Water Air Soil Pollut (2011) 219:401–415
DOI 10.1007/s11270-010-0716-2

Organic Arsenic in the Soil Environment: Speciation, Occurrence, Transformation, and Adsorption Behavior

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Received: 27 July 2010 / Accepted: 1 December 2010 / Published online: 15 December 2010

Abstract An attempt is made to describe the fate and behavior of organic arsenic (As) compounds in the soil environment, based on an extensive literature researches. The objective of this review is to provide an overview on the state of knowledge to date about the occurrence and potential transformation of organic As, including methylation, degradation, and hydration, in soils and their uptake and accumulation in plants and animals. Accordingly, the biogeochemical cycle of organic As in the soil environment is proposed.

Keywords Organic arsenic · Soil · Speciation · Transformation · Adsorption

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1 Introduction

Arsenic (As) is a ubiquitous trace metalloid and can be found in virtually all environmental media. Arsenic occurs mainly as inorganic species in natural systems. Under aerobic environments, arsenate (As(V)) is the stable species, whereas arsenite (As(III)) predominates under anaerobic conditions (Smedley and Kinniburgh 2002). Inorganic As can be methylated by aerobic and anaerobic microorganisms, producing methyl As, such as monomethylarsonic acid (MMAA (V)), dimethylarsinic acid (DMAA(V)), and trimethylarsine oxide (TMAO(V); Cullen and Reimer 1989). Under anaerobic conditions, organic As can be reduced to volatile arsine, including monomethylarsine (MMA(-III)), dimethylarsine (DMA(-III)), and trimethylarsine (TMA(-III); Cullen and Reimer 1989). Organic As with more complicated structures like arsenobetaine (AsB), arsenocholine (AsC), and arsenosugars is usually found in the marine ecosystem (Cullen and Reimer 1989). However, recent studies have demonstrated that these recalcitrant organic As may also occur in the terrestrial environment (Kuehnelt and Goessler 2003). Aside from biomethylation, anthropogenic activity has also resulted in the widespread of organic As in soils. Agricultural practice including the historical use of organic As-based pesticides and herbicides, e.g., sodium salts of MMAA(V) and DMAA(V), has led to accumulation of organic As in topsoils. Phenyl As found in the environment are mostly originated from As chemical warfare agents due to improper treatment and storage (Köhler et al. 2001; Baba et al. 2008). Figures 1 and 2 show the structures of organic As found in soils.

The concentrations of organic As are usually less than 5% of total As (Cullen and Reimer 1989). Moreover, the toxicity of (pentavalent) organic As is not so strong as As(III) and As(V); especially, more recalcitrant organic As such as AsB and arsenosugars are regarded as nontoxic. Therefore, the impact of organic As on environmental quality is usually regarded as small. Their role in As biogeochemical cycle in the environment seems to be of minor importance. Nevertheless, recent studies demonstrated that organic As may account for up to 70% of total As in peatland porewater (Huang and Matzner 2006) and 30% of the extractable As in the forest floor (Huang and Matzner 2007a). Arsenic methylation was thus suggested as an important mechanism of As mobilization. Due to the higher toxicity of trivalent organic As than inorganic As, the occurrence of MMAA(III) and DMAA(III) has drawn ever growing attentions (Petrick et al. 2000). MMAA(III) and DMAA(III) have been detected in aquatic environment (Sohrin et al. 1997) and freeze-dried carrots (Yathavakilla et al. 2008). The occurrence of trivalent methyl As in the soil environment seems to be plausible. Considering the probable high relevance of organic As and the potential occurrence of highly toxic trivalent organic As, understanding the environmental behavior of organic As becomes indispensable for exact risk assessment of As environmental contamination and potential human hazards.

2 Organic Arsenic in Soils

2.1 Speciation of Organic Arsenic in Soils

Most investigation about soils reported mainly inorganic As, whereas organic As are usually the minor

