

环境介质中十溴二苯乙烷和 1,2-双(2,4,6-三溴苯氧基)乙烷分布特征的研究进展

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摘要: 十溴二苯乙烷(DBDPE)和 1,2-双(2,4,6-三溴苯氧基)乙烷(BTBPE)作为新型溴系阻燃剂,因具有亲脂性和持久性而易于在环境介质中累积。总结了 DBDPE 和 BTBPE 在生物和非生物环境介质中的分布特征。DBDPE 和 BTBPE 易与固相紧密结合,土壤、污泥和粉尘中的浓度远高于其他环境介质中。DBDPE 和 BTBPE 在生物中的分布与生物种类、器官组织等有一定关系,并且在人体母乳、血液和头发中也有检出。商业化 DBDPE 和 BTBPE 的生产和使用以及电子垃圾拆解活动是 DBDPE 和 BTBPE 在环境中的主要来源。未来需对 DBDPE 和 BTBPE 在不同环境介质中的迁移转化行为、生物效应的分子机制进一步展开研究。

关键词: 环境介质;十溴二苯乙烷(DBDPE);1,2-双(2,4,6-三溴苯氧基)乙烷(BTBPE);分布特征

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Research Progress on Distribution Characteristics of DBDPE and BTBPE in Environment

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Abstract: Decabromodiphenyl ethane (DBDPE) and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), as novel brominated flame retardants, are liable to accumulate in the environmental matrices due to their persistence and lipophilic characteristics. The distribution characteristics of DBDPE and BTBPE in biological and abiotic environmental matrices are reviewed. DBDPE and BTBPE combine easily with solid phase, therefore, their concentration in soil, sludge and indoor dust is much

higher than other environmental media. The distribution characteristics of DBDPE and BTBPE in biological matrices are related with biological species, tissues, organs, etc. Moreover, DBDPE and BTBPE were also found in human breast milk, blood and hair. The production and the use of commercial DBDPE and BTBPE, as well as e-waste recycling activities are their main sources in the environment. It is necessary to further explore the transport and transformation behavior of DBDPE and BTBPE in different environmental matrices, and the molecular mechanism of biological effects.

Key words: environmental medium; decabromodiphenyl ethane (DBDPE); 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE); distribution characteristics

溴代阻燃剂(BFRs)是全世界应用最广泛的阻燃剂,被添加于电子电气设备、建筑材料和塑料制品等产品中^[1-2]。以多溴联苯醚(PBDEs)为代表的传统 BFRs 由于难降解性、生物毒性和生物累积性^[3],逐步被美国、欧盟、中国等相继淘汰^[4-5],而替代传统 BFRs 的新型溴代阻燃剂(NBFRs)被大量使用。其中,十溴二苯乙烷(DBDPE)和 1,2-双(2,4,6-三溴苯氧基)乙烷(BTBPE)分别是 PBDEs 中十溴联苯醚(deca-BDEs)和八溴联苯醚(octa-BDEs)的替代品,而且 DBDPE 也是目前全球使用量较大的 NBFRs^[6]。

DBDPE 与 BTBPE 都属于添加型阻燃剂,与添加载体间没有化学键束缚,而且在室温下有较低的蒸汽压^[6],因此很容易释放到环境中。目前 DBDPE 和 BTBPE 已在大气、水体、沉积物、土壤以及生物体

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中检出^[6-19]。DBDPE于2004年首次在瑞典的污泥、室内空气以及荷兰的沉积物等环境介质中检出^[7],而早在20世纪70年代,BTBPE在其生产工厂(美国阿肯色州Great Lakes公司)附近的河流沉积物中有较高检出($466 \mu\text{g}\cdot\text{kg}^{-1}$)^[8]。近年来,在青藏高原、北极等偏远地区的大气中也检出DBDPE和BTBPE^[16-17],并且在部分地区DBDPE含量高于十溴联苯醚(BDE-209)^[1,15]。因为DBDPE和BTBPE具有较高的辛醇-水分配系数($\log K_{ow}$)和分子量,可能难以被生物利用^[9-10],然而有研究证实它们可以进入生物体内并沿食物链放大^[11-13],同时在人体母乳和头发中也有一定程度的检出^[18-19]。

