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# 有机磷酸酯污染现状及其生物富集和生物转化研究进展 *

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**摘 要** 有机磷酸酯（Organophosphate esters, OPEs）主要作为阻燃剂和塑化剂被广泛生产和使用. 随着包括多溴联苯醚在内的溴代阻燃剂逐步受控，作为溴代阻燃剂主要代替品之一的 OPEs 产量大幅增长，OPEs 环境问题日益引起人们的关注. 本文从 OPEs 的理化性质着手，简要梳理了其在环境中的赋存状况. 地表水中 OPEs 浓度大多为几百 ng·L$^{-1}$，磷酸三（2-氯异丙基）酯（TCPP）和磷酸三 (2-丁氧基乙基）酯（TBEP）为主要检出物质；沉积物中 OPEs 浓度大多处于几十 ng·g$^{-1}$ dw（干重）水平，主要检出物质为磷酸三（2-乙基己基）酯（TEHP）和磷酸三苯酯（TPHP）；在大气与土壤中 OPEs 以 TCPP 和磷酸三（2-氯乙基）酯（TCEP）为主，浓度多为几十 ng·m$^{-3}$ 和几十 ng·g$^{-1}$ dw. 此外，本文重点针对 OPEs 在生物体内的富集和代谢转化情况进行了综述，水生生物中 OPEs 浓度大多处于几十 ng·g$^{-1}$ ww（湿重）水平，陆生生物中 OPEs 浓度大多处于几百 ng·g$^{-1}$ lw（脂重）水平，对于 OPEs 是否具有生物累积效应，相关的研究结果差异较大，OPEs 在生物体内快速的代谢转化很可能是影响其生物富集作用的主要因素. 最后，针对目前的研究现状，对存在的问题及后续的研究方向进行了讨论与展望.

**关键词** 有机磷酸酯，代谢产物，生物富集，生物转化.

# Pollution status, bioaccumulation and biotransformation of organophosphate esters: A review

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**Abstract** Organophosphate esters (OPEs) have been widely used as flame retardants and plasticizers. With the restriction on brominated flame retardants including PBDEs, the production and consumption of the main alternatives, OPEs have grown substantially in recent years, which has raised increasing environmental concerns. This review commences on the physic-chemical properties

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of OPEs, and summarizes the occurrence of OPEs in environment. The concentrations of OPEs in surface water were mostly at the level of several hundred ng·L$^{-1}$, tris (2-chloroisopropyl) phosphate (TCPP) and tributoxyethyl phosphate (TBEP) were the abundant substance; the concentration of OPEs in sediments were mostly tens of ng·g$^{-1}$ dw, and the main detected substances were tris (2-ethylhexyl) phosphate (TEHP) and triphenyl phosphate (TPHP). In the atmosphere and soil, the concentrations of OPEs were mostly tens of ng·m$^{-3}$ and tens of ng·g$^{-1}$ dw, the main detected substance was TCPP and tris (2-chloroethyl) phosphate (TCEP). The review emphasized on bioaccumulation and biotransformation of OPEs in biota. The concentrations of OPEs in aquatic organisms were mostly at the level of several tens ng·g$^{-1}$ ww, and in terrestrial organisms the concentrations of OPEs were mostly at the level of several hundred ng·g$^{-1}$ lw. Inconsistent results were observed in bioaccumulation of OPEs in biota, and rapid metabolic transformation of OPEs in organisms was likely to be the main factor for the variation. Based on the current research progress, the existing problems and prospects for future studies are also discussed.

**Keywords** organophosphate esters (OPEs), metabolites, bioaccumulation, biotransformation.

随着溴系阻燃剂在全球范围内的限制使用，作为其主要替代品之一的有机磷酸酯（organophosphate esters, OPEs）的生产和使用量大幅度增长[1－4]. OPEs 主要作为阻燃剂、增塑剂和消泡剂，广泛用于电子产品、建筑材料、家具、纺织、塑料和食品包装等行业中[5]. 我国 2007 年有机磷酸酯类物质的年产量接近 7 万 t，并且以 15% 的速度逐年增长[6]. 2011 年，全球 OPEs 的消耗量为 50 万吨[7－8]，预计到 2018 年消费量将达到 105 万 t[9]. 由于 OPEs 主要以物理添加而非化学键合方式加入到材料中[10－11]，容易在产品的生产、使用、处置、回收过程中因挥发、磨损和浸出等原因，释放到各种环境介质中，并通过饮食摄入、呼吸吸入、皮肤接触等方式进入人体，造成潜在健康风险[12].

根据取代基的不同，OPEs 可以划分为含氯、烷基以及芳香基 OPEs 三大类化合物，不同 OPEs 的物理化学性质存在很大差异（表 1），如磷酸三甲酯的辛醇-水分配系数（lg $K_{ow}$）值为-0.65，而磷酸三辛酯的 lg $K_{ow}$ 值为 10.6[13]. 化合物的生物富集潜力与其物理化学性质紧密相关[7]，研究显示，lg $K_{ow}$ 值在 7 左右的卤代有机污染物更容易发生生物富集[14]. 此外，OPEs 的环境浓度水平、生物积累和放大能力及代谢能力也是影响 OPEs 在生物体内富集的主要因素[15]. 目前关于 OPEs 是否存在生物富集和生物放大尚存在一定争议，相关的研究普遍认为 OPEs 生物富集能力较弱，这可能与其在生物体内容易快速代谢有关[16].

**表 1** 有机磷酸酯名称及理化性质

**Table 1** Full name, abbreviation, and physic-chemical properties of OPEs

| 中文全称 Chinese name | 缩写 Abbreviation | CAS号 | 沸点/℃ | 熔点/℃ | 正辛醇-水分配系数（lg $K_{OW}$） | 25 ℃时蒸气压/mm Hg | 25 ℃时亨利常数/（atm·m$^3$·mol$^{-1}$） | 25 ℃时水中溶解度/（mg·L$^{-1}$） |
|---|---|---|---|---|---|---|---|---|
| 磷酸三(2-氯乙基)酯 | TCEP | 115-96-8 | 351 | −55 | 1.44 | $1.1\times10^{-4}$ | $3.3\times10^{-6}$ | $7.0\times10^{3}$ |
| 磷酸三(2-氯异丙基)酯 | TCPP | 13674−84-5 | 359 | 72 | 2.59 | 0.75 | $6.0\times10^{-8}$ | $1.6\times10^{3}$ |
| 磷酸三(1,3-二氯-2-丙基)酯 | TDCPP | 13674−87-8 | 457 | 88 | 3.8 | $7.4\times10^{-8}$ | $2.6\times10^{-9}$ | 1.5 |
| 磷酸三(2-丁氧基乙基)酯 | TBEP | 78-51-3 | 414 | −70 | 3.75 | $2.1\times10^{-6}$ | $1.2\times10^{-11}$ | $1.2\times10^{3}$ |
| 磷酸三丁酯 | TNBP | 126-73-8 | 289 | −80 | 4.00 | $1.5\times10^{-7}$ | $1.5\times10^{-7}$ | 280 |
| 磷酸三异丁酯 | TiBP | 126-71-6 | 264 | 16 | 3.6 | $1.3\times10^{-2}$ | $2.8\times10^{-4}$ | 3.72 |
| 磷酸三苯酯 | TPHP | 115-86-6 | 370 | 4 | 4.59 | $1.2\times10^{-6}$ | $3.3\times10^{-6}$ | 1.9 |
| 磷酸三(2-乙基己基)酯 | TEHP | 78-42-2 | 220 | 87 | 9.49 | $1.1\times10^{-3}$ | $9.6\times10^{-5}$ | 0.6 |
| 磷酸2-乙基己基二苯酯 | EHDPHP | 1241−94-7 | 375 | −54 | 5.73 | $3.3\times10^{-5}$ | — | 1.9 |
| 磷酸三甲酯 | TMP | 512-56-1 | 197 | −10 | −0.65 | $5.6\times10^{-3}$ | $2.5\times10^{-7}$ | $3.0\times10^{3}$ |
| 磷酸三乙酯 | TEP | 78-40-0 | 216 | −56 | 0.80 | 0.29 | $3.5\times10^{-6}$ | $5.0\times10^{5}$ |

