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# 持久性、迁移性和潜在毒性化学品环境健康风险与控制研究现状及趋势分析

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**摘要:**持久性、迁移性、毒性或高持久和高迁移性化学品(PMT/vPvM)在全球地表水、地下水和饮用水水体已被广泛检出,是未来可能显著影响人类健康和环境的一类重要新兴污染物。按照欧盟提议的鉴别标准,现有化学品中的PMT/vPvM数以千计,涉及用途广泛,包括三聚氰胺等数10种较高产量的工业化学品。PMT/vPvM可通过农田径流、工业废水和生活污水排入环境,污水处理厂目前被认为是其主要排放途径。因难以被现行常规水处理技术有效去除,PMT/vPvM可长期存在于城镇人居环境水循环系统中,危及居民饮用水及生态系统安全。欧盟已率先开始将PMT/vPvM专门纳入现行化学品风险管理体系中的优先范畴。目前,环境中仍有众多潜在PMT/vPvM,其监测方法亟待进一步完善,物质鉴定、类别范围及清单建立均尚需时日;PMT/vPvM在全球各地区的环境分布和暴露研究十分有限,其潜在、长期的生态毒性和人体健康危害效应研究较为匮乏。与此同时,替代品或替代技术以及污水处理、污染场地修复等环境工程治理技术的研究和开发,都将成为未来PMT/vPvM风险科学研究与管理决策的迫切需求。

**关键词:**持久性、迁移性、毒性或高持久和高迁移性化学品(PMT/vPvM);新兴污染物;环境暴露;饮用水安全;化学品管理中图分类号: X820.4 文献标识码: A 文章编号: 0250-3301(2023)06-3017-07 DOI: 10.13227/j.hjxx.202207182

## Research Status and Trend Analysis of Environmental and Health Risk and Control of Persistent, Mobile, and Toxic Chemicals

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**Abstract:** Persistent, mobile, and toxic or very persistent and very mobile (PMT/vPvM) chemicals have been widely detected in surface water, groundwater, and drinking water around the world and are important emerging contaminants that may significantly affect human health and the environment in the future. According to the identification criteria proposed by the European Union, there are thousands of PMT/vPvM substances in existing chemicals, covering a wide range of applications, including dozens of high-yield industrial chemicals such as melamine. PMT/vPvM chemicals can be discharged into the environment through farmland runoff, industrial wastewater, and domestic sewage, and sewage treatment plants are currently considered to be their main discharge route. It is difficult to effectively remove PMT/vPvM chemicals through the current conventional water treatment technology; they can exist in the water circulation system of the urban human settlement environment for a long time, endangering the safety of drinking water and the ecosystem. The European Union has taken the lead in introducing PMT/vPvM chemicals specifically into the priority areas of the current chemical risk management system. At present, there are still many potential PMT/vPvM chemicals in the environment, and their monitoring methods need to be further improved. It will take time for the identification of substances, the scope of categories, and the establishment of lists. Studies on the environmental fate and exposure of PMT/vPvM in various regions of the world are still very limited, and research on the potential, long-term ecotoxicity, and human health hazard effects remains scarce. At the same time, the research and development of substitute or alternative technologies, as well as environmental engineering treatment technologies such as sewage treatment and contaminated site remediation, will become an urgent need for future PMT/vPvM risk scientific research and management decisions.

**Key words:** persistent, mobile, and toxic or very persistent and very mobile (PMT/vPvM); emerging contaminants; environmental exposure; drinking water safety; chemical management

随着《关于持久性有机污染物的斯德哥尔摩公约》化学品管控名单逐年增列及世界各国对持久性(persistent)、生物累积性(bioaccumulative)和毒性(toxic)类化学品(PBT)的逐步淘汰,其环境和人体健康风险在全世界范围内正在得到逐步控制。近年来,一类生物累积性较低但具持久性尤其在水环境中更具迁移性(mobile)和潜在毒性的化学品(PMT)或高度持久性和高度迁移性的化学品(vPvM),即PMT/vPvM,正在逐渐成为国际学术界和环保机构高度关注的新兴污染物<sup>[1]</sup>。