由于DBDPE和BTBPE具有持久性、生物累积性、毒性和长距离迁移性,因此受到越来越多的关注。总结了近些年来DBDPE和BTBPE在国内外大气、水体、污泥、土壤、植物、动物和人体等多种环境介质中的分布特征,并对今后的研究方向做了展望,为DBDPE和BTBPE的控制及管理提供科学依据。

1 DBDPE和BTBPE的理化性质及生产应用

DBDPE是一种添加型BFRs,化学结构(见图1a)与BDE-209相似,被广泛应用于高聚物合成材料、塑料、电器、建材、树脂等领域,具有优良的热稳定性(见表1)^[20]。DBDPE的阻燃效果接近于甚至优于BDE-209^[21],已成为deca-BDEs最理想的替代品。中国是商业化DBDPE的主要生产国,2006年—2012年的产量约占全球总产量的50%^[22],并且以每年80%的速率持续增长^[6]。

BTBPE是一种具有低挥发性、良好热稳定性和耐光性的添加型BFRs(见表1)^[23],主要用于电子电器和玩具等产品中^[24],从2005年起被大量生产以替代被禁用的octa-BDEs^[25]。我国目前也有生产和使用BTBPE,随着传统BFRs的淘汰,BTBPE的市场需求也会不断增加^[26]。

2 DBDPE和BTBPE在非生物环境介质中的分布特征

2.1 大气中DBDPE和BTBPE的分布特征

DBDPE和BTBPE作为添加型BFRs,室温下具有较低的蒸汽压,很容易在生产、使用和处理过程

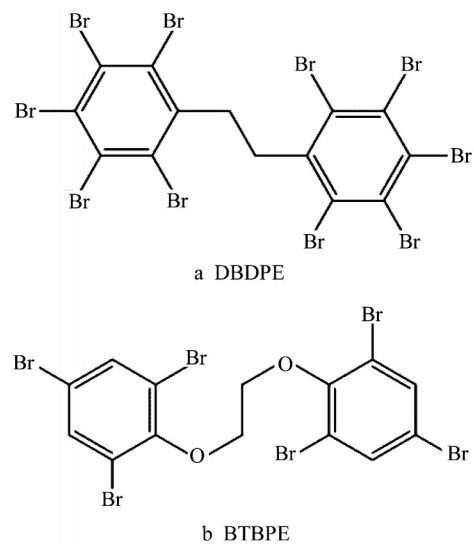


图1 DBDPE及BTBPE的结构式

Fig. 1 Structural formulas of DBDPE and BTBPE

表1 DBDPE和BTBPE的物理化学特性^[6]

Tab. 1 Physicochemical properties of DBDPE and BTBPE^[6]

参数	DBDPE	BTBPE
分子式	$\text{C}_{14}\text{H}_4\text{Br}_{10}$	$\text{C}_{14}\text{H}_8\text{Br}_5\text{O}_2$
分子量	971.2	687.6
蒸汽压(25 °C)/Pa	6.00×10^{-15}	3.88×10^{-10}
溶解度(25 °C)/($\text{g}\cdot\text{L}^{-1}$)	2.10×10^{-7}	1.90×10^{-5}
$\log K_{ow}$	11.10	7.88 ± 0.86

中进入大气,在世界各地大气中都有不同程度检出,甚至在一些偏远地区也有发现^[16-17,27]。因具有较高的 $\log K_{ow}$,DBDPE和BTBPE在大气中易与颗粒物紧密结合,在大气颗粒物中的浓度要远高于气相^[28-30]。Li等^[30]的研究发现,在中国9个城市的大气中,DBDPE在大气颗粒物中的平均质量浓度($63.5 \text{ pg}\cdot\text{m}^{-3}$)远高于在气相中($5.32 \text{ pg}\cdot\text{m}^{-3}$)。在美国中东部和加拿大多伦多地区也仅在大气颗粒物中检测到BTBPE^[31-32]。