生物转化是外源化合物进入生物体后的一个重要的代谢转化过程, 对于外源化合物在生物体内的富集和清除以及毒性效应均有重要影响. 现有研究结果表明, OPEs 可以在生物体内发生快速代谢转化[17－18], 反应路径主要包括Ⅰ相代谢磷酸酯氧脱烷基 (DAPs)[19－20]、氧化羟基化 (HO-OPEs)、氧化羧基化、氧化脱卤, 以及Ⅱ相代谢谷胱甘肽结合、葡萄糖醛酸结合和硫酸结合等, 形成多种代谢产物[12]. 尽管目前已有大量的研究报道了不同环境介质中的 OPEs 浓度水平, 并且已经证实 OPEs 具有内分泌干扰效应以及生殖毒性、发育毒性和神经毒性等, 但目前还少有研究关注 OPEs 的生物富集与生物转化, 对于 OPEs 与其代谢产物在生物体内的环境行为与归趋缺少系统的研究和总结. 为此, 本文梳理和综述了近年来国内外关于 OPEs 在环境中的赋存状况以及生物富集与生物转化的研究进展, 对目前仍存在的问题及未来的研究关注方向进行了总结和展望.

## 1　环境介质中的有机磷酸酯 (OPEs in environmental matrix)

### 1.1　地表水

受城市化和工业化的影响, OPEs 目前已在全球范围内的水体中广泛检出[21－22]. 国内部分地表水中 OPEs 的浓度, 如天津[23]、上海[24] 和北京[25] 地表水中 OPEs 的平均浓度分别为 228.7、850、954 ng·L$^{-1}$, 大多处于几百 ng·L$^{-1}$ 的水平. 而受人为影响较大的松花江[26], 太湖[27] 中 OPEs 平均浓度达到 1171 ng·L$^{-1}$ 和 1363 ng·L$^{-1}$. 成都锦江[28] 中 OPEs 的平均浓度为 3747.6 ng·L$^{-1}$, 大幅高于国内其他地区河流, 主要原因是其沿岸有数百排污口, 日均污水排放量达数十万吨[29]. 国外的相关研究也呈现类似的结果, 欧洲多国地表水如法国[30]、德国[31]、意大利[32]、奥地利[21] 地表水中 OPEs 大多处于几百 ng·L$^{-1}$ 的水平. 在受人为活动影响较小的乡村地区的水体中 OPEs 的浓度相对较低, 如对德国乡村地区[33] 水体中浓度最高的 OPEs 是磷酸三(2-氯异丙基)酯(TCPP), 其浓度范围为 85—126 ng·L$^{-1}$. 而在高度城市化地区 OPEs 浓度相对较高, 如西班牙纳隆河、阿尔加和贝索斯河[34] 的 3 条河中 OPEs 浓度范围为 7.6—7200 ng·L$^{-1}$. 目前报道的 OPEs 最高浓度在英国的亚尔河[35], 浓度最高的污染物是 TCPP, 该污染物的平均浓度超过 6000 ng·L$^{-1}$, 最大浓度可达 26050 ng·L$^{-1}$, 亚尔河沿岸大量污水处理厂的排放很可能是 OPEs 的重要来源.

由于海水的稀释作用, 海水中的 OPEs 浓度大多低于河流. 我国大连黄海沿岸[36] 水体中 OPEs 的浓度范围为 21.6—61.5 ng·L$^{-1}$, 与美国纽约州海滨海水[37] 中的 OPEs 浓度(40.0—60.8 ng·L$^{-1}$)处于同一水平. 中国南海、日本东京湾[38] 中 OPEs 的浓度范围为 1.25—284 ng·L$^{-1}$, 这两个海域受周边工业化影响程度较高. 值得注意的是, 研究人员已在南极费尔德斯半岛[39] 附近的海水中检出了 OPEs, 浓度范围从低于检出限(ND)到 44.37 ng·L$^{-1}$. 随着全球变暖、气候变化和各地人为影响的加剧, 有机磷酸酯释放并分布于全球各地[39].

总体而言, 不同地区水体中 OPEs 的组成存在一定差异, 可能是由于城市化程度有所不同造成的. 具体见表 2, 但大多以 TCPP、磷酸三(2-丁氧基乙基)酯(TBEP)和磷酸三(2-氯乙基)酯(TCEP)的 3 种化合物为主. 在欧洲[21]、澳大利亚[40] 和美国[37, 41] 的地表水中 TCPP 和 TBEP 的浓度相对较高, 而在我国[23, 27] 的地表水体中, 除 TCPP 以外, TCEP 的浓度也大多处于相对较高的水平. 此外, 对南极周边海域的研究发现 OPEs 的主要组分为磷酸三(2-乙基己基)酯(TEHP)和磷酸 2-乙基己基二苯酯(EHDPHP)[39], 与人口稠密地区的结果存在较大差异, 这可能是研究站人为活动中 OPEs 的使用不同导致的结果.

### 1.2　沉积物

沉积物是环境中 OPEs 的主要蓄积库之一(表 2). 日本早在 1977—1979 年就检测出沉积物中的磷酸三丁酯(TNBP)[42], 20 世纪 80 年代进一步发现沉积物中含 TCEP[43]. 我国近年来也逐步开展了沉积物中 OPEs 研究工作, 太湖[44]、东江[45]、海南[46] 近海岸沉积物中 OPEs 浓度范围均处在几十 ng·g$^{-1}$ dw(干重)的水平. 渤海与黄海[47] 表层沉积物中 OPEs 浓度范围为 0.083—4.552 ng·g$^{-1}$ dw. 渤海和黄海的采样点距离海岸线较远, 检出值较近岸降低 1—2 个数量级. 国外, 如荷兰西谢尔特河口[48]、奥地利[21] 河流和北美五大湖[49] 沉积物中 OPEs 平均浓度为几十 ng·g$^{-1}$ dw, 与国内浓度水平相似. 而欧洲萨瓦河、埃夫罗塔斯河和阿迪奇河[50]3 条河沉积物中 OPEs 浓度范围为 0.31—549 ng·g$^{-1}$ dw, 这 3 处主要受到农业废物和工业污染影响, 检出值较高. Ma[51] 评估了白令海至北冰洋中部的海洋沉积物中的 OPEs 浓度水

平, 发现∑OPEs 随着纬度的增加而增加, 表明 OPEs 通过大气转移到地表水, 更进一步转移到深水和偏远海洋环境的沉积物中, 从而被输送到北冰洋. 沉积物中的 OPEs 组成与水体中不同, 主要以 TEHP 和磷酸三苯酯(TPHP)为主, 如在美国旧金山和我国太湖沉积物中以 TEHP 为主, 我国珠三角地区以 TPHP 为主. 这两种 OPEs 化合物的水溶性相对较低, 更加倾向于吸附在有机质颗粒上, 而非溶解于水中[21], 表明 OPEs 的物理化学性质对其环境分布具有重要影响.

