, water and air. According to the previous studies, EDCs were widely detected in areas with high urbanization and industrialization levels. The results of risk assessment with risk quotient method and hazard index method implied that the typical EDCs showed certain risks to ecosystems, especially aquatic ecosystems. Finally, the current researches on EDCs were prospected by focusing on the perspective of the environmental health.

Keywords: endocrine disruptors, classification and application, distribution, risk assessment.

内分泌干扰物(EDCs)是一类具有与生物内分泌激素作用类似的外源性物质[1-2],具有低剂量效

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应,对生物有很大危害,能够引起神经、免疫和生殖等毒性效应[3-7].EDCs 种类繁多,如双酚类、烷基酚类、邻苯二甲酸酯类、高氯酸盐、多溴联苯醚类和多氯联苯类等,被广泛应用于洗涤剂、增塑剂、阻燃剂等生产中[1,8].研究发现,不同国家和地区的土壤、水体和沉积物等环境中均有 EDCs 的检出.Eriko 等[9]发现印度某河流中 BPA 浓度高达 54—1950 ng·L^{-1};我国北方某废旧塑料处置地土壤中 PBDEs 总浓度范围为 1.25—3673.41 ng·g^{-1}[10];广州某办公室室内灰尘中总 OPEs 浓度范围为 5360—6830 ng·g^{-1}[11].大部分 EDCs 具有半衰期长和生物富集等特点,对生态系统和人类健康造成了不同程度的风险.

近年来,随着世界经济水平的发展, EDCs 已成为继臭氧层破坏、全球变暖之后的第三大环境污染问题,被许多国家和国际组织关注[2].本文选择 5 种环境中暴露水平较高、近年来关注度较大的典型 EDCs,包括双酚类、多溴联苯醚类、烷基酚类、邻苯二甲酸酯类和有机磷酸酯类内分泌干扰物,从应用、分布和风险评估等方面对他们进行了综述,为 EDCs 的环境监管、制定 EDCs 的污染防治策略和 EDCs 在环境中的迁移和转化研究等方面提供数据支撑,对保障环境健康具有重要意义.

1 环境内分泌干扰物的分类及应用(Classification and application of EDCs)

1.1 双酚类

双酚类(bisphenol,BPs)是由两个羟苯基用碳原子、硫原子或氧原子连接在一起的化合物,主要包括双酚 A(BPA)、双酚 F(BPF)、双酚 S(BPS)、双酚 B(BPB)、双酚 C(BPC)和双酚 E(BPE)等[12-13],在生产聚碳酸酯塑料、环氧树脂、食品容器、纸制品和牙科密封剂等日常产品中广泛应用[14].其中应用最广泛产量最高的是 BPA[12,15].据统计,2016 年全球 BPA 需求量约为 800 万吨,预计到 2022 年全球 BPA 需求量将增加到 1060 万吨[16].由于 BPA 具有较强的毒性,已被欧洲联盟、美国和加拿大禁止用于奶瓶和儿童饮料容器中[16-17].为了满足市场的需求,一些更安全且稳定性更好的 BPA 结构类似物,如 BPB、BPS 和 BPF 等,被用来替代 BPA 添加到材料中[18].其中,由于 BPS 热稳定性和光稳定性较强,在环氧树脂、婴儿奶瓶和热敏纸等制造中应用较多[19].随着对 BPA 使用的受限,BPA 类似物的使用量逐年增多,这在一定程度上促进了 BPs 生产技术的不断更新与优化.但 BPA 类似物已在多种环境介质和人体中都有检出,并且已证实 BPA 类似物也存在一定的毒性效应[18,20].BPA 及 BPA 的类似物多用于与人密切接触的日常消费品中,给人类带来很大的潜在健康风险.未来几十年其仍可能在工业生产和日常生活中占据重要地位,因此,BPA 及 BPA 类似物在环境中的污染水平也引起了广泛的关注.

1.2 多溴联苯醚类

多溴联苯醚(poly brominated diphenyl ethers,PBDEs)是一种溴代芳香烃类阻燃剂,根据溴的个数及位置,PBDEs 共有 209 种同系物[21].作为一类典型的添加型溴代阻燃剂,已广泛应于塑料、纺织品、电子工业和汽车等产品中[22-23].工业化生产中主要应用五溴联苯醚、八溴联苯醚和十溴联苯醚混合物,其中十溴联苯醚的用途最为广泛[24].PBDEs 的全球需求量增长迅速,1992 年 PBDEs 的全球产量大约有 40000 吨,到 2001 年已经增加到约 67000 吨.中国作为工业大国,2005 年十溴联苯醚的产量达到了 30000 吨[25].大量研究表明,PBDEs 存在严重的环境和健康问题,五溴联苯醚和八溴联苯醚已被全球禁止生产和应用[26].随着十溴联苯醚的研究日益深入,加拿大、瑞士和美国已经开始对十溴联苯醚的生产和使用进行限制[27].PBDEs 引起的环境及健康问题受到了广泛的关注,因其污染具有持久性、生物累积性和高亲脂性等特点,目前在环境中的检出量仍不容忽视[22,26,28-29].环境介质中的 PBDEs 可以通过食物链等途径富集到人体,进而危害人类健康.为降低 PBDEs 产生的危害,应制定严格的法律法规来控制 PBDEs 特别是低溴代 PBDEs 的使用、加强对 PBDEs 废弃物的处理,并研究新型无污染替代品.