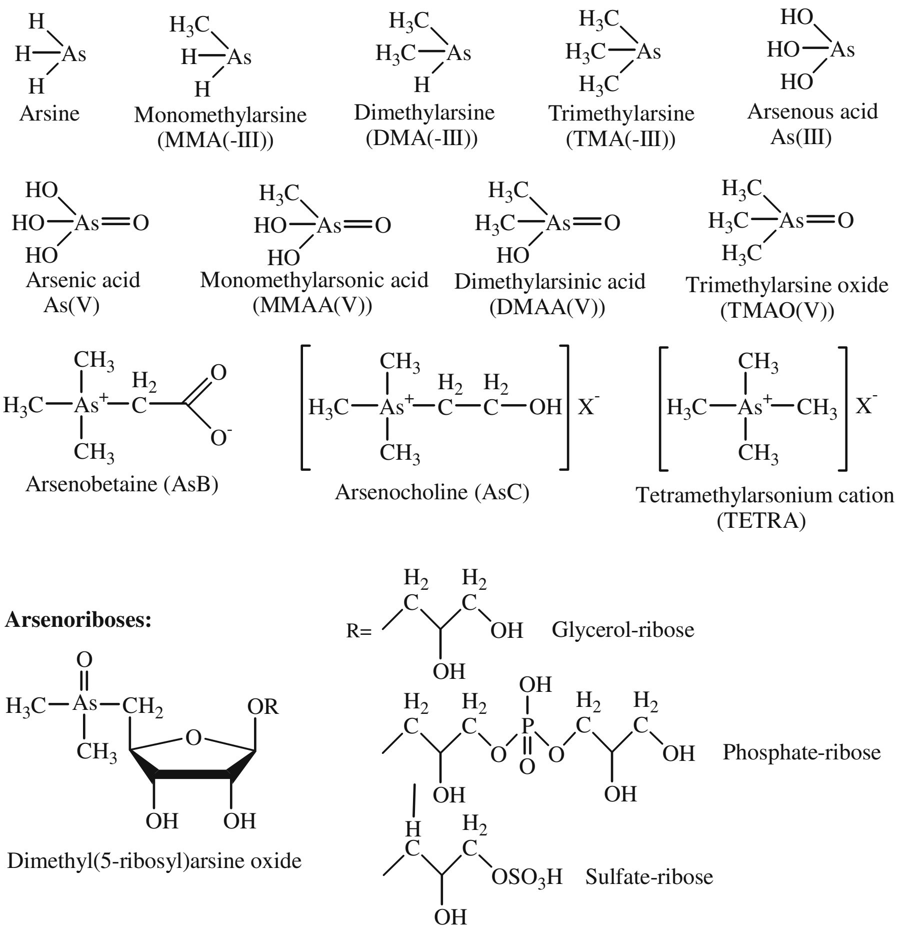

Fig. 1 Structures of As compounds found in the soil environment

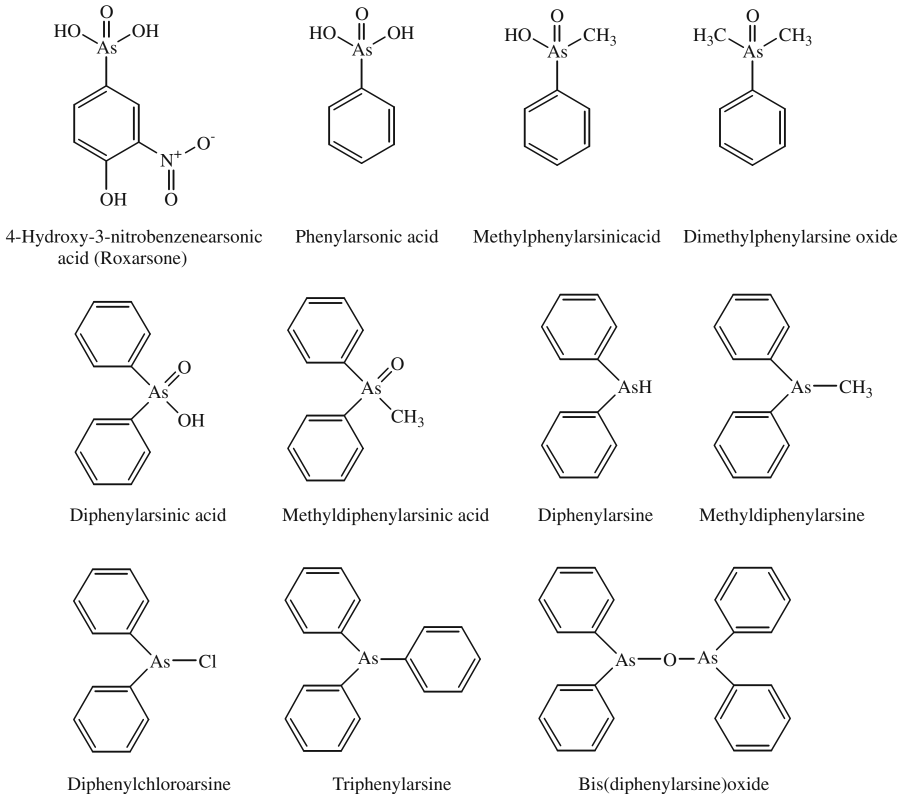

Fig. 2 Structures of phenyl arsenic compounds found in the soil environment

component, or even not detected in soils (Helgesen and Larsen 1998; Geiszinger et al. 1998; Geiszinger et al. 2002; Kuehnelt and Goessler 2003). The high soil As concentration may benefit As biomethylation as more available As are available for the process; this was partially evidenced by the general observation of higher concentrations/proportion and variety of organic As in As-polluted than As-unpolluted soils. At polluted sites in Japan, DMAA(V) was detected with concentrations of 4–69 ppb in paddy soils, and 2–7 ppb in upland and orchard soils. Concentrations of MMAA (V) up to 88 ppb were found in paddy, upland, and orchard soils (Takamatsu et al. 1982). In soils on top of ore vein with total As concentrations ranging from 0.7‰ to 4‰, TMAO(V) accounted for ~17%, and AsB for ~3% of the As extractable with 9:1 methanol–water extract (~1% of total soil As; Geiszinger et al. 2002). Traces of AsB, DMAA(V), MMAA(V), and TMAO(V) were detected in anti-hill material collected at former As roasting facility in Austria (Kuehnelt and Goessler 2003). In Löcknitz, Germany, where chemical warfare agents were stored and attempted to eliminate by burning and reaction with sodium hypochlorite after World War II, diphenylarsine, methyldiphenylarsine, diphenylchloroarsine, triphenylarsine, triphenylarsine-sulfide, bis(diphenylarsine)oxide, and bisdiphenylarsine were detected in soils (Köhler et al. 2001). In Japanese paddy soils contaminated with aromatic As, phenylarsonic acid, diphenylarsinic acid, methylphenylarsinicacid, dimethylphenylarsine oxide, and methyldiphenylarsine oxide were identified with concentrations up to 1.4 ppm (Baba et al. 2008).

