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土壤—水环境中二苯砷酸污染及其修复研究进展*

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摘要 化学武器残留的二苯砷酸(Diphenylarsinic acid, DPAA)引起的土壤—水环境砷污染事件近年来受到广泛关注。国内外学者对土壤—水环境中DPAA的分析方法、污染状况、迁移转化和修复技术等的研究已取得一定进展。鉴于DPAA污染问题的严峻性和污染修复的迫切性,本文通过系统调研并结合笔者的研究工作,综述了土壤-水环境中DPAA分析方法、来源及污染状况的研究进展,探讨了DPAA吸附/解吸、迁移、转化过程及其关键影响因素和作用机制,阐述了对其污染的物理/化学、生物学修复机理研究;认为建立DPAA污染数据库,开展宏观及微观尺度上DPAA环境行为特征的研究,并系统构建DPAA污染的修复技术方法体系将是该领域今后研究的重点。同时,展望了未来的研究方向,旨在为促进土壤-水环境中DPAA污染及其修复的深入研究、有效降低DPAA的环境健康风险提供理论参考。

关键词 二苯砷酸; 土壤—水环境污染; 提取检测; 吸附/解吸; 迁移转化; 物化/生物修复

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在 20 世纪一战和二战期间,二苯氰砷(Diphenylcyanoarsine, DA)和二苯氯砷(Diphenylchloroarsine, DC)等含砷化学武器被大量生产,并在战争中作为呕吐剂和糜烂剂使用。战后,这些遗弃的化学武器通常仅采用土地填埋和海洋倾倒的方式进行处置,因而填埋和倾倒场所周边的土壤-水环境很容易受到化学武器中砷的污染。目前,已在日本^[1]、德国^[2]和中国^[3]多处化学武器埋藏区检测到DA、DC、二苯砷酸(Diphenylarsinic acid, DPAA)和苯砷酸

(Phenylarsonic acid, PAA)等苯砷酸类化合物。其中,DPAA是DA和DC在环境中经水解、氧化后生成的一种结构稳定的化合物^[4]。由于DPAA检出率高、存留时间长,且具有很大的细胞毒性与基因毒性^[5],目前有关化学武器残留的苯砷酸类化合物污染的研究大多聚焦于DPAA。尤其是2002年日本发生一起生活饮用水DPAA中毒事件,更促使研究人员将目光转向这种化合物。

如何消除化学武器残留的DA、DC及其降解产物已经引起了政府机构、国际组织和学术界的高度

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关注。1993年，DA和DC作为必须销毁的化学填料列入《关于禁止发展、生产、储存和使用化学武器及销毁此种武器的公约》附件。2003年，DA和DC作为限制性污染物列入《销毁日本遗弃在华化学武器土壤污染控制标准》（GB19062-2003）^[6]，并被纳入我国强制的环保标准目录。自2005年起，由欧盟框架计划资助的“化学武器在海洋环境中的风险评估模型（MERCW）”和“化学武器搜查与评估（CHEMSEA）”项目陆续启动，旨在呼吁公众关注化学武器污染问题。因此，全面了解DPAA在土壤-水环境中的污染状况，深入认识其环境行为，同时加强研究DPAA污染的修复机理与技术，对有效降低DPAA的环境健康风险非常必要。

目前，日本已经对其境内DPAA的分析方法、污染状况、迁移转化和修复技术等开展了较多研究。近年来，欧洲国家针对DPAA的研究逐渐增多，研究内容主要集中于DPAA的污染调查与修复，我国的情况基本相同。鉴于土壤-水环境中DPAA污染问题的严峻性与解决的迫切性，本文将就其分析方法、污染现状、环境行为和修复技术等最新研究进展进行综述，并展望其发展趋势。

1 土壤—水环境中二苯砷酸的分析方法

目前，DPAA检测的研究主要集中在样品前处理和检测方法上。已报道的前处理方法有固相萃取^[7]、固相微萃取^[8]、超声提取^[9]、振荡提取^[10]和加热提取^[11]。其中，固相萃取和固相微萃取主要用于富集井水和海水中的低浓度DPAA。随着检测方法的改进，DPAA的检出限已达 $\mu\text{g}\cdot\text{L}^{-1}$ 级别，大大降低了对水样中DPAA预富集效率的要求。与水样相比，土壤样品中DPAA的提取就显得更为重要，相关研究主要集中在高效提取剂的筛选。

