#### SEPA United States Environmental Protection Agency

# **Engineering Issue**

# **Biotransformation of Dimethylarsinic Acid**

Table Contents

1.0	PURPOSE	1
2.0	INTRODUCTION	1
3.0	BACKGROUND	2
	3.1 Chemical Properties	2
	3.2 Toxicity	3
4.0	BIOTRANSFORMATION OF DMA(V)	4
	4.1 Microbial Arsenic Tolerance	6
	4.2 Biotransformation of DMA(V) and Related Arsenic-Containing Compounds	6
	4.2.1 Studies in Aerobic Biotransformation	7
	4.2.2 Studies in Anaerobic Biotransformation	7
5.0	FATE AND TRANSPORT IN THE ENVIRONMENT	10
6.0	SUMMARY	10
7.0	ACKNOWLEDGEMENTS	10
9.0	REFERENCES	11
ACE		12

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# 1.0 PURPOSE

The U.S. Environmental Protection Agency (EPA) Engineering Issue Papers (EIPs) are a series of documents that summarize the available information on specific contaminants, selected treatment and site remediation technologies, and related issues. This EIP is intended to provide remedial project managers (RPMs), on-scene coordinators (OSCs), contractors, and other state or private remediation managers with an overview regarding the biotransformation of dimethylarsinic acid (DMA[V]). The (V) suffix in DMA(V) denotes the +5 oxidation state of arsenic.

This EIP summarizes the state of the science regarding the biotransformation of DMA(V) and was developed from peer-reviewed literature, scientific documents, EPA reports, internet sources, input from experts in the field, and other pertinent sources. This EIP includes a review of the current understanding of biologically-mediated transformation of DMA(V) and its metabolites. Given the challenges remaining in transitioning from laboratory studies to field applications, this EIP provides summary guidance for implementing currently recommended remediation strategies for DMA(V) at contaminated sites.

The table of contents shows the type of information covered in this EIP. Important information has been summarized, while references and web site links are provided for readers interested in additional information. The web site links, verified as accurate at the time of publication, are subject to change.

# 2.0 INTRODUCTION

Historically, DMA(V) and its salts have been used as herbicides and defoliants and became one of the most popular herbicides used worldwide in terms of volume [1-3]. It is estimated that during the 1970s and 1980s, 10 to 12 million acres were treated annually with 2.1 million kilograms (kg) of monomethylarsonic acid (MMA[V]) and DMA(V) in the U.S. [4]. At present, large amounts of organic arsenical herbicides are used for agricultural and aesthetic reasons (e.g., golf course maintenance) [5, 6]. DMA is also one of the primary sources of arsenic in orchards, and is likely a source of arsenic in apples and juice that the public became keenly aware of in 2011. In 2011, it was estimated that 100,000 pounds of DMA(V) were commercially used in the U.S. in over 150 products [5]. However, EPA banned the use of organic arsenicals (including DMA[V]) after December 31, 2013. A mixture of DMA(V) and sodium cacodylate was applied to crops during the Vietnam conflict. This herbicidal mixture was named 'Agent Blue'. Between 1962 and 1971, an estimated 1.2 million gallons of varying concentrations of Agent Blue were released under the herbicide program known as "Operation Trail Dust" [3]. Information available regarding this program indicates that Agent Blue was applied to crops using low-flying aircraft equipped with sprayers. The intention of this herbicide application program was to reduce crop growth through desiccation.

In addition to anthropogenic sources of DMA(V), it is likely that biotransformation processes within the environmental arsenic cycle are significant sources of organic arsenicals [5]. For example, phytoplankton have been observed to methylate arsenate to MMA(V) and DMA(V) within marine environments [7]. Within the arsenic biogeochemical cycle, it is important to note that pentavalent organoarsenicals are less toxic than inorganic arsenates, whereas trivalent inorganic arsenic species are generally both more toxic and more mobile in the environment than pentavalent inorganic arsenic species. Thus, understanding the potential biotransformation pathways of organoarsenicals within the environment as well as the fate, transport, and risk associated with the various arsenic species will help to guide remediation strategies for DMA(V). This EIP discusses the following in sections below:

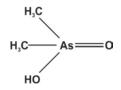
- 1. Chemical properties and toxicity;
- 2. Biological transformation processes, and;
- 3. Fate of these compounds in the environment.

