

# 有机固废资源化过程中新污染物的赋存与消减

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**摘要:** 近年来, 有机固废中逐渐检测出各种新污染物, 由于其生物毒性、环境持久性、生物累积性等特征, 对生态环境和人体健康构成了严重威胁。有机固废生物转化(好氧堆肥和厌氧消化)是实现废弃物资源化利用和新污染物消减的重要方法。然而, 目前关于新污染物在生物转化过程中的赋存特征和消减规律尚缺乏系统认识。在梳理文献的基础上, 总结了持久性有机污染物、内分泌干扰物、抗生素和微塑料等典型污染物在有机固废资源化过程中的研究现状, 分析了不同有机固废新污染物的赋存特征, 探讨了好氧堆肥和厌氧消化对新污染物的去除效果和强化去除策略。总体上, 持久性有机污染物、内分泌干扰物和微塑料浓度在污泥中显著更高, 而抗生素浓度在畜禽粪污中显著更高。有机固废生物转化能够有效控制和削减废弃物中的新污染物, 其中好氧堆肥对污染物的去除能力普遍高于厌氧消化。最后, 对有机固废资源化过程中新污染物研究方向进行了展望, 以期为未来的研究提供参考。

**关键词:** 新污染物; 有机固废; 好氧堆肥; 厌氧消化; 赋存; 消减

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## Occurrence and reduction of emerging pollutants in process of organic solid waste recycling

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**Abstract:** Various emerging pollutants have been detected in organic solid waste in recent years, posing a significant threat to the ecological environment and human health due to biotoxicity, environmental persistence, and bioaccumulation. Organic solid waste bioconversion (aerobic composting and anaerobic digestion) is a crucial method for achieving resource utilization of waste and mitigating emerging pollutants. However, the characteristics and mitigation patterns of emerging pollutants in bioconversion processes are not well understood. This paper summarizes the current research status of typical emerging pollutants in organic solid waste resource utilization, including persistent organic pollutants, endocrine disruptors, antibiotics, and microplastics, based on the literature. It analyzes the characteristics of emerging pollutants in various types of organic solid wastes and explores the effectiveness of aerobic composting and anaerobic digestion in removing these pollutants,

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as well as strategies for improving removal. The study revealed that sludge exhibited significantly higher concentrations of persistent organic pollutants, endocrine disruptors, and microplastics, while antibiotics were notably more concentrated in livestock manure. Organic solid waste bioconversion was effective in controlling and reducing emerging pollutants in waste. Aerobic composting generally demonstrated a higher pollutant removal capacity compared to anaerobic digestion. Finally, the paper delves into further research directions concerning emerging pollutants in organic solid waste resource utilization.

**Keywords:** Emerging pollutants; Organic solid waste; Aerobic composting; Anaerobic digestion; Occurrence; Reduction

## 0 引 言

新污染物是指发现或关注时间较晚、具有环境健康风险但尚未被现有法律制度加以有效约束的污染物<sup>[1]</sup>。目前,国际上广泛关注的污染物主要包括持久性有机污染物(Persistent Organic Pollutants, POPs)、内分泌干扰物(Endocrine Disrupting Chemicals, EDCs)、抗生素(Antibiotics)和微塑料(Microplastics, MPs)。与传统污染物相比,新污染物的环境浓度总体较低,但由于其生物毒性、环境持久性、生物累积性等特征,对生态环境和人体健康造成严重威胁,日益受到各国政府和民众的广泛关注<sup>[2]</sup>。2022年我国生态环境部将新污染物治理纳入“十四五”规划和2035年远景目标。

有毒有害化学物质的生产和使用是新污染物的主要来源,随着生产和消费水平的激增,新污染物在陆地、水体和大气等生态系统中普遍存在<sup>[3]</sup>。近年来,有机固废(厨余垃圾、市政污泥、畜禽粪污等)中频繁检测出多种新污染物,已成为环境中新污染物污染的重要来源<sup>[4-6]</sup>。工业化发展、城市化加速以及人口增长导致有机固废产生率急剧上升,全球有机固废年产量约为1 050亿t,其中中国超过60亿t,位居世界首位<sup>[7]</sup>。有机固废除富含有机物和氮、磷、钾等营养物质外,还含有大量污染介质,特别是新污染物,如不妥善处理,将会造成严重的资源浪费和环境污染<sup>[4]</sup>。

有机固废资源化处理处置是实现“双碳”目标和建设无废城市的重要部分和前提。相对于焚烧和填埋,好氧堆肥和厌氧消化不仅可以实现废弃物的高效减量化、无害化(杀死有害病原微生物和寄生虫卵等)和资源化(制备土壤肥料/改良剂和产生甲烷等),而且还可以在一定程度上降解新污染物,带来巨大的经济和环境效益<sup>[8]</sup>。目前大多数

研究主要关注有机固废好氧堆肥或厌氧消化中特定新污染物的迁移转化,尚缺乏关于有机固废资源化过程中多种新污染物赋存特征和消减规律的系统认识。本文梳理了近5年来 POPs、EDCs、抗生素和 MPs 等为主的典型新污染物在有机固废好氧堆肥和厌氧消化中的研究现状,分析了新污染物在不同有机固废中的赋存特征,探讨了堆肥和厌氧消化中新污染物的去除效果,最后展望了未来的研究前景和方向,以期改善有机固废管理,高效去除新污染物提供理论支撑。