1.1 土壤中二苯砷酸高效提取剂的筛选

分析DPAA常用的有机提取剂有丙酮^[12]、正己烷^[13]和乙腈^[9]。上述有机提取剂在同时提取多种化学毒剂及其降解产物方面具有一定优势，但也存在明显的缺陷，包括需要进行多次提取，提取过程较为复杂；所需土壤样品量较多；有机试剂价格高且毒性强等，因而很难进行大规模推广应用。

与有机提取剂相比，无机提取剂在DPAA检

测中的应用更为广泛。其中，NaOH常用于土壤中DPAA的提取^[14-15]，且已被证实对不同类型土壤中DPAA的回收率均超过80%^[16]。Baba等^[17]对比了NaOH和NaOH-CH₃OH对土壤中DPAA的回收率，发现两者并无显著差异。考虑到添加CH₃OH有助于样品过滤，部分学者仍采用NaOH-CH₃OH作为提取剂^[18]。还有研究采用HCl^[19]和HNO₃^[17]提取土壤中的DPAA。其中，HNO₃对土壤中DPAA等苯砷酸类化合物的回收率高达98.3%，但HNO₃提取会导致As(III)的氧化，因而需同时分析无机砷形态时不宜采用^[17]。李士杏等^[20]进一步结合我国化学武器埋藏区的土壤类型，考察了Na₂HPO₄对红壤、水稻土、黄棕壤和黑土中DPAA的回收率，结果显示回收率均在90%以上，说明Na₂HPO₄提取可广泛应用于我国化学武器埋藏区土壤DPAA污染的研究。

1.2 二苯砷酸的测定方法

已报道的DPAA测定方法有石墨炉原子吸收光谱法^[7]、气相色谱法（GC）、液相色谱法（HPLC）、气质联用法（GC-MS）和液质联用法（HPLC-MS/MS）^[21]。其中，石墨炉原子吸收光谱法由于定性能力差，因而目前在DPAA检测中的应用较少，而GC和HPLC方法能够通过色谱柱实现复杂环境样品中DPAA的高效分离，基本可以满足常规的检测要求。

GC方法最早被用于化学武器残留的苯砷酸类化合物的定量分析。对于DPAA，目前主要采用衍生化GC-MS方法^[22]。由于需要进行复杂的衍生化前处理，且衍生化效率的降低直接影响测定的准确度^[13]，这可能导致了GC未成为DPAA测定的主流方法。

与GC相比，HPLC方法在DPAA检测中的应用更为广泛。Witkiewicz等^[23]综述过化学武器残留的苯砷酸类化合物的HPLC检测方法。本文仅列出针对DPAA等常见苯砷酸类化合物的HPLC分析方法及其测定参数（表1）。其中，HPLC-ICP-MS是目前检测土壤^[13]、地下水^[24-26]中DPAA最常用的方法。与HPLC-ICP-MS相比，HPLC-MS/MS还能同时对DPAA的降解产物进行定性分析，因而近年来在DPAA相关研究中的应用逐渐增多。但HPLC-MS/MS方法普遍存在基质效应，严重降低了测定的准确度。最近，笔者首次通过提取剂的

筛选降低了土壤DPAA在HPLC-MS/MS分析中的基质效应^[16], 填补了已报道的DPAA分析方法未对基质效应进行系统评估的不足之处。总体而言,

目前土壤-水环境中DPAA的检测尚无统一、规范性的方法, 这给科学研究和实际工作带来了诸多不便。

表1 化学武器残留的苯砷酸类化合物的HPLC-MS/MS分析方法及其测定参数

Table 1 HPLC-MS/MS analytical method and determined parameters of phenylarsinic compounds hung over from chemical weapons

