

有机磷酸酯在环境/生物相中的分布、分析方法及毒理效应*

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摘要 有机磷酸酯(organophosphate esters, OPEs)主要作为阻燃剂及增塑剂等而被广泛使用,且极易释放于环境。近年来,由于溴系阻燃剂的禁用,有机磷酸酯类阻燃剂的产量及消费量大幅增加,OPEs已经成为一种新兴污染物并受到广泛关注,多篇文献报道了其在环境及生物相中的分布和毒理效应。本文主要对OPEs在地表水、沉积物、大气及生物相中的分布、分析方法及毒理效应进行综述,并对未来OPEs分布及毒理学研究进行展望,以为后续该类物质的研究提供借鉴。

关键词 有机磷酸酯;分布;分析方法;毒性

有机磷酸酯(organophosphate esters, OPEs)是以磷为中心原子的一类有机物,其结构通式见图1。常见的OPEs化合物有磷酸三甲酯(TMP)、磷酸三(1-氯-2-丙基)酯(TCPP)、磷酸三(2-氯乙基)酯(TCEP)、磷酸三(1,3-二氯-2-丙基)酯(TDCPP)、磷酸三异丁酯(TiBP)、磷酸三正丁酯(TnBP)、磷酸三丁氧乙酯(TBEP)、磷酸三己基酯(THP)、磷酸三戊基酯(TPeP)、磷酸三(2-乙基己基)酯(TEHP)、磷酸三苯酯(TPhP)、磷酸三甲苯酯(TCrP)及三苯基氧磷(TPPO)等。根据其取代R基团的不同,可大致分为烷基取代、含卤烷基取代以及芳基取代等,这也决定了不同OPEs的性质有很大差异。如TMP分子量最小,辛醇-水分配系数($\log K_{ow}$)为-0.65,这导致其易溶于水且极易挥发。而对于较大分子量的OPEs,如TEHP,其 $\log K_{ow}$ 为9.49,故其水溶性很差且不易挥发。不同的OPEs的理化性质见表1。

OPEs用途广泛(表1),但其主要作为阻燃剂、增塑剂等应用于纺织、化工、电子及建筑等行业^[1],如磷酸三氯代烷基酯及磷酸三芳基酯作为添加型阻

燃剂被广泛应用于塑料、电子产品、纺织物、建筑及家装材料等^[2]。而非氯代烷基磷酸酯则更多作为增塑剂及抗发泡剂等发挥作用,如TBEP及TnBP等^[3,4]。此外,一些OPEs还有其他用途,如TEHP作为抗真菌剂发挥作用^[1],而乙烯四乙基二磷酸酯(TEEdP)则被添加于化妆品中^[5]。

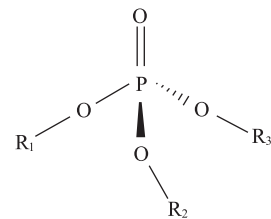


图1 有机磷酸酯的结构通式

Fig. 1 Chemical structure of organophosphate esters

近年来,随着一系列消防安全法案的出台以及联合国环境规划署及世界各国对溴系阻燃剂的禁用^[6,7],有机磷酸酯类阻燃剂的产量(图2)^[8]及消费量(图3)^[9]大幅增长。在全球范围内,其消费量已与溴系阻燃剂相当。我国2013年阻燃剂的消费

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量占世界总量的 27%, 与西欧 (22%) 及北美 (22%) 共列为世界三大阻燃剂消费国家和地区 (图 3)^[9]。中国 2010 ~ 2013 年阻燃剂消费增长率为 15%, 远远高于世界平均水平 (3%)。预计至 2018 年, 中国仍将作为最大消费国占有世界约 30% 阻燃剂消费份额, OPEs 作为阻燃剂在中国将有着巨大的需求^[9]。与此同时, 世界卫生组织及若干研究组对 OPEs 致癌性及神经毒性的报道屡见不鲜 (表 1)。OPEs 已经对环境安全和人类健康构成了潜在的威胁^[8]。

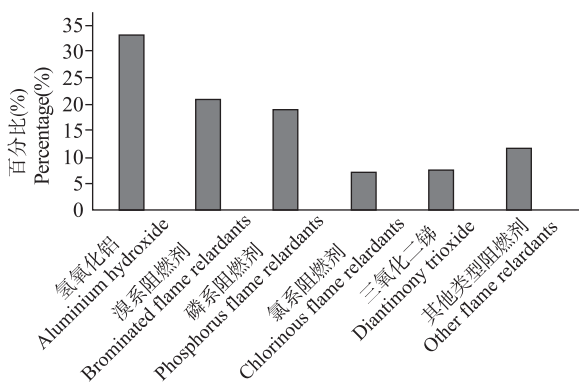


图 2 世界不同类型阻燃剂的消费量 (2013 年)

Fig. 2 Consumption of different flame retardants in worldwide

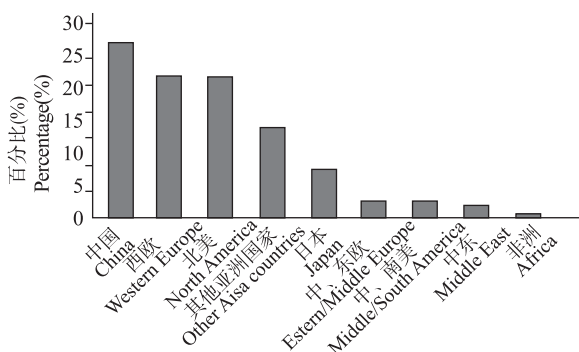


图 3 世界各国和地区阻燃剂消费量 (2013 年)

Fig. 3 Consumption of flame retardants worldwide

1 OPEs 在环境及生物相中的分布和富集

对 OPEs 环境分布的报道最早出现于 1978 年, 根据该报道, 美国德拉瓦河中 3 种 OPEs 的浓度范围为 $0.06 \sim 3 \mu\text{g L}^{-1}$ ^[10]。随后, 由于相关研究认为大部分芳烃基及烷基取代的 OPEs 可在自然环境中降解, 20 世纪 80 年代至 90 年代末, 人们对 OPEs 的关注度逐渐减小。直至 1997 年, Carlsson 等^[11]在室内空气中检测出较高浓度的 TCEP, 及 2000 年欧

盟将氯代 OPEs 列入优先控制污染物名单^[12], 有关 OPEs 环境分布的研究才重新得到重视。至今, 随着 OPEs 作为阻燃剂及增塑剂等被大规模应用, 多篇论文报道了其在地表水、沉积物、空气及生物相中的分布。总体而言, TCEP, TCPP, TDCPP, TPhP 及 TPPO 在环境及生物相中检出率较高, 同时这些物质也具有较高的浓度。