## 1 有机固废资源化过程中新污染物研究现状

通过中国知网和 Web of Science 数据库检索了近5年(2019年1月—2024年8月)有机固废(厨余垃圾、市政污泥和畜禽粪污)好氧堆肥和厌氧消化过程中典型新污染物(POPs、EDCs、抗生素、MPs)的研究文献,总共505篇,统计数据如图1所示。由图1(a)可知,从2019年到2022年相关研究逐渐增多,2023年出现了略微下降,其中中文和英文文献各占18%和82%,综述型和研究型文献各占27%和73%,仅研究好氧堆肥的文献占37%,仅研究厌氧消化的文献占55%,共同研究好氧堆肥和厌氧消化的文献占8%。新污染物的研究重点与农业、工业化生产和人类活动紧密相连。抗生素是目前研究最多的新污染物,主要在畜禽粪便中进行研究,这与抗生素作为抗菌剂和生长促进剂广泛用于畜牧业有关(图1(b)(c))。针对 POPs、EDCs 和 MPs 的研究则主要集中在市政污泥上,这与工业化生产和人类日常生活有关,其产生的污染物通过各种途径排放到污水处理厂并富集到污泥中。携带新污染物的污泥和畜禽粪污在土地施用后可能迁移到作物中,因此,食物和衍生的厨余垃圾也会受到污染。目前关于厨余垃圾及处理中新污染物研究相对较少。

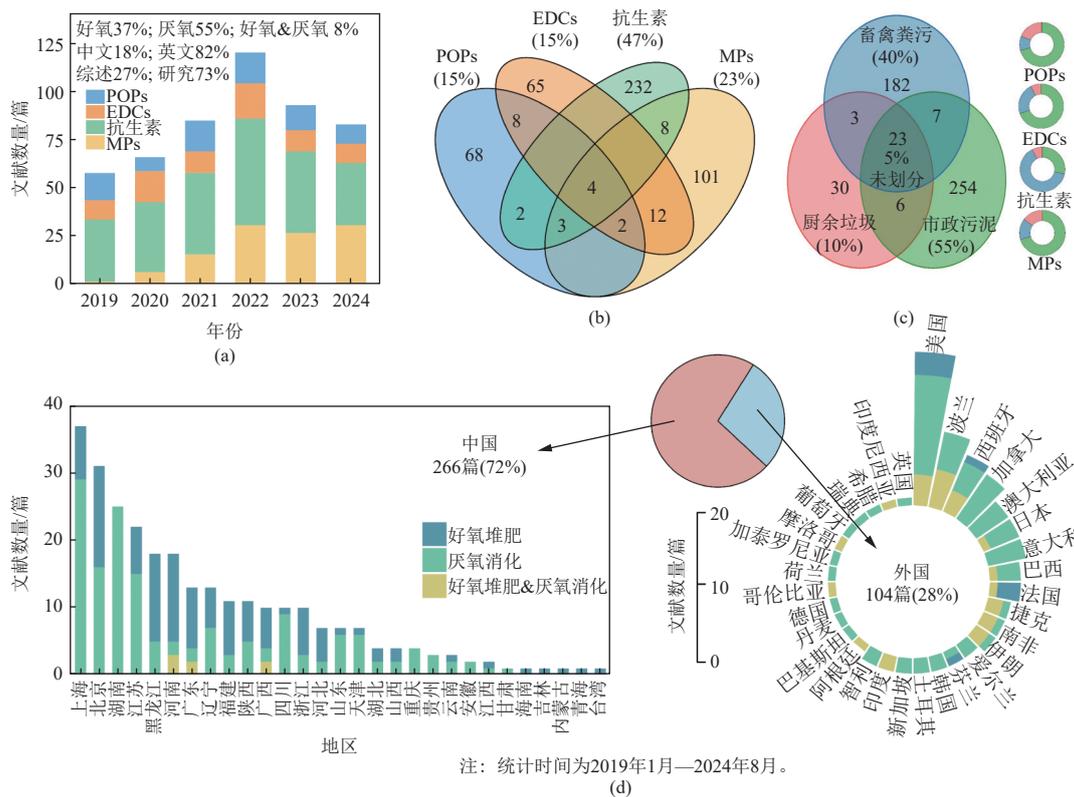


图 1 好氧堆肥和厌氧消化中(a)不同年份、(b)不同类别、(c)不同有机固废和 (d)不同国家及地区新污染物文献统计分析

Fig. 1 Statistical analysis of literature on emerging pollutants in aerobic composting and anaerobic digestion for (a) different year, (b) category, (c) organic solid waste, and (d) countries and regions

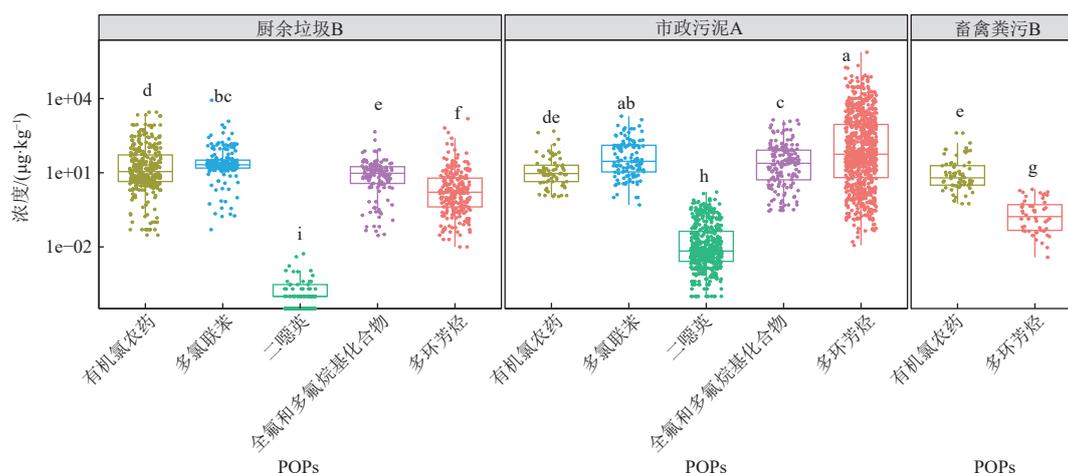
从文献统计分析可知,有机固废资源化过程中新污染物研究覆盖 33 个国家,中国是研究最多的国家(占比 72%),其次是美国、波兰、西班牙、加拿大和澳大利亚(图 1(d))。研究表明我国高度重视有机固废处理中新污染物研究。整体来看,新污染物研究以厌氧消化为主,存在区域性差异。其中上海、湖南、江苏等地区以及国外,以厌氧消化为主;黑龙江、河南和广东等地区,以好氧堆肥为主。目前,由于经济发展水平、消费需求、有机固废管理模式等因素差异,有机固废中新污染研究存在污染物种类、底物类型、处理方式和区域性发展不平衡现象,亟需深入全面调查研究不同国家和地区有机固废好氧堆肥和厌氧消化中新污染物的赋存及消减情况,对了解世界新污染物分布格局、促进好氧堆肥和厌氧消化发展具有重要意义。