The concentrations and variety of organic As are usually low in unpolluted soils. Trace amount of TMAO (V) was detected in unpolluted soils in Austria (Geiszinger et al. 2002). Duester et al. (2005) investigated the occurrence of methyl As in different types of urban soils of the Germany Ruhr basin, including arable, gardening, flooded, and abandoned industrial soils (<30 ppm As). MMAA(V) was the most predominated methyl As with concentrations all <12 ppb. DMAA(V) and TMAO(V) were also observed but less frequently. In remote forest soils, organic As accounted for up to 30% of the extractable fraction in the forest floor, but never exceed 9% in the mineral soil (Huang and Matzner 2007a). The surface O horizons (forest floors) are with specific interests due to high diversity of organic As, comprising DMAA(V), TMAO(V), AsB, and four unidentified species. Peatland and flooded soils may be a hot spot of organic As due to its redox-fluctuated conditions. Huang and Matzner (2006) observed unusual high proportion of organic As in peatland porewater. Tetramethylarsonium ion, which was first time detected in soils, together with MMAA(V), DMAA(V), TMAO(V), AsB, and three unidentified species, was responsible for 70% of total As in porewater at deeper horizons.

The occurrence of methyl As in soils is usually accepted as a consequence of bimethylation. However, the detection of refractory organic As in soils is more doubtful. Due to low concentrations, the presence of these As compounds was usually not able to be confirmed with electrospray ionization mass spectrometry (ESI-MS; Geiszinger et al. 2002; Kuehnelt and Goessler 2003; Huang and Matzner 2006, 2007a). To date, the identification of AsB in soil extracts was mostly based on chromatographic retention time (Geiszinger et al. 2002; Kuehnelt and Goessler 2003; Huang et al. 2007). In studies with specific care, the peak identification was performed with at least two chromatographic methods. For example, identification of AsB in soil extracts was done with chromatographic methods based on Dionex AS-7 column with HNO_3 eluents and Zorbax 300-SCX column with a mobile phase of pyridine (Huang and Matzner 2007a).

2.2 Source of Organic Arsenic in Soils

2.2.1 Anthropogenic Source

The widely application of organic As in agriculture and industry gave significant contribution to soil pools of organic As. Mono- and disodium MMAA(V) and DMAA(V) are used to control weeds in cotton fields and as defoliation agents applied prior to cotton harvesting (Bednar et al. 2002). They are also allowed to be used as herbicides on agricultural lands, orchards, and golf courses in the USA (Sarkar et al. 2005). The monosodium salt of MMAA(V) is among the top pesticides utilized in the USA with approximately 1.2 million kilogram of As applied annually to 3.8 million acres (Baba et al. 2008). In addition, approximately 35,000 kg of As from DMAA(V) is applied annually. Roxarsone, 3-nitro-4-hydroxybenzene arsonic acid (Fig. 1), has seen extensively used in the production of broiler chickens (Stolz et al. 2007). According to the USDA, the USA produced 8.9 billion broiler chickens in 2005. The majority of As uptake is not retained by the chickens but excreted. The litter produced by chicken feed with roxarsone may contain from 15 to 48 mg kg^{-1} of the organoarsenical. Its disposal presents thus a problem for waste management. Chemical warfare reagents containing aromatic As, such as ADAMSITE (10-chloro-5,10-dihydrophenarsine), CLARK I (diphenylchloroarsine), CLARK II (diphenylcyanoarsine), and PFIFFIKUS (phenyldichloroarsine), are mainly produced as vomiting or vesicant agents during World War I and World War II (Köhler et al. 2001; Baba et al. 2008). These agents were afterward abandoned in Europe, China, Japan, and other countries by sea-dumping or earth-burying. There is potential leakage of these aromatic As from munitions to the conjunct environment.

2.2.2 Methylation

Methylation is a strictly biological process and was suggested be a useful detoxication method for microbes (Turpeinen et al. 1999). Formation of methyl As was demonstrated by different aerobic and anaerobic microorganisms (Kuehnelt and Goessler 2003). The As methylation in soils depends on the soil types, the microbes, and the conditions they are exposed to. The most common organic As found in soils are MMAA (V), DMAA(V), TMAO(V), and AsB (Woolson 1977; Pongratz 1998; Kuehnelt and Goessler 2003; Huang and Matzner 2006, 2007a). Microbial As methylation in soils is supported by the fact that no evolution of methyl arsines from sterilized soils treated with DMAA(V) occurred, whereas generation of methyl arsines from nonsterilized soil treated with DMAA(V) was observed (Gao and Burau 1997). There was transformation of As(V) to As(III), MMAA(V), DMAA(V), and TMA(-III) in contaminated soils (2,125–3,632 ppm As) under aerobic and anaerobic conditions, but not in formaldehyde controls (Turpeinen et al. 2002). In a soil containing high amount of geogenic As (2,000 ppm), only As(V) was detected before incubation. After an aerobic incubation for a week, DMAA(V), MMAA(V), and AsB were found (Pongratz 1998). The author suggested that AsB is derived from microorganisms, from where it was released during the shaking applied for the extraction of the As from soil. This is supported by no finding of AsB in the soil porewater after incubation (Pongratz 1998). In soils containing 6,928–9,119 ppm As in the presence of microbes, minor As methylation (<0.1%) was observed under aerobic environments. Nevertheless, no methylation was found in the anaerobic environments (Turpeinen et al. 1999). In columns packed with uncoated and clay mineral-coated sand, fast methylation was indicated as high DMAA(V) concentrations observed when spiking MMAA(V) but not As(III) and As(V) in soil extracts as initial effluent (Chen et al. 2008).

