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微波辅助提取 GC-MS/MS 测定复杂基质底泥中德克隆类化合物及处理效果初探

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摘要： 德克隆类物质在污泥样品中以痕量水平 (ng/g 级) 存在，加之污泥基质复杂，对污泥中德克隆类化合物的分析带来极大挑战。鉴于此，本文建立了微波辅助提取与气相色谱-三重四极杆串联质谱 (GC-MS/MS) 相结合，测定污水处理厂底泥中德克隆类化合物的分析方法。底泥样品采用微波辅助提取在线净化的方法，以丙酮-正己烷 (1∶1，*V*/*V*) 作为提取溶剂，在 120℃ 温度和 1500W 功率条件下，该方法能够高效地从基质复杂的底泥样品中提取出德克隆类化合物，提取回收率超过 80%。样品提取后，利用石墨化碳黑 (GCB) 和乙二胺基-N-丙基 (PSA) 固相萃取柱进一步净化，可有效地去除色素、脂类和非极性干扰物，减少基质干扰。借助质谱多反应监测 (MRM) 模式，针对目标化合物的特定离子对进行选择性监测，排除其他干扰离子的影响，从而实现了对德克隆类化合物的准确定量。该方法在 5～400ng/mL 浓度范围内线性关系良好，相关系数 (*r*) 不小于 0.998，检出限为 0.017～0.040ng/g。在低、中、高三个浓度水平底泥基质中，德克隆类化合物的平均回收率分别为 79.8%～99.5%、86.2%～104.8%、91.2%～106.1%，相对标准偏差 (RSD)＜7%。将该方法应用于实际底泥样品的检测，在 11 个污水处理厂底泥中均检出德克隆类化合物，且含量较高 (31.4～195.6ng/g)。底泥中顺式德克隆 (syn-DP) 异构体比例的平均值 f_{syn}=0.27，低于德克隆 (DP) 产品的 f_{syn} 值，这是由于底泥对反式德克隆 (anti-DP) 的吸附性更强，或底泥中的顺式德克隆 (syn-DP) 优先发生了生物降解。初步比较了 11 个污水处理厂采用不同的污水处理工艺处理底泥中德克隆化合物的效果，与活性污泥法水处理相比，采用 A^2/O 工艺处理的德克隆类化合物的浓度显著降低，f_{syn} 值显著增高，但其影响机制仍待深入探究。

关键词： 德克隆化合物；污泥；微波辅助提取；气相色谱-三重四极杆串联质谱法；污水处理厂；顺式德克隆 (syn-DP) 异构体比例 (f_{syn})

要点：

(1) 通过新鲜底泥直接提取、GCB/PSA 固相萃取柱净化与质谱多反应监测 (MRM) 模式相结合，降低基质干扰，实现德克隆类化合物准确定量。

(2) 污水处理厂底泥中的德克隆类化合物以 anti-DP 为主要贡献单体，f_{syn} 值为 0.27，低于商业 DP 产品 f_{syn} 值，底泥对 anti-DP 具有更强的吸附能力，或 syn-DP 更容易发生降解。

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(3) 不同的污水处理工艺对德克隆类化合物在底泥中的累积有显著影响，与活性污泥法水处理工艺相比，采用 A^2/O 工艺处理的德克隆类化合物的浓度显著降低 ($p<0.05$)，f_{syn} 值显著增高 ($p<0.05$)，具有更好的处理效果。

中图分类号：O657.63；X832　　**文献标识码：**A

德克隆 (Dechlorane Plus，简称 DP，化学式 $C_{18}H_{12}Cl_{12}$)，通过 Diels-Alder 加成反应合成，在十九世纪五十年代由美国 OxyChem 公司生产，其产品不仅包括顺式德克隆 (syn-DP) 和反式德克隆 (anti-DP)，还包括德克隆 602(Dec602)、德克隆 603(Dec603) 和德克隆 604(Dec604) 等产物。这些高氯代添加型阻燃剂被广泛应用于各种行业的材料制造中[1-2]，在工业生产、使用和处置时易渗入环境，最早由 Hoh 等[3]于大湖地区环境空气、沉积物和鱼类中发现，现在世界各地环境样本中频繁检出，在青藏高原[4]、北极地等地偏远环境亦有发现[5]，已成为严峻环境问题。德克隆类化合物具持久性有机污染物特征，如低光降解性 (＞24 年)[6]、高亲脂性、可生物积累[7]，其生物毒性受关注，德克隆暴露影响动物[8]和人体健康[9]。德克隆已被列入中国的《重点管控新污染物清单》，在环境中的分布与归趋引起了科学界的高度关注。污水处理厂作为城市污水的集中处理场所，是持久性有机污染物的重要来源[10]，同时也是环境中新兴污染物的来源[11]。污泥是污水处理厂的副产物，德克隆类化合物具有亲脂性，易在污水及污泥中富集。虽然污泥有焚烧、填埋、堆肥等几种处置方式，但多数处置方式会使处理或未经处理的污泥沉积到环境中，从而引发潜在的生态毒理学风险[12]。目前，针对污水厂处理污泥中德克隆类化合物的研究较少，准确测定污水厂底泥中德克隆的含量，对于评估环境风险、掌握迁移转化规律及制定污染控制策略意义重大。

德克隆类物质在环境介质中以痕量水平 (ng/g 级)存在[13]，并且污泥基质的复杂性对污泥中德克隆类化合物的分析非常具有挑战性，且目前针对污水处理厂底泥中德克隆的检测方法报道极少。现有方法适用于土壤和沉积物中德克隆化合物的分析测定，在样品前处理中索氏提取被用于固体样品中有机污染物的分离富集，虽对固体基质中化合物提取效率高，但存在耗时长、溶剂用量大等缺点[14]。快速溶剂萃取 (ASE) 在高压高温下用常规溶剂提取，能提高溶解度和传质速率，减少溶剂用量和提取时间，自动化程度高，在污泥中有机物提取上应用较多[15]。快速、简单、有效、坚固和安全 (QuEChERS) 方法可以与在线 SPE 相结合，用于测定污泥中的药物化合物[16]，但存在回收率变化大 (59.6% ~ 115.9%)、分析效率较低等问题[17]。与其他提取方法相比，微波辅助提取法 (MAE) 具有样品量小、溶剂消耗低、提取时间短且可同时处理多个样品的优点，已成功应用于从各种环境样品中提取药品、个人护理品以及工业污染物等新污染物[18]。

鉴于德克隆类化合物大多具有一定挥发性，当前主要运用气相色谱法 (GC) 进行分离，常见的检测手段包括气相色谱-质谱法 (GC-MS)[19]以及气相色谱-高分辨质谱法 (GC-HRMS)[20]。但 GC-HRMS 存在操作要求高、普及率低、价格昂贵等弊端；GC-MS 易受基质干扰，特别是在分析底泥样品时，基质干扰情况十分严重，进而致使浓度测定结果不准确[21]。气相色谱-三重四极杆串联质谱 (GC-MS/MS) 以其高灵敏度和特异性定量分析在有机污染物检测领域的应用越来越多[22]。GC-MS/MS 在多组分分析方面优势显著，Maguire 等[23]利用 GC-MS/MS 对大麻花基质进行全面的多残留农药分析，一次即可同时测定多达 367 种农药。并且，GC-MS/MS 在基质复杂程度高且对分析灵敏度要求极高的超痕量分析领域，同样得到了良好的应用。Lyu 等[24]通过对比 GC-MS/MS 和 GC-HRMS 在动物食品样品中多氯二苯并二噁英和呋喃 (PCDD/Fs) 的测定，证实 GC-MS/MS 与 GC-HRMS 具有相似的灵敏度、选择性和稳定性，可作为动物食品中痕量 PCDD/Fs 分析的确认方法。