## 2 有机固废资源化过程中新污染物赋存特征及消减

### 2.1 POPs 赋存特征及消减

POPs 是指具有高毒性、持久性、生物积累

性、远距离迁移性,可对生物体产生致癌、致畸、致突变作用,造成神经系统损伤,甚至对生物体生殖能力造成严重侵害的有机污染物<sup>[9]</sup>。POPs 主要包括《斯德哥尔摩公约》中首批禁止或管控的有机氯农药、多氯联苯和二噁英,《重点管控新污染物清单(2023 年版)》中的全氟和多氟烷基化合物,以及首批公认的环境致癌物质多环芳烃等<sup>[9]</sup>。这些污染物在有机固废中普遍存在,浓度范围为 0~751 000  $\mu\text{g}/\text{kg}$ ,平均值为 1 268  $\mu\text{g}/\text{kg}$ ,目前在污泥和厨余垃圾中多有研究(图 2)<sup>[9-23]</sup>。从图 2 可知,污泥中 POPs 浓度(范围为 0~751 000  $\mu\text{g}/\text{kg}$ ,平均值为 2 160  $\mu\text{g}/\text{kg}$ )显著高于厨余垃圾(0~8 567  $\mu\text{g}/\text{kg}$ , 62  $\mu\text{g}/\text{kg}$ )和 畜禽粪污(0~406  $\mu\text{g}/\text{kg}$ , 17  $\mu\text{g}/\text{kg}$ )。与其他 POPs 相比,具有较强疏水性的多环芳烃在污泥中浓度最高,范围为 0.01~751 000  $\mu\text{g}/\text{kg}$ ,平均值为 2 160  $\mu\text{g}/\text{kg}$ ,主要以 3~4 环多环芳烃为主,其苯环数量越多,致癌性越强,是有机固废处理过程中最常研究的污染物之一<sup>[24]</sup>。在厨余垃圾中,浓度最高的是多氯联苯,范围为 0.05~8 567  $\mu\text{g}/\text{kg}$ ,平均值为 165  $\mu\text{g}/\text{kg}$ 。这与多氯联苯的抗性和亲脂性有关,其可通过食物链在生物体



注:同一字母表示组间没有显著差异,不同字母表示组间存在显著差异( $p < 0.05$ ),其中不同有机固废之间差异用大写字母表示,不同污染物之间差异用小写字母表示,A或a代表统计学上显著最高,B或b其次,字母依次类推。下同。

图2 有机固废中 POPs 浓度<sup>[9-23]</sup>

Fig. 2 Concentration of POPs in organic solid waste<sup>[9-23]</sup>

内(水产品 and 哺乳动物等)积聚和浓缩有关<sup>[6]</sup>。虽然 POPs 生产和使用已得到管控,但由于人为(工业制造和有机化合物的不完全燃烧等)和自然(火灾、火山喷发等)等不可控性因素,其造成的环境污染持续增加,后续应重点关注 POPs 的全流程管控并解决历史遗留污染问题。

在好氧堆肥过程中,微生物群落不断交替演变,生物酶活性升高,有利于 POPs 及其他新污染物的高效降解。申艳萍等<sup>[23]</sup>研究表明高温堆肥可分别去除 51%、44% 和 63% 的六六六、滴滴涕和六氯苯,引入产漆酶血红密孔菌后去除率分别提高 41%、35% 和 20%。多项研究表明,多环芳烃在堆肥过程中的去除率可达 90% 以上,这主要归因于低分子量易挥发性以及微生物降解作用,其主要的降解菌包括芽孢杆菌、假单胞菌和甲基单胞菌<sup>[9,25]</sup>。然而,顽固性多氯联苯和二噁英在堆肥中去除效果较差,甚至出现了浓度增加。GOMEZ 等<sup>[19]</sup>发现多氯联苯和二噁英浓度由 1.2~2.4 ng WHO-TEQ/kg 增加到 2.3~7.8 ng WHO-TEQ/kg。这可能与堆体体积减小、高分子量向低分子量同系物的转变以及污染物对有机物的强烈吸附有关<sup>[26]</sup>,但多氯联苯和二噁英的浓度值仍低于国家规定限值。随着多氯联苯和二噁英前体浓度增加,毒性可能会大幅度增加,因此其潜在风险不容忽视。

厌氧消化去除 POPs 的能力弱于好氧堆肥。ABRIL 等<sup>[27]</sup>发现全氟化合物和双酚 A 经厌氧消化后浓度有所增加,而经好氧堆肥后分别去除了

84% 和 23%。与好氧消化相比,厌氧消化污泥中多环芳烃和多氯联苯的含量显著更高( $p < 0.05$ ),进一步说明好氧条件有助于促进 POPs 的降解<sup>[15]</sup>。多环芳烃和多氯联苯在厌氧消化过程中均具有较宽的去除率范围,其去除率/半衰期分别为 6%~93%/35~495 d<sup>[28-29]</sup> 和 8%~100%/9~3 277 d<sup>[30]</sup>,且高温比中温厌氧消化的去除率更高<sup>[31-32]</sup>。多环芳烃在厌氧消化中的去除率与其分子结构中苯环数量有关,一般认为分子结构中含有 4 个以上苯环的多环芳烃较难降解<sup>[33]</sup>。多氯联苯的分子结构,特别是异构现象,也会影响其生物降解性。一般来说,间位和对位的氯比邻位的氯更易去除<sup>[34]</sup>。然而,在另一项研究中得出矛盾的结果,即通过污水处理厂采样和小试实验,发现温度变化并不会显著影响厌氧处理过程中多环芳烃、多氯联苯和有机氯农药的降解。这可能是高温厌氧消化技术在当地罕见,样本数量不均衡导致<sup>[15]</sup>。沼渣中二噁英浓度(6.2~8.3 ng WHO-TEQ/kg)要高于堆肥产品,接近国标(GB 36600—2018)中开发用地的筛选值,因此今后应关注沼渣土地使用的潜在环境风险<sup>[35]</sup>。厌氧微生物具有脱毒和利用难降解有机污染物以及开环裂解某些芳香烃和杂环化合物的作用,而这正是好氧堆肥的限速步骤,因而将厌氧消化和好氧堆肥联合为进一步降解 POPs 以及其他新污染物提供了更大的可能。AEMIG 等<sup>[36]</sup>发现单独的厌氧消化只能去除 22%、7% 和 19% 的荧蒽、苯并[b]荧蒽和苯并[a]芘,而将厌氧消化产物进行 66 d 堆肥后发现它们分别下降了 35%、