Arsenic methylation in peatland was demonstrated by the high abundance and variety of organic As in porewater, inclusive of MMAA(V), DMAA(V), TMAO (V), TETRA, AsB, and several unknown As (Huang and Matzner 2006). The order of abundance of methyl As (MMAA(V)>DMAA(V)>TMAO(V)) supports As methylation since methylation of As follows the pathway: inorganic As→MMAA(V)→DMAA (V)→TMAO(V). The absence of nitrate, the order of magnitude lower concentrations of sulfate, and the much higher concentrations of dissolved Fe in porewater in growing season compared with those in dormant season reflected the microbial activity which may be responsible for methylation under anaerobic conditions. In comparison, no organic As was detected in porewater in dormant season. The surface O horizon soil is the first barrier of atmospherically deposited As and thus may accumulate significant amounts of As (Gustafsson and Jacks 1995; Suchara and Sucharova 2002). Together with the high content of organic matters and microbial activities, surface O horizon was suggested as a potential hot spot for As biomethylation. Gustafsson and Jacks (1995) indicated a predominance of non-$NaBH_4$-reducible organic As forms in surface O horizons, whereas non-$NaBH_4$-reducible organic As account only a very small part of the solid-phase As in the mineral soils. However, the study about speciation of organic As in surface O horizons of As polluted and unpolluted forest soils with total As concentrations of 2–13 and 2,000 ppm, respectively, suggested little in situ As methylation (Huang and Matzner 2007a). This conclusion was made based on the fact that the higher variety of organic As in unpolluted (DMAA(V), TMAO(V), AsB, and four unknown organic As) than in polluted soils (DMAA(V) and AsB). The concentrations of organic As in both soils were almost the same, suggesting that the 1,000 times higher total As concentrations in polluted surface horizon did not benefit As methylation. Since the variety of organic As in surface O horizons reflected well with that in atmospheric deposition at the unpolluted site (Huang and Matzner 2007a, b), atmospheric deposition was postulated as the main source of organic As in soils, especially in surface O horizons.

2.2.3 Atmospheric Deposition

Aside from anthropogenic source and biomethylation, atmospheric deposition is another important source. Di- and tri-methyl As were found in both vapor and particle phase in a variety of indoor and outdoor environments. The high organic As levels associated with plants were interpreted in terms of biological processes releasing volatile organic As (Johnson and Braman 1975). This emphasizes the relevance of biomethylation in the global As budget. Although TMA(-III) was suggested to be able to travel considerable long distances without chemical change, the methyl arsines will be oxidized to MMAA(V), DMAA(V), and TMAO(V) or undergo other reactions, possible on the surface of particles (Brinckman et al. 1982). DMAA(V) and MMAA(V) can be demethylated by UV irradiation (Stringer and Attrep 1979). This may be more significant at high altitude, as MMAA(V) and DMAA(V) have been found to be unaffected by exposure to sunlight at ground level (Mukai et al. 1986). The concentrations of methyl As at two Japanese sites have been shown to be subjected to seasonal variation: higher in summer and lower in winter, in accordance with the temperature changes. The ratio of DMA(-III) and TMA(-III) was usually 0.15–0.34, indicating that TMA(-III) was the dominant species produced by biomethylation (Mukai et al. 1986). Although the ratio of methyl to inorganic As was <10% in the airborne particulate matter, their overall concentration was up to 18 ppm. Since this in itself represents a significant enrichment over crustal As concentration (~3 ppm), these data provide strong support for a biomethylation contribution to the atmospheric As cycle. In Austria, As in rainwater was determined to amount 5.8 ppb, including 0.2 ppb DMAA(V) (Pongratz 1998). At forested site in northeastern Bavaria, Germany, MMAA(V), DMAA (V), TMAO(V), AsB, and two unknown organic As were found in throughfall (Huang and Matzner 2007b). The proportion of organic As reached a maximum of 45% of total As concentrations in throughfall. The concentrations of organic As in throughfall were apparently higher in the growing season than in the dormant season, suggesting As biomethylation in phyllosphere.

2.2.4 Terrestrial Plants

The formation of organic As is thought to be a detoxification process to enable organisms to cope with potentially toxic inorganic As (Geiszinger et al. 2002). For example, As methylation was reported under nitrate- and/or phosphate-deficient condition in pine seedling, corn, melon, and tomato prior to exposure to ^{74}As-As(V) (Nissen and Benson 1982). Thus, organic As may be found in terrestrial plants and animals with high varieties and high proportion to total As. Although the transfer mechanism is rarely studied, the contribution of organic As in plant and animal materials to their soil pools leaves no room for doubt. Huang and Matzner (2007b) demonstrated that litterfall may be 16% of annual total As input to forest soils, and in litter of Norway spruce, DMAA(V), AsB, and one unknown As were found, which together were 10% of total As. The occurrence of organic As in terrestrial plants has been detailed in Kuehnelt and Goessler (2003). Not only methyl As, i.e. MMAA(V), DMAA(V), TMAO(V), and TETRA, but also AsB, AsC, and arsenosugars were identified in terrestrial fungi, lichens, and green plants (Kuehnelt and Goessler 2003), suggesting that terrestrial plants own the similar ability to detoxify As to their aquatic relatives. In this paragraph, only new findings not included in Kuehnelt and Goessler (2003) are reviewed.