**表 2** 环境介质中 OPEs 的浓度

**Table 2** Concentrations of OPEs in environmental matrix

| | 地点 Sites | TCEP | TCPP | TDCPP | TNBP | EHDPHP | TEHP | TPHP | TBEP | TiBP | ∑OPEs | 浓度范围 Concentration Range | 数据来源 Ref |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 地表水(平均值)/(ng·L$^{-1}$) | 中国海河 | 53.1 | 76.6 | 0.74 | — | 0.88 | — | 1.16 | 32.2 | — | 228.7 | 23.9—824.7 | [23] |
| | 中国上海 | 67—865 | 124—523 | ND—45 | 12—64 | — | — | 2—48 | 16—101 | 11—69 | 850.2 | 340—1688.7 | [24] |
| | 中国北京 | 219 | 291 | 46.3 | 19.6 | 0.38 | 0.91 | 4.49 | 116 | — | 954 | 3.24—10945 | [25] |
| | 中国太湖 | 1197 | 11.3 | 20.6 | 7.1 | — | ND | ND—1.8 | 4.2 | 13.4 | 1363 | 313—2700 | [27] |
| | 中国锦江 | 27—273 | 35—143 | ND | 36—85 | — | 30—299 | 47—164 | 274—10186 | — | 3747 | 689—10623 | [28] |
| | 中国40条河 | 80.2 | 186 | 4.3 | 6.3 | — | 0.4 | 1 | 4.2 | 13.4 | 300 | 9.1—1549 | [85] |
| | 中国松花江 | 520 | 130 | 10 | 230 | 25 | — | 15 | 31 | — | 1171 | — | [26] |
| | 德国易北河 | 81 | 126 | 155 | 23 | — | — | — | — | 73 | 627 | — | [31] |
| | 美国 | 7—300 | 46—2900 | 14—450 | 7—43 | 0.4—2.3 | 0.4—11 | 41—360 | 24—1000 | 0.2—3.2 | — | 170—5100 | [41] |
| | 美国 | 14.6 | 74.6 | 21.2 | — | — | 1.06 | 6.9 | — | — | 191 | 37.2—510 | [37] |
| | 奥地利 | 23 | 43 | 7 | 110 | — | ND | 6 | 52 | — | — | ND—500 | [21] |
| 沉积物(平均值)/(ng·g$^{-1}$ dw) | 中国太湖 | 0.6—3.17 | ND—2.27 | ND—5.54 | — | — | — | ND—2.65 | 1.0—5.0 | — | 7.8 | 3.4—14.2 | [44] |
| | 中国东湖 | 2.57 | 14.04 | 2.29 | — | — | — | — | — | — | 25.4 | 1.5—86.2 | [45] |
| | 中国河流 | 1.18 | 1.59 | 0.29 | 1.2 | 0.4 | 1.59 | 0.48 | — | — | 19.1 | 12.2—25.9 | [46] |
| | 中国近海岸 | 1.62 | 3.28 | 0.55 | 1.04 | 0.48 | 0.85 | 0.51 | — | — | 16.4 | ND—60.0 | [46] |
| | 奥地利 | 160 | 1300 | ND | 15 | — | 160 | 160 | 43 | 8.7 | — | — | [21] |
| | 美国 | 0.03—0.1 | 0.3—1.6 | 0.7—2.0 | 0.3—1.2 | 0.1—1.5 | 2.3—20 | 0.4—7.5 | 0.5—4.8 | — | — | 9.5—33 | [41] |
| | 荷兰 | 0.5 | 3.6 | 0.6 | — | 0.2 | 1.5 | 6 | — | 6.9 | — | 0.1—19.6 | [48] |
| | 希腊 | ND—2.3 | Nq—7.6 | ND—2.96 | ND—5.5 | ND—6.4 | ND—4.7 | ND—0.6 | — | ND—3.4 | 10.4 | 0.31—31.0 | [50] |
| | 意大利 | 0.3—3.6 | 0.5—53.7 | Nq—6.8 | 0.1—42.6 | 4.3—288 | Nq—35.1 | Nq—9.7 | — | Nq—10 | 82.6 | 11.5—549 | [50] |
| 大气(中值)/(ng·m$^{-3}$) | 室内 | | | | | | | | | | | | |
| | 中国北京 | 0.17 | 3.8 | ND | 0.17 | 0.008 | ND | 0.034 | 0.003 | 0.15 | 4.7 | 1.0—20 | [53] |
| | 中国杭州 | 3.11 | 7.76 | 0.63 | 0.17 | 0.35 | 0.84 | 1.41 | 0.27 | — | 17.24 | 5.0—147.7 | [55] |
| | 挪威 | 3 | 128 | ND | 14 | ND | — | 1 | 0.598 | — | 163 | — | [56] |
| | 德国 | ND | 10.77 | 0.36 | 2.87 | — | ND | — | ND | 7.44 | 40.2 | 3.3—751 | [57] |
| | 澳大利亚 | 2.6 | 48 | ND | 1.6 | 0.27 | 0.013 | 0.43 | 0.089 | — | 44 | 7.2—760 | [58] |
| | 室外 | | | | | | | | | | | | |
| | 中国广州 | 0.174 | 1.059 | — | 0.237 | 0.073 | 0.111 | 0.298 | ND | — | 2.854 | — | [86] |
| | 中国北京 | 0.202 | 2.325 | 0.056 | 0.111 | — | — | 0.165 | — | — | 2.999 | — | [87] |
| | 加拿大 | 0.608 | 0.575 | 0.097 | — | 0.092 | — | 0.7 | — | — | 2.64 | — | [61] |
| | 德国 | ND | 1.49 | ND | 0.13 | — | ND | — | ND | 1.51 | 5.13 | — | [57] |
| | 美国 | 0.373 | 0.591 | 0.219 | 0.259 | 0.172 | 0.038 | 0.493 | 0.168 | 0.261 | 3.88 | — | [66] |
| 土壤(平均值)/(ng·g$^{-1}$ dw) | 中国重庆 | 11.3 | 3.3 | 5 | 3.5 | 4.2 | 3.6 | 4.8 | — | — | 77.4 | 10.1—315 | [65] |
| | 中国广州 | ND—110 | ND—14 | ND—50 | 12—46 | 1—40 | 1—39 | 2—9 | — | — | 460 | 25—1730 | [70] |
| | 中国广州 | 30—140 | 1—16 | 5—91 | 10—210 | 6—40 | 4—29 | 5—46 | — | — | 230 | 110—500 | [70] |