31% 和 38%。此外,有机固废预处理如超声波应用、热处理和臭氧化与厌氧消化相结合,可以进一步提高 POPs 降解。

## 2.2 EDCs 赋存特征及消减

EDCs 又称环境激素,是一种外源性干扰生物体内分泌系统的化学物质,包括激素类、双酚类、邻苯二甲酸酯类和烷基酚类等<sup>[37]</sup>。这类物质大多具有较好的脂溶性、疏水性和化学稳定性,痕量级浓度便可产生慢性毒性效应并引起内分泌系统紊乱,具有极高的生态风险。随着工业的不断发展,大量 EDCs 在激素类药物、添加剂、塑料制品和农药的生产、使用和垃圾处理过程中不断被释放到环境中。有机固废中 EDCs 浓度范围为 0.03~1 400 000  $\mu\text{g}/\text{kg}$ ,平均值为 23 158  $\mu\text{g}/\text{kg}$ ,其中市政

污泥中 EDCs 种类和浓度显著高于畜禽粪污,这与污水处理厂具有广泛的 EDCs 来源有关(图 3)。在市政污泥中,EDCs 浓度范围为 0.03~1 400 000  $\mu\text{g}/\text{kg}$ ,中位数排序为邻苯二甲酸酯(4 700  $\mu\text{g}/\text{kg}$ )>壬基酚(1 890  $\mu\text{g}/\text{kg}$ )>三氯生(619  $\mu\text{g}/\text{kg}$ )>辛基酚(270  $\mu\text{g}/\text{kg}$ )>三氯卡班(117  $\mu\text{g}/\text{kg}$ )>双酚 A(84  $\mu\text{g}/\text{kg}$ )>雌激素(18  $\mu\text{g}/\text{kg}$ )。邻苯二甲酸酯作为一种普遍使用的增塑剂,广泛应用于工业、医疗、生活等领域。其中邻苯二甲酸二(2-乙基己基)酯和邻苯二甲酸二丁酯是有机固废中含量最高的 2 类物质,浓度介于 130 000~1 094 000  $\mu\text{g}/\text{kg}$  之间,超过了欧盟委员会建议的污泥土地利用限值(100 000  $\mu\text{g}/\text{kg}$ ),对受纳土壤构成了潜在风险<sup>[38]</sup>。

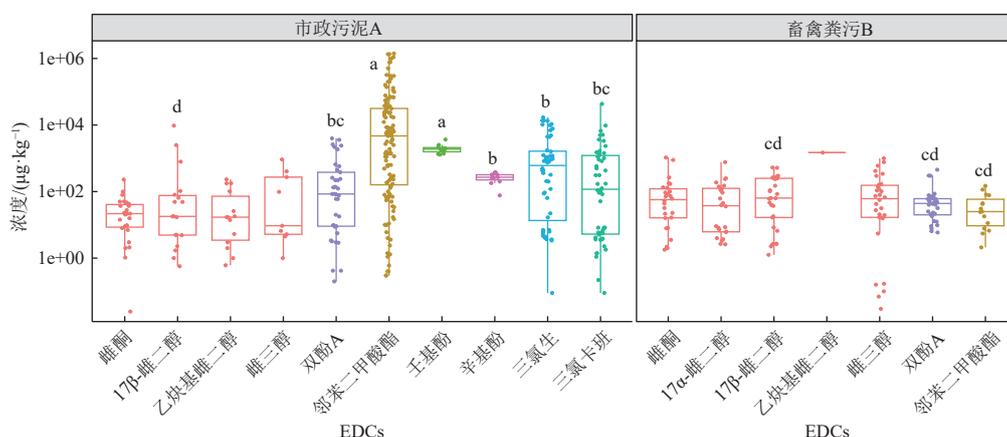


图 3 有机固废中 EDCs 浓度<sup>[9, 14, 27, 39-47]</sup>

Fig. 3 Concentration of EDCs in organic solid waste<sup>[9, 14, 27, 39-47]</sup>

好氧堆肥可有效去除 EDCs。邻苯二甲酸在堆肥中的去除率为 32%~90%,邻苯二甲酸二(2-乙基己基)酯去除率可以高达 90%~99%,其降解途径主要包括烷基侧链的  $\beta$  氧化、脱酯反应和堆肥过程中的酯交换反应<sup>[9]</sup>。好氧堆肥对雌激素的去除率在 71% 至 99% 之间,其中去除效果最好的是雌三醇和 17 $\alpha$ -乙炔基雌二醇,去除率分别为 99% 和 92%<sup>[39]</sup>。加入微生物菌剂<sup>[48]</sup>和生物炭<sup>[49]</sup>可进一步提高雌激素去除率并减少氨气排放。HUSSAIN 等<sup>[50]</sup>研究表明堆肥可以去除 99% 的双酚 A,这可能得益于适当的通气、水分和理想的微生物活性,其中芽孢杆菌和假单胞菌是降解双酚 A 的主要细菌。此外,三氯生和三氯卡班主要在堆肥中温和高温阶段进行生物降解,其去除率随通风强度的增加而有所提高,强制通风后生物去除率可以达到 65% 和 83%<sup>[51]</sup>。