#### 3.0 BACKGROUND

#### 3.1 Chemical Properties

DMA(V) is comprised of a single arsenic atom connected by three single covalent bonds (two methyl groups and one hydroxyl group) and a double bond to oxygen (see Figure 1). This results in a +5 oxidation state for arsenic.

DMA(V) is an amphoteric compound (exhibiting properties of both an acid and base) with an acid dissociation constant (pKa) value of 6.4. DMA(V) exists in a white crystalline solid form with a melting point of 195°C. Its water solubility is 2,000 g/L at 25°C [8]. The soil organic carbon-water partitioning coefficient (Koc) for DMA(V) is reported to be 43.89 L/kg [9].



#### Figure 1. Chemical structure of DMA(V)

There are a relatively small number of related organic and inorganic arsenic compounds which have been identified as the main chemical species involved in the transformation of DMA(V) (see Table 1). The compounds in Table 1 contain arsenic in either the +3 or +5 valence state. These compounds include inorganic forms (As[III] and As[V]) as well as mono- and di-methyl species (MMA[III], MMA[V], DMA[III] and DMA[V]), and one relatively non-toxic and volatile trimethyl species (TMAO). These compounds have been chosen for further discussion as they represent the main products of transformations of DMA(V) in the natural environment. They have been detected and quantified in laboratory studies relating to the amount and rate of biotransformation of DMA(V).

Table 1. Chemical Properties of Select Inorganic and Organic Arsenic Compounds				
Compound	Molecular Formula	Arsenic Oxidation State	Chemical Structure (fully protonated forms)	
Arsenite (As[III])	AsO <sub>3</sub> <sup>3.</sup>	3+	O As	
Arsenate (As[V])	AsO <sub>4</sub> <sup>3.</sup>	5+		
Monomethylarsonous acid (MMA[III])	As(CH <sub>3</sub> )(OH) <sub>2</sub>	3+		
Monomethylarsonic acid (MMA[V])	As(CH <sub>3</sub> )(OH) <sub>2</sub> O	5+		
Dimethylarsinous acid (DMA[III])	As(CH <sub>3</sub> ) <sub>2</sub> (OH)	3+	HO H <sub>3</sub> C H <sub>3</sub> C As	
Dimethylarsinic acid (DMA[V])	As(CH <sub>3</sub> ) <sub>2</sub> (OH)O	5+	H <sub>3</sub> C H <sub>3</sub> C H <sub>0</sub> C H <sub>0</sub> C	
Trimethylarsine Oxide (TMAO)	As(CH <sub>3</sub> ) <sub>3</sub> O	5+	$H_3C$ $H_3C$ $H_3C$ $H_3C$	

#### 3.2 Toxicity

Overall, DMA(V) and other pentavalent organoarsenicals are less toxic than inorganic arsenic. All trivalent forms of arsenic species (both inorganic and organic) are generally both more mobile and more toxic to humans than the pentavalent forms of arsenic compounds (organic and inorganic). This is apparent in both the minimum risk level (MRL) values derived by the Agency for Toxic Substances and Disease Registry [8] and from EPA regional screening levels (RSLs) for soil and tap water. The MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse, noncancer health effects over a specified duration of exposure. Table 2 summarizes available MRLs and RSLs for inorganic arsenic and organic arsenic (V) species discussed in this paper.

Biotransformation of Dimethylarsinic Acid: Engineering Issue

Table 2. Summary of MRL and RSL Values for Inorganic Arsenic and Organoarsenicals

	Inorganic Arsenic	MMA(V)	DMA(V)
MRL, acute duration (14 days or less) oral exposure [8]	0.005 mg As/kg/day	NE	NE
MRL, intermediate duration (15 to 364 days) oral exposure [8]	NE	0.1 mg MMA/kg/day	NE
MRL, chronic duration (365 days or more) oral exposure [8]	0.0003 mg As/kg/day	0.1 mg MMA/kg/day	0.2 mg DMA/kg/day
Residential Soil RSL [9]	0.39 mg/kg	610 mg/kg	1,200 mg/kg
Tapwater RSL [9]	0.045 µg/L	160 µg/L	3,100 µg/L

NE - Not established

#### 4.0 BIOTRANSFORMATION OF DMA(V)

The term "biotransformation" refers to biologicallymediated reactions which change the composition and/ or distribution of contaminants in the environment. "Bioremediation" is a process where microorganisms biotransform hazardous contaminants to other compounds that are intended to be less hazardous than the parent material. Therefore, the term "biotransformation" should not be interpreted as a synonym for "bioremediation". Understanding biotransformation processes for DMA(V) will help to inform the optimum operating conditions for potential application in remediation efforts.