就全球而言,美国五大湖的偏远地区大气中DBDPE质量浓度($0.34 \sim 0.50 \text{ pg}\cdot\text{m}^{-3}$)^[17]远低于全球其他地区,而中国广州大气中DBDPE质量浓度(平均值为 $1916.00 \text{ pg}\cdot\text{m}^{-3}$)远高于其他国家和地区(瑞典和东非(质量浓度平均值分别为 1.40 、 $7.23 \text{ pg}\cdot\text{m}^{-3}$))^[14,33-34],并且远高于国内其他城市(哈尔滨、北京和昆明(质量浓度平均值分别为 11.00 、 55.40 、 $3.90 \text{ pg}\cdot\text{m}^{-3}$))^[28,30]。广州高度发达的汽车制造业和电子电器产业及其周边的电子垃圾拆解活动可能是浓度较高的主要原因^[14,30,35-37]。BTBPE也在包括偏远地区的世界各地大气中检出,其中北极(质量浓度中位值为 $0.044 \text{ pg}\cdot\text{m}^{-3}$)低于青藏高原纳木

错湖地区(质量浓度中位值为 $0.220 \text{ pg}\cdot\text{m}^{-3}$)和美国五大湖偏远地区(质量浓度中位值为 $0.310 \text{ pg}\cdot\text{m}^{-3}$)^[16-17,27],美国阿肯色州农村地区(质量浓度平均值为 $3.40 \text{ pg}\cdot\text{m}^{-3}$)与中国南方农村地区水平相当(质量浓度平均值为 $2.97 \text{ pg}\cdot\text{m}^{-3}$)^[29,31]。电子垃圾拆解活动同样也是大气中BTBPE的主要来源,如中国广东清远电子垃圾拆解地 $\text{PM}_{2.5}$ 的BTBPE质量浓度(平均值为 $34.20 \text{ pg}\cdot\text{m}^{-3}$)是广州市区(平均值为 $1.64 \text{ pg}\cdot\text{m}^{-3}$)的20倍左右^[38]。整体来说,BTBPE在大气中的浓度普遍低于DBDPE^[14,17,30],这可能是由于BTBPE全球使用量低于DBDPE^[6,25]。

室内粉尘可能是人体吸入和皮肤摄入BFRs的主要途径^[39-40]。其中,DBDPE是室内粉尘中最丰富且常见的NBFRs^[40-41]。如澳大利亚墨尔本地区的室内粉尘中,DBDPE含量(中位值为 $1800 \text{ ng}\cdot\text{g}^{-1}$)要比其他NBFRs(五溴甲苯(PBT)、2,3,4,5,6-五溴乙苯(PBEB)、六溴苯(HBB)和2-乙基己基-四溴苯甲酸(EH-TBB))高出2~3个数量级^[42]。广州室内粉尘中DBDPE含量(中位值为 $4600.0 \text{ ng}\cdot\text{g}^{-1}$)处于较高水平^[39],比欧洲(捷克、比利时和德国(中位值分别为 140.8 、 153.0 、 $146.0 \text{ ng}\cdot\text{g}^{-1}$))和北美(美国和加拿大(中位值分别为 148.0 、 $15.0 \text{ ng}\cdot\text{g}^{-1}$))要高出1~2个数量级^[2,24,43-45]。室内粉尘中DBDPE主要来自各类电器的使用^[46-47],因此拥有较多电器的办公室中DBDPE含量通常大于居家环境^[24,48]。BTBPE在室内灰尘中也能检测到,但低于DBDPE^[44-45],如中国、英国、比利时和美国室内粉尘中BTBPE的含量都比DBDPE低1个数量级左右^[24,40,48-49]。不同国家室内粉尘中BTBPE的含量差异显著。加拿大(中位值为 $12.0 \text{ ng}\cdot\text{g}^{-1}$)与英国(中位值为 $11.2 \text{ ng}\cdot\text{g}^{-1}$)和巴基斯坦(中位值为 $15.0 \text{ ng}\cdot\text{g}^{-1}$)相当^[45,50-51],高于比利时(中位值为 $2.0 \text{ ng}\cdot\text{g}^{-1}$)和捷克(中位值为 $3.9 \text{ ng}\cdot\text{g}^{-1}$)^[24,45],低于美国(中位值为 $30.0 \text{ ng}\cdot\text{g}^{-1}$)和挪威(中位值为 $42.0 \text{ ng}\cdot\text{g}^{-1}$)^[49,52]。

2.2 水体和沉积物中DBDPE和BTBPE的分布特征

大气中的DBDPE和BTBPE主要通过干湿沉降迁移到水体和土壤等环境介质中,土壤中的DBDPE和BTBPE也可以通过地表径流进入水体。同时,由于DBDPE和BTBPE具有较高的 $\log K_{ow}$ 和有机碳-水分配系数($\log K_{oc}$),因此对水体中的悬浮颗粒物和沉积物具有较高的亲和力^[53]。研究表明,总有机碳含量(TOC)和沉积物粒径可能是影响沉积物中BFRs分布的重要因素,因此DBDPE等BFRs很容易吸附在粒径较小且TOC较高的沉积物中^[1]。