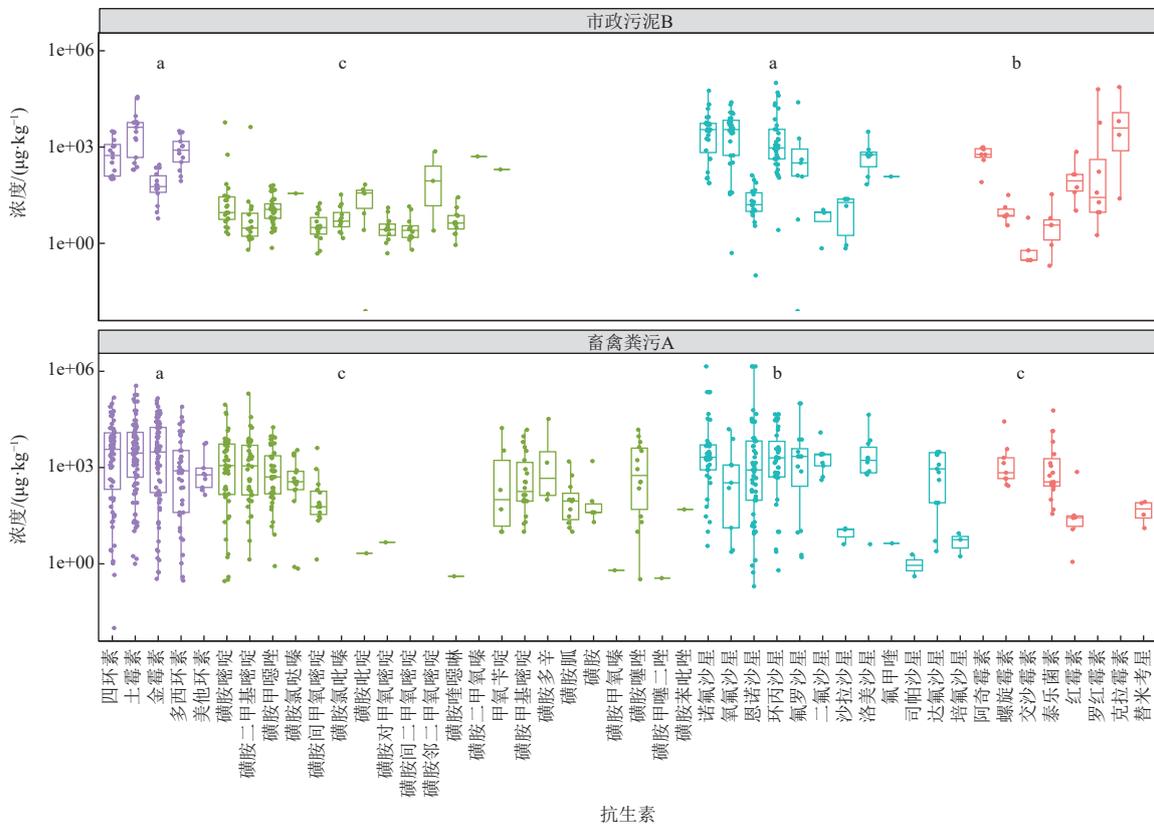
厌氧消化对 EDCs 的去除效果有限。ARMSTRONG 等<sup>[47]</sup>研究发现,无论是否进行热水解预处理,厌氧消化后三氯生、三氯卡班及其代谢产物的浓度均出现了增加,而邻苯二甲酸酯浓度变化各不相同。例如,邻苯二甲酸二(2-乙基己基)酯浓度降低,邻苯二甲酸二异壬酯浓度保持不变,邻苯二甲酸丁苄酯在经过预处理的系统中增加,而在未进行预处理的系统中减少。然而不论如何变化,不同种类邻苯二甲酸酯代谢产物的浓度在实验过程中普遍增加。REYES 等<sup>[42]</sup>研究也发现双酚 A 和辛基酚浓度在厌氧消化以及经超声和热水解预处理的厌氧消化后出现了增加,增长 8%~265% 之间。《重点管控新污染物清单(2023 年版)》中的壬基酚在好氧堆肥中去除率为 52%,而在厌氧消化过程中几乎不降解,这可能是厌氧消化过程中壬基酚乙氧基化物和壬基酚醚羧酸盐降

解为壬基酚,从而导致生产和降解之间的质量平衡,壬基酚浓度增加<sup>[36]</sup>。不同雌激素对温度的响应不同,雌三醇在中温厌氧消化中去除效果更好(中温 45%,高温 17%),雌酮和乙炔基雌二醇在高温厌氧消化中去除效果更好(雌酮:中温 79%,高温 96%;乙炔基雌二醇:中温 34%,高温 43%),而 17β-雌二醇在中温厌氧消化后浓度大幅度增加<sup>[52]</sup>。虽然好氧堆肥和厌氧消化在一定程度上可以降低 EDCs 含量,但仍有部分污染物残留在系统当中。环境风险评估显示,在有机固废好氧堆肥和厌氧消化过程中,23 种目标 EDCs 中 21 种存在环境风险,这可能会对参与好氧堆肥和厌氧消化的微生物以及后续的土地利用产生负面影响<sup>[27]</sup>。因此,需要对有机固废处理中,尤其是厌氧消化中不同种类 EDCs 的去除机制进行深入研究并找到更合适的降解策略。

### 2.3 抗生素赋存特征及消减

抗生素通常是指由细菌、真菌和放线菌等微生物产生的次级代谢产物或通过人工化学合成的类似物,通过抑制微生物生长或杀死微生物,治疗或预防由微生物引起的感染,目前广泛应用于人