As presented in Table 3 and Figure 2, the four biotransformation reactions associated with arsenic are:

- 1. Methylation. The process in which a compound gains a methyl group. For example, methylation of the organic compound MMA(V) to the organic compound DMA(V).
- 2. Demethylation. The process in which a compound loses a methyl group. For example, demethylation of the organic compound MMA(V) to the inorganic compound As(V).
- 3. Oxidation. The process in which the valence state of the compound is increased. For example, oxidation of the organic compound MMA(III) to the organic compound MMA(V) increases the valence state of arsenic from +3 to +5.
- 4. Reduction. The process in which the valence state of the compound is decreased. For example, reduction of the inorganic compound As(V) to the inorganic compound As(III) decreases the valence state from +5 to +3.

Organic and inorganic arsenic compounds can undergo any of these four reactions based on environmental conditions. In general, methylation and demethylation of arsenic are facilitated by microorganisms via enzymatic processes [7, 10]. As illustrated in Figure 2, DMA(V) can be demethylated to MMA(V), which can be further demethylated to inorganic As(V) biotically. Conversely, inorganic As(V) has been shown to be biotically methylated to MMA(V) and DMA(V). While arsines can be formed from As(V) compounds, the contribution of this mechanism to the fate of DMA(V) is minimal and therefore will not be described in detail in this paper [10]. Oxidation and reduction reactions may occur abiotically when environmental conditions change, such as photochemical oxidation of reduced arsenic compounds. However, oxidation and reduction processes can be a result of biotic processes. As shown in Figure 2, microorganisms have been observed to reduce As(V) to As(III) as well as oxidize As(III) to As(V) [7]. As shown in Table 2, As(V) species (organic and inorganic) are less toxic than As(III) species (organic and inorganic). The general toxicity trend by species increases in the TMAO(V) < DMA(V)< MMA (V)< [As(V), As(III)] < MMA(III) [10]. Given the wide variety of potential reactions in the arsenic biogeochemical cycle, the following sections focus on the role that microorganisms play with respect to DMA(V) biotransformation processes.

Table 3. Summary of the Potential Biotransformation Reactions for DMA(V) and Related Co	ompounds
with Respect to Relative Toxicity	

Reactant	Transformation Reaction	Product	Relative Toxicity
DMA (V)	Demethylation	MMA (V)	More Toxic
DMA (V)	Demethylation	Inorganic As (V)	More Toxic
DMA (V)	Reduction	Arsines	More Toxic
MMA (V)	Demethylation	Inorganic As (V)	More Toxic
MMA (V)	Methylation	TMAO (V)	Less Toxic
MMA (V)	Methylation	DMA (V)	Less Toxic
MMA (V)	Reduction	Arsines	More Toxic
MMA (V)	Reduction	MMA (III)	More Toxic
Inorganic As(V)	Methylation	MMA (V)	Less Toxic
Inorganic As(V)	Methylation	DMA (V)	Less Toxic
Inorganic As (V)	Reduction	Arsines	More Toxic
Inorganic As (V)	Reduction	Inorganic As (III)	More Toxic
Inorganic As (III)	Methylation	MMA (III)	More Toxic
Inorganic As (III)	Oxidation	Inorganic As (V)	Less Toxic
MMA (III)	Demethylation	Inorganic As (III)	Less Toxic
MMA (III)	Oxidation	MMA (V)	Less Toxic
MMA (III)	Oxidization	TMAO (V)	Less Toxic
TMAO (V)	Reduction	MMA (III)	More Toxic