1.3 烷基酚类

烷基酚类(alkyl phenols,APs)是指由酚进行烷基化后的一类化合物,代表物质主要包括壬基酚(NP)和辛基酚(OP)等[30].APs 类物质具有良好的润湿、渗透、乳化、分散、增溶和洗涤作用,通常用作洗涤剂中的添加剂和生产烷基酚聚氧乙烯醚(APEOs)的主要原料[31-32].APEOs 是一种常用的非离子型表面活性剂,具有良好的表面活性,已被广泛用于工业、农业和日常消费品中,已成为全球主要商业用非离子表面活性剂[33-34].但是,APs 在环境中不稳定,易被微生物降解为毒性更强的短链 APEOs 和 APs,可通过食物链积累放大,危害人类健康和生态环境,已在全球范围内被限用或禁用[34-36].APs 作为一种环境

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激素,引起的环境毒性问题已经得到广泛关注.欧盟 2003/53/EC 指令规定纺织品等商品中 NP 的含量不得高于 0.1%[37].我国在 2004 年 9 月 1 日起实施的国家标准 GB/T 13171—2004《洗衣粉》,规定禁止使用 APEOs 类型的洗衣粉[30].现在很多 APs 替代品已经相继出现,但从使用性能、原料获取方式和经济性等方面综合考虑,能全面替代 APs 的产品几乎没有,且存在不少的问题.因此,为了防止 APs 的滥用,研究出全面替代 APs 的替产品迫在眉睫.同时,为了人类和生态健康,针对 APs 已经引起的环境问题,我们应该重视并采取相应的措施来降低其风险.

1.4　邻苯二甲酸酯类

邻苯二甲酸酯类(phthalic acid esters,PAEs)是由邻苯二甲酸和不同碳链结构的醇形成的酯,主要包括邻苯二甲酸二(2-乙基己酯)(DEHP 或 DOP)、邻苯二甲酸二甲酯(DMP)和邻苯二甲酸二乙酯(DEP)等[38-39].PAEs 作为增塑剂广泛应用于玩具、化妆品、食品包装和医疗器械等产品中[40].中国是 PAEs 生产和消费大国,每年生产的 PAEs 超过 450 万吨,消费量高达 220 万吨[41].由于 PAEs 不是以化学键合到聚合物基质上,它们容易从塑料制品中释放进入环境,且难以降解[40,42-43].美国环保局(US EPA)将 DMP、DEP 和 DEHP 等 6 种 PAEs 列为优先控制的有毒污染物[44].随着 PAEs 增塑剂的限用,迫切需要大量环保型增塑剂替代品进入市场.目前增塑剂行业研究出多种可代替 DOP 的环保型增塑剂,如柠檬酸酯、偏苯三酸酯和脂肪族二元酸酯类等[45].新型增塑剂的出现减少了对 PAEs 的依赖以及对环境的危害,但其安全性仍需要一个较长的周期来验证.因此,不仅要开展 PAEs 毒性研究,还要开展新型增塑剂的毒性研究并检测其在环境中的暴露水平.为降低 PAEs 的环境危害,除了严格限用 PAEs 并研究其替代品外,我们还应加强环境介质中已存在的 PAEs 分布和降解方式的研究.

1.5　有机磷酸酯类

有机磷酸酯(organophosphate esters,OPEs)简称有机磷,是高产量化学品,主要用作阻燃剂[46-47].有机磷酸酯类阻燃剂(OPFRs)除具有阻燃性能外,还具有增塑和热稳定等作用,广泛用于喷涂泡沫保温材料、聚氨酯泡沫塑料、家具、塑料、电子设备和纺织品等产品中[47-48].据报道,全球 OPEs 的生产和使用量急剧增加,从 2004 年的 29.6 万吨增加到 2011 年的 50 万吨,2015 年达到了 68 万吨,2018 年将增加至 105 万吨[49-50].与溴系阻燃剂相比,OPEs 除了具有良好的阻燃效果,还有低烟、低毒和低卤等优点,近年来有逐渐取代溴代阻燃剂的趋势[48,51].但是,有机磷酸酯类阻燃剂因和材料之间的结合属非化学键结合,易通过挥发或磨损从产品释放到环境中引起不良的环境效应[52].日本和欧盟等开始逐渐禁止生产过程中添加某些 OPEs,并将其列入致癌物质清单[53].有机磷酸酯类阻燃剂虽然比溴系阻燃剂具有优点,但其在环境中的污染水平也随着其生产量和使用量的增加而逐年增大,同时带来一系列的环境问题.因此,为了人类的健康,研发环境友好型阻燃剂是必然的趋势.电子设备、家具和纺织品等产品中有机磷酸酯类阻燃剂增加了人类室内暴露的风险;其次,电子垃圾处理不当使得环境介质中 OPEs 的污染浓度增加.所以,我们要做好电子垃圾回收及 OPEs 污染治理.

2　环境中 EDCs 的污染现状(Status of EDCs pollution in environments)

2.1　土壤

土壤是重要的自然资源之一,是农业发展的重要物质基础,也是复杂污染物的重要储层.大多数 EDCs 具有脂溶性、疏水性和化学稳定性等特点,易被吸附在土壤中,在全球土壤中已被广泛检测到[54-55].宋善军[56]在我国浙江省某生产工厂周边采集并分析了样品,首次在我国土壤介质中发现 BPA 结构类似物双酚 AF(BPAF)的存在,它在土壤中浓度范围为 nd(未检出)—331 $ng\cdot g^{-1}$ dw(干重),BPAF 浓度水平随到工厂距离呈指数下降.有报道指出,美国和欧洲的土壤基质中 BPA 的浓度范围分别为 4—14 $ng\cdot g^{-1}$ dw 和 nd—140 $ng\cdot g^{-1}$ dw,显然欧洲土壤基质中 BPA 浓度较美国更高[57].Harrad 等[58]测得英国横跨西米兰德的城市乡村带土壤中总 PBDEs 的浓度范围为 0.07—3.9 $ng\cdot g^{-1}$ dw,其明显低于我国典型电子废弃物拆解地清远龙塘-石角地区农田土壤中 PBDEs 的平均浓度(19.0±20.1)$ng\cdot g^{-1}$ dw[59].有研究指出,广州城市土壤中 DEHP 浓度的最高值为 264000 $ng\cdot g^{-1}$ dw,苏格兰和丹麦土壤中 DEHP 浓度范围分别为 25—1600 $ng\cdot g^{-1}$ dw 和 12—1900 $ng\cdot g^{-1}$ dw[60].丹麦与苏格兰土壤中 DEHP 的浓度范围差别不大;与苏格兰或丹麦相比,广州城市土壤中 DEHP 的浓度更高.Kurt-karakus [61]测得土耳其一个高度工

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业化城市布尔萨的 8 个样本收集点(包括城市、郊区、工业和农村等)土壤中总 OPEs 范围为 38—468 ng·g^{-1} dw.Cui 等[62]对收集来自中国广州城市道路绿地、水田/蔬菜田、公园、商业和居民区的 67 份土壤样品中 11 种 OPEs 进行分析,结果表明,在所有样品中均有 OPEs 测出,11 种 OPEs 的总浓度范围为 41—1370 ng·g^{-1} dw.可知,高度城市化的广州和高度工业化的布尔萨土壤中 OPEs 浓度都挺高.