体医疗和畜禽养殖<sup>[53]</sup>。据估计,30%~90% 生物体使用或摄入的抗生素会以原药或代谢物形式排出体外,最终进入市政污泥和畜禽粪污等有机固废中。有机固废中抗生素主要包括四环素类、磺胺类、喹诺酮类和大环内酯类,浓度范围为 0~1 420 800 μg/kg,平均值为 12 418 μg/kg,其中四环素类和喹诺酮类浓度普遍较高,而磺胺类检测出的种类最多(图 4)。在市政污泥中,抗生素浓度范围为 0.1~100 000 μg/kg,中位数浓度排序为喹诺酮类(580 μg/kg)>四环素类(469 μg/kg)>大环内酯类(28 μg/kg)>磺胺类(6 μg/kg)。在喹诺酮类中,中位数和平均值浓度最高分别是氧氟沙星和环丙沙星。与市政污泥相比,畜禽粪污中抗生素浓度显著更高,检出种类也更多。畜禽粪污中抗生素浓度范围为 0.01~1 420 800 μg/kg,中位数浓度排序为四环素类(2 200 μg/kg)>喹诺酮类(1 400 μg/kg)>磺胺类(360 μg/kg)>大环内酯类(328 μg/kg)。在四环素类中,中位数和平均值浓度最高的分别是四环素和土霉素。近期,周贤等<sup>[54]</sup>对南京某养殖场中 32 种抗生素浓度进行检测,发现鸡粪中总抗生素浓度(123 μg/kg)>猪粪(107 μg/kg)>牛粪(68 μg/



注:图中紫色为四环素类,绿色为磺胺类,蓝色为喹诺酮类,红色为β-内酰胺类抗生素。

图 4 有机固废中抗生素浓度<sup>[54, 56-62]</sup>

Fig. 4 Concentration of antibiotics in organic solid waste<sup>[54, 56-62]</sup>

kg)。这与抗生素使用剂量、畜禽对抗生素的吸收能力以及畜禽粪污对抗生素的吸附能力有关。目前,关于厨余垃圾中抗生素赋存的研究较少,ZHAO等<sup>[55]</sup>检测到厨余垃圾中四环素类、喹诺酮类、磺胺类和大环内酯类总浓度范围分别为14~57、7~157、0.4~21和0.3~8 μg/kg,远低于畜禽粪污和市政污泥。

好氧堆肥可以有效去除多种抗生素,其中磺胺类、喹诺酮类、四环素类、大环内酯类、β-内酰胺类抗生素甚至可以降至检测限以下<sup>[63]</sup>。然而,抗生素的去除情况受多种因素影响。不同堆肥工艺会影响抗生素的去除效果,ZHAO等<sup>[55]</sup>发现厨余垃圾经静态条垛堆肥和太阳能辅助堆肥后,总抗生素浓度分别下降了86%和58%,而动态条垛堆肥和机械堆肥分别增加了8%和72%。抗生素的初始浓度也会影响其在堆肥中的去除效率,浓度过高会抑制微生物活性,影响去除效果,过低时会吸附在堆体物质上,不利于其彻底去除。刘志平等<sup>[61]</sup>研究表明随着四环素、土霉素和金霉素浓度的增加,堆肥后的残留率也逐渐增加。通过改变堆肥操作参数、预处理方法和外源添加剂(生物炭和微生物菌剂等)可以促进抗生素的高效去除。刘志平等<sup>[61]</sup>发现随着培养温度逐渐增加,四环素、土霉素和金霉素的残留率呈现逐渐降低趋势,当C/N比为25时,残留率最低。周贤等<sup>[54]</sup>发现牛粪、猪粪和鸡粪经过堆肥后抗生素总去除率分别为92%、78%和90%,其中初始含水率和翻堆频率是影响畜禽粪污中抗生素消减的主要因素。当堆肥初始含水率为68%,采用2天1次的翻堆频率时,畜禽粪污中抗生素去除率可达100%。阚泽鑫等<sup>[64]</sup>发现高温预处理联合生物炭堆肥可实现抗生素的高效去除,在堆肥14 d后四环素类抗生素去除率高达100%,28 d后喹诺酮类和磺胺类抗生素去除率分别为100%和99%,去除时间可缩短14~28 d。复合菌剂施用效果往往优于单一菌剂,LIU等<sup>[65]</sup>通过添加黄孢原毛平革菌、黑曲霉和芽孢杆菌复合菌剂改变了原有微生物群落,诱导降解菌的大量繁殖,进而高效去除抗生素。

厌氧消化对抗生素也有较好的去除效果。厌氧条件下抗生素的去除途径包括降解、吸附、挥发和水解,其中生物降解和吸附是厌氧消化过程中抗生素去除的最主要途径<sup>[66]</sup>。靳红梅等<sup>[66]</sup>研究表明中温厌氧消化条件下,磺胺嘧啶和磺胺二甲嘧啶的去除率分别为59%和74%,降解半衰期分

别为5.85 d和5.90 d,其中生物降解作用是磺胺类抗生素去除的主要方式,贡献率均在80%以上。陈理等<sup>[67]</sup>研究表明不同抗生素在厌氧消化过程中的降解表现出较大差异,其中恩诺沙星和土霉素分别在厌氧消化的第5天和第15天基本达到100%的去除,而磺胺嘧啶在厌氧消化第30天去除率才达到53%。影响抗生素降解的因素有很多,魏晓曼等<sup>[68]</sup>采用响应面法,同时考虑抗生素初始质量分数、有机固废含固率和厌氧消化时间3种因素的影响,通过探究各个因素的相互作用,得出有机固废含固率是影响抗生素降解的主要因素。同时通过模型优化,得出抗生素残留质量分数最低的最优工艺条件,如猪粪含固率为3%,初始质量分数为40 000 μg/kg,厌氧消化时间为30 d,预测的磺胺甲嘧啶残留质量分数最低为428 μg/kg。此外,研究表明超声、酶处理、生物炭均可以提高厌氧消化期间抗生素的去除率,其中超声预处理是最有效的消减策略,而酶解(如木瓜蛋白酶、纤维素和溶菌酶)对抗生素的去除效果非常有限,但这可以通过延长污泥水力停留时间改善<sup>[69]</sup>。生物炭则主要通过促进厌氧消化过程中直接间电子转移以减轻抗生素抑制和促进甲烷生成<sup>[70]</sup>。