化合物 Compound	基质 Matrix	检测器 Detector	线性范围 Linear range	检出限 Detection limit	参考文献 References
PAA/PAO/DPAA/ BDPAO/TPA	地下水 Groundwater	PDA	8 ~ 30/5 ~ 40/20 ~ 4 000/ 120 ~ 8 000/1 ~ 60 mg·L ⁻¹	0.1/0.1/0.2/10/ 0.1 mg·L ⁻¹	[9]
DPAA	土壤 Soil	PDA	0.1 ~ 20 mg·L ⁻¹	53 μg·L ⁻¹	[20]
DPAA/PAA/PAO	地下水 Groundwater	ICP-MS	0 ~ 120 μg·L ⁻¹	2.8/2.5/2.5 pg	[26]
PAA/PAO	地下水 Groundwater	ICP-MS	0 ~ 1000 mg·L ⁻¹	0.2 ~ 0.8 μg·L ⁻¹	[25]
MPAA/DMPAO/ MDPAO/DPAA	土壤 Soil	ICP-MS	0 ~ 100 μg·L ⁻¹	0.1 ~ 0.2 μg·L ⁻¹	[17]
DA/DC/BDPAO/TPA	土壤/地下水 Soil/groundwater	MS			[13]
PAA/PAO/DPAA/ BDPAO	地下水 Groundwater	MS/MS	0 ~ 1 mg·L	0.0001 ~ 0.01 mg·L ⁻¹	[24]
DPAA/PAA	土壤 Soil	MS/MS	0.01 ~ 1 mg·L	0.01/1 μg·L ⁻¹	[16]

注: PAA, 苯砷酸; PAO, 氧化苯砷; DPAA, 二苯砷酸; BDPAO, 联二苯砷氧化物; TPA, 三苯砷; MPAA, 甲基苯砷酸; DMPAO, 二甲基苯砷酸; MDPAO, 甲基二苯砷酸; DA, 二苯氯砷; DC, 二苯氯砷; PDA, 二极管阵列检测器
Note: PAA, phenylarsonic acid; PAO, phenylarsinic oxide; DPAA, diphenylarsinic acid; BDPAO, bis(diphenylarsine) oxide; TPA, triphenylarsinic; MPAA, methylphenylarsinic acid; DMPAO, dimethylphenylarsine oxide; MDPAO, methyl diphenylarsine oxide; DA, diphenylchloroarsine; DC, diphenylcyanoarsine; PDA, photo-diode array

2 土壤—水环境中二苯砷酸的来源及污染现状

2.1 二苯砷酸污染的来源

DPAA尚未发现有天然形成的例子, 其在环境中的出现均归结为人类活动。在一战和二战期间, 大量化学武器被生产、制造和使用。资料显示, 仅日本在侵华战争时期就曾生产过746万发毒气弹, 且几乎研制了世界各国所装备的所有毒气^[27]。我国是化学武器的最大受害者之一, 目前已在19个省市近100个地点发现了日遗化学武器^[28], 其中大部分集中在东北区域^[29]。这些埋藏在土壤中的化学武器由于长期腐蚀, 内部毒剂继而发生泄漏, 导致埋藏区土壤和地下水受到不同程度的苯

砷酸类化合物污染, 其中以DPAA、PAA和三苯砷 (Triphenylarsinic, TPA) 污染为主^[30]。自20世纪90年代以来, 我国政府高度重视日遗化学武器砷污染问题, 多家研究机构 (包括防化指挥工程学院、防化学院履约事务部、中国地质调查局水文地质环境地质调查中心、沈阳军区处理遗弃化学武器事务办公室和吉林省敦化市环境保护局总工办等) 陆续开展了化学武器埋藏区砷污染的调查工作。

2.2 二苯砷酸污染的浓度水平

DPAA污染的研究区域主要集中在我国东北、日本南部及东南部地区。表2归纳了化学武器埋藏区土壤^[2-3, 9, 13, 17, 19, 31-32]、地下水^[1, 13-14, 25, 28, 33-35]和沉积物^[36-37]中DPAA及总砷的浓度范围。总体上, 与化学武器接触的土壤总砷含量往往严重超

标, 达到几十甚至上千 $\text{mg}\cdot\text{kg}^{-1}$ 。在土壤DPAA污染浓度的调研上, 目前相关数据较少, 这在很大程度上是由于化学武器掩埋点位于地下, 增加了污染调查的难度。在地下水DPAA污染浓度的调研上, 日本在2002年后陆续开展了较多工作, 但至