综上可知,典型 EDCs 在世界范围内的土壤中广泛存在,其分布受土壤自身独特性质及地区经济发展水平的影响较大,一般工业化、城市化程度较高地区的土壤中 EDCs 浓度较高.EDCs 不断释放到土壤中会对陆地生态系统构成风险,如土壤中 EDCs 通过植物进入食物链并可能产生生物放大及毒性效应,同时,受污染的土壤通过直接接触土壤或通过土壤污染渗入地下水、地表水和大气来影响人类和野生生物的健康.所以要及时检测并修复受污染的土壤,降低其毒性作用对生态系统的健康极其重要.

2.2 水体

水体是对人类影响极大的一类环境介质,水环境中污染物的存在状况一直是人们关注的焦点.近年来,工农业废水和生活污水的排放对水生生态系统构成严重威胁,在许多国家的饮用水、自来水和自然水体中都检测到了 EDCs 的存在.Staniszewska 等[63]研究发现,来自格丹斯克海湾沿岸地区的地表水中的 BPA、4-辛基酚(4-t-OP)和 4-壬基酚(4-NP)的浓度范围分别为<5.0—277.9、<1.0—834.5 和<4.0—228.6 ng·L^{-1}.刘畅伶等[64]在珠江口典型河段内检测到 4-t-OP、4-NP 和 BPA 的平均浓度分别为:49.19—512.82 ng·L^{-1}(均值为 325.46 ng·L^{-1})、112.66—717.31 ng·L^{-1}(112.66 ng·L^{-1})、23.54—2189.88 ng·L^{-1}(313.46 ng·L^{-1}),自上游到下游入海口污染浓度逐渐降低,在广州市区河段含量有所回升.可知,珠江口典型河段总体上 4-t-OP、4-NP 和 BPA 的污染比格但斯克湾沿岸地区的水体更严重.单晓梅等[65]研究结果表明,选取的合肥两水厂不同水期 PAEs 和 BPA 检出含量分别为 2.73—8.14 μg·L^{-1}、9.57—15.70 ng·L^{-1}(水源水),1.91—5.06 μg·L^{-1}、nd—2.74 ng·L^{-1}(出厂水)和 1.12—6.59 μg·L^{-1}、1.03—3.01 ng·L^{-1}(管网末梢水),由此可见,合肥市水源与饮用水不同程度地受到 PAEs 和 BPA 的污染.Shao 等[66]研究结果表明,北京周边地表水中 PBDEs 的浓度范围为 0.0797—2.80 ng·L^{-1},平均值为(1.44±0.57) ng·L^{-1},此浓度高于珠江流域(平均值:0.388 ng·L^{-1})、海南(0.315 ng·L^{-1})和香港(0.089 ng·L^{-1})等;与全球水源相比,北京的 PBDEs 污染水平明显高于美国(0.001 ng·L^{-1})、欧洲(浓度范围:0.005—0.64 ng·L^{-1})或英国(0.062 ng·L^{-1})等.Liang 等[67]测得深圳市快速城市化地区观澜河流域 PBDEs 的旱季浓度范围为 58.40—186.35 ng·L^{-1}(平均值:115.72 ng·L^{-1}),雨季为 8.20—37.80 ng·L^{-1},(22.15 ng·L^{-1}).雨季 PBDEs 浓度明显低于旱季的浓度,这可能是由于雨季河流的稀释形成的;此外,旱季或者雨季污染物的空间分布显示出从上游到下游的浓度呈下降趋势.峨山湖是韩国最大的人工湖之一,周围是工业园区和农田,Lee 等[68]在其水中检测到 PAEs 的浓度范围为 nd—2290 ng·L^{-1},且 DEHP 和邻苯二甲酸二正丁酯(DBP)是检出率较大的物质.Zhang 等[69]得出渤海(BS)和黄海(YS)的海水中 PAEs 的浓度范围为 453—5108 ng·L^{-1},且其水样品中主要的 PAEs 也是 DEHP 和 DBP.磷酸三(2-氯乙基)酯(TCEP)作为一种典型的 OPEs 内分泌干扰物,被欧盟列入高度关注度的污染物,2011 年在我国松花江浓度范围为 38—3700 ng·L^{-1},远超过 2012 年德国莱茵河的 12—25 ng·L^{-1}[70].2014 年测得韩国饮用水中 OPEs 总浓度范围从低于方法检出限(MDL)至 1660 ng·L^{-1}[71],与 2012 测的中国饮用水中 OPEs 的总浓度范围85.1 ng·L^{-1}至 325 ng·L^{-1}相比[72],其最高浓度明显大于中国饮用水.

由此可知,典型 EDCs 在全球水体中广泛存在,其质量浓度在 ng·L^{-1}至 μg·L^{-1}级别.EDCs 在水体中的分布基本遵循上游到下游逐渐减少的趋势,可能是由于下游比上游人为活动弱且下游临近河口区域.水体中的 EDCs 对水环境质量有不良影响,可能会威胁部分地区饮用水安全.因此,应积极采取 EDCs 危害防治措施,保护鱼类和水生植物资源和水生态系统.