#### 2.4 MPs 赋存特征及消减

MPs是指直径小于5 mm的塑料碎片或颗粒,主要来源于家庭用品(个人化妆品、护理品等)、包装材料(食品、饮料包装等)和纺织品等<sup>[71]</sup>。MPs可分为初生和次生MPs,初生MPs是工业生产时形成的微米尺寸的塑料,次生MPs是大块塑料经过各种物理、化学和生物过程裂解形成的塑料微粒。尽管人们普遍认为塑料具有稳定性和生物化学惰性,但塑料添加剂(双酚A、邻苯二甲酸酯等)以及MPs吸附的各类污染物和病原菌等会随MPs一起进入环境中,严重威胁生态健康<sup>[72]</sup>。有机固废是MPs的重要储存库,丰度范围为36~495 000个/kg,平均值为34 703个/kg,其中市政污泥中MPs丰度(平均值为42 608个/kg)显著高于厨余垃圾(6 732个/kg)和畜禽粪污(1 627个/kg),这主要与污水处理过程中超过90%的MPs吸附在污泥中有关(图5)。该统计结果与TAN等<sup>[73]</sup>研究结果一致,即MPs污染程度为污泥>餐厅厨余垃圾>家庭厨余垃圾>猪粪>牛粪,其中MPs形状以纤维和薄膜为主,颜色以黑色、红色、蓝色和绿色为主,聚合物类型以聚乙烯(PE)、聚对苯二甲酸乙二醇酯(PET)、聚丙烯(PP)和聚

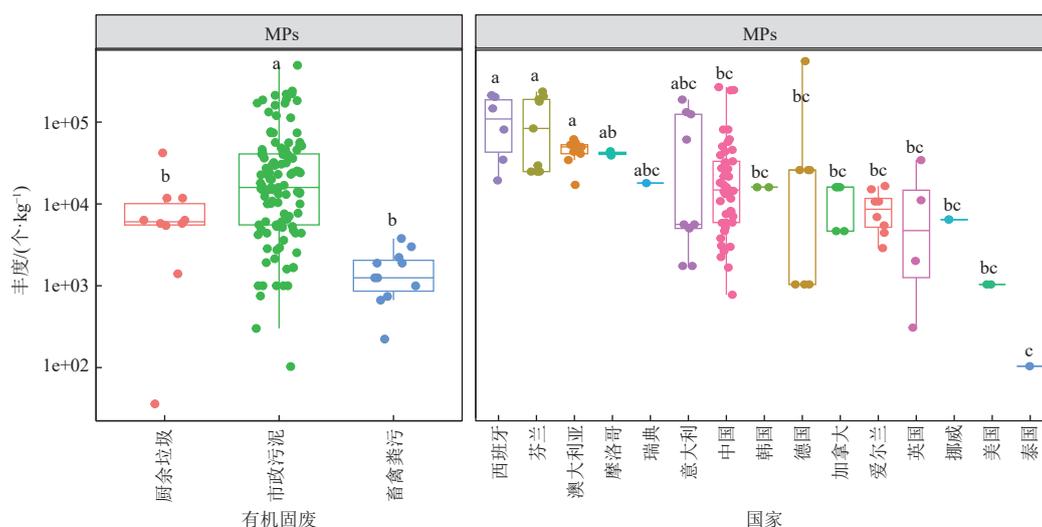


图5 不同有机固废中 MPs 丰度<sup>[62, 73-80]</sup>

Fig. 5 Concentration of MPs in organic solid waste<sup>[62, 73-80]</sup>

苯乙烯(PS)为主。污泥作为 MPs 丰度最高且研究最多的有机固废,进一步对 15 个国家的 MPs 赋存特征进行分析,发现西班牙、芬兰和澳大利亚是 MPs 丰度最高的国家,而美国和泰国 MPs 丰度最低,这可能与不同国家污水处理厂处理能力和生活模式有关。其中,中国是污泥样品中 MPs 研究最多的国家,丰度范围在 750~240 300 个/kg。

在好氧堆肥过程中,高温、高湿和高含氧量环境会加速 MPs 裂解,增加 MPs 的粗糙度和含氧官能团,从而有利于微生物黏附进而降解 MPs。CHEN 等<sup>[80]</sup>研究表明,超高温堆肥(44%)比传统堆肥(4%)具有更高的 MPs 去除率,这主要是因为更高的温度可以更好地促进 MPs 长链裂解,并向低分子量转移,8 种水溶性副产品的检出证明了这一点。此外,高温不仅可以加速 MPs 氧化生成 C=O 和 C—O 官能团,降低 MPs 的表面疏水性,而且使粒径大于 0.3 mm 的 MPs 含量显著减少,小于 0.3 mm 的逐渐增加,从而有利于微生物的吸附和降解,其主要的潜在降解微生物包括栖热菌、芽孢杆菌和地芽孢杆菌。堆肥中的 MPs 为微生物的生长提供良好的生态位,微生物可在塑料上进行频繁的物质交换和能量代谢,同时产生羧化酶、蛋白酶、过氧化物酶、氧化酶和漆酶等多种酶。在胞外酶的作用下,MPs 会解聚生成低聚合物和单体,然后被微生物利用转化为水和 CO<sub>2</sub> 等无机产物<sup>[75]</sup>。堆肥中的自由基也可以极大地促进 MPs 降解,为消除堆肥中的塑料污染提供有效策略。研究发现,在堆肥的氧化/缺氧交替条件下,微生物介导的 MPs 表面铁氧化物氧化还原转化

可促进活性自由基的产生,从而导致 MPs 的原位降解<sup>[81]</sup>。然而,MPs 的疏水特性容易从周围介质中吸收有机污染物,同时 MPs 在降解过程会增加有毒物质(增塑剂和重金属等)的释放或产生抑制微生物生长的活性酶,因而 MPs 的生物降解被抑制并对堆肥系统构成风险。目前,高温菌剂、超高温菌剂和生物炭已被证明可以提高 MPs 的去除效率<sup>[75, 82]</sup>。