今仍未查到国内有相关方面的报道。此外, 化学武器经海洋倾倒处理后造成的沉积物砷污染问题逐渐引起了广泛关注^[38]。目前相关的调查工作主要关注总砷浓度, 仅少数文献报道了DPAA的污染浓度。

表2 化学武器埋藏区环境样品中DPAA及总砷的浓度范围

Table 2 Range of concentrations of diphenylarsinic acid and total arsenic in environmental samples taken from chemical weapon dumping areas

调查区域 Investigation area	基质 Matrix	DPAA浓度 DPAA concentration	总砷浓度 Total arsenic concentration	参考文献 References
中国东北 Northeast China	土壤 Soil	0.14% ~ 12.87%		[9]
中国东北 Northeast China	土壤 Soil	—	62.9 ~ 1 321 $\text{mg}\cdot\text{kg}^{-1}$	[31]
中国东北 Northeast China	土壤 Soil	—	22.66 ~ 2 967 $\text{mg}\cdot\text{kg}^{-1}$	[19]
中国东北 Northeast China	土壤 Soil	—	30 ~ 1 372 $\text{mg}\cdot\text{kg}^{-1}$	[32]
中国吉林 Jilin, China	土壤 Soil	—	0.09 ~ 758.4 $\text{mg}\cdot\text{kg}^{-1}$	[3]
日本茨城县 Ibaraki County, Japan	地下水 Groundwater	<15 $\text{mg}\cdot\text{L}^{-1}$	—	[35]
日本平冢市 Hiratsuka City, Japan	土壤 Soil	<0.53 $\text{mg}\cdot\text{kg}^{-1}$	—	[13]
日本平冢市 Hiratsuka City, Japan	地下水 Groundwater	<10 $\text{mg}\cdot\text{L}^{-1}$	—	[14]
日本茨城县 Ibaraki County, Japan	地下水 Groundwater	0.162 ~ 7.98 $\text{mg}\cdot\text{L}^{-1}$	—	[28]
日本筑波市 Tsukuba City, Japan	地下水 Groundwater	<15 $\text{mg}\cdot\text{L}^{-1}$	—	[1]
日本卡米苏 Kamisu Town, Japan	土壤 Soil	1.18 $\text{mg}\cdot\text{kg}^{-1}$	9.80 $\text{mg}\cdot\text{kg}^{-1}$	[17]
日本茨城县 Ibaraki County, Japan	地下水 Groundwater	<0.56 $\text{mg}\cdot\text{L}^{-1}$	<0.85 $\text{mg}\cdot\text{L}^{-1}$	[33]
德国-波兰边境 German-Polish border	土壤 Soil	—	250 000 $\text{mg}\cdot\text{kg}^{-1}$	[2]
德国 Germany	地下水 Groundwater	2.1 $\text{mg}\cdot\text{L}^{-1}$	—	[25]
德国 Germany	地下水 Groundwater	—	<16 $\text{mg}\cdot\text{L}^{-1}$	[34]
波罗的海 Baltic Sea	沉积物 Sediment	—	5.1 ~ 17.0 $\text{mg}\cdot\text{kg}^{-1}$	[36]
波罗的海 Baltic Sea	沉积物 Sediment	<9 583 $\text{mg}\cdot\text{kg}^{-1}$	—	[37]

3 土壤—水环境中二苯砷酸的环境行为

3.1 二苯砷酸在土壤中的吸附/解吸及其影响因素

pH是影响DPAA吸附的关键因素。Wang等^[39]的研究表明, DPAA在土壤中的吸附量随pH增加显著降低, 这与pH对DPAA存在形式及土壤矿物表面电荷的影响有关。背景溶液的离子强度对DPAA吸附的影响较小, 但 PO_4^{3-} 对DPAA吸附能够产生强烈的竞争作用^[40]。上述结果说明DPAA在土壤中的吸附主要受离子交换和专性吸附作用控制, 且专性吸附的作用更加明显。