续表 2

| | 地点 Sites | TCEP | TCPP | TDCPP | TNBP | EHDPHP | TEHP | TPHP | TBEP | TiBP | ∑OPEs | 浓度范围 Concentration Range | 数据来源 Ref |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 土壤（平均值）/（ng·g$^{-1}$ dw） | 中国天津 | 2.03 | 8.86 | 3.89 | 3.07 | 1.57 | 5.62 | 3 | — | 2.45 | 65.2 | 37.7—156 | [64] |
| | 中国天津 | 114 | 444 | 42.1 | 1.14 | 1.75 | 4.51 | 100 | — | 4.49 | 829 | 122—2100 | [64] |
| | 中国河北 | 92 | 21 | — | 22 | 11 | — | 26 | 200 | 47 | 398 | 39—1250 | [69] |
| | 尼泊尔 | 19.8 | 125 | 21.2 | 18.7 | 37.9 | 92.4 | 12.9 | — | — | 1830 | 64.7—27500 | [72] |
| | 越南 | 4.0 | 19 | 21 | — | 24 | — | 620 | — | — | 724 | 13—3430 | [71] |
| 灰尘（中值）/（μg·g$^{-1}$） | 室内灰尘 | | | | | | | | | | | | |
| | 中国上海 | 1.0 | 1.6 | 0.7 | 0.3 | 0.9 | 1.4 | 0.9 | 2.0 | — | 11.5 | 8.0—165.5 | [73] |
| | 中国广州 | 0.41 | 0.62 | 3.23 | 0.11 | 1.02 | 0.77 | 0.61 | 0.4 | — | 9.2 | 2.06—19.95 | [74] |
| | 中国大陆 | 0.24 | 0.69 | 0.12 | 0.053 | 0.037 | 0.147 | 0.089 | 0.03 | 0.009 | 2.38 | 0.292—9.54 | [78] |
| | 韩国 | 2.49 | 0.722 | 0.079 | 0.13 | 0.132 | 0.091 | 0.524 | 23.3 | 0.028 | 31.3 | 3.09—249 | [75] |
| | 澳大利亚 | 0.66 | 6.4 | 0.92 | ND | 0.88 | ND | 0.74 | 10 | — | 40.0 | 7.4—880- | [58] |
| | 美国 | 2.7 | 2.2 | 2.1 | 0.08 | 0.56 | 0.2 | — | 11 | 0.08 | 19.24 | — | [81] |
| | 希腊 | 0.335 | 0.59 | 0.667 | 0.067 | 0.09 | 0.069 | 0.544 | 2.87 | 0.041 | 7.14 | 1.69—90.2 | [75] |
| | 尼泊尔 | 0.018 | 0.026 | 0.001 | 0.018 | 0.026 | 0.081 | 0.017 | — | — | 13 | 0.203—240 | [79] |
| | 挪威 | 0.435 | 5.241 | 1.13 | ND | 0.617 | 0.71 | 1.228 | 6.796 | — | 33.1 | — | [56] |
| | 室外灰尘 | | | | | | | | | | | | |
| | 中国重庆 | 0.205 | 0.07 | 0.05 | 0.025 | 0.032 | 0.794 | 0.069 | 0.227 | — | 0.794 | 0.348—1369 | [65] |
| | 中国北京 | 0.274 | 0.384 | 0.037 | 0.025 | 0.022 | 0.005 | 0.065 | 0.073 | 0.071 | 0.933 | 1.315—2.407 | [82] |
| | 中国大连 | 0.05 | 0.32 | 0.034 | 0.082 | 0.06 | 0.55 | 0.096 | 0.109 | — | 1.62 | 0.3—7.48 | [84] |

ND., 未检出; —., 无数据; Nq., 未定量。ND., not detected; —., no data; Nq., not quantifiable.

### 1.3　大气

现有的研究表明, OPEs 主要分布在颗粒相而非气相中, 因此近来的研究大多将颗粒相中的 OPEs 浓度作为其在空气中的总浓度[52](表 2). 北京[53] 室内空气中 OPEs 平均值浓度为 5.2 ng·m$^{-3}$. 广州[54] 室内空气和杭州[55] 室内空气 OPEs 平均值浓度均在 45 ng·m$^{-3}$ 左右. 北京检出值相较于国内其他两城市, 低了 1 个数量级, 是由于在监测点室内有使用空气净化器. 挪威奥斯陆[56]、德国[57] 及澳大利亚[58] 室内空气 OPEs 平均浓度在 44 ng·m$^{-3}$ 左右. 国内外室内空气中 OPEs 的浓度差异较小.

无论是国内城市如北京、天津、石家庄[59] 和上海[60], 还是国外城市如加拿大多伦多[61], 城市室外空气中 OPEs 浓度范围均在几 ng·m$^{-3}$ 水平. 海洋上空大气中, 对 OPEs 同样有检出. 在地中海大气[62] 中 OPEs 浓度范围为 0.4—5.0 ng·m$^{-3}$, 西南黑海中测得 OPEs 浓度范围为 2.0—6.0 ng·m$^{-3}$. 与城市空气中 OPEs 检出浓度处于同一数量级.

现有的研究结果显示, 室内空气中 OPEs 浓度普遍比室外空气浓度高 1—3 个数量级, 表明 OPEs 主要从室内环境向室外环境释放. 不论是在国内、国外, 室内室外空气中 TCPP 检出率和浓度都较高, 出现这种检出结果, 可能是由于 TCPP 相对于 TCEP 毒性低, 而在欧洲被作为工业代替; 且 TCPP 产量占欧洲氯化有机磷酸酯的 80%[7].

### 1.4　土壤

关于土壤中 OPEs 浓度和分布的研究较为有限. 国内[63] 西部地区、中部地区和东南地区土壤中 OPEs 的中值浓度分别为 29.7、35.8、57.4 ng·g$^{-1}$ dw, OPEs 的浓度与天津[64]、重庆[65] 检出结果相似. 美国[66]、德国[67] 和巴西[68] 土壤中 OPEs 的平均浓度分为 14.3、18.9、67 ng·g$^{-1}$ dw, 其中美国与德国土壤 OPEs 检出较低, 可能是由于土壤取自相较于城市中污染较小的校园.

电子拆解区附近土壤中的 OPEs 浓度相较于城市土壤, 升高 1—3 个数量级. 河北[69]、广州[70] 和天

津[64] 电子拆解区附近土壤 OPEs 的总浓度分别为 398、460、829 ng·g$^{-1}$ dw. 越南[71] 电子拆解区 OPEs 平均浓度为 724 ng·g$^{-1}$ dw. 而高度污染的尼泊尔[72] 加德满都土壤中 OPEs 平均浓度 1830 ng·g$^{-1}$ dw, 主要受到交通、大型工业区和商业区影响, 土壤中不同目标物检出值不同(表 2), 表明城市化地区和工业程度较高地区对这些化学品的使用模式不同. TCPP 这类含氯 OPEs 在国内土壤中普遍检出率较高[63], 这与地表水结果相似. 尼泊尔[72] 磷酸三甲酯(TMP)检出浓度最高, 这受当地的交通环境、消费品中 OPEs 的使用量及工业区分布影响. 国内电子拆解区主要污染物为 TCEP 和 TBEP, 而越南电子拆解区[71]TPHP 检出浓度最高. 可能是由于不同国家电子废弃物中 OPEs 使用种类之间的差异造成[65].