污水处理厂底泥的基质特性与土壤、沉积物差异显著，成分复杂多样，并且底泥中干扰物种类繁多、浓度高，还含多种特异性污染物，这些因素极大地影响了检测结果的准确性与可靠性。目前，大部分检测方法是依据土壤和沉积物的特性进行设计与开发的，难以满足污水处理厂底泥检测工作的专业需求，无法直接应用于该类底泥的检测。因此，亟需建立适配底泥样品的分析方法。本文拟采用微波辅助提取法，并在提取进程中添加吸附剂以实现初步净化，再与固相萃取柱相结合，进一步强化净化效果，随后运用 GC-MS/MS 进行测定，以此克服底泥样品成分复杂和基质干扰严重的难题，建立一种可操作性强、

精密度高、适合大批量底泥中德克隆类化合物的分析方法。并将该方法应用于分析城市污水处理厂的污泥样品，获得污泥中德克隆类化合物的污染特征，为进一步研究德克隆类化合物的环境归趋提供依据。

1 实验部分

1.1 仪器和主要试剂

气相色谱-三重四极杆串联质谱联用仪 (TQ8040，日本岛津公司)；微波消解萃取仪 (ETHOS UP，Milestone 公司)；全自动浓缩仪 (AutoVap S8 Plus，美国 ATR 公司)。

目标物：灭蚁灵 (Mirex，100μg/mL，甲苯溶液)；顺式-德克隆 (syn-DP，100μg/mL，甲苯溶液)；反式-德克隆 (anti-DP，100μg/mL，甲苯溶液)；德克隆 602(Dec602，100μg/mL，甲苯溶液)；德克隆 603 (Dec603，100μg/mL，甲苯溶液)；德克隆 604(Dec604，100μg/mL，甲苯溶液)；反式-十氯德克隆 (anti-Cl_{10}DP，50μg/mL，甲苯溶液)；反式-十一氯德克隆 (ant-Cl_{11}DP，50μg/mL，甲苯溶液)。

净化内标：顺式-德克隆-$^{13}C_{10}$(syn-DP-$^{13}C_{10}$，100μg/mL，壬烷溶液)；反式-德克隆-$^{13}C_{10}$(anti-DP-$^{13}C_{10}$，50μg/mL，甲苯溶液)；$^{13}C_{12}$ 标记的多氯联苯 209($^{13}C_{12}$PCB209，40μg/mL，壬烷溶液)。

进样内标：$^{13}C_{12}$ 标记的多氯联苯 198($^{13}C_{12}$PCB198，40μg/mL，壬烷溶液)。

以上标准物质均购自阿尔塔科技有限公司。

铜粉(分析纯，纯度 99.9%)、无水 Na_2SO_4(分析纯，纯度≥99.0%)、C_{18} 层析填料(粒径：40-63um)、石墨化碳黑(GCB，粒径：100-300 目)、乙二胺-N-丙基硅烷(PSA，粒度：45μm)、硅胶固相萃取柱(规格 500mg/3mL)、C_{18}/PSA 固相萃取柱(规格 50mg PSA/50mg C_{18}，3mL)、GCB/PSA 固相萃取柱(规格 250mg GCB/250mg PSA，3mL)和弗罗里硅土(Florisil)固相萃取柱(规格 500mg/3mL)，均购自安谱公司。

1.2 样品采集

2024 年 4 月和 6 月，项目组在北京、河北、河南、天津、山东等城市 11 个污水处理厂采集底泥样本和未受德克隆类化合物污染的底泥样品 (德克隆化合物未检出)，其中的 1～5 号污水处理厂采用活性污泥法，6～11 号污水处理厂采用 A^2/O 工艺 (即厌氧-缺氧-好氧生物脱氮除磷工艺)。所有样品均收集在用丙酮-正己烷混合溶剂 (1∶1，*V/V*) 预清洗棕色玻璃容器中，每个样品采集三个平行样，同时采集空白样品。采集的样品在 4℃ 左右冷藏保存直至运回实验室。根据《土壤和沉积物 半挥发性有机物的测定 气相色谱-质谱法》(HJ 834—2017)，从样品采集到完成样品提取的时间不超过 14 天。

1.3 样品提取与净化

准确称取 10.00g 新鲜底泥样品，置于洁净的研磨钵中。首先，向其中加入 3.00g 铜粉，充分研磨混合。之后加入适量无水硫酸钠继续研磨，再依次加入 0.50g 石墨化碳黑 (GBC)、0.50g 乙二胺-N-丙基硅烷 (PSA)，并确保每加入一种物质后都研磨均匀。将经过预处理的底泥样品加入到 100mL 改性聚四氟乙烯材质的微波消解管内。加入 10μL 浓度为 10μg/mL 的净化内标混合溶液 ($^{13}C_{10}$-syn-DP、$^{13}C_{10}$-anti-DP 和 $^{13}C_{12}$-PCB209)。设置微波萃取参数为：微波萃取功率 1500W，萃取温度 120℃，升温程序为：初始温度 20℃，以 10℃/min 升温至 120℃，保持 20min。以 30mL 丙酮-正己烷 (1∶1，*V/V*) 为萃取溶剂，萃取完成后转移至含有 5g 无水硫酸钠砂芯漏斗上将底泥和萃取溶剂分离，浓缩至 1mL。用 GCB/PSA 固相萃取进一步净化，净化液氮吹浓缩后，加入 10μL 浓度为 10μg/mL 的 $^{13}C_{12}$ PCB198 进样内标溶液，并用正己烷定容至 1.0mL 后进气相色谱-三重四极杆串联质谱分析。

1.4 气相色谱-三重四极杆串联质谱分析条件

气相色谱参数：进样口温度 260℃，不分流进样；进样量 1.0μL，色谱柱 DB-5(15m×0.25mm，0.1μm)，柱流量 1.0mL/min。升温程序：初温 120℃，保持 2min；以 20℃/min 升温至 220℃ 保持 1min，以 10℃/min 升温至 310℃ 保持 2min。

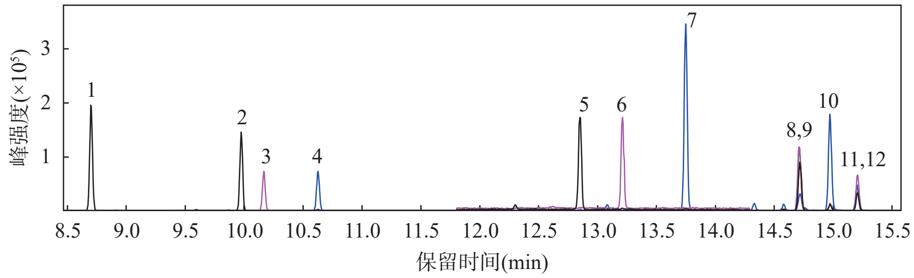
质谱参数：离子源为 EI 源；离子源温度 240℃；离子化能量 70eV；接口温度 280℃；溶剂延迟时间 4.5min。数据采集方式：质谱多反应监测 (MRM) 模式。

数据采集的德克隆类化合物色谱图见图 1，质谱条件参数列于表 1。

2 结果与讨论

2.1 样品的制备

针对同一含水分的新鲜样品，开展直接提取与干燥后提取的实验对照研究。各称取 10.0g 空白底泥制备新鲜样品和干样，新鲜样是与无水硫酸钠搅拌研磨后加标至浓度 10ng/g，干样是经阴干、研磨后加标至同浓度，再按照步骤提取底泥样品。结果如图 2 所示，各化合物在干样和湿样中的回收率相近，



1. Mirex；2. Dec602；3. $^{13}C_{12}$-PCB198；4. $^{13}C_{12}$-PCB209；5. Dec603；6. Dec604；7. anti-Cl_{10}-DP；8. syn-DP；9. $^{13}C_{10}$-syn-DP；10. anti-Cl_{11}-DP；11. anti-DP；12. $^{13}C_{10}$-anti-DP。

图1　德克隆类化合物的色谱图

Fig. 1　Chromatograms of dechlorane plus and related compounds.