氧化物和有机质也是影响土壤中DPAA吸附的重要因素。Maejima^[41]和Wang^[39]等的研究均表明, 铁/铝氧化物含量高的土壤对DPAA的吸附能力更强。去除有机质反而增强了土壤对DPAA的吸附, 这可能与去除有机质暴露了氧化物和硅酸盐矿物的吸附位点有关^[41]。此外, Zhu等^[42]发现外源添加乳酸钠显著促进了土壤中DPAA的解吸, 推测可能与乳酸钠的竞争吸附或掩蔽氧化物表面的吸附位点有关。以上研究表明, DPAA在土壤中的吸附主要受氧化物的配位交换作用而非有机质的疏水作用控制, 这与无机砷^[43]、洛克沙肿^[44]和阿散酸^[45]的吸附机制类似。最近, Tanaka等^[46]采用扩展X射线吸收精细结构光谱(Extended X-ray absorption fine structure, EXAFS)技术鉴定出DPAA在水铁矿上的吸附结构为内圈层双齿双核和单齿单核。虽然DPAA在土壤中的吸附主要以牢固的专性吸附为主, 但与前人报道的无机砷的吸附量^[47]相比, DPAA的吸附量明显降低。这很可能与苯环取代基增加了DPAA分子的疏水性和空间位阻, 进而影响了砷酸根与羟基基团的配位交换作用有关。类似现象也发生在甲基砷的吸附过程中^[48]。

氧化还原电位对无机砷吸附/解吸的影响主要体现在碳、铁和硫的价态变化上, 其中, 有机质作为电子供体促进铁还原通常被认为是导致土壤中无机砷释放的重要原因^[49], 相关研究已经成为环境地学的热点。然而, 碳/铁循环对DPAA吸附/解吸的影响罕见报道, 目前仅有笔者结果显示, 淹水土壤中添加的乳酸钠通过促进铁还原进而促进了DPAA的释放^[42]。虽然这方面的研究刚起步, 很多问题有待进一步研究, 但上述结果足以说明碳/

铁循环是驱动土壤中DPAA释放的重要因素。总体而言, 目前对DPAA吸附/解吸的研究涉及的土壤类型有限, 对氧化还原电位等条件变化引起的DPAA结合/释放等关键问题缺乏认识, 对其吸附机制的研究缺乏分子水平的依据。

3.2 二苯砷酸在土壤中的迁移及其影响因素

DPAA在土壤中的迁移一方面与吸附作用密切相关, 另一方面与DPAA本身的吸附特性有关。目前, 仅查到Maejima等^[41]采用柱试验开展了相关研究, 发现DPAA在对其吸附能力弱的冲积土中容易发生迁移, 而在对其吸附能力强的火山灰土中的迁移距离明显降低。Maejima等^[41]的研究还发现, 与DPAA、PAA和MPAA相比, DMPAO和MDPAO的迁移能力明显增强, 说明苯砷酸类化合物的迁移能力随分子结构疏水性的增加而增强。

3.3 二苯砷酸在土壤中的转化及其影响因素

土壤中DPAA的有效转化发生在淹水厌氧条件下, 且与厌氧微生物的作用密切相关。Maejima等^[18]研究发现, 淹水条件下火山灰土和新成土中的DPAA在24周时的转化率分别为31.4%和79.5%, 其中, 火山灰土中高含量的氧化物很可能通过降低DPAA的生物有效性进而降低其转化率。Maejima等^[18]研究还发现, DPAA在淹水土壤中主要发生脱苯环反应, 加入葡萄糖后则主要发生甲基化反应。另有研究从污染稻田土壤中同时检测到DPAA的甲基化和脱苯环产物^[50], 说明碳源也是影响DPAA转化的重要因素。

硫化是淹水土壤中DPAA的另一个重要转化途径。Nakamiya等^[33]在污染地下水中检测到DPAA的硫化产物, 包括二苯基硫代砷酸(Diphenylthioarsinic acid, DPTAA)和甲基化二苯基硫代砷酸(Methylphenyldithioarsinic acid, MPDTAA)。近来, 日本Naoki Harada课题组开展了一系列有关DPAA硫化的研究。Guan等^[14]的研究发现, 向淹水土壤中添加碳源和硫酸盐显著促进了DPAA转化。Hisatomi等^[15]进一步鉴定出DPAA的转化产物为DPTAA。从上述土壤中分离得到的硫酸盐还原菌*Desulfovibrio aerotolerans* JCM 12613在溶液中能够直接介导DPAA的硫化^[51]。Zhu等^[42]还考察了DPAA释放对其硫化的影响, 发现碳/铁循环通过促进黑土中DPAA的释放进而促进其硫化。该研究首次揭示了碳铁硫耦合作用下土