目前关于水体中DBDPE和BTBPE的研究较少,主要集中在中国、新加坡和加拿大^[11,53-54]。如中国山东莱州湾地区的DBDPE质量浓度($0.310\sim 107.000 \text{ ng}\cdot\text{L}^{-1}$)远高于其他地区^[11,54],主要由于该地区是中国最大的BFRs生产地^[55]。由于BTBPE产量较低,因此在水体中的浓度远低于DBDPE。新加坡城市流域水体中BTBPE的质量浓度($0.040\sim 5.220 \text{ ng}\cdot\text{L}^{-1}$)远高于新加坡沿海流域($N_d\sim 62.000 \text{ pg}\cdot\text{L}^{-1}$, N_d 为检测限)以及中国渤海流域($0.030\sim 0.150 \text{ ng}\cdot\text{L}^{-1}$)和加拿大温尼伯湖流域($N_d\sim 2.690 \text{ pg}\cdot\text{L}^{-1}$)^[11,53,56-57]。此外,水相中DBDPE和BTBPE的浓度远低于包含悬浮颗粒相的水体以及沉积物^[12,54-55]。如在广东东江水体中,DBDPE含量呈现为溶解相($13\sim 38 \text{ pg}\cdot\text{L}^{-1}$)<颗粒相($37\sim 110 \text{ ng}\cdot\text{g}^{-1}$ 干重)<<沉积物($N_d\sim 1700 \text{ ng}\cdot\text{g}^{-1}$ 干重)^[12],在山东莱州湾地区也仅在颗粒相中检测到了BTBPE^[55]。

由于DBDPE和BTBPE的强疏水性,因此一旦进入水体中,其主要分布相是沉积物。近年来随着DBDPE的广泛生产和使用,DBDPE已成为沉积物中主要的BFRs之一^[55,58-59],并且许多研究表明DBDPE在沉积物中的含量已高于BDE-209^[1,58-60]。如在中国黄海和东海沉积物中,DBDPE含量($N_d\sim 9460.0 \text{ pg}\cdot\text{g}^{-1}$ 干重)比BDE-209($1.1\sim 924.0 \text{ pg}\cdot\text{g}^{-1}$ 干重)高1个数量级^[1]。就全球而言,DBDPE在北美五大湖、智利、北冰洋、中国河北白洋淀、长三角等地区的水平相近($N_d\sim 5.29 \text{ ng}\cdot\text{g}^{-1}$ 干重)^[59-63],而西班牙、中国黄海和福建九龙江口红树林($N_d\sim 39.70 \text{ ng}\cdot\text{g}^{-1}$ 干重)则比前者高1~2个数量级^[58,64-65]。污染最为严重的是中国珠江三角洲的东江河($N_d\sim 1728.00 \text{ ng}\cdot\text{g}^{-1}$ 干重)^[66],这是由于东江河流的沿岸城市东莞是中国主要电子产品生产地^[67]。BTBPE在沉积物中的含量通常低于DBDPE(见表2)。如在越南以及中国莱州湾、珠江三角洲、黄河中下游地区的DBDPE含量($N_d\sim 1728.00 \text{ ng}\cdot\text{g}^{-1}$ 干重)均高于BTBPE($N_d\sim 73.40 \text{ ng}\cdot\text{g}^{-1}$ 干重)^[55,66,68-69]。中国珠江三角洲大堰河流域中BTBPE的含量^[66]高于新加坡城市流域、北美五大湖地区以及荷兰^[53,61,70],这主要是由于大堰河下游靠近电子垃圾拆解地。

2.3 污泥中DBDPE和BTBPE的分布特征

污水处理厂污泥中DBDPE和BTBPE是最常检测到的NBFRs,检出率要高于PBT、PBEB和HBB等NBFRs^[14,36,71-74]。其中,DBDPE检出率最高,浓度最高。如Ricklund等^[75]从12个国家收集的