2.3 沉积物

大部分 EDCs 亲脂性较高,进入水体后的 EDCs 容易吸附到沉积物中,在全球很多地区的沉积物中均发现了 EDCs 的存在.Liao 等[73]2012 年在韩国、美国和日本等 3 个国家工业地区的沉积物中发现了多种 BPs,其中 BPA、BPS、BPF 的平均检出浓度分别为 117、12.37、69.7 ng·g^{-1} dw.Wang 等[74]2015 年在中国太湖沉积物样品中测得 BPA、BPF 和 BPS 的浓度范围分别为 3.94—33.2、0.503—3.28、0.323—27.3 ng·g^{-1} dw.可知,BPs 在沉积物中分布广泛,且工业地区沉积物中的浓度偏高.笪春年等[75]于

2015 年测得巢湖沉积物中 9 种 PBDEs 的含量为 0.001—2.75 ng·g^{-1},平均值为 1.15 ng·g^{-1}.有研究指出,亚洲地区沉积物中 PBDEs 污染水平总的来说低于欧洲和北美,且污水排放区和电子废弃物污染地区污染更为严重[76].在对珠江广州河段和其邻近河流中 28 个表层沉积物中 APs 分析时发现,NP 和 OP 在所有样品中均有检出,其浓度范围分别是 31—21885 ng·g^{-1} dw(均值为 3686 ng·g^{-1} dw)和 0.01—463.01 ng·g^{-1} dw(40.29 ng·g^{-1} dw)[77].据报道,尼泊尔加德满都谷地的巴格马蒂河沉积物中 8 种 OPEs 的总浓度范围为 983—7460 ng·g^{-1} dw,此检测浓度高于西班牙沉积物的浓度(3.8—824 ng·g^{-1} dw)、3 条欧洲河流(埃夫罗塔斯河、阿迪杰河和萨瓦河)沉积物的浓度(0.31—549 ng·g^{-1} dw)低于挪威沉积物中的浓度(486—22500 ng·g^{-1} dw)[78-80].在对印度科钦河口表层沉积物中 PAEs 调查中发现,PAEs 的浓度范围在季风前为 44—1723 ng·g^{-1} dw,季风时为 331—1747 ng·g^{-1} dw,季风后为 1402—3121 ng·g^{-1} dw,结果表明该河口已受到严重污染,且主要的 PAEs 是 DEHP、邻苯二甲酸丁基苄酯(BBP)和邻苯二甲酸正二丁酯(DnBP)[43].廖日权等[81]发现,钦州湾入海口沉积物中 5 种 PAEs 检出率均为 100%,浓度范围为 4158—8455 ng·g^{-1} dw,平均值为 7011 ng·g^{-1} dw,以 DEHP 和 DEP 为主.

沉积物中的 EDCs 可经解析和扩散等环境过程重新释放到水体,即沉积物的污染状况在一定程度上反应了水质的好坏.EDCs 在沉积物中广泛检出且检出量不容乐观.EDCs 在沉积物中的分布有一定规律,一般工业地区、污水排放区和电子废弃物污染地区污染更为严重.这可能是由于工业废水、生活污水和电子废弃物处理过程不合格造成的.

2.4　空气

空气是人类赖以生存的环境,空气污染给人类健康所带来的影响受到了广泛关注.由于大气的流动性,空气污染带来的环境问题是全球性的.近年来 EDCs 广泛添加到建筑、家装材料以及电子设备中,在办公室、卧室甚至私家车等密闭环境中都检出了较高浓度的 EDCs.Xue 等[82]于 2014 年从美国纽约奥尔巴尼的不同地点(包括车库、超市、车、理发店等)收集了 83 个室内空气样本,在测量的 8 种 BPs 中,BPA、BPF 和 BPS 在大量空气样本中被发现,平均浓度分别为 0.43、0.69、0.09 ng·m^{-3},其中 BPs 浓度最高的收集点是汽车.早前有报告指出,日本和美国的室内空气中平均 BPA 浓度分别为 0.70 ng·m^{-3}[83]和 0.73 ng·m^{-3}[84].珠江三角洲是中国最繁华的地区之一,工业化和城市化的快速发展,造成户外工业来源多.据报道,珠三角一个城市的室外空气中 PBDEs 平均浓度高达 2.45 ng·m^{-3}[85],远高于在北美、欧洲和其他亚洲国家城市空气中观察到的浓度(0.05—0.15 ng·m^{-3})[86].Ding 等[87]于 2015 年收集了杭州浙江工业大学实验室的空气样品,测得 PBDEs 的平均浓度为 0.54564 ng·m^{-3},相当于中等水平的空气污染,最高水平记录在冬季,夏季最低,为大学实验室室内空气污染提供了依据.2016 年 9 月至 2017 年 1 月期间,Tran 等[88]从越南北部采集的 97 个室内空气样本中,10 种 PAEs 的检出浓度范围为 106—16000 ng·m^{-3},其中发廊中含量最高.据报道,2014 年在美国纽约奥尔巴尼收集的 60 个室内空气样本中测出来 9 种 PAEs 污染物,其中美发沙龙中 PAEs 的浓度中值(2600 ng·m^{-3})最高[89].由上述两例可知,美发场所空气受 PAEs 污染较重,需要相关工作人员的重视.Song 等[90]在中国医院室内空气中检测到 PAEs 的存在,并且经过不同病房之间比较发现,产科病房的 PAEs 浓度比其他病房高 1.63 倍,较高的 PAEs 可能影响到孕妇和婴儿的健康.Axel 等[91]于 2010 年在北海德国部分海洋大气中,首次检测到 OPEs,其可在大气中迁移,含量范围高达 1 ng·m^{-3},TCPP 是主要化合物.Kim 等[92]于 2018 年测得美国纽约州奥尔巴尼地区不同微环境的散装空气中 15 种 OPEs 的总浓度介于 2.96 ng·m^{-3}和 635 ng·m^{-3}之间,其中汽车零件商店 OPEs 的总浓度最高.