壤中DPAA的结合/释放与硫化过程,说明碳铁硫循环是影响土壤-水环境中DPAA转化的关键因素,具体可能产生的影响见图1。总体而言,虽然厌氧

微生物显著促进了DPAA发生脱苯环、甲基化或硫化,但仅依靠土著微生物破坏DPAA的As-C键并释放出无机砷仍比较困难。

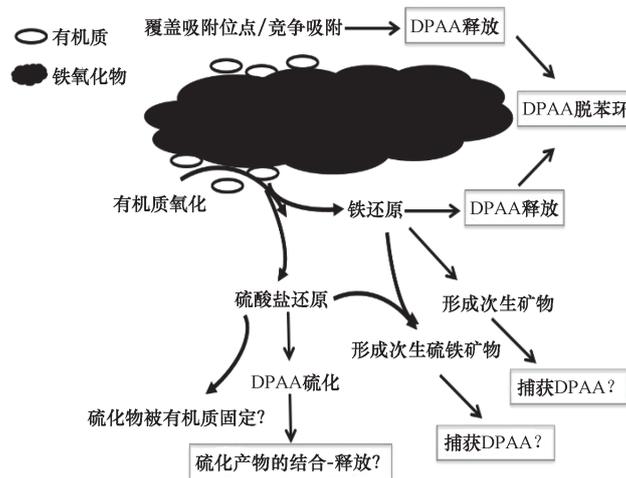


图1 碳-铁-硫耦合作用下土壤中DPAA形态转化与分配过程的示意图

Fig. 1 Schematic diagram for morphological transformation and partitioning of DPAA under the coupling effects of carbon, iron and sulfur

4 土壤—水环境中二苯砷酸污染的修复

有机污染土壤的修复技术主要分为物理/化学修复和生物修复。其中,物理/化学修复尤其适用于高浓度有机物污染场地土壤。由于我国化学武器埋藏区土壤总砷含量往往严重超标^[31],采用物理/化学修复技术处理其中的高浓度有机砷很可能卓有成效。与物理/化学修复相比,生物修复具有成本低和绿色环保等优点。我国已发现的化学武器有不少直接埋于农田土壤^[52],而生物修复尤其适用于中、低浓度有机物污染农田土壤。因此,本文将重点综述物理/化学和生物修复技术在DPAA污染修复中的修复机制与技术发展。

4.1 物理/化学修复

物理/化学方法能有效钝化或消除土壤中的DPAA。Arao等^[11]在化学武器污染土壤上施用0.04%活性炭并种植一季水稻后,在水稻秸秆中未检测到DPAA。这说明活性炭吸附降低了DPAA的生物有效性,但由于活性炭吸附并未破坏苯环结构,因而不能消除环境中的DPAA。化学氧化则能够实现将DPAA降解为小分子有机物,甚至是无机砷。周廷等^[32]提出利用芬顿试剂的强氧化性去除土壤中DPAA的思路。最近,笔者进一步开展了试

验研究,结果表明,芬顿和类芬顿氧化法均能够有效去除土壤中的DPAA,去除率在65%以上,且DPAA通过逐步脱苯环最终降解为无机砷^[53]。

光化学氧化也能达到消除DPAA的目的,这方面的研究近年来开展的较多。Wang等^[54]的研究表明,纯水中的DPAA经紫外光照射全部发生了光降解,最终生成小分子有机物、砷酸盐和亚砷酸盐,加入纳米TiO₂光催化剂还能避免生成毒性较高的亚砷酸盐^[55]。TiO₂光催化同样能有效去除土壤中的DPAA。王阿楠和骆永明^[10]的研究显示,原位施用TiO₂光催化剂时,对DPAA的光催化能力受限于土层厚度和土壤含水量,采用异位泥浆法则显著提高了DPAA降解率(>57.0%),且降解终产物为无机砷^[56]。上述结果提示,利用(光)化学氧化法将DPAA降解为无机砷和植物超富集无机砷同时进行,理论上能够彻底去除土壤-水环境中的DPAA,这为DPAA污染的(光)化学-植物联合修复提供了新思路。