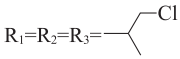
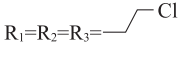
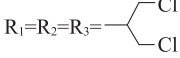
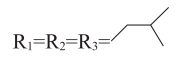
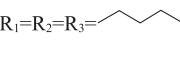
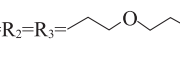
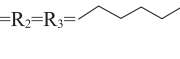
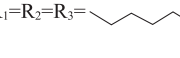
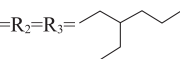
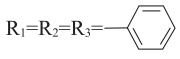
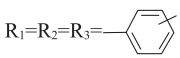
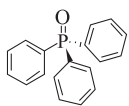
1.1 OPEs 在地表水中的分布

自 2000 年以来, 已经有较多的研究证明 OPEs 在地表水中广泛存在^[13-19]。Fries 等报道了德国 Oder 河 Frankfurt, Nieschen 及 Bahnbrücke 段水样及其周边地区雨水及屋顶径流中 TBP, TCEP 及 TBEP 的分布情况 (图 4a)^[13]。Bacaloni 等分析了意大利 Tiber 河中 12 种 OPEs 的含量, 发现 TBEP, TiBP 及 TnBP 等为主要污染物 (图 4b), 并指出 OPEs 的含量与季节变化无明显关联^[14]。Regnery 等对德国城市和农村湖泊的 OPEs 进行了对比研究, 监测发现城市的湖泊中 OPEs 含量显著高于农村湖泊, 说明位于人口密集城市地区的湖泊可能更易受到该类物质的污染, 且 TCEP 及 TCPP 为主要 OPEs 污染物 (图 4c)^[15]。Bollmann 等分析了德国 6 条河流的 OPEs, 发现 TCPP 及 TPPO 为主要的污染物 (图 4d)^[16]。Cristale 等在英国 Aire 河中检出 TCEP, TCPP, TDCPP 和 TPhP 等化合物, 其中 TCPP 的浓度最高达 26050 ng L^{-1} (图 4e), 远远高于该河流中 BDE-209 的含量 ($17 \sim 295 \text{ ng L}^{-1}$)^[17]。而 Wang 等分析了环渤海 40 条河流中 12 种 OPEs 的含量, 发现 TCPP, TCEP 及 TPPO 为主要污染物 (图 4f), 并指出 TPPO 作为有机合成及制药产业的中间产物可能具有独立的污染源^[18]。

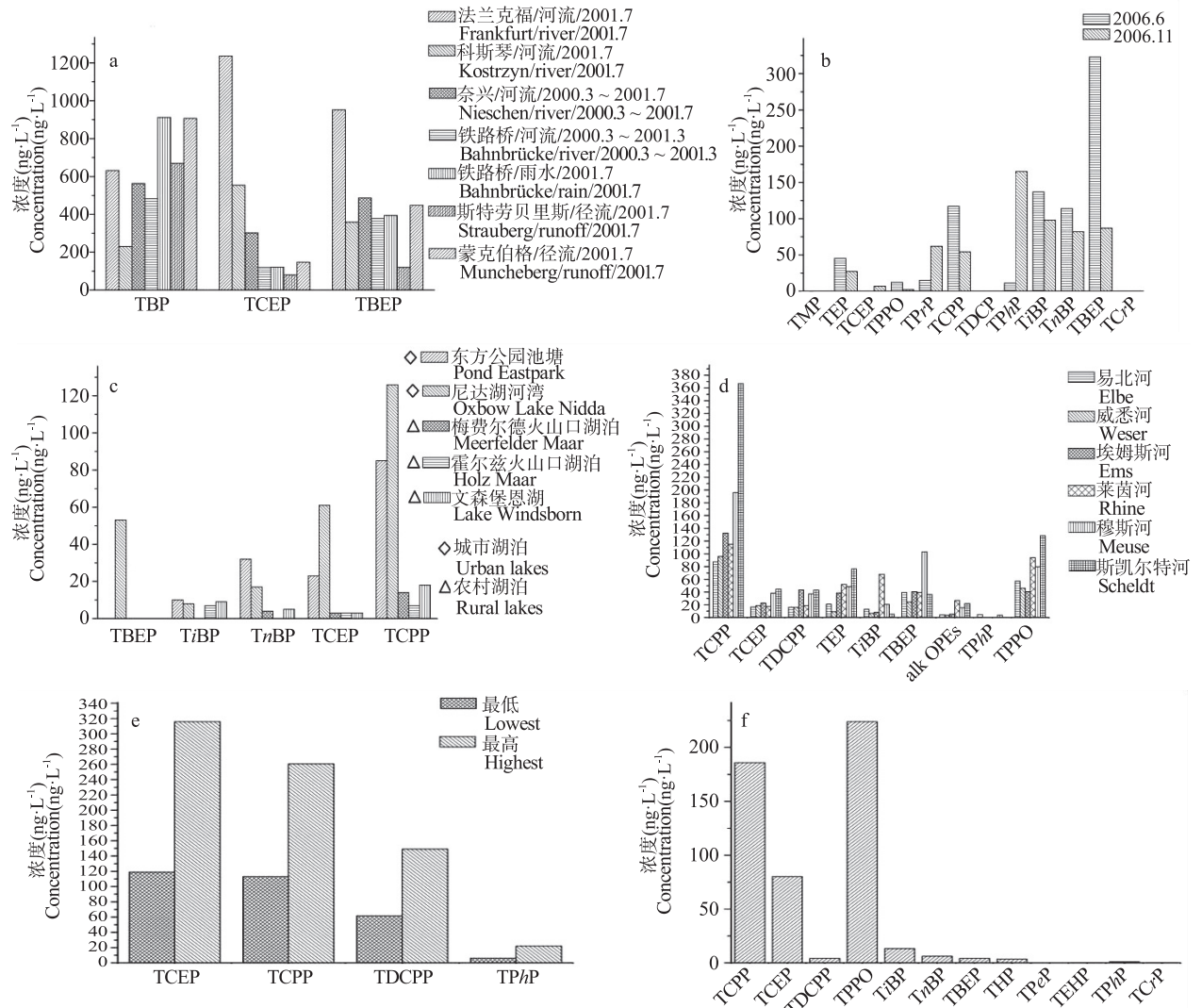
此外, Bacaloni, Regnery 及 Bollmann 等均分析讨论了 OPEs 浓度随季节变化的现象^[14-16]。而 Kawagoshi 和 Fries 等还分别对地表水中 OPEs 的时空迁移和转化进行了研究: Kawagoshi 等发现水溶性较强的 OPEs 从填埋点释放后主要以溶解态存在于水体中, 且只有 TCPP 在水体和悬浮颗粒物中的浓度具有显著联系, 而沉积物中更易积累水溶性较差的 OPEs, 并据此推断 K_{ow} 较大的 OPEs 可能是与垃圾填埋场产生的固体废物一起直接沉降富集在底部沉积物中, 其在水体中的迁移性并不强^[19]。而 Fries 等则通过分析河水、井水、雨水及屋顶径流中 OPEs 的含量, 推断 OPEs 可能通过渗滤作用从河水向地下水迁移^[13]。