44个污泥样本中有42个检测到DBDPE,而且在2017年广州污水处理厂污泥中DBDPE与BDE-209的比值已超过1^[15]。中国广州某污水处理厂污泥中DBDPE的含量(675.40~27 438.60 ng·g⁻¹干重)比全国62个污水处理厂高出近100倍(0.82~215.00 ng·g⁻¹干重)。东部地区污泥中DBDPE含量要高于中西部地区,这可能是由于电子电器产业、汽车制造业主要分布在东部地区^[15,35-36]。韩国污泥中DBDPE的含量高于西班牙(N_d ~257.0 ng·g⁻¹干重)、瑞士(73.0~160.0 ng·g⁻¹干重)、德国(N_d ~

220.0 ng·g⁻¹干重)、美国(1.4~160.0 ng·g⁻¹干重)和捷克共和国(6.0~140.0 ng·g⁻¹干重),而新西兰(5.1~31.0 ng·g⁻¹干重)、澳大利亚(7.7~31.0 ng·g⁻¹干重)和挪威(1.9~6.3 ng·g⁻¹干重)等国家则处于相对较低的污染水平^[71-72,74-75]。对于BTBPE,中国(平均值为0.95 ng·g⁻¹干重)与韩国(平均值为1.57 ng·g⁻¹干重)和挪威(平均值为1.27 ng·g⁻¹干重)水平相近^[36,72,74],但比美国(平均值为10.10 ng·g⁻¹干重)和中国哈尔滨地区(平均值为15.62 ng·g⁻¹干重)要低1个数量级^[73,76]。

表2 DBDPE和BTBPE在沉积物和污泥中的分布

Tab. 2 Distribution of DBDPE and BTBPE in sediments and sludge

种类	国家或地区	采样时间	含量/(ng·g ⁻¹ 干重)		文献
			DBDPE (中位值)	BTBPE (中位值)	
沉积物	新加坡	2014年—2015年		1.73~4.46	[53]
	智利	2009年—2010年	N_d ~2.26		[60]
	荷兰	2005年	0.65~9.80	N_d ~0.31	[70]
	西班牙伊比利亚地区	2010年	N_d ~31.50		[64]
	北美五大湖地区	2007年	0.11~2.80	0.13~8.30	[61]
	越南北部地区		N_d ~20.00(3.10)	N_d ~5.70(0.89)	[68]
	中国黄河中下游	2014年	0.04~18.70	0.01~0.20	[69]
	中国福建九龙江口地区	2013年	5.10~32.00	0.03~0.25	[65]
	中国山东莱州湾地区	2014年	3.52~218.00(39.50)	N_d ~3.05(0.01)	[55]
	中国珠江三角洲地区	2009年—2010年	N_d ~1 728.00	N_d ~73.4	[66]
污水处理厂污泥	中国广州地区	2007年	266.00~1 995.00	0.31~1.66	[14]
	中国哈尔滨地区	2012年—2013年	33.86~607.32	0.77~156.60	[76]
	韩国	2011年	N_d ~3 100.00	N_d ~21.00	[72]
	美国	1999年—2000年	1.4~160.00		[75]
	加拿大	2004年	N_d ~65.00		[75]
	瑞典斯德哥尔摩地区	2006年—2007年	66.00~95.00		[77]

2.4 土壤中DBDPE和BTBPE的分布特征

土壤是持久性有机污染物最主要的汇,目前在多个国家和地区的土壤中检出DBDPE和BTBPE,并且DBDPE是土壤中最主要的NBFRs^[78-79]。广东贵屿非电子垃圾拆解区域土壤中检出的DBDPE含量(0.53~0.57 ng·g⁻¹干重)与广东某稻田的(0.88~1.00 ng·g⁻¹干重)较为相近^[80-81],但低于越南北部稻田(N_d ~2.9 ng·g⁻¹干重)和广州郊区农田(17.6~35.8 ng·g⁻¹干重)^[14,82]。工业活动和电子垃圾拆解活动是土壤中DBDPE的主要污染物来源。在印尼苏腊巴亚地区,乡村(N_d ~3.400 ng·g⁻¹干重)和农田土壤(0.058~0.160 ng·g⁻¹干重)中的DBDPE含量要低于城市(0.650~7.600 ng·g⁻¹干重)和工业区(N_d ~4.300 ng·g⁻¹干重)^[83];中国华北地区土壤中山东省DBDPE含量最高(0.06~