现有研究显示,PMT/vPvM所涉物质种类众多、

用途广泛,包含个人护理品、药物以及涂料、油漆、阻燃剂等多种工业产品,并且其中部分物质的生产、使用量巨大<sup>[2]</sup>。PMT/vPvM进入自然环境后,极易通过土壤层并穿透河岸等天然屏障沿着河流水道进入水生生态系统,在数周或更长时间尺度上迁移<sup>[1]</sup>。持久性和迁移性的结合使此类化学品在饮用水净化、污水处理厂或生物降解和地下水过滤等过程中很难

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被去除,随着时间推移 PMT/vPvM 浓度将在水体中不断增加,对生态系统和人类健康构成了潜在的风险<sup>[3-5]</sup>.当前,PMT/vPvM 化学品已被欧盟健康、环境和新兴风险科学委员会 (scientific committee on health, environmental and emerging risks, SCHEER) 列为未来可能影响人类健康和环境的 14 个新兴问题之一<sup>[6]</sup>,并且欧盟化学品注册、评估、许可和限制法规 (REACH) 和物质和混合物分类、标签和包装法规 (CLP) 均提出需要加强对 PMT/vPvM 化学品的审查监管<sup>[7,8]</sup>.

本文旨在系统梳理和分析当前 PMT/vPvM 的现有鉴别标准、物质清单、排放强度和环境暴露等风险评估研究现状以及风险管理政策趋势,展望未来 PMT/vPvM 风险科学研究与管理的需求和挑战.

## 1 PMT/vPvM 鉴别标准、种类和物质清单

### 1.1 定义和鉴别标准

PMT/vPvM 与大多数定期监测和管制的污染

物最大区别体现在,其水生环境中的迁移性本质上与强极性有关<sup>[9]</sup>.早期学术界尚未对“迁移性”作出确切定义和量化,大多使用“极性 (polar)”如持久性极性污染物 (P<sup>3</sup>)<sup>[10]</sup>、极性持久性有机污染物 (polar-POPs/P-POPs)<sup>[11]</sup> 描述,后发现个别非极性分子也可在水中远距离移动<sup>[12]</sup>,极性不再适用于此类化学品的通用内在属性.目前国际上主要采用 Neumann 等<sup>[13]</sup> 提出的持久性、迁移性及毒性和高度持久、高度迁移特性的物质定义,将其简称为 PMT/vPvM;此外,也有研究者将持久性和迁移性有机污染物 (persistent, mobile organic contaminants, PMOC)<sup>[14,15]</sup> 作为统称开展相关研究.

德国环境署 (Umweltbundesamt, UBA) 通过多年开展的 PMT/vPvM 物质特性研究、模型优先级审查、决策工具模型开发以及对 REACH 注册物质进行全面性评估<sup>[16]</sup>,提出了如表 1 所示的 PMT/vPvM 鉴别标准<sup>[17]</sup>.

表 1 UBA-PMT/vPvM 的鉴别标准

Table 1 Current evaluation criteria for UBA-PMT/vPvM

化学品	物质特性	鉴别标准
PMT	持久性	满足以下任一条件则视为符合 P 标准 (pH 在 4~9 之间):①海水 (9℃) 中半衰期 > 60 d;②淡水或河水 (12℃) 中半衰期 > 40 d;③海洋沉积物 (9℃) 中半衰期 > 180 d;④淡水或河水沉积物 (12℃) 中半衰期 > 120 d;⑤土壤 (12℃) 中半衰期 > 120 d
	迁移性	满足下列条件则视为符合 M 标准:pH 4~9 范围内最低 $\lg K_{oc} < 4$
	毒性	满足以下任一条件则视为符合 T 标准:①海洋或淡水生物 NOEC 或 EC10 < 0.01 mg·L <sup>-1</sup> ;②EC No 1272/2008 规定的致癌 (1A 或 1B 类)、生殖细胞诱变 (1A 或 1B 类) 或生殖毒性 (1A, 1B 或 2 类);③ EC No 1272/2008 其他慢性毒性证据:重复接触后特定靶器官毒性 (1 或 2 类);④ EC No 1272/2008 规定的致癌物 (2 类) 或生殖细胞诱变 (2 类);⑤ EC No 1272/2008 规定的“对哺乳或通过哺乳产生影响”的附加类别;⑥ Derived-No-Adverse-Effect-Level (DNEL) ≤ 9 μg·kg <sup>-1</sup> ·d <sup>-1</sup> (普通人群长期口服);⑦根据世界卫生组织/国际化学品安全规划署定义,该物质对人类和/或野生动物物种具有内分泌扰乱作用
vPvM	非常持久性	满足以下任一条件则视为符合 P 标准 (pH 在 4~9 之间):①海水 (9℃)、淡水或河水 (12℃) 中半衰期 > 60 d;②海洋沉积物 (9℃)、淡水或河水沉积物 (12℃) 中半衰期 > 180 d;③土壤 (12℃) 中半衰期 > 180 d
	非常迁移性	满足下列条件则视为符合 M 标准:pH 4~9 范围内最低 $\lg K_{oc} < 3$