### 1.5 灰尘

关于灰尘中 OPEs 的研究主要集中在室内, 室内灰尘被认为是人体 OPEs 暴露的主要来源. 目前已在不同国家如中国[73－74]、韩国[75]、比利时[76] 和西班牙[77] 的室内灰尘中检测到多种 OPEs(表 2), 检出浓度通常在几 μg·g$^{-1}$ 到几十 μg·g$^{-1}$ 之间. 北京[78]、上海[73] 和广州[74] 室内灰尘中 OPEs 的中值浓度是 2.38、11.5、9.2 μg·g$^{-1}$. 澳大利亚[58]、韩国[75] 室内灰尘中 OPEs 的中值浓度为 33.0 μg·g$^{-1}$ 和 31.3 μg·g$^{-1}$. 但尼泊尔[79]、菲律宾[80] 检出浓度为 13、0.53 μg·g$^{-1}$.

工业化程度较高的国家(如美国[81]、韩国[75]、澳大利亚[58]、挪威[56]、希腊[75] 等)OPEs 检出浓度高于工业化程度较低的国家 (如菲律宾[80] 等). 与其他国家相比, 我国室内灰尘 OPEs 的浓度处在中间水平. 室内灰尘中 TBEP 和 TCPP 的检出率高、浓度高, 其中 TBEP 主要添加于涂漆、橡胶产品以及地板抛光剂中, 这可能是其释放于室内环境中, 使得检出浓度高的原因.

室外灰尘中 OPEs 研究较少, 中国重庆[65]、北京[82]、苏州[83] 和大连[84] 的室外灰尘的平均浓度分别为 0.794、1.861、0.915、2.02 μg·g$^{-1}$, 与室内灰尘相比, 室外灰尘中 OPEs 检出浓度较低. TCPP 在不同地区的检出率较高. 室外灰尘中 OPEs 的组成会受当地的生产、使用阻燃剂的种类和复杂的环境条件影响[83].

## 2 有机磷酸酯的生物富集 (Bioaccumulation of OPEs)

尽管已有大量研究报道了各类环境介质中的 OPEs, 但对生物体中 OPEs 的研究仍相对较少, 且大多集中在水生生物. 近来有研究指出, 部分生物体内 OPEs 的浓度高于其环境背景值[13], 表明 OPEs 可能具有一定的生物累积效应. 同时也有研究结果显示, OPEs 在生物体内不存在明显的生物放大作用, 甚至存在生物稀释现象, 这可能与研究物种以及不同 OPEs 之间结构和性质的差异有关.

### 2.1 水生生物

鱼类等水生生物能够通过水、沉积物以及食物的摄入富集环境中的污染物, 是研究污染物生物蓄积的有效指示物[88]. 部分水生生物体内有机磷酸酯的浓度见(表 3). 珠江三角洲[89] 主要河流中 3 种鱼, 鲮鱼(*Cirrhinus molitorella*)、罗非鱼(*Tilapia nilotica*)和清道夫(*Hypostomus plecostomus*)体内 OPEs 浓度范围为 2.3—30 ng·g$^{-1}$ ww(湿重). 广东[90] 清远电子拆解厂附近的鲤鱼(*Cyprinus carpio*)和水蛇(*water snake Enhydris chinensis*)中 OPEs 浓度为(14±2.4) ng·g$^{-1}$ ww 和(1.9±1.2) ng·g$^{-1}$ ww. 太湖[91] 中多种鱼 OPEs 浓度范围为(9.8±6.2)ng·g$^{-1}$ ww. 韩国洛东河[92] 鲫鱼(*Carassius auratus*)肌肉中 9 种 OPEs 浓度范围为 4.27—7.75 ng·g$^{-1}$ ww. 加拿大[93] 湖泊鱼体中 OPEs 浓度范围为 0.07—9.8 ng·g$^{-1}$ ww. 对鲫鱼和泥鳅(*(Misgurnus anguillicaudatus*)[16] 的不同组织, 如肌肉、肝脏、卵巢、肠道和肾脏进行 OPEs 检测, 肝脏中 OPEs 相较于肠道和肾脏检出较高, 鲫鱼和泥鳅肝脏中 OPEs 浓度分别为 576 ng·g$^{-1}$ lw 和 861 ng·g$^{-1}$ lw. 珠江三角洲水生生物中 OPEs 检出浓度较高, 可能受到城市化及周边地区的工业化程度高影响.

我国莱州湾[94] 沿岸鱼体中 OPEs 的浓度范围为 6.6—107 ng·g$^{-1}$ dw, 肝脏和肌肉的生物累积因子(BAF)分别为 2.8—4.4 和 2.3—3.8, 表明 OPEs 具有生物富集潜力. 太湖[95] 竹山湾水生食物网中, EHDPHP 的营养放大因子(TMF)为 3.61, 具有放大作用, 其他目标物 TCEP、TCPP、TDCPP、TPHP、磷酸三异丁酯(TiBP)和磷酸三甲酯(TMP)没有得到有效的 TMF, 不具有放大作用. 菲律宾马尼拉湾[96] 鱼类样品中 TPHP 的浓度为 1100 ng·g$^{-1}$ lw(脂重), 通过对稳定氮同位素的分析发现, 不同鱼类的$\delta^{15}$N 值

与 TPHP 浓度之间存在显著相关, 表明 TPHP 具有营养级放大效应. 在荷兰西部谢尔德河口[48] 的食物网中, 底栖动物如杜父鱼(*sculpin*)、虾虎鱼(*goby*)和沙蚕(*lugworm*)中浓度较高的两种 OPEs 为 TBEP 和 TCPP, 浓度分别为 17 ng·g$^{-1}$ ww 和 4.6 ng·g$^{-1}$ ww, 高于浮游植物及以浮游植物为食的鱼类中的浓度. TBEP 和 TCPP 生物放大因子(BMF)分别为 3.5 和 2.2, 表明这两种 OPEs 在底栖食物网中具有生物放大作用.

**表 3**　水生生物体内有机磷酸酯的浓度(平均浓度±标准偏差, ng·g$^{-1}$)

**Table 3**　Concentrations of OPEs in Aquatic organisms(mean±sd, ng·g$^{-1}$)

| 物种 Species | 地点 Sites | TCEP | TCPP | TDCPP | TNBP | EHDPHP | TEHP | TPHP | TBEP | 数据来源 Ref |
|---|---|---|---|---|---|---|---|---|---|---|
| 脂眼凹肩鲹 *S. crumenthalmops* | 菲律宾 | — | — | — | 4.7±4.1 | 1.8±3.2 | 23±20 | 1.3±2.2 | 0.18±0.31 | [96] |
| 短钻嘴鱼 *Gerres erythrourus* | 菲律宾 | — | — | — | 64±39 | 38±33 | 160±150 | ND | 34±29 | [96] |
| 沙尖鱼 *S. sihama* | 菲律宾 | — | — | — | 420±120 | 180±32 | 1000±2.1 | ND | 7.9±4.3 | [96] |
| 水蛇 *Enhydris chinensis* | 中国 | 0.046±0.032 | 0.31±0.17 | 0.32±0.78 | 0.79±0.81 | ND | 0.014±0.011 | 0.23±0.11 | — | [90] |
| 鲤鱼 *Cyprinus carpio* | 中国 | 0.21±0.10 | 3.1±0.48 | 0.24±0.21 | 3.0±1.4 | 0.24±0.32 | 0.13±0.045 | 6.2±1.8 | — | [90] |
| 鲫鱼 *Carassius auratus* | 韩国 | 0.688—1.06 | 0.25—0.512 | ND | 0.848—1.52 | — | ND—0.586 | ND | — | [92] |
| 鲫鱼 *Carassius auratus* | 韩国 | 0.53—1.03 | 0.262—0.739 | ND | 1.31—4.32 | — | ND | ND—0.798 | — | [92] |
| 鲮鱼 *Cirrhinus molitorella* | 中国 | 0.81±0.17 | 0.72±0.12 | ND | 0.19±0.02 | 0.05±0.01 | 2.1±0.01 | 0.15±0.06 | — | [89] |
| 罗非鱼 *Tilapia nilotica* | 中国 | 1.0±0.09 | 0.66±0.14 | ND | 0.23±0.11 | 0.07±0.03 | 9.0±2.9 | 0.20±0.16 | — | [89] |
| 清道夫 *Hypostomus plecostomus* | 中国 | 1.5±0.47 | 1.6±0.50 | 0.04±0.03 | 0.18±0.14 | 0.05±0.05 | 4.4±0.55 | 0.36±0.32 | — | [89] |
| 胡子鲶、白鲩 *Claris fuscus*、*Ctenopharyngodon idellus* | 中国 | 82.7—4692 | — | — | 43.9—46 | ND—1.8 | ND—3.61 | ND—45.7 | 164—8842 | [104] |