The methanol–water-extractable As from plants (*Dactylis glomerata*, *Trifolium pratense*, *Plantago lanceolata*) above an ore vein contain As(V), As (III), MMAA(V), DMAA(V), AsB, TMAO(V), and TETRA with concentrations ranged from 0.5 to 6 ppm (Geiszinger et al. 2002). In spike rush (*Eleochairs* spp.) collected from Moira watershed, Ontario, Canada, trace amounts of MMAA(V), DMAA(V), TMAO(V), and TETRA may also be detected (Zheng et al. 2003). The detailed investigation of As species in plant samples collected in mining-contaminated sites in Spain revealed the influence of contamination extent on As speciation (Ruiz-Chancho et al. 2008). Arsenic in plant extracts from uncontaminated site (6.5–15.2 ppm As) showed the typical pattern with dominance of inorganic As. In comparison, organic As became more significant in plant extracts from contaminated sites (1,886–21,200 ppm As). The major components were MMAA(V) and DMAA(V), and TMAO(V) may be in significant amounts in some samples. TETRA with a concentration of 0.19 ppm As was quantified in moss (*Brachythecium cf. reflexum*) containing 1,750 ppm As in whole plant. The most striking was the difference of As speciation in downy oak (*Quercus pubescens*) among different sites. The majority of extractable As was As(V) in plants from uncontaminated sites, whereas MMAA(V) and TMAO(V) were 44% and 24% of total As pool of plant extracts from contaminated sites, respectively. The As speciation in corresponding soil solutions showed only the presence of As(III) and As(V) (Ruiz-Chancho et al. 2007), suggesting that the occurrence of organic As in plants was rather via methylation by the plant than translocation from the surrounding environments. Accordingly, the authors suggested that As speciation in plants was different due to plant characteristics and environment conditions.

For the first time, MMAA(III) and monomethylthioarsonic acid were detected in freeze-dried carrots collected 25 years ago (Yathavakilla et al. 2008). Additionally, MMAA(V) and DMAA(V) were observed with concentrations at least a level of magnitude higher than MMAA(III). However, the occurrence of methyl As in carrots with long-term storage is not clear. In the same study, carrots collected from markets in 2006 were found to contain only inorganic As. No methyl As was detectable in the carrots growing in soils with different As concentrations (6.5 to 917 ppm), reflecting that carrots were not able to metabolize inorganic As to methyl As (Helgesen and Larsen 1998). Thus, methyl As in these carrots was then suspected as a result of translocation from surrounding environments. Whether the long-term storage has caused the occurrence of MMAA(III) and monomethylthioarsonic acid in carrots with long-term storage must be addressed in further research.

A two-step sequential extraction was proposed to recover more As from plant than the typical one-step extraction for As speciation in plant materials (Mir et al. 2007). Air-dried plant materials were extracted first by 1:1 water–methanol followed by 0.1 M HCl. Arsenic speciation in Yellowknife and Deloro plants indicated that MMAA(V) and DMAA(V) can only be found in water–methanol fraction but not in HCl fraction. Still, there were significant portions of As pools in plants not extractable. The low extraction efficiencies were suggested due to a number of factors such as the insoluble forms of As, the chemical and/or physical bonding of As to the plant matrix, and the trapping of As inside the plant vascular tissues.

2.2.5 Terrestrial Animals

A variety of studies have been focused on As metabolism in terrestrial mammals such as mice, rats, hamsters, and rabbits (Kuehnelt and Goessler 2003; Reimer et al. 2010). Knowledge about organic As in terrestrial nonmammals was mostly related to aquatic species, whereas the occurrence of organic As in terrestrial nonaquatic nonmammalians, which may contribute more significantly to organic As in soils, is rare. In ants (*Formica* sp.) and earthworms (*Lumbricus terrestris*) from contaminated sites in Styria, Austria, MMAA (V), DMAA(V), AsB, and TMAO(V) were identified as minor constituent (Kuehnelt et al. 1997; Geiszinger et al. 1998; Geiszinger et al. 2002). The surprisingly low As concentrations in ants (12 ppm) compared with ant-hill material (5,420 ppm As) hint a specific mechanism for As exclusion (Kuehnelt et al. 1997). Earthworms (*Lumbricus rubellus* and *Dendrodrilus rubidus*) collected at Devon Great Consols, UK, with different extent of As soil contamination (up to 1.3%) confirmed again the findings of MMAA(V), DMAA (V), and AsB (Watts et al. 2008; Button et al. 2009). Dimethylarsinoylribosides (glycerol, phosphate, and sulfate) were also identified in earthworms, suggesting probable biotransformation and bioaccumulation of arsenosugars in the soil environments (Geiszinger et al. 1998; Geiszinger et al. 2002; Watts et al. 2008; Button et al. 2009). The occurrence of arsenosugars in earthworm casts but not in the surrounding soil suggested that earthworm or microorganisms in contact with the worms might elaborate these compounds (Geiszinger et al. 2002). However, Button et al. 2009 indicated the increased inorganic As concentrations with increasing As body burden of earthworms, but the concentrations of organic As remained relatively constant. This observation suggests that biomethylation seems not to contribute to As resistance in the sampled earthworm populations (Button et al. 2009). Organoarsenicals, including MMA, DMA, TMAO, AsB, and AsC, were identified in caterpillars, moths, grasshoppers, slugs, ants, spiders, mosquitoes, and dragonflies from a contaminated site in Nova Scotia, Canada, but the amount did not exceed 20% of total extractable As using 1:1 methanol–water solution (Moriarty et al. 2009). However, there was no direct evidence for As methylation in metabolic processes in the invertebrates (Reimer et al. 2010).