由表 1 可见,在 PMT/vPvM 鉴别标准中,持久性 (P) 的鉴定方法与 PBT 物质相同,毒性 (T) 是在 REACH 附件 XIII 1.1.3 规定指标以外增加了其他与人类健康和环境风险有关的限制条件,而迁移性 (M) 则是最新定义和量化的受关注物质特性.近年来,科学界关于如何定义与量化迁移性 (M) 内在物质特征进行了广泛讨论,包括众多指标如水溶性 ( $S_w$ )、辛醇-水分配系数 ( $K_{ow}$ )、土壤-水分配系数 ( $K_d$ ) 和有机碳-水分配系数 ( $K_{oc}$ ) 等<sup>[15]</sup>.由于有机碳通常是土壤和沉积物中诸多中性化合物和离子化合物的吸附相,且该参数对于不同土壤的变异性小于  $K_d$ ,故目前对 M/vM 的评估大都基于  $\lg K_{oc}$  指标.需要注意的是,离子化合物与不同类型有机碳间相互

作用差异较大,尤其阳离子化合物易与带负电荷的土壤和矿物质表面吸附使迁移性降低,导致不同环境下  $K_{oc}$  测量值变化较大<sup>[18]</sup>.目前,国际上主要根据批次实验结果,将在实际土壤、水体沉积物和污泥中测得的最小  $\lg K_{oc}$  值作为迁移性参考指标<sup>[19]</sup>.

### 1.2 物质种类和优先清单

基于定量构效关系 (quantitative structure-activity relationship, QSAR) 模型对欧盟登记的工业化学品的评估研究表明,按照 REACH 早期关于化学物质持久性和迁移性的最低标准,即淡水中半衰期 > 40 d 和 pH 在 4~10 范围内  $\lg K_{oc} < 4.5$ ,有 5 155 种工业化学品可被初步鉴定为 PM 类有机化学品 (PMOC)<sup>[15]</sup>,其中具有较高持久性和迁移性的化

学品及其前体物约有2 167种<sup>[20]</sup>. UBA 按照如表 1 所示的评估标准对欧盟 REACH 登记的现有15 469 种化学品进行评估表明,至少有 260 种符合 PMT/vPvM 标准,224 种符合 PM 标准,有2 377种因数据不足有待进一步评估;在已鉴别的 PMT/vPvM 中,有 122 种化学品需要优先给予进一步地调查以采取风险管理措施<sup>[19]</sup>.

由于 PMT/vPvM 监测方法较为有限,学术界对于自然环境中此类化学品的存在状况迄今尚未充分了解. Neumann 等<sup>[17]</sup>对 2000 ~ 2018 年期间文献报道的饮用水和地下水环境中监测到的化学品进行甄别,得出 333 种 PMT/vPvM 污染物清单,其中有 142 种化学品在 REACH 中登记备案. Neuwald 等<sup>[21]</sup>在

德国的两条河流中开展环境监测,识别出 64 种可疑 PM 化学品( $< 1 \sim 10\,000\text{ng}\cdot\text{L}^{-1}$ ),主要有含氮化合物(44 种)、磺酸盐(14 种)和离子液体(20 种).

基于现有筛选和监测研究,不同研究机构和国际组织给出了一系列重点关注的 PMT/vPvM(及潜在)清单<sup>[17,20~23]</sup>. 其中,国际非政府组织 ChemSec 列出了包括三聚氰胺、1,4-二噁烷和四氯化碳等在内的 35 种 PMT/vPvM 名录<sup>[23]</sup>,部分在 REACH 中登记量超过  $100\text{t}\cdot\text{a}^{-1}$  的 PMT/vPvM 及其应用范围见表 2. 由此可见, PMT/vPvM 种类多样,主要作为阻燃剂、增塑剂、表面活性剂、乳化剂和杀虫剂等,广泛应用于家具材料、塑料制品、家用护理品、电子电器和农药生产等领域.