ND., 未检出; —., 无数据.

ND., not detected; —., no data.

广东清远[90] 电子拆解区附近水塘中水蛇和鲤鱼的 OPEs 浓度分别为 12 ng·g$^{-1}$ ww 和 14 ng·g$^{-1}$ ww, 检测发现 TCEP、TCIPP、TNBP、TDCIPP、TPHP、EHDPHP、TEHP、磷酸三乙酯(TEP)和磷酸三甲酚酯(TPTP), 这 9 种 OPEs 的 BMF 均小于 1, 表明 OPEs 在该食物链中表现出生物稀释作用. 同样广东[97] 清远虾中检测到的 OPEs 浓度范围为 1.7—47 ng·g$^{-1}$ ww, 其中 TNBP 和 TPHP 的 TMF 均小于 1, 分别为 0.57 和 0.62, 表现出营养级稀释现象. 对于 OPEs 是否具有生物蓄积效应, 现有研究结果仍没有一致性结论. 不同 OPEs 的物理化学性质、生物可利用度的差异, 以及不同物种代谢能力的差异都可能对生物累积的结果产生影响.

## 2.2　陆生生物

相比于水生生物, OPEs 在陆生生物体内富集的研究就更为缺乏, 目前主要集中于鸟类和哺乳动物. 陆生生物体内有机磷酸酯的浓度见表 4.

鸟类多处于食物链的较高位置, 容易富集环境中的污染物, 因而成为研究区域环境污染状况的重要生物监测工具之一. 研究人员在挪威[98] 白尾鹰雏鸟(*Haliaeetus albicilla*)的羽毛中检出了 OPEs, 其中 TCEP 和 TCPP 的检出浓度较高, 分别为 110 ng·g$^{-1}$dw 和 91 ng·g$^{-1}$ dw. 加拿大[99] 东部极地地区游隼(*Falco peregrinus*)体内, TBEP 和 TCPP 的比例较高, 浓度分别为 0—7.5 ng·g$^{-1}$ ww 和 0.1—5.5 ng·g$^{-1}$ ww. 鸟蛋中的 OPEs 也表现出类似的结果, 如澳大利亚昆士兰州[100] 鸡蛋中 OPEs 浓度为 1.0 ng·g$^{-1}$ ww.

**表 4** 陆生生物体内有机磷酸酯的浓度(浓度范围, ng·g$^{-1}$)

**Table 4** Concentrations of OPEs in Terrestrial organisms(Concentration range, ng·g$^{-1}$)

| 物种 Species | 地点 Sites | TCEP | TCPP | TNBP | TDCPP | EHDPHP | TEHP | TPHP | TBEP | 数据来源 Ref |
|---|---|---|---|---|---|---|---|---|---|---|
| 禽类 | 中国 | 33.7—16.2 | 3.89—21.4 | 11.7—281 | — | ND—21.6 | ND—13.9 | ND—209 | 48.1—266 | [104] |
| 白尾鹰羽毛 *Haliaeetus albicilla* | 挪威 | 14—3000 | 14—220 | ND | 0.95—21 | 5.4—25 | — | 5.9—250 | 3.1—22 | [98] |
| 北极狐 *Vulpes lagopus* | 挪威 | <0.2—.8 | <1.3—15 | — | <0.1—89 | <0.3—1 | 4.76±2.2 | <0.—1.3 | 955 ±294 | [109] |
| 黑冠夜鹭卵 *Nycticorax nycticorax* | 中国 | <5.0—14.5 | <0.2—25.7 | 1.04—39.0 | <4.0—11.5 | <0.2 | <5.0—31.0 | 1.32—34.1 | <0.2—40.3 | [106] |
| 小白鹭卵 *Egretta garzetta* | 中国 | <5.0—8.92 | 0.83—8.39 | 3.28—38.2 | <4.0 | <0.2 | <5.0—7.22 | 1.69—5.9 | <0.2—0.4 | [106] |
| 中国池鹭卵 *Ardeola bacchus* | 中国 | <5.0—6.44 | <0.2—4.10 | 3.14—26.7 | <4.0 | <0.2 | <5.0—7.49 | 1.40—2.58 | <0.2—0.3 | [106] |
| 牛白鹭卵 *Bubulcus ibis* | 中国 | 5.6 | 10.15 | 6.55 | <4.0 | <0.2 | 8.39 | 3.12 | <0.2 | [106] |
| 黑斑蛙 *Rana nigromaculata* | 中国 | 0.93±0.53 | 0.8±0.56 | 0.17±0.13 | 0.043±0.066 | 0.14±0.13 | 0.076±0.046 | 0.073±0.049 | 0.017±0.17 | [107] |
| 牛蛙 *Rana catesbeiana* | 中国 | 6.6±4.6 | 0.41±0.16 | 0.13±0.03 | 0.11±0.06 | 0.34±0.18 | 0.07±0.03 | 0.39±0.17 | 0.03±0.02 | [107] |

ND., 未检出; —., 无数据.

ND., not detected; —., no data.

休伦湖[101]银鸥蛋(*Larus argentatus*)中 TCPP、TCEP 和 TBEP 检出率较高. 美国劳伦斯湖[99, 102]的银鸥卵中被检测到的目标物浓度范围为 0.31—2.14 ng·g$^{-1}$ ww, TNBP 和 TCEP 的检出频率最高. 美国五大湖[103]密歇根聚集地中银鸥卵中 OPEs 的浓度范围, 从 ND—2.89 ng·g$^{-1}$ ww, 其中 TBEP 检出率最高. 广东清远[104]藏香鸡(*Gallus gallus domesticus*)和金定鸭(*Anas platyrhynchos domesticus*)体内 TNBP、TBEP 和 TPHP 为主要组分, 其浓度分别为 11.7—281、48.1—266、ND—209 ng·g$^{-1}$ lw. 重庆某农业区[65]鸡体内的 OPEs, 浓度为 676 ng·g$^{-1}$ lw. 广东清远[105]电子废弃物回收区域鸡蛋中 OPEs 浓度范围分别为 0.48—15.8 ng·g$^{-1}$ ww, 其中 TCEP 浓度最高. 对中国西南长江上游[106]地区的黑冠夜鹭卵(*Nycticorax nycticorax*)、小白鹭卵(*Egretta garzetta*)、中国池鹭卵((*Ardeola bacchus*)和牛白鹭卵(*Bubulcus ibis*)中 OPEs 进行检测, 平均浓度分别为 51、38、34、47 ng·g$^{-1}$ ww. 与国内外其他地区 OPEs 检出相比, 检出浓度较高, 可能归因于长江周围的工业程度高, 鸟类摄取的食物种类多样化.