3 Transformation of Methyl As in Soils: Demethylation and Gas Evolution

The organic As may undergo further transformation in soils. These compounds may further methylate or reduce and volatilize to the atmosphere. The volatile arsines are extremely toxic. Fortunately, these arsines are readily oxidized to give corresponding products less toxic. On the other hand, microorganisms in soils are able to decompose organic As (Gao and Burau 1997; Huang et al. 2007). Organic As may be stepwise demethylated, and the final production is usually inorganic As. Both demethylation and gas evolution are potential pathways for organic As loss in soils. Arsenic transformation in soils is usually related to microbial activity. In addition to microorganisms involved, As transformation can be influenced by some abiotic factors, such as soil pH (Cox 1975) and soil temperature (Huysmans and Frankenberger 1991)

3.1 Arsine Evolution

Arsenic in soils can be transformed by microbial activity to volatile arsines. Although arsines are very toxic, their volatilization lowers the As concentration in both the medium and in the microbial cell, preventing its accumulation in cells and augmenting its detoxification (Qin et al. 2006). Studies on arsine evolution from soil have shown that the process was affected by the soil environment and chemical forms of As (Woolson and Kearney 1973; Akins and Lewis 1976; Woolson 1977). Evolution of arsine is much higher from organic As than from inorganic As (Woolson 1977). Woolson and Isensee (1981) estimated that as much as 14% to 15% of the As applied in soil can be lost through volatilization of organic As each year.

A study of arsine evolution from soils treated with ^{74}As-MMAA(V) at 100 ppm (Akins and Lewis 1976) showed that the greatest loss of As (~11%) was found from a soil with 11% organic matter and maintained under reduced (wet) soil conditions for 60 days. In another study (Woolson 1977), the soil was treated with 10 ppm As as ^{74}As-sodium As(V), ^{14}C-MMAA

(V), and ^{14}C-DMAA(V). In 160 days, while continuously flushing a closed system with air, 18.0%, 12.5%, and 1.0% of As were volatilized from DMAA(V), MMAA(V), and As(V), respectively. When flushed with N_2, 7.8%, 0.8%, and 1.8% were lost. The main volatile forms were identified as DMA(-III) and TMA (-III). The loss of DMAA(V) from soils under aerobic and anaerobic conditions was also reported (Woolson and Kearney 1973). Over 24 weeks, about 35% was evolved as a volatile organic As under aerobic incubation, but 61% was evolved under anaerobic incubation as DMA(-III). When As was applied to the surface of an established lawn, the most rapid evolution was from DMAA(V), a slightly slower rate was found from MMAA(V), but a very much slower rate was observed with As(III) (Braman 1975). A similar trend (DMAA(V)>MMAA(V)>As(V)=As (III)) of evolution rates of As from Sacramento silty clay soils incubated with 100 ppm As of DMAA(V), MMAA(V), As(V), and As(III) for 70 days was found (Gao and Burau 1997). Arsine production by microorganisms in soils was verified. The amount of arsine evolution at 25°C was about twice that at 5°C. Arsine evolution reached its maximum when the soil moisture was between 25% and 35%. Cellulose addition enhanced the arsine evolution rates.

Three different types of soils (pH 5.6–7.6 and 0.9–2.3% C) were spiked with 160 ppm as As(V), As(III), MMAA(V), and DMAA(V) and incubated anaerobically for 3 weeks (Cheng and Focht 1979). Arsine was produced in all three soils from all substrates, whereas MMA(-III) and DMA(-III) were produced only from MMAA(V) and DMAA(V), respectively. No TMA (-III) was observed and methylation of any As substrates in soils here. *Alcaligenes* sp. and *Pseudomonas* sp. isolated from soils were found to produce arsine from the reduction of As(V) and As(III) (Cheng and Focht 1979). Under aerobic and anaerobic laboratory conditions, production of gaseous TMA(-III) was positively related to As concentrations in soils (2,125–3,632 ppm As; Turpeinen et al. 2002). The production of TMA(-III) was observed to decline within 2–4 days after its peak occurrence. No TMA(-III) formation in formaldehyde-treated controls that suggested TMA (-III) formation was driven by microorganisms. In field sampling from As-contaminated soils in Helsinki, TMA(-III) with concentrations up to 1.5 mg L^{-1} in soil air was detected. The lifetime of TMA(-III) in air was short. It is known that gaseous methyl arsines develop first, and after that, arsines will be converted to water-soluble species (Ridley et al. 1977; Takamatsu et al. 1982). The stability test indicated that TMA(-III) reached water rapidly and converted to As(V) and TMAO(V) in a few hours (Turpeinen et al. 2002). Arsine, methyl arsines, and two unidentified volatile As species were observed in the headspace of an anaerobic incubation of an alluvial soil for over 3 months under He atmosphere (Meyer et al. 2007). A strictly anaerobic Gram-positive strain ASI-1 isolated from this alluvial soil is known to be able to produce volatile arsines.

The fungi (*Aspergillus niger*, *Aspergillus clavatus*, and *Nassarius fischeri*) isolated from mining soils highly contaminated with As (Pezinok, Slovakia) were demonstrated to be able to produce volatile arsines from As(III) and As(V) in Sabouraud medium (Čererňanský et al. 2009). The order of ability of As biovolatilization was *N. fischeri*>*A. clavatus*>*A. niger*. There was no extremely significant difference between the biovolatilization of As(III) and As(V). Using laboratory soil column setup, Islam et al. (2007) estimated the rate of As evolution by anaerobic microorganisms in agricultural soils (total As 7.9–61 ppm) in Bangladesh that could be as high as 0.014 μg As kg^{-1} day^{-1} as MMA(-III) and arsine. By supplying medium for methanogen growth, As evolution increased to 0.017–0.68 μg As kg^{-1} day^{-1}. Arsenic evolution was all <0.3% of total As in the soil during 100 days of incubation. A microcosm study was performed to examine the relevance of As evolution from field-contaminated Bangladeshi paddy soils containing 24.2 ppm As (Mestrot et al. 2009). Arsenic evolution was responsible for loss of 0.014% of total soil As in a 3-week period for manuring and flooding. Trimethylarsine(-III) was shown to be the dominant species with lesser quantities of DMA(-III). No As evolution was observed for nonmanured treatments, and arsine release from the nonflooded, manured treatment was much less than the flooded treatment. Nevertheless, the As speciation in headspace was based on silver nitrate chemotrapping, elution of this chemotrap with hot boiling diluted HNO_3 with subsequent addition of H_2O_2 to oxidize arsine to pentavalent As, and analysis of eluent with HPLC–ICP-MS. This technique is thus disadvantaged by not being able to differentiate methylarsine from pentavalent methyl As, e.g., associated with aerosol particles.