由上述例子可知,EDCs 在车库、超市、车、理发店和医院等气体中都有检出,且不同区域中主要的 EDCs 可能不同,如美发场所空气受 PAEs 污染较重.同时,人类活动频繁,工业化和城市化发展快速的地区,其空气中 EDCs 污染较严重,这可能是由于被添加到各类产品中的 EDCs 释放到空气中造成的.空气中 EDCs 时刻影响人类健康,因此需及时监测空气中的 EDCs,为空气质量提供理论依据.

2.5　尘埃

空气中的灰尘可能含有较高浓度的环境污染物,并且已被证明是人体暴露于多种有毒物质的重要来源[93-94].室内尘埃上附着的污染物能够通过皮肤和吸入等途径对人体健康产生影响,尤其是对于婴幼儿.室内是人类生活工作的重要场所,据估算人类大概有 70%—90%的时间是在室内度过的,室内污染

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正日益受到关注[95].Wei 等[96]从 12 个国家(中国、哥伦比亚、希腊、印度、日本、科威特、巴基斯坦、罗马尼亚、沙特阿拉伯、韩国、美国和越南)收集了 388 个室内灰尘样品(包括家庭和微环境),结果表明 BPA 在所有室内灰尘样品中均有检出,浓度范围为 9.6—32000 ng·g^{-1},全球中值浓度为 440 ng·g^{-1};除 BPA 外,BPF 也在尘埃样本中广泛分布,高 BPF 污染地区多为韩国、希腊、日本和美国等 BPF 高使用量的国家.韩国已有报道 BPF 作为 BPA 的主要替代物而被广泛使用[97].有研究报道,美国密歇根居室尘土中 PBDEs 浓度中值为 8754 ng·g^{-1},高于加拿大渥太华居室尘土浓度中值 1800 ng·g^{-1}[98-99].有研究指出,中国广东清远电子垃圾拆解地的家庭居室尘埃中 PBDEs 浓度最大值是 157.5 mg·g^{-1},其室内尘埃中 PBDEs 浓度偏高可能是受该地区室外电子垃圾处理活动的影响,通过大气颗粒物传输等途径进入了室内[100].Abafe 等[101]于 2012 年收集了南非德班的 3 个微环境中粉尘(家庭、计算机实验室和办公室),结果显示,APs 中,所有微环境中观察到的 t-NP 浓度较高,其在家庭、计算机实验室和办公室的浓度范围分别是 127—686 ng·g^{-1}、43—557 ng·g^{-1}和 123—602 ng·g^{-1},表明在所研究的微环境中广泛使用添加 NP 的产品.PAEs 在中国室内灰尘中广泛存在,秦晓雷等[102]于 2013 年研究得出 PAEs 在中国室内灰尘中总浓度均值为 599 μg·g^{-1} dw,其中 DEHP 是优先污染物,其浓度最大值为 4012 μg·g^{-1} dw,均值为470 μg·g^{-1} dw.2016 年,刘琴等[95]研究发现,成都市高校和居民住房的各个室内环境中灰尘的总 OPEs 浓度范围为 317.44—2566.97 ng·g^{-1},并表明低于发达国家,其中体育馆、寝室、教室和复印店的总 OPEs 浓度明显高于停车场,说明室内灰尘中 OPEs 的污染水平与人群活动频率及国家经济发展水平有一定关系.

综上可知,EDCs 在全球范围内的家庭、办公室、教室和体育馆等室内的尘埃中广泛分布.EDCs 在室内尘埃中分布的种类和含量,与室内产品中添加的 EDCs 和室外周围环境中的 EDCs 有关.另外,国家的经济发展和人类活动也会影响 EDCs 在室内尘埃中的分布.为了健康的生存环境,监测空气中 EDCs 的同时,也要特别重视尘埃中 EDCs 的检出.

EDCs 在无机环境中分布广泛,列举一些典型的区域来说明分布特征,详见表 1.由表 1 可知,所调研的 5 类 EDCs 在全球范围内被频繁检出,应加强对其生态风险的监控和污染治理方法的开发.

3 内分泌干扰物对环境的风险评估(Environmental risk assessment of endocrine disruptors)

EDCs 应用和分布广泛,在多种环境介质中均有检出.EDCs 在低浓度时就会对生态环境带来风险,因此,对 EDCs 进行环境的风险评估是很有必要的.通过查阅文献可知,近年来对水体及沉积中 EDCs 的风险研究较多,其他环境介质中的风险评估很少.由于其他环境介质中的 EDCs 通过大气沉降、地表径流、土壤淋溶和直接排放等方式进入水体,从而使水体成为 EDCs 存在的主要场所之一[103].已有研究对 EDCs 的风险评价主要采用生态风险评估法和健康风险评估法.

生态风险评估:即风险熵法,简称 RQ 法,公式如下:

$$RQ = EEC/PNEC$$

式中,RQ 为风险熵值,EEC 为污染物的环境暴露浓度,PNEC 为污染物的预测无效应浓度;根据 RQ 值,EDCs 的风险程度可以划分为:RQ<0.01(无风险)、0.01<RQ<0.1(低风险)、0.1<RQ<1(中风险)和 RQ>1(高风险).

危害指数法,简称 HI 法,公式如下:

$$HI = \sum HQ_i = \sum EDI/RV_i$$

式中,HI 指危害指数;RV_i为某种 EDCs 每日允许摄入量的参考限值;HQ_i为根据 EDI 值和 RV_i值计算出的某种 EDCs 的危害商;当 HI≥1 时,一般认为该个体 EDCs 的累积暴露超过了允许的摄入量,可能对健康造成危害.