表 1 OPEs 的理化性质、毒性及应用

Table 1 Physical and chemical structure, toxicity and application of OPEs

名称(英文缩写) Name(Abbreviation)	化学检索号 CAS No.	化学结构 Chemical structure	理化特征 Physical and chemical characteristics	毒性 ^[17, 22-25] Toxicity	应用 ^[16, 26, 27] Application
磷酸三(1-氯-2-丙基)酯 (T CPP)	13674-84-5		$\log K_{OW} = 2.59$ $W_S = 1.2 \text{ g L}^{-1}$ $V_P = 2.7 \times 10^{-3} \text{ Pa}$	疑似致癌性 Suspected carcinogenicity	阻燃剂、增塑剂 Flame retardants, plasticizer
磷酸三(2-氯乙基)酯 T CEP	115-96-8		$\log K_{OW} = 1.44$ $W_S = 7.0 \text{ g L}^{-1}$ $V_P = 8.2 \text{ Pa}$	致癌性、神经毒性 Carcinogenicity, neurotoxicity	阻燃剂、增塑剂、油漆 颜料、胶水、工业过程 Flame retardants, plasticizer paint, glue, industrial process
磷酸三(1,3-二氯-2-丙基)酯 T DCPP	13674-87-8		$\log K_{OW} = 3.65$ $W_S = 7.0 \times 10^{-3} \text{ g L}^{-1}$ $V_P = 9.8 \times 10^{-6} \text{ Pa}$	致癌性、神经毒性 Carcinogenicity, neurotoxicity	阻燃剂、增塑剂、油漆 颜料、胶水 Flame retardants, plasticizer paint, glue
磷酸三异丁酯 T iBP	126-71-6		$\log K_{OW} = 3.6$ $W_S = 1.6 \times 10^{-2} \text{ g L}^{-1}$ $V_P = 1.71 \text{ Pa}$	n. a.	油漆、颜料、胶水、 阻泡剂、工业过程 Paint, glue, foam inhibitor industrial process
磷酸三正丁酯 T BP (T nBP)	126-73-8		$\log K_{OW} = 4.0$ $W_S = 0.28 \text{ g L}^{-1}$ $V_P = 0.15 \text{ Pa}$	疑似神经毒性 Suspected neurotoxicity	增塑剂、液压剂、油漆 颜料、胶水 阻泡剂、工业过程 Plasticizer, hydraulic pressure, paint, glue, foam inhibitor, industrial process
磷酸三丁氧乙酯 T BEP	78-51-3		$\log K_{OW} = 3.75$ $W_S = 1.1 \text{ g L}^{-1}$ $V_P = 3.3 \times 10^{-6} \text{ Pa}$	疑似致癌性 Suspected carcinogenicity	阻燃剂、增塑剂、抗真菌剂、 油漆、颜料、胶水、阻泡剂 Flame retardants, plasticizer antifungal agent, paint, glue, foam inhibitor
磷酸三己基酯 T HP	2528-39-4		n. a.	n. a.	n. a.
磷酸三戊基酯 T PeP	2528-38-3		$\log K_{OW} = 5.29$ $W_S = 3.3 \times 10^{-4} \text{ g L}^{-1}$ $V_P = 2.2 \times 10^{-3} \text{ Pa}$	n. a.	n. a.
磷酸三(2-乙基己基)酯 T EHP	78-42-2		$\log K_{OW} = 9.49$ $W_S = 6.0 \times 10^{-4} \text{ g L}^{-1}$ $V_P = 1.1 \times 10^{-5} \text{ Pa}$	n. a.	阻燃剂、增塑剂、抗真菌剂 Flame retardants, plasticizer antifungal agent
磷酸三苯酯 T PP (T PhP)	115-86-6		$\log K_{OW} = 4.59$ $W_S = 1.9 \times 10^{-3} \text{ g L}^{-1}$ $V_P = 8.4 \times 10^{-4} \text{ Pa}$	疑似神经毒性 Suspected neurotoxicity	阻燃剂、增塑剂、液压剂、 油漆、颜料、胶水 Flame retardants, plasticizer hydraulic pressure, paint, glue
磷酸三甲苯酯 T CP (T CP)	1330-78-5		$\log K_{OW} = 5.11$ $W_S = 3.6 \times 10^{-4} \text{ g L}^{-1}$ $V_P = 8.0 \times 10^{-5} \text{ Pa}$	n. a.	阻燃剂、液压剂、油漆 颜料、胶水、工业过程 Flame retardants, hydraulic pressure, paint, glue, industrial process
三苯基氧磷 T PPO	791-28-6		$\log K_{OW} = 2.83$ $W_S = 6.3 \times 10^{-2} \text{ g L}^{-1}$ $V_P = 3.47 \times 10^{-7} \text{ Pa}$	对水生生物具有毒性 Toxicity to aquatic organism	阻燃剂、金属配体、提取剂、 合成中间体、助结晶剂 Flame retardants, metal ligand, extractant, synthetic intermediates, crystallization agent

注: n. a. : 该栏不适用 Note: n. a. : not applicable



注: a: Oder 河水样及其周围雨水及屋顶径流中 OPEs 平均含量; b: Tiber 河中 OPEs 平均含量; c: 德国城区及农村湖水 OPEs 的含量; d: 德国 6 条河流中 OPEs 平均含量; e: 英国 Aire 河 OPEs 含量; f: 环渤海 40 条河流 OPEs 平均含量

Note: a; mean content of OPEs in River Oder and nearby rain water and roof runoff; b; mean content of OPEs in River Tiber; c; OPEs in German urban and suburban lakes; d; mean content of OPEs in 6 rivers in German; e; OPEs in River Aire in Britain; f; mean content of OPEs in 40 rivers around Bohai Sea in China