3.2 Degradation of Organic Arsenic Compounds

Biological demethylation is the dominant process for the generation of inorganic As from organic As (Andreae 1979). DMAA(V) was shown to degrade to As(V) in soil under aerobic but not anaerobic conditions, and the persistence of DMAA(V) was not function of soil type (Woolson and Kearney 1973). In a loamy soil, degradation of MMAA(V) increased with increasing soil organic matter content and also from the addition of plant materials (Dickens and Hiltbold 1967). Degradation of MMAA(V) (0–5 ppm As) in soil followed first-order kinetics. The rate constants are temperature dependent at water contents under field capacity, and the temperature effect was less under flooded conditions (Akkari et al. 1986).

DMAA(V) degrades (incubated with 100 ppm As) in Sacramento silty clay soils more rapidly than MMAA (V) and simultaneously losing both methyl groups with first-order kinetics (Gao and Burau 1997). DMAA(V) mineralized with a slower rate at 5°C than 25°C. Cellulose addition (0–5% *w/w*) depressed DMAA(V) degradation in soils. Mineralization of organic As in soils after 70 days (3–87%) of incubation was much higher than the loss as arsine (0.001–0.4%), suggesting that degradation was the major pathway of MMAA(V) and DMAA(V) loss than gaseous evolution in soils. The mineralization of DMAA(V) was indicated as first-order kinetic and increased as soil moisture (5–55% *w/w*). A strong effect was shown only when soil moisture is over 35% *w/w*.

Application of 50 g seaweed to 1 kg soil led to an increase of As in the soils, and the dominating species found in the soil porewater were DMAA(V), As(V), and As(III) after the initial appearance of arsenosugars. Thus, the decomposition pathway is proposed, arsenosugars→DMAA(V)→inorganic As, without appreciable amounts of MMAA(V) (Castlehouse et al. 2003). In paddy soils, seasonal fluctuations between As(III) and DMAA(V) or As(V) and MMAA(V) were very similar. An explanation may be offered: even if DMAA(V) and MMAA(V) are produced through the same metabolic pathways, either the production of MMAA(V) from As(III) or degradation of MMAA(V) to As(III) is very stable and slow under both anaerobic and aerobic conditions. On the other hand, although DMAA(V) can be degraded more easily than MMAA (V), it is formed from MMAA(V) with an accelerated rate under anaerobic condition (Takamatsu et al. 1982).

The degradation of AsB was demonstrated to be faster than that of DMAA(V) in extracts of nonpolluted surface O horizon (Oa horizon) and peatland soils (≤24 ppm As, Huang et al. 2007). Based on first-order kinetics, AsB were degraded in extracts of O horizon and peatland soils at 5°C under oxic and anoxic conditions with half-lives 3.6 to 12 days. Demethylation of DMAA(V) was relatively slow with half-lives of 187 and 46 days in extracts of O horizon and peatland soils under aerobic condition, respectively. Under anaerobic condition, DMAA(V) may be stable for at least 100 days in peatland extracts. Arsenic speciation during AsB degradation indicated rapid demethylation of AsB probably via the pathway AsB→dimethylarsenoylacetate→DMAA(V), followed up by slow demethylation of DMAA(V)→MMAA(V)→inorganic As.

A number of bacteria isolated from highly contaminated soils were shown to be able to degrade water-insoluble compounds triphenylarsine and triphenylarsineoxide (Köhler et al. 2001). The bacteria comprised *Stenotrophomonas maltophilia* As2, *Pseudomonas* sp. As3 and As4, *Arthrobacter* sp. As9, and *Bacillus* sp. As10. The release of As(III), As(V), and soluble organic As from soils by these bacteria highlighted the potential of using autochthonic soil bacteria for bioremediation of chemical warfare reagent-contaminated soils. Similarly, Hofmann et al. (2001) demonstrated the ability of As-resistant fungi (*Trichoderma harzianum* As11) to oxidize triphenylarsine to triphenylarsineoxide. *Phanerochaete chrysosporium* transformed phenylarsineoxide to phenylsronic acid under oxic condition. Biodegradation of diphenylarsinic acid by *Ensifer adhaerens*-related strains L22406 and L2431 was proposed via the metabolic pathway diphenylarsinic acid→monohydroxilated diphenylarsinic acid→phenylarsonic acid→As(V) (Harada et al. 2010). The monohydroxilation of diphenylarsinic acid seemed to be mediated by monooxygenase, as supported by the positive relation between diphenylarsinic acid degradation and iron concentration up to 7.2 μM.

4 Sorption Behavior and Mobility of Organic Arsenic Compounds in Soils

Understanding sorption behavior of organic As on soils and soil minerals is important to access their mobility in soil systems and potential impacts on environment. Chemical forms of As were indicated to influence their sorption affinity. Arsenic is generally more mobile in the III oxidation state than in the V oxidation state (Chiu and Hering 2000). The past findings revealed that as As becomes more methylated, its adsorption affinity decreases (Lafferty and Loeppert 2005). For example, the order of sorption was DMAA<MMAA≈As(V) in aerobic soils (Wauchope 1975). In aerobic river sediment, the order of sorption was DMAA<MMAA<As(V) (Holm et al. 1980). Thus, As may become more mobile and bioavailable in soil systems where As methylation is favored. Turpeinen et al. (1999) and Huang and Matzner (2007b) observed more As releases in soils with increased microbial activity toward As methylation.