表 1　德克隆类化合物的质谱分析参数

Table 1　Mass spectrometric analysis parameters of dechlorane plus and related compounds.

序号 No.	德克隆类化合物 Dechlorane plus and related compounds	保留时间 Retention time (min)	定量离子对 Quantitative ion pair		定性离子对 Qualitative ion pair	
			m/z	CE(eV)	*m/z*	CE(eV)
1	Mirex	8.753	272.00>236.80	15	274.00>238.80	15
2	Dec602	10.028	272.00>236.80	18	274.00>238.90	18
3	$^{13}C_{12}$-PCB198	10.217	476.00>405.70	39	474.00>403.70	24
4	$^{13}C_{12}$-PCB209	10.678	510.00>439.60	27	512.00>439.90	33
5	Dec603	12.90	263.00>192.90	30	261.00>191.00	33
6	Dec604	13.258	420.00>259.80	30	441.00>281.00	36
7	anti-Cl_{10}-DP	13.796	204.00>168.90	18	202.00>166.90	21
8	syn-DP	14.775	272.00>236.80	15	274.00>238.90	15
9	$^{13}C_{10}$-syn-DP	14.77	277.00>241.80	18	278.85>244.00	15
10	anti-Cl_{11}-DP	15.027	238.00>202.90	18	240.00>204.90	18
11	anti-DP	15.262	272.00>236.90	15	274.00>238.80	15
12	$^{13}C_{10}$-anti-DP	15.259	277.00>241.90	18	278.85>243.90	15

经双样本 *t* 检验, 在假定方差齐性以及假定方差不齐 (采用 Welch 校正) 的两种情况下, 所得到的概率值均大于 0.05, 表明“湿样”与“干样”并无显著差异。但多数化合物在湿样条件下所呈现的回收率较干样略高, 这可能是因为在微波提取中湿样中含有一定水分, 水是一种能够高效地吸收微波能的极性分子, 有助于目标化合物从基质中解吸和溶解到提取溶剂中。此外, 提取溶剂为丙酮-正己烷 (1 ∶ 1, *V/V*), 样品中存在少量水分时能够促进丙酮更好地与土壤颗粒接触, 提高提取效率。因此, 本研究采取新鲜底泥样品直接提取测定, 省却干燥步骤的操作与时间成本, 提高分析效率。

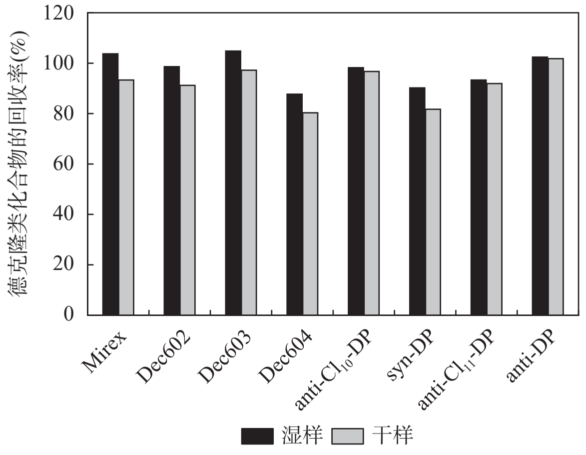


图2　不同样品制备方法条件下德克隆类化合物提取回收率

Fig. 2　Recoveries of dechlorane plus and related compounds extracted by different sample preparation methods.

2.2　微波辅助提取与净化样品实验条件的优化

微波辅助萃取 (MAE) 是利用微波能量加热样品-溶剂混合物, 该技术减少了从固体基质中提取有机化合物的萃取次数和萃取剂用量。它被用于从污水处理厂的污泥中提取目标分析物[25-27]。MAE 提取溶剂的选择、微波功率、萃取时间等因素对萃取物提取效率有很大影响[28]。为了研究最佳条件, 对

最相关的变量进行了实验设计 (n=7)。

2.2.1　微波辅助提取溶剂的选择与优化

根据目标物的理化性质与微波辅助提取对溶剂的要求，选用二氯甲烷、丙酮、正己烷、二氯甲烷-丙酮 (1∶1, V/V)、二氯甲烷-正己烷 (1∶1, V/V)、丙酮-正己烷 (1∶1, V/V) 共 6 种常用有机试剂进行提取，不同提取溶剂条件下德克隆类化合物提取回收率如图 3 所示。实验发现，以正己烷、二氯甲烷、二氯甲烷-丙酮 (1∶1, V/V) 和二氯甲烷-正己烷 (1∶1, V/V) 作为提取剂时，目标物在土壤中的回收率均不理想。当丙酮作为提取溶剂时，回收率可达 98.6%～108.7%。但因丙酮的极性较大，提取液中干扰物增多，影响定性、定量的准确性。综合考量回收率与干扰因素，最终确定选择丙酮-正己烷 (1∶1, V/V) 作为提取溶剂。

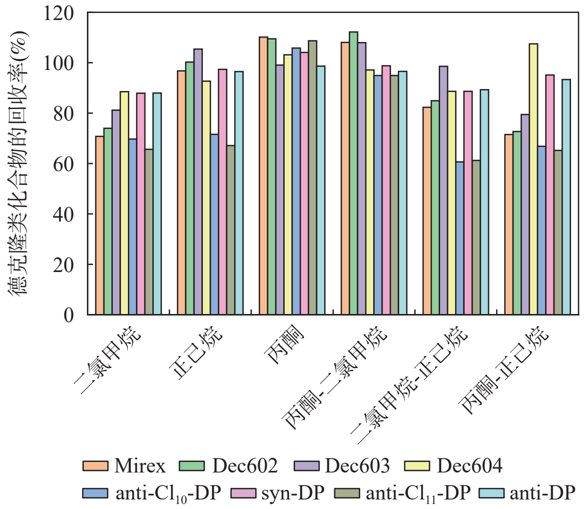


图3　不同提取溶剂条件下德克隆类化合物提取回收率

Fig. 3　Recoveries of dechlorane plus and related compounds extracted by different solvents.