表 2 ChemSec-高产量 PMT/vPvM 化学品清单<sup>1)</sup>

Table 2 High-yield PMT/vPvM chemical list from ChemSec

CAS	名称	产量 $\times 10^3/\text{t}\cdot\text{a}^{-1}$	应用范围
108-78-1	三聚氰胺(melamine)	100 ~ 1 000	阻燃剂、填料、粘合剂、着色剂和发泡剂
115-27-5	氯酸酐(chlorendic anhydride)	1 ~ 10	粘合剂和阻燃剂
123-91-1	1,4-二噁烷(1,4-dioxane)	> 1	脱水剂和稳定剂
29420-49-3	全氟丁基磺酸钾(PFBS)	0.1 ~ 1	表面活性剂、阻燃剂和乳化稳定剂
3622-84-2	N-丁基苯磺酰胺(N-butyl benzenesulphonamide)	1 ~ 10	增塑剂
382-28-5	全氟-N-甲基吗啉(FC-3284)	1-10	功能性液体
56-23-5	四氯化碳(carbon tetrachloride)	1 ~ 10	溶剂、胶粘剂和杀虫剂
67-66-3	氯仿(chloroform)	100 ~ 1 000	溶剂、表面活性剂和麻醉剂
76-05-1	三氟乙酸(trifluoroacetic acid)	1 ~ 10	氧化剂
78-67-1	2,2'-二甲基-2,2'-偶氮二丙腈(2,2'-dimethyl-2,2'-azodipropionitrile)	1 ~ 10	粘合剂、催化剂和载气推进剂

1)所列化学品来自 ChemSec-SINLIST<sup>[23]</sup>; 筛选条件:登记量  $> 100\text{t}\cdot\text{a}^{-1}$

## 2 PMT/vPvM 的环境排放、归趋与暴露

### 2.1 环境排放

PMT/vPvM 种类众多,环境排放源广泛. 根据目前已识别的主要化学品清单及应用领域,农田径流、工业废水和生活污水是 PMT/vPvM 主要环境排放源. 此类化学品难以在常规的污水处理条件下去除,而通常情况下污水处理厂作为连接人类生产生活和自然水体环境的纽带,目前被认为是 PMT/vPvM 环境排放的主要途径<sup>[24,25]</sup>.

Schulze 等<sup>[20]</sup>以 REACH 注册数据为参数开发了化学品定性排放评分系统,对登记的2 167种潜在的 PM 化学品排放潜力进行建模排序,结合文献调研发现,三聚氰胺、双酚 S、安赛蜜和糖精等高排放潜力的 PM 化学品在水体中均被广泛检出. 值得关注的是,有研究表明三聚氰胺已成为我国华南地区生活污水和受纳水体中的首要污染物,其在水体中浓度是目前已知水环境中三聚氰胺最高报道水平( $\mu\text{g}\cdot\text{L}^{-1}$ )<sup>[24]</sup>. 此外,现有监测研究发现甲基叔丁基醚<sup>[26]</sup>、乙二胺四乙酸<sup>[27]</sup>、全氟丙酸酐<sup>[28]</sup>和三氟

乙酸<sup>[29]</sup>等 PMT/vPvM 已广泛存在于地表水和饮用水源地中.

大量工业化学品、药物和个人护理品在生产生活中广泛使用并通过工业废水与生活污水排放到自然环境,河流作为主要的环境纳污介质和污染物转化场所,在人类活动影响下成为 PMT/vPvM 的流动载体. PMT/vPvM 通过直排、经污水处理厂处理和部分渗透作用等途径进入河流地表水和地下水环境,以自来水厂为主要汲水设施再次流通进入生产、生活流程. 因此,在水加工、处理过程中几乎均有 PMT/vPvM 的存在. 例如, Sjerps 等<sup>[3]</sup>对荷兰水样在污水处理厂流出物到地表水、再到地下水并最终进入饮用水环节开展了系统性分析,发现尽管总有有机污染物浓度水平下降两个数量级,但迁移性(极性)最强的 PMT/vPvM 在整个过程水样中一直被检出. 基于当前对 PMT/vPvM 排放来源、途径及归趋的认识,城镇人居环境水循环系统中的 PMT/vPvM 环境排放与归趋过程可归纳如图 1 所示.