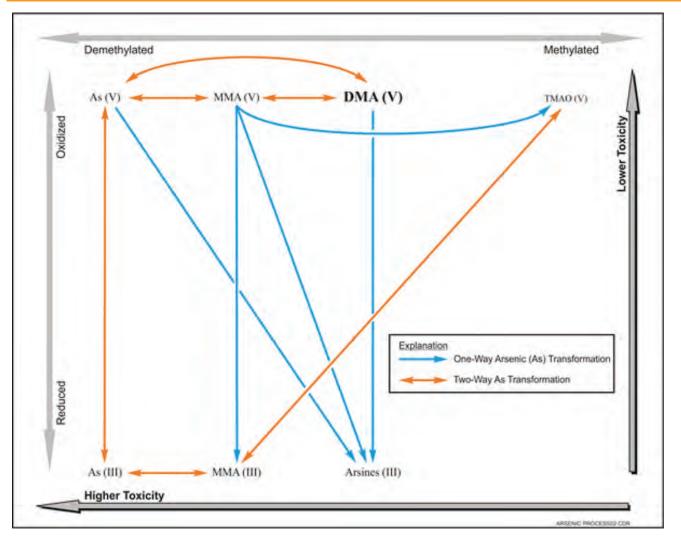


Figure 2. Overview of Biological Transformation Processes of Organic and Inorganic Arsenic Compounds

#### 4.1 Microbial Arsenic Tolerance

Biotransformation processes can only occur if active biological species capable of transforming DMA(V) and related compounds thrive within the environment. For example, microbial arsenic-tolerant species have been isolated from gold and antimony mines [11, 12], highlycontaminated soils and sediments [13-16], and golf course greens [6, 17]. In general, it is unusual for organisms to be arsenic-tolerant as arsenic is generally used as an antimicrobial agent. These microorganisms are either tolerant of arsenic uptake or have developed the ability to detoxify arsenic. One detoxification mechanism uses an arsenic-resistance operon (denoted 'ars') that facilitates biological transformation [18, 19]. Tolerance to arseniccontaining compounds is highly species-, environment-, and compound-specific [20, 21]. For example, reported arsenic tolerance for Stenotrophomonas maltophilia ranged over two orders of magnitude [11]. Additionally, phytoplankton are thought to accumulate inorganic

arsenic species and generate organoarsenic compounds as a detoxification mechanism [22, 23]. Regardless of the detoxification mechanism, microbial action contributes to the arsenic biogeochemical cycle and can include methylated, demethylated, oxidized or reduced forms of arsenic.

# 4.2 Biotransformation of DMA(V) and Related Arsenic-Containing Compounds

Tables 4 and 5 present key aspects of research conducted over the past 40 years under controlled conditions to study methylation, demethylation, oxidation and reduction. The tables include, to a lesser extent, oxidation and reduction of organoarsenic compounds related to DMA(V). The studies reviewed here have been separated into those conducted under aerobic (or oxic) conditions (Table 4) and those conducted under anaerobic (or anoxic) conditions (Table 5). The following discussion will provide insight into the research work conducted in understanding the complexity of biotransformation of DMA(V) and related organoarsenicals.

# 4.2.1 Studies in Aerobic Biotransformation

Research conducted in aerobic environments has studied the ability of indigenous microorganisms from contaminated soils, sediments and aqueous environments to transform organoarsenicals. Overall, DMA(V) biotransforms to MMA(V), inorganic As(V), and arsines over time in the environment with inorganic As(V) as the predominant end product. The reverse pathways of methlyation of inorganic As(V) to MMA(V) and DMA(V) are also possible; however, anaerobic methlyation of As(V) appears more prevalent in the environment [10].

In an early study by Von Endt et al. [24], demethylation rates were observed to be much higher in pure cultures than in soils as would be expected. In later studies, three similar soil types were used to evaluate DMA(V) degradation and three metabolites were identified: As(V), MMA(V), and arsines [25, 26]. Although the organisms responsible for DMA(V) transformation were not specifically identified, a large consortium of microorganisms was assumed responsible for the biotransformation. Specific organisms responsible for the biotransformation of these compounds were not identified until recently when advanced microbiological techniques were employed [10]. Additionally, impacts of amendments such as manure, hay or sewage sludge were investigated on DMA(V) biotransformation [26]. Although no difference in transformation rate was observed between amendments, DMA(V) was degraded more rapidly in unamended soils. This difference is assumed to be due to reduced DMA(V) bioavailability through adsorption to amended organic matter. More recent studies used low concentrations of DMA(V) as the reactant organic arsenic compound. Huang et al. [27] studied the demethylation and reduction of 755 to 1,035 parts per billion concentrations of DMA(V) in soils collected from Germany. In contrast to Gao and Burau shown in Table 4 [28], Huang et al. observed the sequential formation of MMA(V) before complete demethylation to inorganic forms of arsenic.