陈玫宏等[104]对 BPA、四溴双酚 A(TBBPA)和 3 种 APs 在太湖及支流表层水和沉积物中的潜在风险进行了评估,研究发现,上述 5 种目标物的联合毒性 RQ(0.02—3.26)相对较高,其生态风险值得重视.Chai 等[105]对中国 6 个红树林湿地表层沉积物中 PBDEs 进行生态风险评估,发现三溴、四溴和六溴联苯醚同源物的 RQ 均小于 0.01,表明这些多溴联苯醚的生态风险可忽略不计,五溴联苯醚和十溴联苯醚同源物的 RQ 达到 0.1 或高于 0.1,具有低或中等风险.

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表 1　国内外无机环境中 EDCs 的浓度水平

Table 1　EDCs concentrations in inorganic environments in China and other countries

化合物 Compounds	土壤 Soil		水体 Water		沉积物 Sediment		空气 Air		尘埃 Dust	
	浓度 Concentration/($ng \cdot g^{-1}$ dw)	地区 Region	浓度 Concentration/($ng \cdot L^{-1}$)	地区 Region	浓度 Concentration	地区	浓度 Concentration	地区 Region	浓度 Concentration	地区 Region
BPs	BPA：4—14	美国[57]	Σ_9BPs：5.4—87	太湖[150]	Σ_8BPs：Nd—138 $ng \cdot g^{-1}$ dw	美国（工业区）[73]	BPA：0.73 $ng \cdot m^{-3}$（平均值）	美国（室内）[84]	Σ_8BPs：23—860 $ng \cdot g^{-1}$	巴基斯坦（室内）[152]
	BPA：Nd—140	欧洲[57]	BPA：1.03—3.01	合肥（自来水）[65]	Σ_8BPs：1.88—28.2 $ng \cdot g^{-1}$dw	日本（工业区）[73]	BPA：0.70 $ng \cdot m^{-3}$（平均值）	日本（室内）[83]	Σ_8BPs：66—1600 $ng \cdot g^{-1}$	越南（室内）[152]
	BPA：Nd—48.68	韩国[57]	BPA：281—3642	美国（初级生活污水）[151]	Σ_8BPs：Nd—25300 $ng \cdot g^{-1}$ dw	韩国（工业区）[73]	BPA：0.43 $ng \cdot m^{-3}$（平均值）	纽约（室内）[82]	Σ_8BPs：43—4400 $ng \cdot g^{-1}$	中国（室内）[152]
	BPAF：Nd—331	浙江省（工厂周围）[56]	BPA：6—50	美国（二级生活污水）[151]	Σ_9BPs：0.37—8.3 $ng \cdot g^{-1}$ dw	太湖[150]	BPF：0.69 $ng \cdot m^{-3}$（平均值）	纽约（室内）[82]	Σ_8BPs：360—12000 $ng \cdot g^{-1}$	日本（室内）[152]
	BPA：24.55（平均值）	浙江省（温州）[162]	BPA：230—149200	加拿大（工业废水）[151]	BPA：< 3.4—9 $ng \cdot g^{-1}$	英国（乌兹河）[151]	BPS：0.09 $ng \cdot m^{-3}$（平均值）	纽约（室内）[82]	Σ_8BPs：550—89000 $ng \cdot g^{-1}$	美国（室内）[152]
PBDEs	$\Sigma_{总}$PBDEs：25.0	墨西哥（工业区）[121]	Σ_9PBDEs：0.316—1.36	南非（地下水）[117]	Σ_9PBDEs：3.00—4.91 $ng \cdot g^{-1}$	南非[117]	ΣPBDEs：69 $pg \cdot m^{-3}$	东北[119]	ΣPBDEs：8754 $ng \cdot g^{-1}$（中值）	美国密歇根（居室）[98]
	$\Sigma_{总}$PBDEs：13.6—13200	澳大利亚（处理源附近）[121]	Σ_{11}PBDEs：0.001（平均值）	美国[66]	Σ_9PBDEs：0.001—2.75 $ng \cdot g^{-1}$	巢湖[75]	$\Sigma_{总}$PBDEs：15—487 $pg \cdot m^{-3}$	澳大利亚（办公室）[120]	ΣPBDEs：1800 $ng \cdot g^{-1}$（中值）	加拿大渥太华居室[99]
	$\Sigma_{总}$PBDEs：0.130—3.000	挪威[121]	Σ_{10}PBDEs：0.005—0.64	欧洲[66]	Σ_{27}PBDEs 0.46—1760 $ng \cdot g^{-1}$ dw	韩国[116]	ΣPBDEs 545.64 $pg \cdot m^{-3}$（平均值）	杭州（实验室）[87]	ΣPBDEs：157.5 $mg \cdot g^{-1}$（最大值）	清远（家庭居室）[100]
	$\Sigma_{总}$PBDEs：0.07—3.9	英国[58]	Σ_9PBDEs：Nd—7.87	华南地区（饮用水）[113]	ΣPBDEs：3.67—2520 $ng \cdot g^{-1}$	珠江三角洲[114]	Σ_{12}PBDEs：0.2—2.9 $pg \cdot m^{-3}$	南极洲西部[112]	ΣPBDEs：<MDL—615 $ng \cdot g^{-1}$	波兰北部（家庭）[118]
	Σ_{14}PBDEs：19.0±20.1	清远龙塘-石角（农田）[59]	Σ_7PBDEs：0.0797—2.80	北京周边（地表水）[66]	Σ_{19}PBDEs：2.3—10490 $ng \cdot g^{-1}$	中国台湾[116]	ΣPBDEs：3.24—247.30 $pg \cdot m^{-3}$	广州[115]	Σ_{14}PBDEs：546.13 $ng \cdot g^{-1}$	杭州（超市）[161]