2.2.2　微波辅助提取温度的选择与优化

以丙酮-正己烷 (1∶1, V/V) 为提取溶剂，提取温度温分别选择 50℃、80℃、100℃、120℃ 和 150℃。如图 4 所示，温度对提取效率有明显的影响，当提取温度≤80℃ 时，大多数德克隆类化合物回收率不足 80%；随着提取温度的升高，目标物回收率有所提升；当温度为 120℃ 时，大部分化合物的回收率达到峰值 (92.1%～110.4%) 并趋于稳定；但在 150℃ 时出现了基质效应。考虑到土壤基质的复杂性，较高提取温度会使共提干扰物增多，影响后续净化效果和仪器分析准确性，综合考虑实验最终选择提取温度为 120℃。

2.2.3　微波辅助提取功率的选择与优化

以丙酮-正己烷 (1∶1, V/V) 为提取溶剂，提取温度设定 120℃ 后考察微波提取功率对提取效率的影响。如图 5 显示，从 1000～1500W 随着提取功率的提高，各目标物回收率逐渐增加。以 Mirex 为例，提取功率为 1000W 时，回收率约为 63.2%；随着功率增加，回收率逐渐上升；在 1500W 时，回收率达到峰值，约为 107.3%。然而，当微波辅助提取功率升至 1700W 时回收率反而降低，Mirex、Dec602、Dec603 等低分子量化合物回收率分别降至约 53.4%、66.4% 和 66.5%。这可能是因为功率的增加使得提取温度升高，造成德克隆类化合物发生分解或者基质效应增强，故最终选择提取功率为 1500W。

2.2.4　样品净化

由于污泥样品基质复杂，富含脂类 (磷脂、脂肪酸等)，色素 (如胡萝卜素、叶绿素) 和其他干扰物质

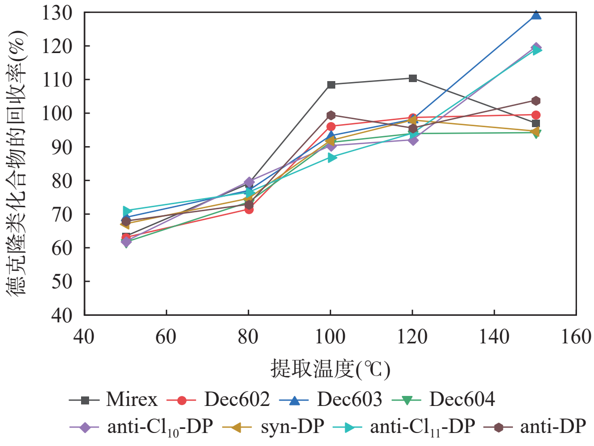


图4　不同提取温度条件下德克隆类化合物提取回收率

Fig. 4　Recoveries of dechlorane plus and related compounds extracted at different extraction temperatures.

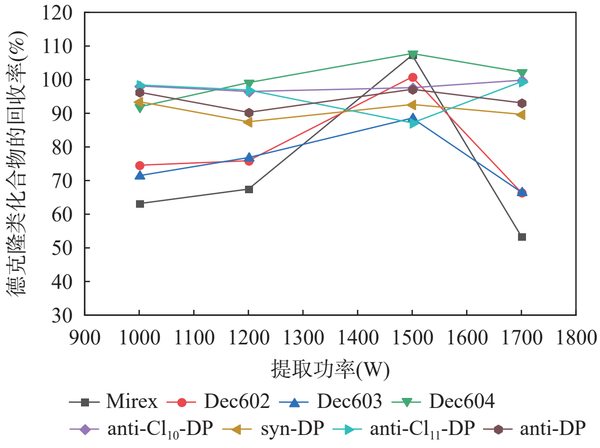


图5　不同提取功率条件下德克隆类化合物提取回收率

Fig. 5　Recoveries of dechlorane plus and related compounds extracted under different extraction power.

(如腐殖酸、黄腐酸) 等，因此样品提取后不能直接上机测定。本研究采用样品提取时加入吸附剂进行初步净化，再结合固相萃取柱进一步净化的方式来提高净化效果。选择实验室常用的铜粉除硫[29]，并考察了不同用量的净化效果，实验表明 10.00g 底泥样品加入 2.50g 铜粉即可达到除硫的效果。为了确保除硫的最佳效果，选择加入 3.00g 铜粉。有文献证实 C_{18} 通常用于去除有机溶剂中提取物中的干扰性脂类和亲脂性化合物。乙二胺基-N-丙基 (PSA) 也被证明能有效地去除酸性干扰物，如腐殖酸和黄腐酸，石墨化碳黑 (GBC) 可去除色素等干扰物质[30]。实验考察了 C_{18}、PSA 和 GBC 三种吸附剂对净化效果的影响，结果表明 10.00g 污泥中加入 0.50g 的 GBC 和 0.50g 的 PSA 净化效果最好，提取液在外观上颜色较浅，表明色素类杂质得到了有效去除；在仪器检测时，背景噪音最低，回收率较高，平均回收率可达 95.2%。

污泥样品经在线提取净化后的提取液仍然含有干扰物质，需要进一步净化。实验对比了硅胶柱、C_{18}、C_{18}/PSA、GCB/PSA、弗罗里硅土 (Florisil) 共 5 种固相萃取小柱的净化效果。图 6 结果表明，德克隆类化合物在硅胶柱和 Florisil 柱上的共提取物较多，回收率较低，分别为 62.4% ~ 77.3% 和 75.9% ~ 96.9%。可能是因为底泥样品基质复杂，硅胶柱和 Florisil 柱存在非特异性吸附、吸附容量与选择性有限，故在硅胶柱和 Florisil 柱上共提取物较多，并且德克隆与硅胶、Florisil 的吸附作用过强，从而使目标化合物不能充分被洗脱下来，最终造成回收率偏低。C_{18}、C_{18}/PSA 和 GCB/PSA 柱的回收率高于硅胶柱和 Florisil 柱，在 C_{18}/PSA 和 GCB/PSA 柱完成净化之后所得到的浓缩液，相较于 C_{18} 净化后的浓缩液，其颜色更浅，谱图上杂峰更少，这表明其净化效果更为理想，主要是因为石墨化碳黑 GCB 可去除色素、甾醇和非极性干扰物[31]，PSA 用于去脂质、碳水化合物和色素等极性干扰物[32]。在保证各目标物回收率的前提下，考虑到底泥中脂肪含量较高，最终选用 GCB/PSA 固相萃取柱。

2.3　方法线性范围、检出限和精密度

配制标准溶液的浓度分别为 5、20、50、100、200、400ng/mL，以 $^{13}C_{10}$-syn-DP、$^{13}C_{10}$-anti-DP 和 $^{13}C_{12}$-PCB209 作为净化内标（100ng/mL），$^{13}C_{12}$-PCB198 作为进样内标（100ng/mL），将配制好的混合标准工作液在优化好的仪器条件下进行测试。以目标物与内标物仪器响应比率 (y) 为纵坐标，对应的目标物与内标物的浓度比率 (x) 为横坐标，绘制标准工作曲线。在 MRM 模式下，德克隆类化合物在对应的质量浓度范围内线性良好，相关系数 (r) 不小于 0.998。以样品浓度为 0.5ng/g 的基质加标样，根据 1.2 和 1.3 所示做样品前处理并上机分析，根据检出限的计算公式 $MDL=S\times t_{(n-1,\ 1-\alpha=0.99)}$，计算德克隆类化合物的方法检出限为 0.017 ~ 0.040ng/g(表 2)。

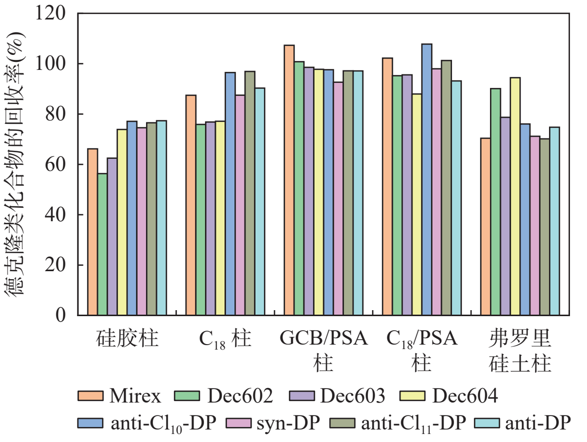


图6　不同净化小柱条件下德克隆类化合物提取回收率

Fig. 6　Recoveries of dechlorane plus and related compounds extracted with different purification columns.