With respect to other organoarsenicals, MMA(V) was the subject of two studies in both soil and pure culture [29, 30]. In soil, parts per million concentrations of MMA(V) were demethylated to As(V). Separate pure cultures of bacteria (Mycobacterium neoaurum and Scopulariopsis koningii) as well as three fungi (Fomitopsis pinicola, Puccinia gladioli

and Scopulariopsis brevicaulis) methylated MMA(V) finally to TMAO. These organisms were also found to oxidize and methylate MMA(III) to TMAO. Therefore, the dynamic nature of the arsenic biogeochemical cycle should be recognized when investigating a contaminated site such that analyzing for specific arsenic compounds and oxidation states is recommended.

# 4.2.2 Studies in Anaerobic Biotransformation

As with aerobic studies, research conducted in anaerobic environments evaluated the ability of indigenous microorganisms to transform organoarsenicals. Overall, the entire range of potential biotransformation pathways (see Figure 2) can be observed under anaerobic conditions. Demethylation of DMA(V) as well as methylation of As(V) can occur under the appropriate conditions. Anoxic contaminated sites with arsenic contamination should be monitored for all As(III) and As(V) species to understand the distribution of arsenic compounds.

Demethylation of DMA(V) can produce in MMA(V) and inorganic As(V). Woolson and Kearney [25] repeated their earlier aerobic experiments on three soils under anoxic conditions. As with the aerobic conditions, DMA(V) was converted to inorganic As(V) as well as arsines, however DMA(V) transformations were not as efficient under anaerobic conditions. Furthermore, As(V) reduction to As(III) has been observed by iron-reducing, sulfate-reducing, and fermenting populations as well as methanogens [10]. This indicates that reduction to the more toxic trivalent forms is a possibility. Another potential pathway for As(III) formation includes the reduction of MMA(V) to MMA(III) as an intermediate compound before producing inorganic As(III).

Studies have also been completed to determine the anaerobic transformation of MMA(V) [2, 5, 15, 29] and inorganic forms of arsenic [31, 32]. In the case of MMA(V), transformation products include either inorganic arsenic or volatile arsines. Yoshinaga et al. [5] identified two specific bacteria that were necessary and sufficient for transformation of MMA(V) to As(III). Reduction of MMA(V) to MMA(III) by Burkholderia species was first required before demethylation of MMA(III) to As(III) by Streptomyces species. This indicates that full transformation of some organoarsenic compounds may not be accomplished by the same organism, but rather as sequential steps of methylation/demethylation and oxidation/reduction.

CO Table 4. Summary of Selected Biotransformation Studies of DMA(V) and Related Compounds in Aerobic Environments

Initial Arsenic Species	Biotransformation	Transformation Pathway (see Figure 2)	Microorganism	Initial Concentration	Temperature	Percent transformed/ time	Media	Reference
		Demethylation $DMA(V) \rightarrow As(V)$	Fungus, Actinomycete, Bacterium	10 ppm	30 °C	3-20%/11 d	Pure Culture	[24]
	Demethylation		Consortium	10 ppm, 100 ppm	28-30 °C	1.7-10%/60 d	Soil	[24]
			Consortium	10 ppb	20 °C	37 % / 24 h	Mixed Culture	[33]
DMA(V)	Demethylation/		Consortium	184 ppm	5 °C, 25 °C	5-90%/70 d	Soil	[28]
	Arsine	$DMA(V) \to As(V), Ars$	Consortium	1 ppm, 10 ppm, 100 ppm	25 °C	76%/168 d	Soil	[25]
	Demethylation/ Reduction	$\begin{array}{c} DMA(V) \to MMA(V) \to \\ iAs \end{array}$	Consortium	1545 ppm	25 °C	25% / 91 d	Mixed Culture	[34]
	Reduction	IAS	Consortium	755 ppb, 1035 ppb	5 °C	80%/100 d	Soil	[27]
	Demethylation	$MMA(V) \to As(V)$	Consortium	3.7 ppm, 9.2 ppm	15 °C, 30 °C	72%/120 d	Soil	[29]
MMA(V)	Methylation	$MMA(V) \to TMAO$	Mycobacterium neoaurum, Scopulariopsis koningii, F. pinicola, P. gladioli, S. brevicaulis	920 ppb	21 °C	3-17% / 28 d	Pure Culture	[30]
MMA(III)	Methylation	MMA(III) → TMAO	Mycobacterium neoaurum, Scopulariopsis koningii, F. pinicola, P. gladioli, S. brevicaulis	930 ppb	21 °C	8-38% / 28 d	Pure Culture	[30]