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续表1

化合物 Compounds	土壤 Soil		水体 Water		沉积物 Sediment		空气 Air		尘埃 Dust	
	浓度 Concentration/($ng \cdot g^{-1}$ dw)	地区 Region	浓度 Concentration/($ng \cdot L^{-1}$)	地区 Region	浓度 Concentration	地区	浓度 Concentration	地区 Region	浓度 Concentration	地区 Region
APs	NP、OP: Nd—156.8	黑龙江(农田)[157]	NP: 212.1—2791.6	沈阳市(自来水)[159]	APEOs: 0.2—2.8 $ng \cdot g^{-1}$ dw	科威特[154]	NP: 21—420 $ng \cdot m^{-3}$	美国[156]	NP: <RL—8.68 $ng \cdot g^{-1}$	美国(室内)[160]
	NP: 1 450	丹麦(农田-停止施用污泥)[158]	4-NP: 112.66—717.31	珠江[64]	APEOs: 5.0—21 $ng \cdot g^{-1}$ dw	沙特阿拉伯[154]	NP: <LOD—56.3 $ng \cdot m^{-3}$	哈得孙河下游河口(沿岸)[156]	–	–
	NP: <5	美国(棉田)[158]	∑APs: 1200—7300	挪威(污水处理厂进水)[155]	NP: 31—21885 $ng \cdot g^{-1}$ dw	珠江[77]	NP: 0.13—81 $ng \cdot m^{-3}$	哈得孙河下游河口(城郊)[156]	OP: <RL—1.99 $\mu g \cdot g^{-1}$	美国(室内)[160]
	NP: Nd—6.38 $\mu g \cdot kg^{-1}$,	深圳(蔬菜农田)[158]	NP: <110—640	美国[156]	OP: 0.01—463.01 $ng \cdot g^{-1}$ dw	珠江[77]	NP: 0.066 $ng \cdot m^{-3}$ (平均值)	北海[156]	4-OP: <RL—0.09 $\mu g \cdot g^{-1}$	美国(室内)[160]
PAEs	$\sum_6$PAEs: 162.9—946.9	东北(三江平原)[140]	$\sum_6$PAEs: 9930—45550	松花江[137]	$\sum_6$PAEs: 381.14—2044.3 $ng \cdot g^{-1}$ dw	松花江[146]	$\sum_{10}$PAEs: 106—16000 $ng \cdot m^{-3}$	越南(室内)[88]	$\sum_{10}$PAEs:9.60—4130 $\mu g \cdot g^{-1}$dw	中国(室内)[102]
	$\sum_{16}$PAEs 1670—322000	广州(市区)[139]	$\sum_7$PAEs: 2730—8140	合肥(水源水)[65]	$\sum_{16}$PAEs: 244—5922 $ng \cdot g^{-1}$ dw	巢湖[141]	$\sum_9$PAEs: 53.6—4850 $ng \cdot m^{-3}$	纽约(室内)[89]	$\sum_{10}$PAEs:0.102—1430 $\mu g \cdot g^{-1}$dw	中国(室外)[102]
	$\sum_9$PAEs: 154	巴黎(乡村)[138]	$\sum_7$PAEs: 1120—6590	合肥(管网末梢水)[65]	$\sum_{16}$PAEs:4260—9401 $ng \cdot g^{-1}$	波斯湾[143]	$\sum_{15}$PAEs: 10623.4—23014.6 $ng \cdot m^{-3}$	杭州(办公室)[147]	$\sum_9$PAEs: 87.1—9670 $\mu g \cdot g^{-1}$dw	纽约(室内)[146]
	$\sum_9$PAEs: 60	巴黎(森林)[138]	$\sum_6$PAEs: 0.05—5.503	北极[142]	$\sum_6$PAEs: 44—1723 $ng \cdot g^{-1}$ dw	科钦-印度(季风前)[43]	$\sum_{15}$PAEs: 2013.79—6121.6 $ng \cdot m^{-3}$	杭州(室外)[147]	$\sum_{10}$PAEs: 144.57—19048.69 $\mu g \cdot g^{-1}$	德国(日托中心)[148]
	$\sum_9$PAEs: 1089	巴黎(市区)[138]	$\sum_6$PAEs: 9243	法国(污水处理厂)[144]	$\sum_6$PAEs:1402—3121 $ng \cdot g^{-1}$ dw	科钦-印度(季风后)[43]	$\sum_{13}$PAEs: 2622—15331 $ng \cdot m^{-3}$	巢湖(市中心)[145]	$\sum_9$PAEs: 3440—106000 $ng \cdot g^{-1}$	越南(室内)[149]
OPEs	$\sum_{12}$OPEs: 1.70—179	中国(住宅区)[122]	∑OPFR: <MDL—1660	韩国(饮用水)[71]	$\sum_7$OPEs: 0.159—4.658 $ng \cdot g^{-1}$ dw	北极[123]	$\sum_8$OPEs: 110—1400 $pg \cdot m^{-3}$	北海(德国部分)[91]	$\sum_7$OPEs: 317.44—2566.97 $ng \cdot g^{-1}$	成都(室内)[95]

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续表1

化合物 Compounds	土壤 Soil		水体 Water		沉积物 Sediment		空气 Air		尘埃 Dust	
	浓度 Concentration/($ng \cdot g^{-1}$ dw)	地区 Region	浓度 Concentration/($ng \cdot L^{-1}$)	地区 Region	浓度 Concentration	地区	浓度 Concentration	地区 Region	浓度 Concentration	地区 Region
	Σ_8OPEs：38—1250	中国(塑料处理厂)[124]	Σ_9OPFR：85.1—325	中国(饮用水)[72]	ΣPFRs 0.31—549 $ng \cdot g^{-1}$ dw	欧洲[79]	Σ_{15}OPEs：2.96—635 $pg \cdot m^{-3}$	纽约(室内)[92]	Σ_{10}OPFRs：2053—72090 $ng \cdot g^{-1}$	巴塞罗那[126]
	$\Sigma_{总}$OPEs：38—468	土耳其(工业区)[61]	Σ_4OPFRs：91.87—1392	中国(海水)[130]	Σ_9OPEs：55.5—4511 $ng \cdot g^{-1}$	太湖(入湖)[125]	Σ_9OPEs：47.1—160.9 $pg \cdot m^{-3}$	南海北部[128]	ΣOPFRs：14400—134000 $ng \cdot g^{-1}$	巴西(住宅内)[129]
	Σ_8OPFRs：25—27900	尼泊尔(城市)[132]	Σ_{14}OPEs：40.0—60.8	纽约(海水)[131]	Σ_9OPEs：47.3—106.9 $ng \cdot g^{-1}$	太湖(出湖)[125]	Σ_{11}OPEs：193—580 $pg \cdot m^{-3}$	重庆市(室外)[135]	ΣOPFRs：108000—2050000 $ng \cdot g^{-1}$	巴西(汽车内)[129]
	Σ_{20}OPEs：1.16—73.1	纽约[133]	ΣOPEs：65.8—2842	中国(废水处理厂)[134]	Σ_{12}PFRs：8.3—470 $ng \cdot g^{-1}$ dw	珠江三角洲[127]	Σ_{11}OPEs：1580—2120 $pg \cdot m^{-3}$	重庆市(室内)[135]	Σ_{12}OPEs：2619 —733260 $ng \cdot g^{-1}$	加拿大(房屋)[136]