1 612.00 ng·g⁻¹干重),京津地区次之(0.03~173.00 ng·g⁻¹干重)。这可能是因为山东省是中国DBDPE的主要生产地,天津的电子垃圾拆解活动是京津地区DBDPE的重要来源^[6,84]。澳大利亚墨尔本电子垃圾拆解地DBDPE的含量(N_d ~37 000 ng·g⁻¹干重)也远高于世界其他国家和地区^[85]。

BTBPE在土壤中也有一定检出,并且在电子垃圾拆解地的含量(0.09~4 150.00 ng·g⁻¹干重)要远高于农田、森林和非电子垃圾拆解区域的土壤(N_d ~0.91 ng·g⁻¹干重)^[14,68,78-83]。越南北部电子垃圾拆解地土壤有BTBPE检出,含量为0.51~350.00 ng·g⁻¹干重,但在该地区农田土壤中未检出^[68]。在巴基斯坦和澳大利亚墨尔本电子垃圾拆解地土壤的NBFRs中,BTBPE的含量仅次于DBDPE^[78,85]。

3 DBDPE和BTBPE在生物体中的分布特征

3.1 植物中DBDPE和BTBPE的分布特征

植物主要从土壤和大气中吸收有机污染物。对于土壤吸收,污染物先溶解到土壤间隙水、被植物根系吸收,再向上传输至植物的其他部位^[86];对于大气吸收,主要是大气中的污染物被吸附到树叶或树皮表面^[87-88]。树皮具有较高的脂质含量和较大的表面积,是大气有机污染物重要的指示物^[89]。目前DBDPE和BTBPE主要在针叶林(松树、冷杉和云杉等)的树皮和叶片以及落叶林的叶片中检出^[88-93]。DBDPE含量在加拿大、捷克共和国和美国芝加哥地区的树皮中水平相近(平均值分别为6.63、3.92、5.70 ng·g⁻¹脂重)^[89-90],但低于中国主要电子产品制造地深圳(1 034.5 ng·g⁻¹脂重)^[91]。DBDPE与BTBPE在美国东北部树皮中含量的平均值(8.5、3.2 ng·g⁻¹脂重)远远低于美国阿肯色州(100.0、24.0 ng·g⁻¹脂重),这是因为阿肯色州有DBDPE和BTBPE的生产厂^[91-92]。落叶和针叶林的叶中DBDPE的含量要比BTBPE高大概1~2个数量级^[88,93]。此外,谷物、蔬菜、水果等食物中也检测出了少量DBDPE(平均值为120.0 pg·g⁻¹湿重)与BTBPE($N_d \sim 21.8$ pg·g⁻¹湿重)^[94-95]。

3.2 动物中DBDPE和BTBPE的分布特征

由于DBDPE和BTBPE具有高亲脂性,在陆生和水生动物体内均能检测到其存在(见表3)^[13,96-102],它们的差异性分布与生存环境、器官组织、动物种类、营养级和生活习性有关^[14,96,99]。中国广东清远池塘中鱼体内的DBDPE和BTBPE(440.00~1 000.00、1.71~518.00 ng·g⁻¹脂重)都远高于加拿大流域($N_d \sim 1.01$ 、0.13~0.95 ng·g⁻¹脂重)^[11,96,100]。由于该池塘底泥中含有较高的DBDPE,鱼类、虾和水蛇DBDPE的含量比两栖生物(青蛙和蟾蜍)高1~2个数量级^[96,100]。在格陵兰岛,DBDPE和BTBPE在鲸脂、脂肪组织中的含量明显高于蛋和肝脏^[101]。

目前陆生动物中DBDPE和BTBPE的研究主要集中在鸟类。蛋的高脂肪含量使其可能积累大量的有机污染物,因此被认为是环境中持久性有机污染物污染水平的良好指示物^[103]。来自美国五大湖、北极、瑞典Faroe岛以及加拿大和西班牙等国家和地区的鸟蛋中DBDPE和BTBPE的含量分别为 $N_d \sim 3 310.30$ ng·g⁻¹和 $N_d \sim 19.20$ ng·g⁻¹(脂重)^[104-107],其中美国五大湖地区DBDPE的含量最高。在中国,