DMAr(III) = dimethylarsine

Ars = volatile arsine compounds (arsine, methylarsine, dimethylarsine, trimethylarsine)

iAs = inorganic arsenic

100% removal indicates final concentration was nondetect for the method employed

Table 5. Summary of Selected Biotransformation Studies of DMA(V) and Related Compounds in Anaerobic Environments

Initial Arsenic Species	Biotransformation	Transformation Pathway (see Figure 2)	Microorganism	Initial Concentration	Temperature	Percent trans- formed/time	Media	Reference
		$DMA(V) \to iAs$	Phytoplankton	138 ppb	4-30 °C	100%/ 21 d	Aqueous	[14]
	Demethylation/ Reduction	$\begin{array}{c} \text{DMA(V)} \rightarrow \text{MMA(V)} \rightarrow \\ \text{iAs} \end{array}$	Consortium	1545 ppm	25 °C	10% / 91 d	Mixed Culture	[34]
		$\begin{array}{c} \text{DMA(V)} \rightarrow \text{MMA(V)} \rightarrow \\ \text{iAs} \end{array}$	Consortium	755 ppb, 1035 ppb	5 °C	66%/100 d	Soil	[27]
DMA(V)	Demethylation	$DMA(V) \to MMA(V)$	Consortium	138 ppm	30 °C	75-95%/217 d	Sludge	[2]
		$DMA(V) \rightarrow iAs \text{ and } Ars$	Consortium	21.4 ppm	Ambient	85-89%/59 d	Soil	[35]
	Demethylation/	$\begin{array}{l} \textbf{DMA(V)} \rightarrow \textbf{MMA(V)}, \\ \textbf{As(V)} \text{ and } \textbf{Ars} \end{array}$	Consortium	10 ppm	Ambient	60%/ 60d	Soil	[26]
	Methylation	$DMA(V) \to Ars$	Consortium	1 ppm, 10 ppm, 100 ppm	25 °C	61% /168 d	Soil	[25]
MMA(V)	Demethylation/ Reduction	$\begin{array}{l} MMA(V) \rightarrow MMA(III) \rightarrow \\ As(III) \end{array}$	Streptomyces sp., Burkholderia sp.	140 ppb	Ambient	100%/7 d	Soil Ex- tracts	[5]
		$\begin{array}{c} MMA(V) \rightarrow MMA(III) \rightarrow \\ As(III) \end{array}$	Pseudomonas putida strain KT2240, Burkhold- eria sp. MR1	140 ppb	Ambient	100%/ 7 d	Soil Ex- tracts	[5]
	Demethylation/ Reduction	$MMA(V) \to iAs$	9 separate isolates of As-resistant bacteria	140 ppb	20 °C	5-100%/14 d	Pure Culture	[15]
	Demethylation/ Meth- ylation	$\begin{array}{c} MMA(V) \to As(V) \text{ and} \\ Ars \end{array}$	Consortium	3.7 ppm, 9.2 ppm	15 °C, 30 °C	100%/120 d	Soil	[29]
	Reduction	$MMA(V) \to MMA(III)$	Consortium	400 ppm, 2000 ppm	30 °C	24-49%/ 240 d	Sludge	[2]
As(V)	Reduction/ Methyla- tion/Oxidation	$\begin{array}{c} As(V) \to As(III) \to \\ MMA(V) \to DMA(V) \to \\ Ars \end{array}$	<i>Methanobacterium</i> strain M.o.H	75 ppb	Ambient	Not quantified	Pure Culture	[31]
As(V)	Methylation	$As(V) \to Ars$	Desulfovibrio vulgaris strain 8303	75 ppb	Ambient	Not quantified	Pure Culture	[31]

Ars = volatile arsine compounds (arsine, methylarsine, dimethylarsine, trimethylarsine)

iAs = inorganic arsenic

100% removal indicates final concentration was nondetect for the method employed

# 5.0 FATE AND TRANSPORT IN THE ENVIRONMENT

The fate of DMA(V) in the environment is difficult to assess in detail because of the number of interrelated abiotic and biological processes that occur simultaneously. Phase transfer, advective, and diffusive transport, methylation, demethylation, oxidation and reduction are examples of these.