4.2 生物修复

至今已报道的DPAA降解菌有不动盖球菌NK0508^[57]、附着剑菌L2406和L2413^[58]。其中,NK0508在溶液体系中对DPAA的降解率最高,3d的降解率可达80%,且DPAA转化为无机砷

的效率约为50%。上述降解菌为DPAA污染土壤的微生物修复提供了菌种资源,但尚未应用到土壤中,降解菌在土壤中的存活率及对DPAA的降解效果仍然未知。Köhler等^[59]从污染土壤中分离出嗜麦芽寡养单胞菌、假单胞菌和节细菌属,上述菌株显著促进了土壤中DPAA等苯甲酸类化合物降解为无机砷,但具体降解过程与机理未知。这是国际上有关微生物降解土壤中DPAA的首次报道。最近,宋芳等^[60]对根际促生菌RC6b进行了化学诱变,并进一步考察了诱变后的菌株对土壤中DPAA的去除效果,结果显示90d的去除率超过了50%。这是国内有关DPAA降解菌的首次报道。总体而言,当今对DPAA微生物降解的研究主要集中在降解菌的分离、降解条件及降解率等前期研究上,对降解机理、降解基因和降解酶等关键问题仍缺乏清晰的认识。

近年来,利用植物去除DPAA的研究也取得了一定进展。冯仕江等^[61]采用水培试验考察了蜈蚣草对DPAA的植物提取作用,发现培养2周后叶子部分的生物富集系数达到140。但蜈蚣草对土壤中DPAA的去除效果非常有限^[40],同时接种根际促生菌RC6b提高了DPAA去除率,90d时可达24.5%;经蜈蚣草吸收的DPAA大部分被转运至地上部分^[62],因而通过移除蜈蚣草地上部分,能够彻底去除土壤中的DPAA。但从目前的结果看,蜈蚣草对土壤中DPAA的植物提取效率还有待提高。此外,鲁胜利等^[63]认为在化学武器污染土壤上接种能将有机砷无机化的高效菌株,再种植蜈蚣草、大叶井边草等无机砷的超积累植物,使有机砷的无机化和植物提取无机砷同时进行,理论上能够彻底去除DPAA等苯甲酸类化合物。但选育能使DPAA向无机砷高效转化的菌株,同时保证该菌株在土壤中的存活仍然是当前面临的难题。

5 研究展望

化学武器残留的DPAA造成的土壤-水环境污染问题已经受到政府机构、国际组织和学术研究机构的高度关注。中国一直致力于解决遗留化学武器污染问题,目前日本遗弃在华化学武器销毁工作已经全面展开,但加强化学武器在长期掩埋过程中的泄露、在销毁过程中产生的弹药污水以及销毁后产生的固体残渣等引起的土壤-水环境DPAA污染的研究

与治理仍然刻不容缓。未来应加强以下几个方面的研究:

1) 土壤-水环境中DPAA分析方法的标准化。注重标准替代物、净化内标和标准参照物的研制,加强不同实验室之间分析结果的比对,完善质量保证与质量控制体系,建立土壤、水体与沉积物样品中DPAA的标准分析方法,为科学研究和污染监控服务。

2) DPAA的土壤-水环境调研与数据库建立。结合我国化学武器埋藏区的地理位置、土壤类型和土地利用方式等特点,开展区域性的环境介质中DPAA污染范围与浓度水平的调研,建立土壤-水环境DPAA污染数据库。

3) 土壤-水环境中DPAA赋存形态和多介质、多界面环境行为。结合化学武器埋藏区的分布特点,研究DPAA在土壤、土壤胶体、黏土矿物、氧化物上的结合形态与分子结合机制,阐明DPAA在多介质环境内部和微观界面的结合/释放、迁移、转化过程及机制,服务于风险评估与污染修复。

4) 土壤-水环境中DPAA污染的修复技术。化学武器的销毁与残留的苯甲酸类化合物的污染治理具有同样的重要性。需要开展新型修复材料的研发,加强物理/化学-植物联合修复的研究;继续筛选DPAA高效降解菌,在分子和基因水平上探明其机制,并融合基因工程、分子生物学与植物修复技术,建立适合不同污染介质类型、性质及条件的生物修复技术方法体系。