北方黄河流域鸟蛋中DBDPE的含量为 $N_d \sim 1.70$ ng·g⁻¹(脂重),低于广东清远电子垃圾拆解地鸡蛋(5.97~37.90 ng·g⁻¹脂重)^[108-109]。在广东清远电子垃圾拆解地鸟类肌肉中DBDPE和BTBPE的含量(10.0~180.0和 $N_d \sim 7.7$ ng·g⁻¹脂重)高于广东鼎湖山和石门台国家级自然保护区(11.0~25.0和0.1~0.3 ng·g⁻¹脂重),并且DBDPE的含量要高于BTBPE^[97,110-114]。然而,韩国普通鸫体内BTBPE含量平均值(431.00 ng·g⁻¹脂重)要比DBDPE(10.10 ng·g⁻¹脂重)高1个数量级左右,其他鸟类体内DBDPE(11.20~80.60 ng·g⁻¹脂重)远高于BTBPE($N_d \sim 2.65$ ng·g⁻¹脂重),这可能与鸟类的捕食习性和迁徙模式有关^[99]。除了鸟类外,中国动物园的大熊猫和小熊猫也被检出DBDPE^[115]。巴基斯坦室内环境的宠物猫和狗的毛发和血清中均检测出一定量的BTBPE^[98]。此外,由于有机污染物在动物不同组织中代谢和累积模式的不同,使其存在组织分布差异性。如DBDPE与BTBPE在广东清远电子垃圾拆解地鸟类肝脏(13.70~54.60、0.27~2.41 ng·g⁻¹脂重)和肾脏(24.50~124.00、0.12~0.89 ng·g⁻¹脂重)的含量比肌肉(9.60~16.30、0.07~0.39 ng·g⁻¹脂重)高^[14]。

研究表明,DBDPE和BTBPE在水生食物链具有一定的生物放大作用。如加拿大温尼伯湖地区水生食物链中DBDPE的营养放大系数(TMF)值为8.60^[11],太湖水生食物链中BTBPE的TMF值为2.83^[13]。研究亦发现,DBDPE与BTBPE在陆地食物链中具有生物放大效应。如广东肇庆地区DBDPE的浓度与氮同位素($\delta^{15}N$)显著正相关^[110],BTBPE在普通翠鸟的捕食关系中生物放大因子(BMF)值也都大于1(1.1~3.6)^[112,114]。也有研究发现,DBDPE和BTBPE在水生食物链中BMF值分别为0.06和0.40,这也表明它们具有营养级稀释效应^[116]。

3.3 人体中DBDPE和BTBPE的分布特征

关于人体内DBDPE和BTBPE的分布,主要以母乳、血液和头发为研究对象。研究发现,中国母乳中DBDPE含量(2.45~21.80 ng·g⁻¹脂重)与加拿大($N_d \sim 25.00$ ng·g⁻¹脂重)相似,都高于新西兰(15.85~325.50 pg·g⁻¹脂重)^[117-119]。对BTBPE而言,在加拿大、坦桑尼亚和爱尔兰母乳中均未检出^[118,120-121],但在中国许多地区有检出,但含量较低($N_d \sim 0.922$ ng·g⁻¹脂重)^[117]。血液中DBDPE的分布与人群所处区域环境状况及从事的职业有关。如

表3 DBDPE和BTBPE在动物体内的分布
Tab. 3 Distribution of DBDPE and BTBPE in animals

国家或地区	种类	组织	采样时间	含量/(ng·g ⁻¹ 脂重)		文献
				DBDPE	BTBPE	
中国太湖地区	黄鳝、团头鲂、银鱼、鲫鱼、鲤鱼、鲢鱼等	肌肉	2014年—2015年	N _d ~64.80	5.70(平均值)	[13]
加拿大温尼伯湖地区	大眼蓝鲈、白鲑、翠闪岁、江鳕、白亚口鱼、鲱鱼	肌肉	2000年—2002年	N _d ~1.01	0.13~0.95	[11]
拉脱维亚共和国	鳗鱼	肌肉	2013年—2014年	N _d ~33.00	N _d	[102]
	黑海鸬	鸟蛋	2012年	N _d ~0.96	0.13~0.18	[101]
格陵兰岛地区	北极鸥	肝脏	2012年	N _d	N _d ~0.67	[101]
	海豹	鲸脂	2012年	N _d ~0.33	N _d ~0.23	[101]
	北极熊	脂肪	2012年	N _d	N _d ~0.33	[101]
中国广东清远电子垃圾回收地	母鸡	鸡蛋	2010年	5.97~37.90	37.20~264.00	[109]
美国五大湖地区	银鸥	鸟蛋	1982年—2006年	N _d ~3 310.30	N _d ~4.00	[104]
中国广东清远电子垃圾拆解地(1)	水鸟	肌肉	2005年—2007年		N _d ~3.30	[111]
中国广东清远电子垃圾拆解地(2)	水鸟	肌肉	2005年—2007年	10.00~180.00		[113]
中国广东鼎湖山国家级自然保护区	普通翠鸟	肌肉	2010年	0.44~90.00	0.04~0.87	[114]