广州清远电子废物拆解区[107]中黑斑蛙(*Rana nigromaculata*)和牛蛙(*Rana catesbeiana*)肌肉中, OPEs 浓度范围分别为 0.62—4.9 ng·g$^{-1}$ ww 和 1.7—15 ng·g$^{-1}$ ww, 且同一采样区域中几种野生昆虫物种[108]中的 OPEs 浓度范围为 54—773 ng·g$^{-1}$ ww. 挪威斯瓦尔巴特群岛[109]北极狐(*Vulpes lagopus*)体内 OPEs 进行检测, 发现 OPEs 的检出率较低, 仅为 17%. 北极狐肝脏中 TBEP 浓度最高, 浓度为(955±294)ng·g$^{-1}$ lw, 可能受到海洋垃圾暴露影响. 可以看出, OPEs 在环境介质中的浓度较高, 但在生物体中检出浓度却大多处于比较低的水平, 这可能是由于 OPEs 在生物体内快速代谢转化[110].

目前关于 OPEs 在陆生生物中的研究仍十分匮乏, 目前大多数的研究结果显示, OPEs 在陆生生物中的浓度也处于相对较低的水平, 这与对水生生物的研究结果相似. 表明 OPEs 在不同类型的生物体内均能够发生快速的代谢转化. 北美五大湖[110]银鸥的脂肪中 OPEs 浓度为(32.3±9.8)ng·g$^{-1}$ ww, 而在肝脏中的检出低于检出限. 暴露实验里小鼠[111]中 OPEs 主要富集在肾脏上. OPEs 在不同物种的组织分布之间也存在着差异. 鸟类[111]体内 OPEs 可能存在一定的亲脂性, 而水生生物[16]中的结果却有所不同. 这可能是由于 OPEs 的物理化学性质差异较大, 导致 OPEs 在水生和陆生生物中不同的暴露、富集和清除模式, 进而导致 OPEs 在水生和陆生生物中不同的迁移转化规律, 这一点目前尚未见有相关的研究报道.

### 2.3　人体

环境中的 OPEs 可以通过饮食、呼吸、皮肤接触及灰尘摄入等方式进入人体[112－113], 目前国内外已有较多关于人体暴露的文献报道, 在人体尿液[114－115]、血液[116]、母乳[117－119]、胎盘[120]、头发[121－122] 等样品中均检测到 OPEs. 澳大利亚[114] 昆士兰州 0—5 岁儿童的尿液中检出部分 OPEs, 主要包括磷酸三(1,3-二氯-2-丙基)酯(TDCPP)、TCEP、TEHP、TMP 和 EHDPHP 等目标化合物, 最高浓度分别为 0.069、0.90、0.61、0.020、1.4 ng·mL$^{-1}$. 瑞典[119] 城镇居民母乳中 OPEs 的浓度范围为 46—108 ng·g$^{-1}$ lw. 美国[117] 母乳中 OPEs 的浓度范围为 0.67—7.83 ng·mL$^{-1}$. 不同地区居民体内 OPEs 的浓度存在一定差异, 可能与 OPEs 在当地的使用量有关. 这个结果同样体现于一项日本、菲律宾和越南居民母乳的研究中, 菲律宾居民母乳样品中 OPEs 的浓度(70 ng·g$^{-1}$ lw)显著高于日本(22 ng·g$^{-1}$ lw)和越南[118](10 ng·g$^{-1}$ lw), 同时菲律宾含有 OPEs 的产品的使用量也高于日本和越南. 现有的研究结果显示, OPEs 在不同地区人群体内的组成情况也存在较大差异. 瑞典[119] 居民母乳中 TCPP 和 TNBP 的比例相对较高; 美国[117] 居民母乳中 OPEs 以 TBEP 为主, 其次是 TiBP 和 TNBP; 而亚洲地区 TCEP 的占比则相对较高, 如日本、菲律宾和越南[118] 居民母乳中 TCEP 和 TPHP 两种化合物的浓度相对较高, 在这 3 个国家 60% 以上的母乳中均能够检出. 而我国东部地区[120] 电子拆解区人群胎盘中 TCEP 的浓度同样最高, 浓度中值数达到 142 ng·g$^{-1}$ lw, 其次是 TBEP 和 TPHP. 不同地区居民体内 OPEs 浓度和组成的差异可能是由于不同国家或地区使用不同类型的 OPEs 工业品所导致.

## 3　有机磷酸酯的生物转化 (Biotransformation of OPEs)

由于 OPEs 能够在生物体内发生快速代谢转化[16], 近年来研究人员开始更多关注生物体内 OPEs 的代谢物, 并取得了一系列研究进展. 目前鉴定出的 OPEs 代谢物(mOPEs)主要为 DAPs 和 HO-OPEs[124]. Van den Eede 等[124] 采用人体肝微粒体对 TBEP、TPHP、TCEP、TCPP 和 TDCPP 进行体外代谢研究, 通过液相色谱-飞行时间质谱筛查和鉴定可能的Ⅰ相和Ⅱ相代谢物, 并根据分子式, 同位素模式和质谱图的质量准确度初步鉴定得到 TBEP 的 O-脱烷基化和羟基化代谢产物; TPHP 的 O-脱芳基转化二酯和羟基化代谢物; TCPP 的氧化脱卤产物; 以及 TDCPP 的二酯代谢产物. 同时发现 TCEP 很难代谢转化为二酯和氧化脱卤产物. 对于Ⅱ相代谢, Ⅰ相代谢物是葡萄糖醛酸化和硫酸化的底物. 其中醚裂解和碳羟基化的产物, 如 TBEP8 和 TPRP4、TNBP4、TBEP7, 可进一步与葡萄糖醛酸联合, 得到Ⅱ相代谢物 TBEP5 和 TPRP3、TNBP3、TBEP6. 部分 OPEs 与其Ⅰ相代谢产物的对应关系见表 5.

近年来部分研究结果显示, 生物体内 mOPEs 的含量高于其母体化合物. 如 Stubbings 等[123] 在白头海雕蛋中检出了高浓度的 mOPEs, Li 等[125] 对鸡蛋的研究同样发现 mOPEs 浓度大多高于其母体化合物. DAPs 目前已被认为是评估 OPEs 暴露的重要生物标志物[126－127]. 美国[128] 和澳大利亚[114] 的人体尿液样品中均检出较高浓度 mOPEs, 并且尿液中 mOPEs 浓度与室内灰尘中的 OPEs 浓度具有较强相关性, 表明暴露于人体中的 OPEs 经代谢转化后, 由尿液排出体外. 总体而言, mOPEs 的亲水性高于 OPEs, 更易于被排出体外[129]. 我国人群研究结果显示, 广东[130] 电子拆解区域怀孕女性尿液中 mOPEs 浓度的几何平均值为 6.1 ng·mL$^{-1}$, 磷酸二正丁酯(DNBP)浓度最高, 浓度为 2.9 ng·mL$^{-1}$, 其次是磷酸二苯酯(DPHP)(0.94 ng·mL$^{-1}$)和双(1, 3-二氯-2-丙基)磷酸酯(BDCIPP)(0.27 ng·mL$^{-1}$), 表明 TNBP 的暴露水平较高; Ya 等[131] 对江苏省成人尿液的研究发现, 磷酸双(2-乙基己基)酯(DEHP)、DPHP 和 DNBP 这 3 种 mOPEs 的检出率大于 60%, 其中 DEHP 浓度最高, 中值浓度为 1.2 ng·mL$^{-1}$. 从多元回归分析中观察到, DPHP 与 TPHP 以及 DPHP 与 EHDPHP 之间的相关性增加, 表明 DPHP 可能源自 TPHP 和 EHDPHP 的代谢.