表 2　德克隆类化合物的线性方程、相关系数、检出限和定量限

Table 2　Linear equations, correlation coefficients, detection limits and quantitation limits of dechlorane plus and related compounds.

德克隆类化合物 Dechlorane plus and related compounds	线性方程 Linear equation	相关系数 Correlation coefficient (r)	检出限 Detection limit (ng/g)
Mirex	y=0.2137x−2.3210	0.9995	0.024
Dec602	y=0.1604x−1.8138	0.9998	0.040
Dec603	y=0.0430x−0.7378	0.9988	0.024
Dec604	y=0.0024x+0.0073	0.9995	0.038
anti-Cl_{10}DP	y=0.1061x+1.8584	0.9993	0.017
syn-DP	y=0.0190x+0.1920	0.9999	0.018
anti-Cl_{11}DP	y=0.1374x+3.1074	0.9987	0.040
anti-DP	y=0.0491x+0.7488	0.9995	0.039

以空白底泥样品为基质进行低、中、高三个浓度水平 (分别为 2、10、30ng/g) 的加标回收实验，每个浓度平行 7 次，在优化条件下测得各个浓度的德克隆类化合物的平均回收率分别为 79.8% ~ 99.5%、86.2% ~ 104.8%、91.2% ~ 106.1%，相对标准偏差 (RSD, n=7) 分别为 2.28% ~ 6.91%、2.24% ~ 5.58%、1.17% ~ 5.87%。同时低、中、高三个浓度水平下净化内标 $^{13}C_{12}$-PCB209、$^{13}C_{10}$-syn-DP 和 $^{13}C_{10}$-anti-DP 的回收率分别为 88.3% ~ 94.8%、92.2% ~ 102.3%、85.9% ~ 100.8%，相对标准偏差 (RSD, n=7) 分别为 2.89% ~ 4.12%、2.39% ~ 3.28%、2.31% ~ 3.56%(表 3)。与 EPA 测定有机污染物的标准方法指标对比，表明本文方法具有较好的准确性和精密度，可满足水体中痕量德克隆类化合物的分析需求。

2.4 本文方法的特性优势与文献方法对比

鉴于当前尚无专门针对底泥中德克隆化合物的分析方法，将本文建立的底泥中德克隆类化合物测定方法，与文献中用于测定土壤和沉积物中德克隆类化合物的方法进行对比 (表 4)，本文方法的特性优势主要体现在以下方面。

(1) 在测定基质方面存在显著差异，这使得本方法的测定难度较大。相较于沉积物和土壤，本文所采用的基质为底泥样品，其成分更为复杂，可能含有大量的微生物、有机物以及各种矿物质等，这些因素相互交织，极大地增加了德克隆类化合物的测定难度。

(2) 本文方法的综合性能具有优势。本文方法采用微波辅助提取与 GC-MS/MS 联用技术，能够测

表 3 德克隆类化合物的加标回收率和精密度

Table 3 Average recoveries and RSD of dechlorane plus and related compounds.

德克隆类化合物 Dechlorane plus and related compounds	添加浓度 2ng/g Spiked concentration of 2ng/g		添加浓度 10ng/g Spiked concentration of 10ng/g		添加浓度 30ng/g Spiked concentration of 30ng/g	
	平均回收率 Average recovery (%)	RSD (%)	平均回收率 Average recovery (%)	RSD (%)	平均回收率 Average recovery (%)	RSD (%)
Mirex	89.8	6.29	93.3	5.58	106.0	2.79
Dec602	79.8	6.60	98.6	5.39	102.4	2.28
Dec603	92.5	2.28	104.8	3.73	91.2	3.70
Dec604	83.5	4.60	87.7	4.79	91.3	5.87
anti-Cl_{10}DP	99.5	6.91	94.2	2.48	106.1	1.17
syn-DP	82.8	3.16	86.2	3.10	95.7	1.62
anti-Cl_{11}DP	99.5	3.03	91.9	2.51	103.3	1.95
anti-DP	91.7	2.39	102.4	2.24	95.8	1.48
$^{13}C_{12}$-PCB209	88.3	4.12	102.3	3.28	100.8	2.97
$^{13}C_{10}$-syn-DP	94.8	3.56	92.2	3.16	85.9	2.31
$^{13}C_{10}$-anti-DP	89.5	2.89	94.9	2.39	91.4	3.56

表 4 本文分析方法与相关文献分析方法的比较

Table 4 Comparison of the analytical methods in this paper and those in related literatures.

目标物 Target compounds	样品基质 Sample matrix	样品前处理方法 Sample pretreatment method	分析仪器 Analytical instrument	方法回收率 Recovery of method	方法检出限 Detection limit of method	参考文献 Reference
syn-DP, anti-DP, Dec602, Dec603, Dec604	干燥沉积物 Dry sediment	索氏提取，多层硅胶柱净化 Soxhlet extraction, multi-layer silica gel column purification	GC-HRMS	61% ~ 106%	0.5 ~ 1pg/g	[33]
Mirex, syn-DP, anti-DP, Dec602, Dec603, Dec604	干燥沉积物和土壤 Dry sediment and soil	加压液相萃取，镁铝层状双金属氢氧化物净化 Pressure liquid phase extraction, Mg-Al layered double oxides purification	GC-MS	90.3% ~ 99.8%	0.01 ~ 0.67ng/g	[34]
Mirex, syn-DP, anti-DP, Dec602, Dec603, Dec604, anti-Cl_{10}DP, anti-Cl_{11}DP	新鲜底泥 Fresh sludge	微波辅助提取，GCB/PSA 固相萃取柱净化 Microwave assisted extraction, GCB/PSA solid phase extraction column purification	GC-MS/MS	79.8% ~ 106.0%	0.017 ~ 0.040ng/g	本文研究 This study

定的化合物种类更多 (8 种); 回收率 (79.8%～106.1%) 与加压液相萃取技术相当, 且优于传统的索氏提取法; 在检出限方面, 虽然本文方法 (GC-MS/MS) 不及 GC-HRMS 的灵敏度高, 但相较于 GC-MS 仍具有明显优势。索氏提取法在文献中报道的提取时间长达 24h[35] 或 36h[36], 而本文采用微波辅助提取, 仅需 45min 即可同时处理 44 个样品。这一显著的时间优势提高了分析效率, 使本文方法更适用于大规模样品的快速检测。

(3) 采用新鲜底泥样品直接进行提取, 省却了干燥步骤的操作与时间成本。若进行干燥处理, 易使样品受环境干扰、改变特性从而会影响结果。直接提取则保持了原始状态, 避免以上这些问题, 从而提高了德克隆类化合物检测结果的准确性, 为研究提供可靠数据。

(4) 与单级质谱 (MS) 相比, 本文方法采用的 GC-MS/MS 技术能够有效地减少共萃取化合物干扰, 为污水处理厂底泥相关领域的样品分析提供了一种高效、准确且具有实际应用价值的检测方法。