While highly soluble in water, both DMA(V) and MMA(V) have high sorption capacities (MMA > DMA) in soil and sediment systems. Organoarsenic as well as inorganic arsenic sorption is dependent on clay and mineral content (i.e., ferrihydrite and alumina) of the soil, as well as pH of the system. For example, DMA(V) [36] and MMA(V) [6] adsorption increased as iron oxide and alumina content increased. Overall, inorganic As(V) species are found in oxic conditions and can strongly adsorb to soil and sediment in acidic and neutral environments, whereas inorganic As(III) species are weakly retained by soil and sediment, and are mobile in both oxic and anoxic environments. Thus, the potential for desorption and remobilization of arsenic into the aqueous environment by reductive transformations of As(V) to As(III) species should be included in evaluating impacts to site conditions when considering remedial technologies.

#### 6.0 SUMMARY

Biotransformation of DMA(V) is a significant part of the arsenic biogeochemical cycle and can produce a variety of end products. Site specific conditions, in particular the predominant redox condition, will direct the most prevalent forms of arsenic species present.

Under aerobic conditions, DMA(V) is predominately demethlyated to inorganic As(V). While inorganic As(V) is more toxic than the organoarsenicals (DMA[V] and MMA[V]), this valence of inorganic As strongly sorbs to iron, aluminum, and manganese oxyhydroxides, and clay minerals under acidic and neutral conditions. Thus, pentavalent species are generally immobile in the aerobic environment. Therefore, maintaining an aerobic environment may aid in reducing transport of arsenic in the environment.

Under anaerobic conditions, DMA(V) is also demethylated to inorganic arsenic. Although the transformation pathways incorporate a variety of intermediate compounds, both inorganic As(V) and As(III) can be produced. Trivalent arsenic [As(III)] species (both organic and inorganic) are generally both more toxic and more mobile than pentavalent arsenic species (organic and inorganic). Therefore, all potential arsenic species produced from biotransformation processes should be considered in the remedy selection process when altering a site's oxidation/reduction environment and pH.

These results indicate that transitioning from aerobic to anaerobic conditions may increase the toxicity and mobility of arsenic in the environment. As such, redox conditions play an important role during remedial alternative evaluation as the redox conditions impact the mobility and toxicity of the arsenic species. Therefore, understanding the potential biotransformation pathways of organoarsenicals within the environment as well as the fate, transport, and risk associated with the various arsenic species are important when assessing remedial alternatives for sites contaminated with DMA(V).

Predominant remediation strategies for As currently include removal and immobilization [37]. Removal consists of excavating the zone identified as contaminated. Once removed, contaminated soil may be treated through ex-situ means or sent to a hazardous waste landfill. Exsitu arsenic treatment includes (from low to high cost) iron seeding for co-precipitation with aqueous As, soil washing with acid extraction, membrane filtration, media adsorption, ion exchange, and pyrometallurgical recovery.

In-situ remediation approaches rely on immobilization of arsenic to reduce the bioavailability of the contaminant and decrease the associated risk. Immobilization can include (from low to high cost) phytoremediation (if concentrations are low), biological treatment/ biotransformation, installation of a permeable reactive barrier, soil flushing, amendments for precipitation or coprecipitation, solidification and stabilization, electrokinetic treatment, and vitrification. In-situ amendments for precipitation or co-precipitation include zero valent iron (ZVI), titanium dioxide (TiO2), and ZVI coupled with a sulfate compound. These immobilization methods are undergoing evaluation to ensure that they can serve as long term, stable sinks for arsenic despite fluctuations in geochemistry.

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# **ACRONYMS AND ABBREVIATIONS**

As(III)	Inorganic/elemental arsenic (arsenite; oxidation state +3)
As (V)	Inorganic/elemental arsenic (arsenate; oxidation state +5)
DMA(V)	dimethylarsinic acid (oxidation state +5)
EPA	U.S. Environmental Protection Agency
kg	Kilogram
MMA(III)	monomethylarsonous acid (oxidation state +3)
MMA(V)	monomethylarsonic acid (oxidation state +5)
MRL	minimum risk level
OSC	on-scene coordinator
ppb	parts per billion
ppm	parts per million
RPM	Remedial Project Manager
RSL	regional screening levels
TMAO	trimethylarsine oxide
U.S.	United States



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