图 4 地表水中 OPEs 的分布

Fig.4 Distribution of OPEs in surface water

1.2 OPEs 在空气中的分布

对于 OPEs 在室内空气分布的报道较多,其在空气中主要以两种形式存在,即以蒸气态直接存在于空气中和以附着在空气灰尘上的形式存在于空气中。其中 TnBP, TCEP, TCPP, TDCPP, TBEP 及 TPp/P 等物质均有检出(表 2)。新西兰室内空气灰尘中各 OPEs 的含量均较高^[20],而美国室内空气灰尘中 TPp/P 则高达 $1.798 \times 10^6 \text{ ng g}^{-1}$ ^[21]。总体而言,空气中卤代 OPEs (TCEP 及 TCPP) 的含量要高

于其他 OPEs,而空气中灰尘附着的 OPEs 要高于以蒸气态存在的 OPEs。

对于 OPEs 在野外空气中的报道相对较少,Castro-Jiménez 等人报道了地中海、黑海及爱琴海大气中 OPEs 的分布。在该区域大气中,多达 14 种 OPEs 被检出,其中 TCPP 在该区域具有很高的丰度,且 TCPP 及 TCEP 在所有样品中均有检出,这表明卤代 OPEs 可能是该区域大气中主要存在的 OPEs^[28]。

表2 OPEs在室内空气的分布(单位: ng m^{-3})
Table 2 Distribution of OPEs in indoor air (unit: ng m^{-3})

磷酸三正丁酯 TnBP	磷酸三 (2-氯乙基)酯 TCEP	磷酸三 (1-氯-2-丙基)酯 TCPP	磷酸三 (1,3-二氯-2-丙基)酯 TDCPP	磷酸三丁氧乙酯 TBEP	磷酸三苯酯 TPhP	参考文献 Reference
1.8 ~ 100 ^a	1.4 ~ 30 ^a	n. d.	n. d.	0.4 ~ 30 ^a	1.2 ~ 10 ^a	[29]
0.2 ~ 120 ^a	0.4 ~ 730 ^a	5.1 ~ 570 ^a	0.2 ~ 150 ^a	0.2 ~ 55 ^a	0.1 ~ 23 ^a	[30]
7 ~ 35 ^a	11 ~ 250 ^a	14 ~ 41 ^a	n. d.	1.4 ~ 5.9 ^a	0.5 ~ 0.8 ^a	[11]
9 ~ 18 ^a	15 ~ 36 ^a	14 ~ 28 ^a	n. d.	20 ~ 36 ^a	12 ~ 40 ^a	[31]
0.1 ~ 29 ^a	0.2 ~ 56 ^a	0.1 ~ 260 ^a	0.1 ^a	3 ^a	1.5 ~ 5.7 ^a	[32]
1 ~ 172 ^a	1 ~ 870 ^a	1 ~ 2300 ^a	5 ~ 7 ^a	1 ~ 130 ^a	1 ~ 17 ^a	[33]
4 ~ 138 ^a	11 ~ 110 ^a	10 ~ 112 ^a	n. d.	0.8 ~ 46 ^a	0.5 ~ 35 ^a	[34]
0.4 ~ 30.6 ^a	0.7 ~ 136 ^a	0.9 ~ 1260 ^a	0.6 ^a	0.6 ~ 14 ^a	5.4 ^a	[35]
n. d.	n. d.	52 ^a	n. d.	n. d.	n. d.	[36]
2.0 ~ 80 ^a	2.0 ~ 33 ^a	2.0 ~ 45 ^a	n. d. ~ 30 ^a	2.0 ~ 1279 ^a	n. d. ~ 0.9 ^a	[37]
0.07 ~ 2.2 ^b	0.2 ~ 94 ^b	0.5 ~ 73 ^b	0.2 ~ 67 ^b	14 ~ 5300 ^b	0.9 ~ 110 ^b	[1]
n. d.	0.1 ~ 121 ^b	0.1 ~ 375 ^b	n. d.	n. d.	n. d.	[36]
0.04 ~ 0.9 ^b	0.1 ~ 40 ^b	1.2 ~ 40 ^b	0.05 ~ 11 ^b	1.6 ~ 48 ^b	0.4 ~ 4.9 ^b	[38]
0.07 ~ 0.65 ^b	0.25 ~ 9.8 ^b	0.35 ~ 10.3 ^b	0.05 ~ 1.1 ^b	1.2 ~ 19 ^b	0.3 ~ 9.5 ^b	[39]
20 ~ 7545 ^b	20 ~ 7605 ^b	20 ~ 7615 ^b	20 ~ 16560 ^b	50 ~ 27325 ^b	20 ~ 35190 ^b	[20]
0.3 ~ 3.7 ^b	0.1 ~ 8.3 ^b	0.7 ~ 47.0 ^b	3.9 ~ 150 ^b	1.6 ~ 4711 ^b	0.3 ~ 64.5 ^b	[37]
n. d.	n. d.	140 ~ 5490 ^b	90 ~ 56090 ^b	n. d.	150 ~ 1798000 ^b	[21]

注: a: 空气中 OPEs 的含量; b: 空气灰尘中 OPEs 的含量; n. d.: 未检测到

Note: a: content of OPEs in air; b: content of OPEs in air dust; n. d.: not detecte

1.3 OPEs 在沉积物中的分布

国内外对于沉积物中 OPEs 污染状况的报道最早出现于 1985 年, Ishikawa 等首先在环境沉积物中检测到 TCEP ($13 \sim 28 \text{ ng g}^{-1}$) 及 TCPP ($9 \sim 17 \text{ ng g}^{-1}$)^[40]。此后, Kawagoshi 等在海洋垃圾固体填埋场检出高浓度的 TBEP (7.4 ng g^{-1}) 及 TCPP (2.0 ng g^{-1}), 并指出上述两种物质是沉积物中检出的主要的化合物^[19]。而 Martínez-Carballo 等同样在奥地利河流沉积物中检出高达 8.7 ng g^{-1} 的 TBEP, 20 ng g^{-1} 的 TCPP 及 50 ng g^{-1} 的 TBP^[41]。García-Lopez 等分析了西班牙 Galicia 地区河流及入海口沉积物中 OPEs 的分布状况, TnBP (7.8 ng g^{-1}), TCEP (45.9 ng g^{-1}), TPhP (6.4 ng g^{-1}) 及 TCPP (6.4 ng g^{-1}) 均有检出^[42]。Chung 等则报道了台湾西南海岸带区域海水沉积物中 TCPP, TCEP, TDCPP 及 TPhP 的分布, 其中 TCPP 浓度高达 9.5 ng g^{-1} ^[43]。2012 年, Cao 等首次报道了太湖沉积物中 7 种 OPEs 的含量, 研究指出 TBEP ($3.38 \sim 14.25 \text{ ng g}^{-1}$), TCEP ($0.62 \sim 3.17 \text{ ng g}^{-1}$) 及 TCPP (MQL $\sim 2.27 \text{ ng g}^{-1}$) 为主要污染物, 并推断人类活动对沉积物中 OPEs 的分布具有重要影响^[44]。由此可以看出, TCPP, TCEP 及 TBEP 为沉积物中主要 OPEs。