2.5　分析方法的应用

2.5.1　污水处理厂底泥中德克隆类化合物的分布特征及 f_{syn} 值分析

DP 的同分异构体有顺、反两种构象。DP 的同分异构体比值可以用分数丰度来描述, syn-DP 的异构体比例 (f_{syn}) 用顺式 DP 浓度除以总 DP 浓度来计算, 即 f_{syn}=syn-DP/(anti-DP+syn-DP)。按照 1.2 节和 1.3 节的方法参数测定污水处理厂底泥中的德克隆含量, 并根据测定结果, 绘制德克隆类单体在不同污水处理厂底泥中的分布特征图 (图 7)。可以看出, 在 11 个污水处理厂底泥中均检测到德克隆类化合物, 总量为 31.4～195.6ng/g, 与文献报道的加拿大多伦多某一污水处理厂底泥中的德克隆含量相近 (34～120ng/g)[37]。可见, 污水处理厂由于其去除工艺存在一定的局限性, 致使有机污染物无法完全被清除[38]。为确保数据的精确性与可靠性, 本文实施了严格的质量控制措施, 空白样德克隆类化合物的浓度均小于检出限 (LOD), 同时进行了加标回收实验, 其回收率为 80.6%～117%, 平行样的相对偏差为 0.14%～8.45%, 质控结果显示实验过程没有出现明显的失误或偏差, 测试结果可靠。

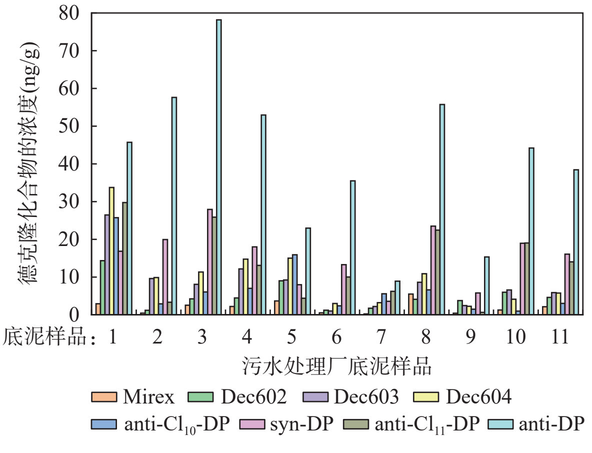


图7　德克隆类化合物在不同污水处理厂底泥中的分布特征

Fig. 7　Distribution characteristics of dechlorane plus compounds in the sludge of sewage treatment plants.

由图 7 可见, 不同污水处理厂底泥中德克隆类化合物中分布不相同, 推测污水处理厂底泥中的德克隆化合物浓度可能与当地生活和工业使用德克隆类化合物有关。底泥样品中的德克隆类化合物均以 anti-DP 是主要的贡献单体, 占比 23.4%～53.0%, Mirex 含量最低, 占比 0.4%～4.0%, 这可能与其自 2009 年起被禁用多年有关。同时发现 DP 的脱氯产物在测定的 8 种德克隆化合物中浓度较高, anti-Cl_{10}-DP 和 anti-Cl_{11}-DP 的浓度加和仅次于 anti-DP 与 syn-DP 之和, DP 的脱氯产物需要引起足够的重视。污水处理厂 1 底泥中, 德克隆类化合物的浓度最高, 可能是该污水处理厂处于潮白河附近, 潮白河上游有电子垃圾拆解基地, 电子垃圾的拆解回收可能会将高浓度的德克隆类物质释放到邻近环境中, 已有研究证实潮白河受到城市污水和工业废水的污染, 河水和沉积物中检测到较高浓度的 DP[33]。Jia 等[39]报告了中国生产的 DP 产品的 f_{syn} 值在 0.20～0.36 之间, 商业 DP 产品的 f_{syn} 值为 0.41。本研究计算获得的平均 f_{syn}=0.27, 要低于 DP 产品的 f_{syn} 值, 可归因于底泥中对 anti-DP 的更高吸附或底泥中 syn-DP 的优先生物降解。

2.5.2　不同水处理工艺对德克隆类化合物的影响及机制分析

污水处理过程中, 有机污染物的去除程度受多种因素影响, 如化合物的物理化学和生物特性、污水处理厂的配置和运行环境、所选用的污水处理技术、周边环境因素等。本文研究在仅考虑底泥浓度的前提下, 将不同水处理工艺的德克隆类化合物含量与 syn-DP 异构体比例绘制箱式图 (图 8)。如图 8a 所示, 与活性污泥法水处理相比, 采用 A^2/O 工艺的德克隆类化合物的浓度显著降低 ($p<0.05$), 其平均浓度从活性污泥法的 135.7ng/g 降至 75.2ng/g。对比不同水处理工艺中获得的 f_{syn} 值 (图 8b), 采用 A^2/O 工艺的

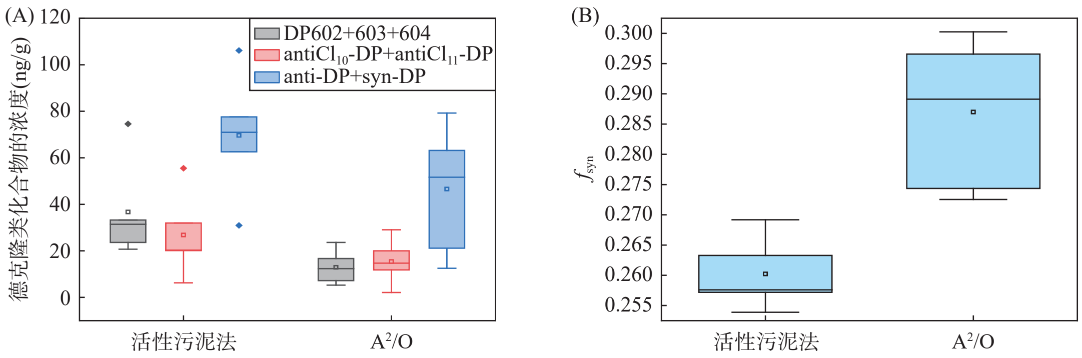


图8 不同水处理工艺处理的德克隆类化合物浓度 (a) **和** syn-DP **异构体比例** (b) **箱式图**

Fig. 8 Box diagrams of dechlorane plus compounds (a) and f_{syn} values (b) in different water treatment processes.

f_{syn} 值显著增高 ($p<0.05$), 由 0.26 上升至 0.29。在采用 A^2/O 工艺处理污水过程中, 在厌氧池中需氧的氨氧化细菌 (如亚硝化单胞菌属 Nitrosomonas europea) 在氧气限制条件下, 可以将 50% 的生物可利用氨转化为亚硝酸盐, 称为部分亚硝化[40], 亚硝酸盐再被硝化杆菌氧化成硝酸盐。在缺氧池中, 反硝化菌利用污水中的有机物作碳源, 将回流混合液中带入大量硝酸盐转化为氮。在好氧池中, 有机物被微生物生化降解, 而继续下降; 磷元素被聚磷菌摄取, 也以较快的速度下降。有研究证实, A^2/O 工艺能够除去城市污水中药物活性化合物[41], 故推测, 在厌氧-缺氧-好氧交替运行下, 德克隆类化合物可能会被降解。此外, 从结构式上看, 与 syn-DP 相比, anti-DP 的环辛烷部分的 4 个内部碳被氯遮挡的程度较小, 这表明 anti-DP 可能更具活性[3], 更容易受到生物降解的影响, 因此其 f_{syn} 值增大。