### 2.2 环境暴露水平及风险

目前,环境中仍有众多潜在 PMT/vPvM 环境监



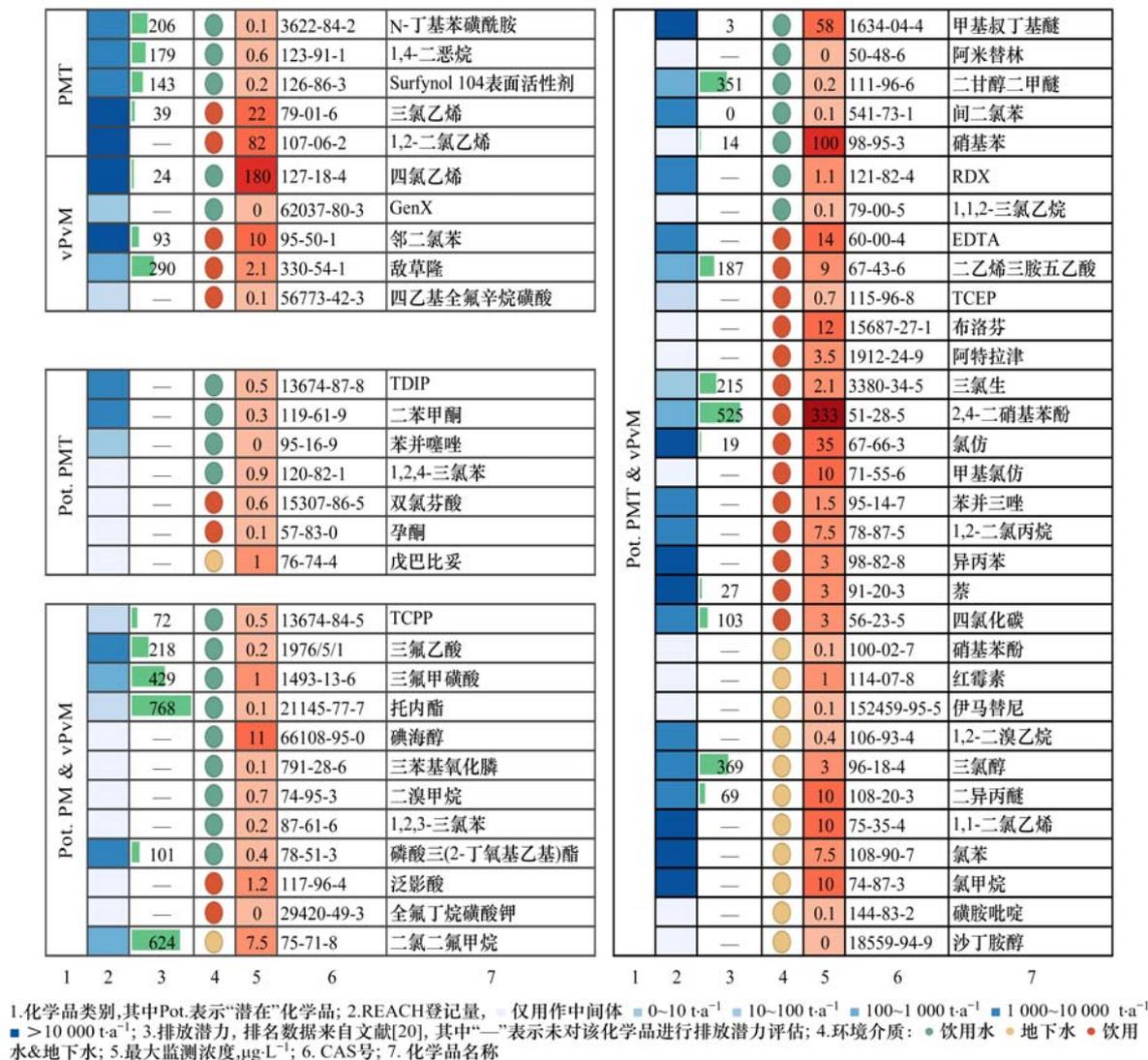


图2 饮用水和地下水中部分 PMT/vPvM 化学品环境排放和暴露水平

Fig. 2 Environmental emissions and exposure levels of some PMT/vPvM chemicals in drinking water and groundwater