与拆解地普通居民(4.2~127.2 ng·g⁻¹脂重)和城镇居民(N_d~33.2 ng·g⁻¹脂重)相比,电子垃圾拆解工人血清中DBDPE含量(26.7~439.5 ng·g⁻¹脂重)显著升高^[122]。加拿大哺乳期妇女血清中BTBPE含量(N_d~16.00 ng·g⁻¹脂重)与巴基斯坦妇女和儿童较为接近(N_d~8.20 ng·g⁻¹脂重)^[118,123]。头发脂质含量高(2%~4%),可以通过外部环境和血液循环吸收污染物^[124]。浙江温岭电子垃圾拆解地工人头发中DBDPE含量(平均值为82.50 ng·g⁻¹干重)分别是该电子垃圾拆解地普通居民(平均值为29.40 ng·g⁻¹干重)和城镇居民(平均值为10.90 ng·g⁻¹干重)的3倍和8倍^[122],也远高于广州中山大学(中位值为3.56 ng·g⁻¹干重)和广东农村居民(中位值为9.57 ng·g⁻¹干重)^[125-126]。BTBPE也呈现相似趋势,广东电子垃圾拆解工人(中位值为1.21 ng·g⁻¹干重)、电子垃圾拆解地普通居民(中位值为0.60 ng·g⁻¹干重)和广州城市居民(中位值为0.10 ng·g⁻¹干重)头发中的含量逐渐增加,这表明DBDPE和BTBPE在人体头发中的含量与其在环境中的污染水平有很大的关联^[126]。

4 结论与展望

近年来,随着PBDEs的禁用,DBDPE和BTBPE等NBRs开始被广泛生产并使用,在世界各地乃至北极、青藏高原等偏远地区的不同环境介质中被陆续检出,尤其是DBDPE浓度呈不断上升趋势,在某些区域甚至超过deca-BDEs。电子垃圾拆解活动、商业化DBDPE和BTBPE的生产和使用是环境中DBDPE和BTBPE的主要来源。因此,

DBDPE和BTBPE在不同区域的分布大致表现为:电子垃圾拆解地要高于非电子垃圾拆解地,城市及工业区高于农村地区,拥有较多电器的办公室高于居家环境。由于DBDPE和BTBPE具有较高的log K_{ow},易与固相结合,在大气颗粒物、室内粉尘、沉积物、污泥和土壤中的浓度高于大气气相和水体溶解相等介质。对于生物介质,植物主要以树皮和叶片为主,动物主要集中在鱼类和鸟类,人体则通过血液、母乳及头发来研究DBDPE和BTBPE分布特征,在生物介质中的分布与生物种属、组织、营养级、生存环境和生活习性等有一定关系。总的来说,BTBPE在非生物环境介质中的浓度都明显低于DBDPE,也有研究发现在部分动物体内BTBPE的浓度高于DBDPE。

由于DBDPE和BTBPE的生物富集作用和毒性,因此未来仍需对其在不同生物介质中的分布特征展开研究,尤其食物链中的生物放大作用也值得格外关注。其次,需重点关注DBDPE和BTBPE在环境介质中的迁移转化行为,尤其是在生物体内的迁移转化过程及机制。最后,需加强DBDPE和BTBPE的生物效应及机制研究,从基因组学、转录组学、蛋白质组学及代谢组学对机理开展深入研究。这对评价DBDPE和BTBPE的生态风险和对人类潜在的健康危害都具有重要意义。电子垃圾拆解活动以及生产和使用DBDPE和BTBPE的企业是目前的主要污染源,因此要从污染源头来减少向环境中的排放,通过先进的处理工艺有效去除“三废”中DBDPE和BTBPE来尽量减少对生态环境和人类健康的影响。

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