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Progress in Researches on Diphenylarsinic Acid Pollution of Soil-water Environment and Its Remediation

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Abstract Chemical warfare agents containing organoarsenic compounds such as Clark I (diphenylcyanoarsine) and Clark II (diphenylchloroarsine) were widely produced and used during World Wars I and II. After the wars, remains of these agents were simply dumped into the sea or buried underground, thus inevitably polluting the soil-water environments of the sites where they were disposed with the arsenic contained in the chemical weapons. In the environment, these abandoned chemical agents are easily hydrolyzed and oxidized into diphenylarsinic acid (DPAA), rather stable in structure, and other organoarsenic compounds. So far, DPAA has been detected in quite a number of the areas where these

chemical weapons were dumped. The detection has aroused extensive concerns because the presence of DPAA may bring about environmental and health risks. Scholars both at home and abroad have already begun doing some researches, trying to find ways to analyze DPAA in the soil and water environments, determine their status and behaviors and remedy the polluted environments. However, few have done any to summarize systematically progresses in the research. In this paper, a review is presented to introduce some high-effect inorganic and organic extractants and GC as well as LC analytical methods for DPAA in the soil, and sources and status of the pollutant in the soil-water environments. Generally speaking, the DPAA contaminated areas are located mainly in Northeast China, and South and Southeast Japan. Especially in the chemical weapons dumping sites, the concentration of total arsenic is far beyond the criteria for safety. At the same time, the paper also discusses how DPAA is adsorbed/desorbed, translocated and transformed in the soil-water environment, what are the factors affecting the processes and what are the mechanisms. Studies in the past reported that the adsorption/desorption of DPAA in soil was controlled by a variety of factors, including pH, inorganic ions, Fe/Al oxides, organic matter, redox potential (Eh), etc. and adsorption of the substance was completed via ligand exchange reactions between hydroxyl groups of Fe/Al oxides and arsenate of DPAA, rather than the hydrophilic effect of organic matter; the effective transformation of DPAA in the soil occurred under flooded anaerobic conditions, and under sulfate-reducing conditions, in particular; and iron reduction and sulfate reduction were the two key factors controlling desorption and transformation of DPAA. In the end, the paper elaborates the physical, chemical and biological technologies available for remediation of DPAA contaminated soil-water environments, and their remediation efficiency, controlling factors and mechanisms as well. In terms of physic-chemical remediation, application of activated carbon, Fenton and Fenton-like oxidation and photochemical degradation has been demonstrated to be able to effectively remove DPAA in soil-water environments. In terms of bioremediation, certain progresses have been made, like screening of highly efficient DPAA degrading bacteria, unfolding microbial remediation and combined microbial-phyto remediation and previewing directions of the future researches. The paper holds that all the relevant research findings will serve as the theoretical reference for future in-depth studies on DPAA pollution of soil-water environments, remediation of DPAA polluted environments, and protection of environmental quality and human health from DPAA pollution. For further researches, emphases should be laid on the following aspects: (1) To perfect quality assurance and quality control system for DPAA analytical methods, with focus on development of standard alternatives, purification of internal standards and markers; (2) To launch investigations on scope and extent of DPAA contamination, while taking into the consideration of geographical locations, soil types and land-use patterns of the chemical weapon burial sites; (3) To explore forms of DPAA bonding with soil colloids, clay minerals and oxides in the soil and molecular binding mechanisms, and elucidate the mechanisms responsible for adsorption/desorption, translocation and transformation of DPAA in multi-media environment and at microscopic interfaces; (4) To explore for developing new remediation materials, intensify researches on physic-chemical-phyto combined remediation and continue to screen out highly efficient DPAA degrading bacteria and probe mechanisms of their effectiveness at molecular as well as genetic levels, while integrating genetic engineering, molecular biology with phytoremediation technologies, so as to eventually establish a bioremediation technical system applicable to DPAA contaminated media different in type and condition.

Key words Diphenylarsinic acid (DPAA); Soil-water environmental pollution; Extraction and determination; Adsorption/desorption; Translocation and transformation; Physico-chemico/bio-remediation

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