推动将 PMT/vPvM 类别和鉴别标准纳入欧盟 CLP 法规中,从而创建一个新的化学品危害性类别和标准<sup>[7]</sup>;并进一步修订 REACH 法规,将 PMT/vPvM 明确列为 SVHC 以加强登记管理<sup>[44]</sup>。为此,欧盟在尝试建立新的模型或完善实验方法,以识别和筛选 REACH 法规内登记在册物质中的 PMT/vPvM。目前,已有 21 种 PMT/vPvM 被纳入到欧盟 REACH 的 SVHC 清单或作为欧盟水质框架的优先关注物质<sup>[19]</sup>。

欧盟“地平线 2020”(Horizon 2020)计划资助启动了 ZeroPM 项目,全面开展环境中 PMT/vPvM 包括多氟和全氟烷基化合物 (poly-and perfluoroalkyl substances, PFAS) 在内的化学品安全替代、优先识别、风险评估及修复去除等研究<sup>[45]</sup>;为实现《欧洲绿色协议》目标而设立的 PROMISCES 项目则主要关注高持久性和迁移性 PFAS,提供创新技术减少环境中的 PM 污染,以建立土壤-沉积物-水环境系统相

关的可持续发展和循环经济路线<sup>[46]</sup>。

北美关于 PMT/vPvM 的管控行动目前主要集中在 PFAS 上。美国环保署 (USEPA) 于 2021 年发布了 PFAS 战略路线图<sup>[47]</sup>,拟通过增加研究资金、限制环境排放和加快污染治理等指导策略,以管控包含 Gen-X 和全氟丁烷磺酸 (perfluorobutane sulfonic acid, PFBA) 等在内的高持久性和迁移性 PFAS。美国各州已发布多项提案,禁止在食品包装、消防防护装备及灭火泡沫等产品中使用 PFAS<sup>[48]</sup>。此外,在安全饮用水法 (safe drinking water act, SDWA) 的监管下,EPA 发布“第 5 项不受管制的污染物监测规则” (fifth unregulated contaminant monitoring rule, UCMR 5),进一步计划对全国范围内饮用水中的 29 种 PFAS 进行扩大监测,保护饮用水安全和公众健康<sup>[49]</sup>。

#### 4 结论与展望

(1) PMT/vPvM 正在成为继 POPs 及 PBT 类化

学品之后国际化学品风险评估与风险管理的关注热点. 目前, 国际上已经形成了比较明确的 PMT/vPvM 鉴别标准; 结合理论推算和环境监测数据分析, 初步确定了其物质范畴以及优先关注物质清单; PMT/vPvM 在城镇人居环境水循环系统中的环境排放和归趋过程, 尤其是其持续循环与积累的过程正逐渐明晰; 一系列优先关注的高产量/排放量的 PMT/vPvM 环境暴露及环境和健康风险已日趋凸显; 欧盟等化学品风险管理先进的地区和国家, 正逐步将 PMT/vPvM 专门纳入现行化学品风险管理体系中的优先范畴.

(2) 因所涉物质种类繁多, 迄今已识别的 PMT/vPvM 还仅占现有登记化学品的一小部分, PMT/vPvM 化学品的评估鉴别和清单确定仍将是未来学术界面临的一项重要且长期的任务. 环境监测数据是 PMT/vPvM 化学品评估鉴别的重要基础条件, 但其目前主要受限于监测方法的欠缺, 各类新兴和潜在 PMT/vPvM 的监测方法开发和应用将成为未来较为迫切的研究需求. 从当前总体研究进展来看, 除欧盟等个别地区及 PFAS 等个别物质类别之外, 全球不同地区及更广泛的 PMT/vPvM 环境分布和暴露水平的研究尚十分有限, 其以低浓度产生的潜在、长期的生态毒性和人体健康危害效应的研究更为匮乏. 因此, PMT/vPvM (尤其是高产量/排放的高关注物质) 的区域和全球环境暴露及其生态和人体健康危害效应的评估研究亟待开展, 这将成为未来区域及全球 PMT/vPvM 风险管理决策的重要前提. 与此同时, PMT/vPvM 替代品或替代技术, 以及污水处理厂去除等环境工程治理技术的研发, 也必将成为未来重要的研究方向.

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