注：MDL：最低检出限；LOD：检测限；RL：报告限制.

Note: MDL: Minimum detection limits; LOD: Low limits of detection; RL: Reporting Limits.

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有研究指出,暴露于尼日利亚南部电视、收音机、立体声和视频播放器维修车间灰尘中的多溴联苯醚的 HI>1,可能会对人体健康造成危险[106].Zhang 等[69]对 BS 和 YS 中 PAEs 进行生态风险评估时发现,对于 BS 中的藻类和甲壳类动物以及 YS 中的藻类,DEHP 的 RQ 大于 1,表明 DEHP 对这些生物体具有高风险.此外,对于 BS 中的鱼以及 YS 中的甲壳类和鱼类,DEHP 的 RQ 值为 0.01—1,表明存在中等风险.王诗雨等[107]对辽河口湿地土壤中 11 种 OPEs 进行风险评估,从单个水平上分析, 磷酸三异丁酯(TiBP)的风险商值是最高的,平均风险商值为 3.207,说明 TiBP 在辽河口湿地土壤中具有较高的风险水平.陈玮华等[108]对上海市 300 名中老年 2 型糖尿病患者(T2DM)PAEs 暴露的肝脏受损风险评估时发现,上海市社区中老年 T2DM 患者的肝脏受损风险主要来源于 DEHP,由于 DEHP 的 HQ 最高,其最高值为 22.06,对 HI 的贡献率最高.谢国建等[109]对奉化江中 3 个采样点中 3 种残留量较大的 BPA、DEP、DBP 进行了健康风险评价,3 个采样点的 HI 均小于 1,故暂不会对人体造成影响.袁子婷等[110]通过对某地区地下水中 EDCs 生态风险评估可知,OP 在该地区地下水和地表水中的风险熵最高分别为 5.56 和 10.27,都具有高生态风险,OP 应列为该地区地表水与地下水中的优先控制污染物.为了更好地了解胶州湾的 PAEs 污染,Liu 等[111]于 2015 年 8 月和 11 月和 2016 年 1 月收集了胶州湾的地表水样品,分析检测到 15 种PAEs,生态风险评估结果表明,DBP 的 RQ 大于 1,生态风险相对较大,而其他 PAEs 的 RQ 小于 1,风险很小.

鉴于内分泌干扰物给水体和沉积物造成风险的复杂性,针对风险商 RQ 较高的区域,需要采取适当的措施控制污染物质的排放,如提高污水处理比例、提高污水处理效率、加强监管非法排放工业废水、保护水体及其周边的生物.在 EDCs 进行生态风险评价时,可以采用多种评价方法,综合考虑来增强评价结果的可靠度.同时,还要进一步研究 EDCs 的行为和他们对环境的生态危害.希望风险评估为有效控制 EDCs 相关风险提供有用信息.

4 总结与展望(Conclusion and expectation)

典型 EDCs 应用广泛,与人类生活密切相关,全球需求量大且增长迅速.大多数 EDCs 易从产品脱落到环境中给环境带来诸多不利影响,部分 EDCs 被禁用或限用.为了市场的需求,许多典型 EDCs 的替代品已研发并得到了广泛应用.典型 EDCs 在土壤等无机环境中被检出,在全球范围内广泛分布.EDCs 的分布与无机环境介质本身的特性和地区经济发展水平有关.一般高度工业化、城市化地区的 EDCs 分布更广,检出量更大,污染相对比较严重.EDCs 作为痕量污染物,它给环境带来的生态风险和健康风险是不容忽视的.为了生态环境健康,需采取适当的措施降低 EDCs 的环境风险.

依据目前典型 EDCs 的应用、分布和风险评估现状,对以下 5 个方面进行展望:(1)EDCs 替代品应用广泛,但鉴于这些化合物与其前身在结构上同源,并且可能具有类似的激素活性和内分泌干扰作用,其安全性、可靠性仍需要一个较长的周期来验证.因此我们不仅要深入开展典型 EDCs 的毒性研究,还要深入开展 EDCs 类似物的毒性实验,给环境健康提供理论支撑.(2)关于典型 EDCs 在各种无机环境中的分布研究较多,但是部分 EDCs 的代谢产物会对环境造成更加不利的影响.因此,有关 EDCs 代谢产物分布的研究也应加强,给环境治理方面给予更多建议.(3)目前文献中关于单个 EDCs 的风险评估较多,而关于 EDCs 联合作用的风险评估不多,而实际环境基质复杂,多种 EDCs 共存,因此,不仅要关注 EDCs 单体的风险评估,多种 EDCs 联合风险评估更加需要关注.(4)空气、水体和土壤等无机环境与人类的日常生活息息相关,因此,应严格控制未经处理的三废进入无机环境造成 EDCs 污染加重.(5)定期检测无机环境中 EDCs 的污染水平,掌握当前无机环境中 EDCs 的污染途径、浓度水平,研发高效适用的风险控制技术.

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