OPEs 生物转化研究主要包括体外代谢和体内代谢两个方面. Su 等[132] 发现 TPHP 在鸡胚肝细胞中被快速代谢, 36 h 后仅剩余原始剂量的 0.2%; Greaves 等[133] 使用鲱鸥肝微粒体研究 OPEs 体外代谢, 结果显示在 100 min 孵育期内, TNBP 代谢速度最快, 耗尽率为(73±4)pmol·(min·mg)$^{-1}$ 蛋白质, 其次是 TBEP、TCPP、TPHP 和 TDCPP; Sasaki 等[18] 采用大鼠肝微粒体对 OPEs 进行体外代谢研究, 结果同样显示 TNBP 代谢效率最快, 其次是 TPHP 和 TDCPP, 表明不同 OPEs 生物转化效率存在一定差异. 仅有的几项体内代谢研究表明, OPEs 在生物体内快速代谢转化为对应的二酯和羟基化代谢产物. Farhat

等[134]将 TCPP 和 TDCPP 注射到鸡蛋中并进行孵化实验,结果发现在孵化第 5 d 仍可检出超出 92% 的暴露剂量,但在孵化第 19 d 蛋内目标物浓度以不足暴露量的 1%.

**表 5** 有机磷酸酯及其 I 相对应代谢产物

**Table 5** OPEs and their phrase I respective metabolites

| 目标化合物缩写 Parent compound abbreviation | 物种 Species | 方式 Methods | 主要代谢产物 Major metabolites | 参考文献 References |
|---|---|---|---|---|
| TNBP | 鲤鱼 | 体内代谢 | 磷酸二正丁酯(DNBP) | [137] |
| | 老鼠肝脏 | 体外代谢 | 2-羟基磷酸三丁酯(di-OH-TNBP) | [18] |
| TPHP | 鲤鱼 | 体内代谢 | 4-羟基磷酸二苯酯(4-HO-DPHP)、磷酸二苯酯(DPHP)、磷酸二苯酯(DPHP)、4-羟基磷酸二苯酯(4-HO-TPHP) | [137] |
| | 鸡胚胎肝细胞 | 体外代谢 | DPHP、羟基磷酸二苯酯(OH-TPHP)、2-羟基磷酸二苯酯基(di-OH-TPHP) | [18] |
| TCEP | 鲤鱼 | 体内代谢 | 双(2-氯乙基)磷酸酯(BCEP) | [137] |
| | 人肝微粒体 | 体外代谢 | BCEP、羟基磷酸三(2-氯乙基)酯 (OH-TCEP) | [124] |
| | 人肝微粒体 | 体外代谢 | BCIPP、羟基磷酸三(2-氯异丙基)酯(OH-TCIPP)、烃基磷酸三(2-氯异丙基)酯(COOH-TCIPP)、、羟基双(1-氯-2-丙基)磷酸酯(OH-BCIPP) | [124] |
| TDCPP | 鲤鱼 | 体内代谢 | 双(1, 3-二氯-2-丙基)磷酸酯(BDCIPP) | [137] |
| | 人肝微粒体 | 体外代谢 | BDCIPP、羟基磷酸三(1,3-二氯-2-丙基)酯(OH-TDCIPP)、羟基双(1, 3-二氯-2-丙基)磷酸酯(OH-BDCIPP) | [124] |
| TBEP | 鲤鱼 | 体内代谢 | 双(丁氧乙基)磷酸酯(BBOEP)、2-羟乙基双(2-丁氧基乙基)磷酸酯(BBOEHEP)、3-羟基-2-丁氧基乙基酯(3-HO-TBOEP) | [137] |
| | 人肝微粒体 | 体外代谢 | BBOEP、BBOEHEP、羟基磷酸三(2-丁氧基乙基)酯TBOEP(1-HO-TBEP)、2-羟基磷酸三(2-丁氧基乙基)酯(2-HO-TBEP)、3-磷酸三(2-丁氧基乙基)酯(3-HO-TBEP) | [124] |
| TEHP | 鲤鱼 | 体内代谢 | 磷酸双(2-乙基己基)酯(DEHP) | [137] |
| EHDPHP | 鲤鱼 | 体内代谢 | 2-乙基己基苯基磷酸酯(EHDPP)、2-乙基-5-羟基己基磷酸二苯酯(5-HO-EHDPHP) | [137] |
| TMP | 鲤鱼 | 体内代谢 | 磷酸二(甲基苯基)酯(BMPP) | [137] |

Wang 等[135]对斑马鱼进行 TPHP 暴露研究,在暴露期内肠道和肝脏均能检出 TPHP,而其主要代谢产物 DPHP 浓度达到母体化合物的 3—3.5 倍. 经过 3 d 净化期后,鱼体内 TPHP 和 DPHP 浓度均大幅下降,同时水中 DPHP 浓度明显升高,表明 TPHP 被快速的代谢清除出体外. Wang 等[136]进一步将成年斑马鱼暴露于多种 OPEs 中,发现 DNBP、双(1, 3-二氯-2-丙基)磷酸酯(BDCIPP)、DPHP 为主要代谢产物. 在肝脏和肠道中均有检出,在暴露期内代谢产物浓度为其母体化合物的 1.2—2 倍. 但在 3 d 净化期结束后,鱼体内代谢产物和母体化合物检出降低. Tang 等[137]对鲤鱼暴露环境相关浓度的多种 OPEs,在暴露期内的肠道和肝脏中检出了 BDCIPP、DPHP 等代谢产物. 经 3 d 净化期后,鱼体组织中未检测到代谢产物,表明 OPEs 被鱼体快递的代谢清除. 上述研究结果均表明鱼类肝胆系统对 OPEs 的代谢和排泄具有重要作用[138]. 生物转化过程会影响鱼类体内疏水亲水性有机化学物质的积累程度[139],代谢产物可能也更具亲水性,因此比母体化合物更快地从组织中代谢.

## 4 结论与展望 (Conclusions and prospects)

作为一类新型的有机磷阻燃剂,环境中 OPEs 的浓度随着生产量和使用量的增加而逐年增大. OPEs 的生物体研究主要集中于人体和水生生物的暴露水平检测,对水生生物的生物富集和生物代谢有较为系统的研究,但是陆生生物的研究在各方面还较为匮乏. 总结相关研究进展,建议未来 OPEs 研究重点考虑以下几个方面: (1) 通过体内或体外实验研究 OPEs 在生物体内的代谢转化途径和潜在代谢产物; (2) 研究 OPEs 在陆生生物中的生物富集及其与水生生物的异同; (3)OPEs 代谢产物的生物毒性研究.

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