此外, Kawagoshi 及 Martínez-Carballo 等的研究均表明水溶性较差的 OPEs 如 TEHP 等, 倾向于在沉积物中富集^[19,41], 这也部分揭示了不同性质的

OPEs 在沉积物中的分布规律。

1.4 OPEs 在生物相中的分布

环境中的 OPEs 主要通过呼吸、食入和皮肤渗透等途径进入生物体内, 但是对其在生物相分布和富集的研究主要在近几年才开始展开。各研究中生物相 OPEs 的分布情况见表 3。Sundkvist 等在瑞典湖泊鱼肉内发现多种 OPEs 的富集, 其中 TPP 及 TCPP 的浓度较高, 最高浓度分别达 770 ng g^{-1} 及 180 ng g^{-1} , 并指出附近污染源的存在是鱼肉内 OPEs 高浓度富集的主要诱因^[45]。同时, 该课题组还研究了 OPEs 在瑞典妇女乳汁中的含量, 发现其中总 OPEs 达 $46 \sim 180 \text{ ng g}^{-1}$, 而 TCPP 及 TBP 含量较高, 分别最高达 82 ng g^{-1} 及 57 ng g^{-1} ^[45]。Kim 等对马尼拉湾多种海洋的生物中 OPEs 的分布进行了调查, 其关注的 9 种 OPEs 几乎在所有海洋生物中均有检出, 其中以 TnBP 为主要污染物, 其在生物体内的浓度最高可达 420 ng g^{-1} 。同时, 该研究还指出, 底栖生物体内可能更易富集 OPEs^[46]。Chen 等调研了 Huron 湖地区海鸥蛋中 OPEs 的含量, 其中 TCEP, TCPP 及 TBEP 为主要污染物, 其浓度分别最高达 0.6 ng g^{-1} 、 4.1 ng g^{-1} 及 2.2 ng g^{-1} ^[47]。Ma 等研究了中国珠江三角洲地区鱼类及家禽中 OPEs 的含量, 其中 TnBP, TCEP 及 TBEP 丰度较高, 在鱼类中分别达 2946 ng g^{-1} 、 4692 ng g^{-1} 及 8842 ng g^{-1} ^[48]。

但根据 Sundkvist 及 Ma 等的研究,处于上级生物链的人及家禽中 OPEs 含量却远低于该地区的鱼类,这提

示 OPEs 在生物相富集和分布的复杂性。

表 3 生物相中 OPEs 的分布(单位: ng g⁻¹)
Table 3 Distribution of OPEs in biota(unit: ng g⁻¹)

采样地点/采集生物 Sampling point/species	磷酸三乙酯 (TEP)	磷酸三正丁酯 (TnBP)	磷酸三(2-氯乙基)酯 (TCEP)	磷酸三(1-氯-2-丙基)酯 (TCPP)	磷酸三(1,3-二氯-2-丙基)酯 (TDCPP)	磷酸三丁氧乙酯 (TBEP)	磷酸三苯酯 (TPhP)	磷酸三(2-乙基己基)酯 (TEHP)	三苯基氧磷 (TPPO)	磷酸三己基酯 (THP)	磷酸三甲苯酯 (TCrP)
菲律宾马尼拉湾/鱼类 ^[46] Manila Bay, Philippines/ Fish	n. d. ~ 410	n. d. ~ 590	-	-	-	n. d. ~ 50	n. d. ~ 120	n. d. ~ 2000	-	-	n. d. ~ 16
瑞典/鱼类 ^[45] Sweden/Fish	-	1.6 ~ 4900	n. d. ~ 160	23 ~ 770	n. d. ~ 140	n. d. ~ 1000	4.2 ~ 810	-	-	-	n. d. ~ 137
瑞典/人类 ^[45] Sweden/Human	-	11 ~ 57	2.1 ~ 8.2	22 ~ 82	1.6 ~ 5.3	n. d. ~ 63	3.2 ~ 11	-	-	-	n. d. ~ 3.7
北美/海鸥蛋 ^[47] North America/Gull eggs	-	-	0.16 ~ 0.28	0.21 ~ 4.1	n. d. ~ 0.17	0.16 ~ 2.2	n. d. ~ 0.13	-	-	-	-
中国珠江三角洲/鱼类 ^[48] Zhujiang Delta, China/Fish	n. d. ~ 8.23	43.9 ~ 2946	82.7 ~ 4692	62.7 ~ 883	n. d. ~ 251	164 ~ 8842	n. d. ~ 45.7	n. d. ~ 3.61	n. d. ~ 12.9	n. d. ~ 1.39	n. d. ~ 83.5
中国珠江三角洲/家禽 ^[48] Zhujiang Delta, China/Poultry	n. d.	11.7 ~ 281	33.7 ~ 162	3.89 ~ 21.4	n. d. ~ 43.7	48.1 ~ 266	n. d. ~ 209	n. d. ~ 13.9	n. d. ~ 37.2	n. d. ~ 2.17	n. d. ~ 11.8

注:n. d.: 未检测到

Note: n. d.: not detected

2 OPEs 的分析方法

如前所述,有机磷酸酯广泛存在于环境及生物相内,因此检测环境及生物相内该类物质的浓度和分布具有重大的意义。现今,对该类物质的分析方法主要是气相色谱—质谱(GC-MS)串联及液相色谱—质谱(LC-MS)串联。但是,由于该类物质在环境和生物相内的含量较低,因此在对其进行分析时往往需要先对其进行富集萃取。对于水质样品,常用的分析方法有液液萃取及固相萃取等。对于大气样品,一般需采样富集后再进行萃取洗脱。而对于沉积物样品及生物样品,由于基质效应复杂,往往需要采用如凝胶渗透色谱(Gel permeation chromatography)以及其他净化柱预处理后才可进行分析。