一般来说,与好氧堆肥相比,厌氧消化不利于 MPs 降解。PE、PS、聚氯乙烯(PVC)、PET、聚酯纤维(PES)和聚酰胺(PA),在厌氧消化中表现为惰性物质,较短的厌氧消化周期内几乎不发生降解<sup>[62]</sup>。此外,研究表明,即使在系统中添加降解菌,也不会促进 PP 和 PET 的明显降解<sup>[83]</sup>。作为塑料的替代品,生物降解塑料在系统中的降解能力存在争议。MASSARDIER 等<sup>[84]</sup>研究表明,在厌氧条件下生物降解塑料 PLA 和 PCL 较少降解或没有降解,但在有氧条件下 PCL 降解程度达 35%。JIN 等<sup>[85]</sup>系统评估了 10 种可降解塑料在中温和高温条件下的厌氧降解性能。结果表明,4 种可降解塑料在中温条件下降解明显,生物去除率为 57.9%~84.6%,5 种可降解塑料在高温条件下降解明显,生物去除率为 53.0%~95.7%。这说明厌氧消化中部分生物降解 MPs 可以作为微生物生长、繁殖和代谢的碳源,并最终转化为生物质、CO<sub>2</sub> 或甲烷。进一步分析表明,聚丁二酸-己二酸丁二酯(PBSA)和聚乳酸(PLA)的降解主要依赖于本体侵蚀,聚己内酯(PCL)和聚甲基乙撑碳酸酯(PPC)的降解主要是表面侵蚀,微生物群落的差

异反映了不同可降解塑料的降解机制。通常情况下,低浓度的 MPs 并不会对厌氧消化造成影响,而较高浓度的 MPs 则会影响水解和产甲烷过程<sup>[86]</sup>。与好氧堆肥一样,MPs 对厌氧消化的影响主要表现在尺寸效应造成的微生物细胞物理损伤以及通过浸出塑化剂、添加剂和寡聚体等诱导活性氧产生导致细胞活力降低,进而抑制水解酸化和甲烷生成<sup>[87-89]</sup>。部分实用的方法如预处理(机械研磨、高温、碱处理)、接种微生物菌剂、添加絮凝剂以及沼渣二次堆肥等被提出来促进厌氧消化中 MPs 降解<sup>[90-91]</sup>。然而,目前关于 MPs 在好氧堆肥和厌氧消化系统中的降解机制研究较少,主要集中在 MPs 对系统的影响上,今后应做好二者之间的平衡。尽管好氧堆肥和厌氧消化可以降解 MPs,但其产品中仍有大量残留。另外,生物处理后,MPs 尺寸减小、疏水性增加,易从周围吸附有机污染物、并会释放增塑剂等污染物,可能带来更大的环境风险<sup>[73]</sup>。目前,有机堆肥产品和沼渣已然成为 MPs 进入农田的重要载体。因此,除了强化堆肥过程中 MPs 的原位降解外,建议尽量减少有机固废中(微)塑料的输入,并为有机固废及其生物处理产品的利用建立相关管理政策。

### 3 结论与展望

POPs、EDCs、抗生素和 MPs 等新污染物在有机固废中频繁检出,从有机固废中新污染物赋存水平来看,浓度范围和平均值排序为 EDCs(0.03~1 400 000  $\mu\text{g}/\text{kg}$ , 23 158  $\mu\text{g}/\text{kg}$ )>抗生素(0~1 420 800  $\mu\text{g}/\text{kg}$ , 12 418  $\mu\text{g}/\text{kg}$ )>POPs(0~751 000  $\mu\text{g}/\text{kg}$ , 1 268  $\mu\text{g}/\text{kg}$ ), MPs 也有较高的存在水平,范围为 36~495 000 个/kg,平均值为 34 703 个/kg。其中,POPs、EDCs 和 MPs 浓度在污泥中显著更高,抗生素浓度在畜禽粪污中显著更高,这与农业、工业化生产以及人类活动密切相关。好氧堆肥和厌氧消化能够有效控制和削减有机固废中的新污染物,一般来说,好氧堆肥去除新污染物的能力要高于厌氧消化。尽管在资源化处理过程去除了大部分新污染物,但部分难降解的有机污染物,如多氯联苯、二噁英等可能会吸附在固废的有机质上,使得降解缓慢,甚至出现浓度增加现象,对后续的土地利用造成潜在风险。为提高新污染物的去除率,可以通过控制和优化关键技术参数、预处理、引入外源添加剂、沼渣二次堆肥以及以上多因子联合等手段,进一步提高新污染物的消减效能。

当前,有机固废中新污染物研究仍不全面,未来需全面调查研究不同国家和地区有机固废好氧堆肥和厌氧消化中各种新污染的赋存、消减及潜在风险,对促进好氧堆肥和厌氧消化发展具有重要意义。新污染物种类繁多,且有机固废类型、资源化处理方式、工艺条件以及处理时间等的不同可能导致处理过程中新污染物和副产物的产生、分布和去除率的差异。机器学习在处理大规模、复杂数据方面具有显著优势。因此,今后有必要引入机器学习算法,在解析大量数据的基础上,对新污染物去除效果、与微生物作用机制,以及对堆肥质量和甲烷产量的影响进行评估和预测,以精准识别高风险污染物和降解产物并给予优先防控。目前,好氧堆肥和厌氧消化中新污染物的降解产物和降解机理仍不清楚,今后应引入基因组学、转录组学、蛋白质组学和代谢组学等技术,以深入探究新污染物降解机制并寻找合适的强化降解策略。值得注意的是,新污染物降解产生的有毒中间产物、抗生素使用导致的微生物耐药性以及 MPs 降解造成的更小塑料富集和增塑剂释放等二次污染问题,使得新污染物即使在微量情况下也具有比母体更加深远和更加持久的危害性。因此,须在全面了解新污染物赋存特征、挖掘新污染物降解机理以及寻找更好的降解技术的同时,应从源头控制新污染物的产生,如淘汰限制能产生新污染物的化工厂,寻找更加清洁、安全的平替工艺和材料,减少抗生素的使用,控制一次性塑料制品的生产和使用等。

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