3 结论

采用微波辅助提取与气相色谱-三重四极杆串联质谱相结合, 建立了一种适合测定污水处理厂底泥等复杂基质中德克隆类化合物的方法。在最优条件下, 获得较低的检出限为 0.017 ~ 0.040ng/g, 高、中、低三个水平的加标回收率和重现性均满足 EPA 测定有机污染物标准方法的要求。对于大批量样品检测工作, 该提取技术省时、省力、省溶剂。将建立的方法应用于分析城市污水处理厂水处理过程中产生的底泥样品, 在 11 个污水处理厂底泥中均检测到德克隆类化合物, 其中 anti-DP 含量最高, Mirex 含量最低。不同污水处理厂产生的德克隆类化合物的分布特征不相同, 可能与当地生活和工业的德克隆类化合物的使用有关。在未考虑进水口德克隆类化合物含量与污水处理厂运行条件, 仅考虑底泥浓度的前提下, 统计 11 个污水处理厂底泥的数据, 发现不同的污水处理工艺对德克隆类化合物在底泥中的累积有着显著的影响, 与活性污泥法水处理相比, 采用 A^2/O 工艺的德克隆类化合物的浓度显著降低 ($p<0.05$), 其 f_{syn} 值显著增高 ($p<0.05$)。

本研究还有不足之处, 需要进一步探索。首先, 当前研究主要集中在单一介质 (污泥) 中的德克隆类化合物分析, 未能全面反映污水处理厂整体工艺对德克隆的影响, 需要同时采集污水处理厂污水和污泥样品, 系统地研究德克隆类化合物在不同介质中的分布特征和迁移规律, 深入探讨不同污水处理工艺对德克隆类化合物的去除效率和机制, 明确各工艺环节的作用。此外, 本文中污泥样品分别采集于 4 月和 6 月, 这两个月份的环境条件 (如温度、湿度、氧气含量等) 存在差异, 这些环境因素会影响底泥中微生物的种类与活性, 进而通过微生物代谢活动影响德克隆类化合物的降解、转化或富集过程, 改变其在底泥中的分布与迁移特性。尤为重要的是, 环境条件的变化会改变底泥的氧化还原状态, 从而影响德克隆类化合物的稳定性和反应活性。然而, 本研究尚未充分考虑这些环境条件对德克隆类化合物的影响。

Determination of Dechlorane Plus Compounds in Complex Matrix Sludge by GC-MS/MS with Microwave-Assisted Extraction and Evaluation of Treatment Efficiency

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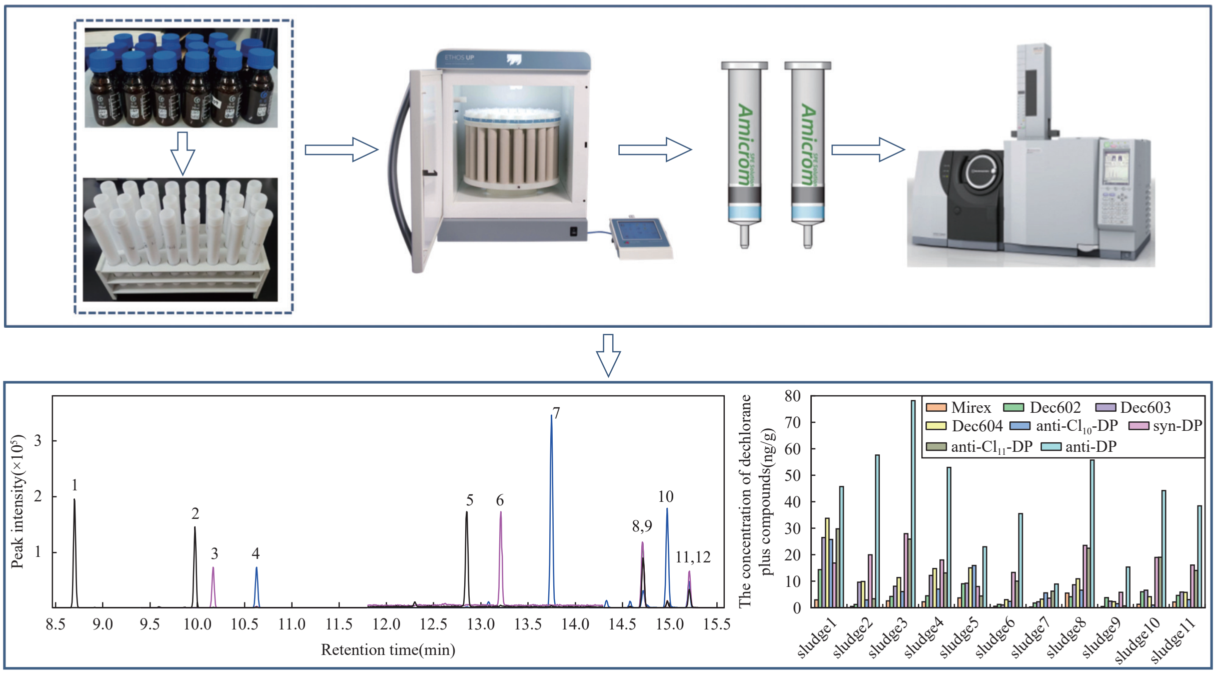
HIGHLIGHTS

(1) By combining direct extraction from fresh sludge, purification using GCB/PSA solid-phase extraction columns, and the multiple reaction monitoring (MRM) mode of mass spectrometry, matrix interference was minimized, and accurate quantification of dechlorane compounds was achieved.

(2) In the sludge of the sewage treatment plants, anti-DP was the main contributing monomer among the dechlorane plus compounds. The f_{syn} value was 0.27, which was lower than that of commercial DP products. This indicates that the sludge in the sewage treatment plants has a stronger adsorption capacity for anti-DP or that syn-DP is more prone to degradation.

(3) Different wastewater treatment processes have a significant impact on the accumulation of dechlorane compounds in sludge. Compared with the activated sludge process, the concentration of dechlorane plus compounds in the A^2/O process was significantly reduced ($p<0.05$), and the f_{syn} value was significantly increased ($p<0.05$), indicating that the A^2/O process is more effective in treating dechlorane plus compounds.



ABSTRACT: Dechlorane plus compounds are present at trace levels (ng/g) in sludge samples. The complex sludge matrix poses a significant challenge for the analysis of these compounds. To address this issue, we established an analytical method for determining dechlorane plus compounds in the sludge of sewage treatment plants, combining microwave-assisted extraction with gas chromatography-triple quadrupole tandem mass spectrometry. Sludge samples were processed using microwave-assisted extraction with online purification, and using acetone-*n*-hexane (1 : 1, *V/V*) as the extraction solvent. After extraction, GCB/PSA solid-phase extraction columns were used for further purification to reduce matrix interference. The multiple reaction monitoring (MRM) mode of mass spectrometry was employed for accurate quantification. This method demonstrated good linearity ($r \geqslant 0.998$) in the 5−400ng/mL range, with a detection limit of 0.017−0.040ng/g. The average recoveries were 79.8%−99.5%, 86.2%−104.8% and 91.2%−106.1% at low, medium and high concentrations, respectively, with relative standard deviations (RSDs) of <7%. When applied to 11 sewage treatment plants, dechlorane plus compounds were detected, and the contents were relatively high (31.4−195.6ng/g). In sludge, average f_{syn} of syn-DP was 0.27, lower than that of DP products. This is due to stronger anti-DP adsorption or preferential syn-DP biodegradation. When the A^2/O process was adopted, the concentration of dechlorane plus compounds was significantly reduced, and the f_{syn} value was significantly increased, but the influencing mechanism still needs to be further explored. The BRIEF REPORT is available for this paper at http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202409190197.

KEY WORDS: dechlorane plus compounds; sludge; microwave assisted extraction; gas chromatography-triple quadrupole tandem mass spectrometry; sewage treatment plant; fraction abundance of syn-DP (f_{syn})

BRIEF REPORT

Significance: Dechlorane plus (DP) is synthesized through the Diels-Alder addition reaction. It was first produced in the United States in the 1950s, and its products are diverse. As a highly chlorinated flame retardant, it is widely used[1-2]. Due to its tendency to enter the environment during production, use, and other processes, DP has been frequently detected in environmental samples around the world[4-5]. It exhibits characteristics of persistent organic pollutants (POPs), affecting the health of organisms[8-9], and has been included in China's list of key controlled emerging pollutants.