2.1 水相中 OPEs 的分析方法

2.1.1 液液萃取

该方法是水样中有机磷酸酯萃取的传统方法,其主要流程可归纳为萃取、分液、旋蒸、去除水分、溶剂置换及氮吹定容等^[49]。但液相萃取具有显著的

缺陷,如需要大量的有机溶剂、产生泡沫及难以实现自动化等^[50]。此外,液液萃取对于极性分析物的回收率较低,如其对 TCEP 的回收率仅为 39%^[51]。因此,液液萃取逐渐被固相萃取所取代。

2.1.2 固相萃取

对于固相萃取,常用的富集介质有二乙烯基苯疏水盘、Oasis HLB 小柱、Supelco LC-18 及 Lichrolut RP-18 等^[52, 53]。其主要流程可归纳为溶剂平衡、介质富集、溶剂洗脱、去除水分、溶剂置换及氮吹定容等^[49]。因固相萃取具有样品保存时间长、溶剂需求小、回收率较高及重复性较好等特点,现已逐渐成为水相中 OPEs 前处理的主要方法。

2.2 大气中 OPEs 的分析方法

大气中 OPEs 的分析方法可归纳为介质富集、萃取洗脱、旋蒸、去除水分、溶剂置换及氮吹定容等^[49]。常见的富集介质有 Isolute NH₂^[30]、聚氨酯泡沫^[11, 34]、C8 Empore 固相萃取膜^[33, 54]、氨基硅胶^[55]、AP10 纤维素滤膜^[56]等。常用的萃取方法有索氏抽提(Soxhlet extraction)及加速溶剂萃取(Accelerated solvent extraction, ASE)等,且后者比前者

具有更高的效率^[49]。

2.3 沉积物中 OPEs 的分析方法

由于基质效应比较复杂,沉积物中 OPEs 的分析方法也相对较为复杂。其前处理方法主要分为两大部分:萃取洗脱和净化除杂。萃取洗脱主要采用的方法有超声辅助溶剂萃取(Ultrasound-assisted solvent extraction, US)^[41,44]、微波辅助萃取(Microwave assisted extraction, MAE)^[43,57]以及加速溶剂萃取^[42]等。相较而言,MAE 因具有较高的萃取效率和较少的溶剂耗费而优于其他两种萃取方法^[49]。净化除杂的方法主要有 HLB 小柱净化^[42,43]、PSA 柱净化^[41]及硅胶柱净化^[57]等。

2.4 生物相中 OPEs 的分析方法

与沉积物相似,生物相因成分较为复杂而会对 OPEs 的分析造成影响和干扰。因此,生物相中 OPEs 的分析方法也可归纳为萃取洗脱和净化除杂两个主要步骤。对于萃取洗脱,最常用的方法是加速溶剂萃取^[45-47]和微波辅助萃取^[48]等。净化洗脱主要采用的方法为硅胶柱净化^[46,47]及凝胶渗透色谱^[45,48]等。

3 OPEs 的毒理效应

OPEs 的毒性主要包括神经毒性、生殖毒性以及致癌性等(表 1, 4)。1989 年,高田幸一等研究了 TCEP 对小鼠的毒性,报道指出一定浓度的 TCEP 可导致小鼠体重减轻,死亡率上升且组织更易发生癌变^[58]。Fautz 等则研究了 TP_hP 及 TPPO 对雌鼠免疫细胞的毒性,报道指出 TP_hP 可抑制巨噬细胞及脾细胞的活性,而 TPPO 则以更复杂的方式影响上述两种细胞^[59]。Follmann 等则就 TCEP 及 TCPP 对微生物的毒性展开讨论,认为较高浓度的 TCEP 及 TCPP 可以对微生物细胞产生毒性^[60]。Ren 等则讨论了 TCEP 对兔近曲小管上皮细胞的毒性,指出高浓度的 TCEP 可影响细胞活性,抑制细胞周期蛋白的表达及 DNA 的合成,同时又可提升细胞乳酸脱氢酶的活性^[61]。Dishaw 等则研究了 TDCPP 对 PC12 细胞的毒性作用,文章指出一定浓度及时间暴露的 TDCPP 可影响细胞 DNA 的合成并影响细胞分化方

向^[62]。Crump 等则认为 TCPP 及 TDCPP 影响禽类肝细胞及神经细胞的异型生物质代谢、TH 途径及脂调节等^[63]。Mcgee 和 Dishaw 等分别就 TCEP, TCPP 及 TDCPP 对斑马鱼的毒性进行了研究,结果表明 TDCPP 对斑马鱼具有发育毒性和神经毒性,且 TDCPP 影响斑马鱼基因组 DNA 的甲基化^[64,65]。Farhat 等的研究指出一定浓度的 TCPP 可影响雏鸡破壳时间及跗骨长度,而一定浓度的 TDCPP 则可影响鸡胚胎重量和胆囊大小。同时,该研究还指出 TCPP 及 TDCPP 可诱导脱碘酶、肝脂肪酸结合蛋白、细胞色素 P4503A37 及 2H1 的表达^[66]。Pillai 等则研究了 FM550(主要成分为 TP_hP)对 COS7 细胞的毒性,研究表明一定浓度的 FM550 可显著激活 PPAR γ ,并可显著诱导细胞分化及脂质积累^[67]。而 Su 等的研究则表明 10 μ M 的 TP_hP 即对鸡胚胎肝细胞产生毒性而其代谢产物 DPhP 却无此效应。同时,该研究还表明 10 μ M TP_hP 及 DPhP 对糖代谢、脂代谢、免疫、氧化胁迫、甲状腺激素代谢、类法尼醇 X 受体及肝 X 受体相关基因的表达具有显著影响^[68]。

4 展望

综上所述,近五年来 OPEs 产出持续增长,应用领域不断扩大,其已经成为一种不容忽视的新兴污染物,对生态环境及人类健康产生了巨大的潜在威胁。目前,OPEs 在多种环境介质及生物相中被检出,有关其毒理效应的研究也已经在多个物种开展,并取得了一定的进展。但对于沉积物及生物相等复杂介质条件下 OPEs 的分析尚需要建立快速通用的分析方法,对于 OPEs 的分布仍需进行系统全面地研究,以期揭示其在环境中的迁移转化规律及在生物相中的富集放大规律。对于 OPEs 的毒理学研究,目前尚缺少以组学手段系统揭示其致毒机制的研究。今后应将组学手段更加深入的应用于这一领域,这将有助于更加全面及系统地阐明 OPEs 的毒理作用,并为 OPEs 的环境风险及健康风险评价打下基础。

表4 相关文献报道中 OPEs 的毒性
Table 4 Toxicity of OPEs in related documents

研究物质 Substance researched	研究对象 Species used	研究结果 Research results	参考文献 Reference
磷酸三(1,3-二氯-2-丙基)酯 (TDCPP) 磷酸三(2-氯乙基)酯 (TCEP) 磷酸三(1-氯-2-丙基)酯 (TCPP) 磷酸三(2,3-二溴丙基)酯 (TDBPP)	斑马鱼 Zebra fish	1. 明显毒性出现阈值:TDBPP (3.3 μM); TDCPP (10 μM); TCPP (n. a.); TCEP (n. a.); Threshold of obvious toxicity:TDBPP(3.3 μM); TDCPP(10 μM); TCPP (n. a.); TCEP (n. a.); 2. 致畸性:TDBPP (无); TDCPP (有); TCPP (无); TCEP (无); Teratogenicity: TDBPP (No); TDCPP (Yes); TCPP (No); TCEP (No); 3. 生存中值 (dpf):TDBPP (4); TDCPP (1); TCPP (n. a.); TCEP (n. a.); Median survival (dpf): TDBPP (4); TDCPP (1); TCPP (n. a.); TCEP (n. a.); 4. 神经症状出现阈值:TDBPP (0.56 μM); TDCPP (3.14 μM); TCPP (100 μM); TCEP (31.4 μM); Treshold of Neurological symptoms: TDBPP (0.56 μM); TDCPP (3.14 μM); TCPP (100 μM); TCEP (31.4 μM).	[65]
磷酸三苯酯 (TPP) FM550 磷酸一苯酯 (ITP)	BMS2 骨髓基质细胞 BMS2 marrow stroma cell Cos7 细胞 Cos7 cell	1. FM550 (90 μM)、TPP (40 μM)、ITP (100 μM) 暴露 24 小时或 FM550 (50 μM)、TPP (20 μM)、ITP (30 μM) 暴露 7 天,BMS2 骨髓基质细胞均无细胞损失; Exposure of FM550 (90 μM), TPP (40 μM), ITP (100 μM) for 24 hours or exposure of FM550 (50 μM), TPP (20 μM), ITP (30 μM) for 7 days can not make BMS2 marrow stroma cell lose; 2. FM550 (20 μM) 及 TPP (20 μM) 暴露 12 天,BMS2 骨髓基质细胞无明显细胞损失,未见 Caspase3 蛋白上调及细胞坏死蛋白释放; Exposure of FM550 (20 μM) and TPP (20 μM) for 12 days can not make BMS2 marrow stroma cell lose and induce no up-regulation of Caspase 3 and release of cell necrosis protein; 3. 20 μM FM550 可显著激活 PPARγ (EC ₅₀ = 47 μM); FM550 at 20 μM can significantly activate PPARγ (EC ₅₀ = 47 μM); 4. 10 μM FM550 可显著脂肪诱导细胞分化并增加脂质积累; FM550 at 10 μM can significantly induce cell differentiation and enhance lipid accumulation.	[67]
磷酸三苯酯 (TPP)	鸡胚胎肝细胞 Chicken embryo liver cells	1. 10 μM TPP 处理组即显现细胞毒性,而 DPP (TPP 代谢物) 在 1000 μM 时仍无明显细胞毒性; TPP at 10 μM shows cell toxicity, but DPP (metabolite of TPP) shows no cell toxicity even at 1000 μM; 2. 10 μM TPP 及 DPP 对糖代谢、脂代谢、免疫、氧化胁迫、甲状腺激素代谢、类法尼醇 X 受体及肝 X 受体相关基因的表达具有显著影响; TPP and DPP at 10 μM significantly influence the expression of genes related to sugar metabolism, fat metabolism, immune system, oxidative stress, thyroid hormone metabolism, Farnesoid X receptor and liver X receptor.	[68]
磷酸三(2-氯乙基)酯 (TCEP) 磷酸三(1,3-二氯-2-丙基)酯 (TDCPP)	鸡蛋 Eggs	1. TECP 及 TDCPP 均不缩短破壳时间; Both TECP and TDCPP can not decrease the incubation period; 2. 9240 及 51600 ng/g 的 TCPP 处理明显延长破壳时间及缩短跗骨的长度; TCPP at 9240 and 51600 ng/g obviously prolong the incubation period and decrease the length of tarsale; 3. 45000 ng/g TDCPP 处理明显减少胚胎的重量和胆囊的大小; TDCPP at 45000 ng/g decrease the weight of embryo and volume of gallbladder; 4. TCPP 明显诱导脱碘酶、肝脂肪酸结合蛋白及细胞色素 P4503A37 等的表达; TCPP obviously induce the expression of deiodinase, liver fatty acid binding protein, cytochrome P4503A37; 5. TDCPP 诱导细胞色素 P4503A37 及 CYP2H1 的表达; TDCPP induce the expression of cytochrome P4503A37 and CYP2H1.	[66]