Sewage treatment plants are important sources of pollutants. DP compounds tend to accumulate in sludge, and the existing disposal methods carry ecological risks[12]. However, there are relatively few studies on DP compounds in the sludge of sewage treatment plants. Accurately determining its content is of great significance. Nevertheless, the complex sludge matrix poses challenges to the analysis. Most of the existing detection methods are designed for soil and sediment. For example, Soxhlet extraction is time-consuming and requires a large amount of solvent[14]. Although QuEChERS has its advantages, it has problems such as large variations in recovery rates (59.6%−115.9%)[16-17]. At present, gas chromatography is primarily employed to separate DP compounds. Common detection methods include GC-MS and GC-HRMS[19-20]. However, GC-MS is prone to matrix interference, while GC-HRMS has high operation requirements and comes at a high cost[21]. GC-MS/MS, on the other hand, boasts high sensitivity and strong specificity, showing distinct advantages in multi-component and ultra-trace analysis[24-25].

Due to the special matrix of the sludge in sewage treatment plants, it is challenging to meet the detection limit requirements with existing methods. This research intends to use microwave-assisted extraction combined with adsorbents for preliminary purification, then strengthen the purification effect with solid-phase extraction columns, and finally determine the content by GC-MS/MS. The recovery rate of the method was comparable to that of pressurized liquid extraction technology and superior to the traditional Soxhlet extraction method. When this method was applied to the detection of actual sludge samples, DP compounds were detected in the sludge of 11 sewage treatment plants, with anti-DP being the main contributing monomer. The f_{syn} value was 0.27, lower than that of commercial DP products. At the same time, it was found that the A^2/O process had a significant impact on the concentration of DP compounds in the sludge and the f_{syn} value and was more effective in treating such compounds.

Methods: In April and June 2024, sludge samples were collected from 11 urban sewage treatment plants in China, including samples not contaminated by DP compounds. The activated sludge process was adopted in sewage treatment plants numbered 1−5, while the anaerobic-anoxic-oxic (A^2/O) process was used in plants numbered 6−11. The samples were collected in pre-cleaned brown glass containers. Three parallel samples and blank samples were taken for each sample. The samples were stored and refrigerated at around 4℃, and extraction was completed within 14d after collection.

Accurately weigh 10.00g of fresh sludge sample. Mix it successively with 3.00g of copper powder, an appropriate amount of anhydrous sodium sulfate, 0.50g of graphitized carbon black (GCB), and 0.50g of primary-secondary amine sorbent (PSA), and grind them evenly. Then add the purification internal standard solution. Next, perform extraction using acetone-n-hexane (1 : 1, *V/V*) under conditions of 1500W power and 120℃. After the extraction, separate and concentrate the extraction solution. Then, purify it through GCB/PSA solid-phase extraction. Add the injection internal standard, and then analyze it by GC-MS/MS.

For gas chromatography, the injection port temperature was set to 260℃ with splitless injection; the injection volume was 1.0μL. The used chromatographic column was a DB-5 (15m×0.25mm, 0.1μm), and the column flow rate was 1.0mL/min. The temperature program was as follows: initial temperature of 120℃, held for 2min; then increased to 220℃ at a rate of 20℃/min and held for 1min and finally increased to 310℃ at a rate of 10℃/min and held for 2min. For mass spectrometry, the EI source was used as the ion source, with an ion source temperature of 240℃, ionization energy of 70eV, interface temperature of 280℃, and solvent delay time of 4.5min. Data acquisition was performed using multiple reaction monitoring (MRM) mode. The chromatograms and mass spectrometry condition parameters for data collection are shown in Fig.1 and Table 1.

Data and Results: (1) This study focuses on the detection of DP compounds in sludge. A comparative experiment of direct extraction and extraction after drying was conducted on the same fresh water-containing sample. It was found that the recovery rate of the wet sample was slightly higher (Fig.2). Therefore, direct extraction of fresh sludge was adopted to improve efficiency.

In the optimization of sample extraction and purification, extraction experiments with different organic reagents were performed, and acetone-*n*-hexane (1 : 1, *V/V*) was determined as the optimal extraction solvent, with a recovery rate of 98.6%−108.7% (Fig.3). The effects of different temperatures and powers on extraction efficiency were studied, as shown in Fig.4 and Fig.5 respectively, and finally 120°C and 1500W were selected as the optimal conditions, with recovery rates of 92.1%−110.4% and 89.2%−107.3%, respectively. For purification, it was determined that adding 3.00g of copper powder to 10.00g of sludge effectively removed sulfur. Simultaneously adding 0.50g of graphitized carbon black (GCB) and 0.50g of primary secondary amine (PSA) in sequence effectively removed interferences such as pigments and lipids. The GCB/PSA solid-phase extraction column was used for further purification, with a recovery rate of 92.6%−105.3% (Fig.6).

The standard solution test showed that DP compounds exhibited good linearity ($r \geqslant 0.998$), with a limit of detection ranging from 0.017 to 0.040ng/g (Table 3). The average recoveries were 79.8%−99.5%, 86.2%−104.8% and 91.2%−106.1% at low, medium and high concentrations, respectively (Table 4), with relative standard deviations of less than 7%, meeting the analysis requirements.

Compared to methods used in the literature for determining DP compounds in soil and sediment, this method faces the challenge of a more complex sludge matrix but offers several advantages. It can detect a wider range of compounds, and its recovery rates are comparable to those achieved by pressurized liquid extraction technology and superior to the traditional Soxhlet extraction method. In terms of detection limits, this method has a clear advantage over GC-MS, although it is not as sensitive as GC-HRMS. Microwave-assisted extraction processes 44 samples in just 45min. Additionally, direct extraction of fresh sludge avoids issues associated with drying. The use of GC-MS/MS technology effectively reduces interference from co-extracted compounds and minimizes the matrix effect, providing an efficient, accurate, and practical detection method for analyzing sludge samples in sewage treatment plants.

(2) DP has two conformational isomers, syn-DP and anti-DP. The ratio of its isomers is described by fractional abundance. The contents of DP compounds in the sludge of 11 sewage treatment plants were measured according to the methods. DP compounds were detected in the sludge of each sewage treatment plant. The total content ranged from 31.4 to 195.6ng/g, which was similar to the values reported in the literature[37]. The quality control in the experiment was strict, ensuring reliable results.

The distribution of DP compounds in the sludge varies. Concentrations may be related to local usage patterns. As shown in Fig.7, anti-DP was the primary contributing monomer, while the content of Mirex was low. The concentration of DP compounds in the sludge of Sewage Treatment Plant 1 was particularly high, possibly due to the presence of an electronic waste dismantling base nearby[33]. The average f_{syn} value in this study was 0.27, which was lower than that of DP products[39]. This may be due to the strong adsorption of anti-DP by the sludge or the preferential degradation of syn-DP.

As shown in Fig.8, different water treatment processes affected DP compounds differently. Compared with water treatment by the activated sludge process, the concentration of DP compounds in the A^2/O process was significantly reduced ($p<0.05$), and its average concentration dropped from 135.7ng/g in the activated sludge process to 75.2ng/g. Comparing the f_{syn} values obtained from different water treatment processes (Fig.8b), when the A^2/O process was adopted, the f_{syn} value increases significantly ($p<0.05$), rising from 0.26 to 0.29.

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