磷酸三(1,3-二氯-2-丙基)酯 (TDCPP) 磷酸三(2-氯乙基)酯 TCEP	禽类肝细胞 Avian hepatocytes 神经细胞 Nerve cell	<ol style="list-style-type: none"> 1. TDCPP 对肝及神经细胞的 LC_{50} 分别为 $60.3 \pm 45.8 \mu\text{M}$ 及 $28.7 \pm 19.1 \mu\text{M}$; LC_{50} of TDCPP to hepatocyte and to neurocyte are $60.3 \pm 45.8 \mu\text{M}$ and $28.7 \pm 19.1 \mu\text{M}$ respectively; 2. TCPP 在 $300 \mu\text{M}$ 时对细胞活性仍无影响; TCPP at $300\mu\text{M}$ shows no influence on cell activity; 3. 大于 $10 \mu\text{M}$ 的 TDCPP 及 TCPP 影响异型生物质代谢、TH 途径及脂调节等; TDCPP and TCPP more than $10 \mu\text{M}$ influence biomass metabolism, TH pathway and lipid regulation. 	[63]
磷酸三(1,3-二氯-2-丙基)酯 (TDCPP) 磷酸三(2-氯乙基)酯 (TCEP) 磷酸三(1-氯-2-丙基)酯 (TCPP) 磷酸三(2,3-二溴丙基)酯 (TDBPP)	PC12 细胞 PC12 cell	<ol style="list-style-type: none"> 1. TDCPP 抑制 DNA 合成,且抑制作用随浓度 ($10 \sim 50 \mu\text{M}$) 及暴露时间 ($1 \sim 6 \text{d}$) 的增加而增加; TDCPP inhibit DNA synthesis and the inhibition increases with the increasement of concentration ($10 \sim 50 \mu\text{M}$) and exposure time ($1 \sim 6 \text{d}$); 2. TDCPP 处理组细胞数量减少; TDCPP decrease the amount of cells; 3. 在用 $50 \mu\text{M}$ TDCPP 暴露 4 天细胞中,其脂质过氧化作用提高了 22%,但细胞活力无明显变化; For cells exposed in $50 \mu\text{M}$ TDCPP, their lipid peroxidation effects increase by 22%, but cell activity doesn't change; 4. TDCPP 各处理浓度 ($10 \sim 50 \mu\text{M}$) 下均促进神经细胞分化为多巴胺能及类胆碱脂能表型; TDCPP ($10 \sim 50 \mu\text{M}$) induce neurocytes to differentiate into dopaminergic and cholinergic lipid phenotype. 	[62]
磷酸三(2-氯乙基)酯 TCEP	兔近曲小管上皮细胞 Rabbit proximal tubule epithelial cells	<ol style="list-style-type: none"> 1. 10mg/L 的 TCEP 降低细胞的生活力但提升乳酸脱氢酶的活力; TCEP at 10mg/L decrease cell activity but enhance the activity of lactate dehydrogenase; 2. 10mg/L 的 TCEP 抑制 <i>CDK4</i>、<i>cyclin D1</i>、<i>CDK2</i> 和 <i>cyclinE</i> 的表达降低细胞数量和 DNA 合成,但提高 <i>p21WAF/Cip1</i> 和 <i>p27Kip1</i> 的表达; TCEP at 10mg/L inhibits the expression of <i>CDK4</i>, <i>cyclin D1</i>, <i>CDK2</i> and <i>cyclinE</i> and DNA synthesis, but increase the expression of <i>p21WAF/Cip1</i> and <i>p27Kip1</i>; 3. $10 \mu\text{g/L}$ 的 TCEP 仅提高 <i>p21WAF/Cip1</i> 和 <i>p27Kip1</i> 的表达和抑制 DNA 的合成; TCEP at $10 \mu\text{g/L}$ only increase the expression of <i>p21WAF/Cip1</i> and <i>p27Kip1</i>, but inhibit DNA synthesis. 	[61]
磷酸三(2-氯乙基)酯 (TCEP) 磷酸三(1-氯-2-丙基)酯 TCPP	仓鼠成纤维细胞 V79 Hamster fibroblasts V79 鼠伤寒沙门氏杆菌 Salmonella typhimurium 酵母 Yeast 人子宫内膜瘤细胞 Human endometrial tumor cells	<ol style="list-style-type: none"> 1. TCEP 在大于 $10 \mu\text{M}$ 时对 V79 细胞显示微弱细胞毒性,而 TCPP 在 $1 \mu\text{M}$ 时即对 V79 细胞产生毒性; TCEP at more than $10 \mu\text{M}$ shows slight cell toxicity to V79 cell and TCPP at $1 \mu\text{M}$ shows toxicity to V79 cell; 2. TCEP 和 TCPP 均不能诱导 DNA 链的断裂; Both TCEP and TCPP can not induce fracture of DNA strands; 3. TCEP 和 TCPP 在大于 $1 \mu\text{M}$ 时均不诱导鼠伤寒沙门氏杆菌的遗传变异; Both TCEP and TCPP at more than $1 \mu\text{M}$ can not induce mutation of Salmonella typhimurium; 4. TCEP 和 TCPP 均不诱导激素毒性; Both TCEP and TCPP can not induce hormone toxicity. 	[60]
磷酸三苯酯 (TPP) 三苯基氧磷 (TPPO)	雌鼠 C57B1 免疫活性细胞; Female mice immune-competent cell	<ol style="list-style-type: none"> 1. TPPO 及 TPP 对巨噬细胞的巨噬作用无明显影响; TPPO and TPP show no obvious influence on macrophage function of macrophage; 2. TPP 可抑制巨噬细胞 TNF 及脾细胞 NK 的活性,其还轻微影响 B 型淋巴细胞抗体合成的活性; TPP inhibit TNF activity of macrophage and NK activity of splenocyte; 3. TPPO 调节巨噬细胞 TNF 及脾细胞 NK 的活性; TPPO regulate the activity of macrophage TNF and splenocyte NK. 	[59]

磷酸三(2-氯乙基)酯
TCEP

小鼠
Mice

1. 1.5 % TCEP 饲喂的小鼠,其体重要明显轻于对照组小鼠,而饲喂组小鼠死亡率高于对照组;
- Mice fed with 1.5 % TCEP shows lighter weigh and higher death rate;
2. 1.5 % 饲喂组雄鼠肾细胞癌变频率要明显高于对照组雄鼠;
- Male mice fed with 1.5 % TCEP shows higher cancerization rate in renal cell than male mice in control group;
3. 0.3 % 及 1.5 % TCEP 饲喂的雄鼠,其肝细胞癌变率明显高于对照组雄鼠;
- Male mice fed with 0.3 % and 1.5 % TCEP shows higher cancerization rate in liver cell than male mice in control group;
4. 1.5 % TCEP 饲喂雌鼠,其乳腺细胞及白细胞的癌变率明显高于对照组雌鼠;
- Female mice fed with 1.5 % TCEP shows higher cancerization rate in mammary glandular cell and in leukocyte than female mice in control group.

[58]

注:n. a. : 该栏不适用

Note:n. a. : not applicable

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DISTRIBUTION AND ANALYTICAL METHOD OF ORGANOPHOSPHATE ESTERS (OPEs) IN ENVIRONMENT/BIOTA AND THEIR TOXICITY

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Abstract The organophosphate esters (OPEs) are widely used as flame retardants and plasticizers and tend to release to the environment quite easily. Because of the banning of brominated flame retardants and the great increase in production and consumption of organophosphate esters flame retardants, OPEs has been regarded as a kind of emerging pollutant to which wide attention has been paid in recent years. There have been many documents reporting the distribution of OPEs in the environment and biota and their toxicity are also investigated. In this paper, distributions of OPEs in the surface water, sediment, atmosphere and biota have been summarized. Additionally, the analytical method of OPEs and its toxicity have also been reviewed. Finally, the prospects of distributional and toxicological researches of OPEs have been discussed aiming at providing reference for subsequent studies.

Key words Organophosphate esters; Distribution; Analytical methods; Toxicity