There has been considerably less research on the interactions of organic As than inorganic As with soil constituents (Xu et al. 1991; Cox and Ghosh 1994; Lafferty and Loeppert 2005; Ramesh et al. (2007)). The adsorption behavior of MMAA(V) and DMAA(V) was previously investigated with several soil minerals, including alumina, hematite, quartz, and hydrous ferric oxide (Xu et al. 1991; Cox and Ghosh 1994). The adsorption affinity of MMAA(V) to ferrihydrite and goethite is slightly less than As(V) (Lafferty and Loeppert 2005). Compared with MMAA(V) and As(V), the adsorption of DMAA (V) was in much smaller amounts on ferrihydrite and goethite. Ramesh et al. (2007) indicated also that the adsorption capacity of As(V) (11.6 and 0.58 mg g^{-1}) was apparently larger than DMAA(V) (5.63 and 0.2 mg g^{-1}) onto goethite and ferrihydrite. Adsorption of MMAA(V) and DMAA(V) on Al and Fe (hydr)oxides was insensitive to changes in ionic strength, indicating that these As species form inner sphere complexes with these minerals (Cox and Ghosh 1994; Lafferty and Loeppert 2005). Apparently, the single methyl group substitution still allows MMAA(V) to form bidentate complexes, which is the predominating form of As(V) surface complex with Fe (hydr)oxides (Fig. 3). The additional methyl group of DMAA(V) compared with MMAA(V) was hypothesized to result in losing possibility to form bidentate complexes and reduction in spatial compatibility with surface adsorption sites (Lafferty and Loeppert 2005). This hypothesis has been demonstrated on nanocrystalline titanium oxide with X-ray absorption spectroscopy (XAS; Jing et al. 2005). It was observed that for MMAA(V) and DMAA(V), maximum adsorption occurred at low pH and decreased with increasing pH, which is similar to the adsorption behavior of As(V) (Lafferty and Loeppert 2005). The adsorption of As on alumina at pH<6 decrease in the order As(V)> MMAA(V)≈DMAA(V)>As(III), whereas at pH>6, the order is As(V)>As(III)>MMAA(V)≈DMAA (V). The adsorption reaches the maximum around pH 5 for As(V), pH 7 for As(III), and pH 4 for MMAA(V) and DMAA(V) (Xu et al. 1991). Overall, phosphate is more effective to desorb MMAA(V) and DMAA(V) than sulfate from ferrihydrite and goethite (Lafferty and Loeppert 2005).

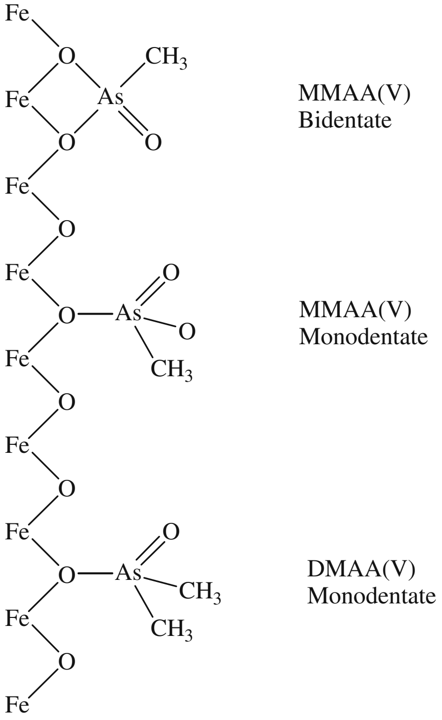

Fig. 3 Schematic illustration of the surface structures of monomethylarsonic acid (*MMAA(V)*) and dimethylarsinic acid (*DMAA(V)*) on iron (hydr)oxides

The adsorption of MMAA(III) and DMAA(III) was almost negligible on goethite and ferrihydrite at pH range examined (3.5 to 11; Lafferty and Loeppert 2005). Compared with inorganic As(III), this lack of any appreciable adsorption of MMAA(III) and DMAA(III) by Fe oxides indicates that the presence of methyl groups drastically altered the bonding characteristics of As(III).

5 Biogeochemical Cycle of Organic Arsenic in the Soil Environment

Based on the existing knowledge, biogeochemical cycle of organic As in soil-associated environment is proposed in Fig. 4. The occurrence of organic As was due to biomethylation, atmospheric deposition, and anthropogenic input. Several strains of soil microorganisms can transform As(V) to methyl As, if appropriate methyl donor becomes available. Organic As can either biotransform to methylarsines or biodegrade to inorganic chemical form. Methylarsines are volatile and may escape to atmosphere. Organic As in the atmosphere may undergo stepwise demethylation by UV light to As(V). Arsenic in different forms in the atmosphere can travel back into soils through different kinds of atmospheric deposition. Arsenic in different forms is able to be taken up by plants and animals directly and indirectly in the terrestrial environment, followed by biotransformation processes, such as methylation, and formation of arsenosugars. These transformations are usually taken as detoxification mechanisms for plants and animals. After the death and decomposition of the plants and animals, all organic As input back into the cycle in soils, dominantly as inorganic As after biodegradation.

6 Conclusion and Future Research Prospective

Overall, the past knowledge has highlighted the important role of organic As in As biogeochemical cycle. This information becomes indispensable for understanding the fate and transport of As in soils, sediments, and aquifers and for assessment of As risk in natural ecosystems. Additionally, understanding the factors affecting As transformation in more depth may offer the key information for developing strategies of

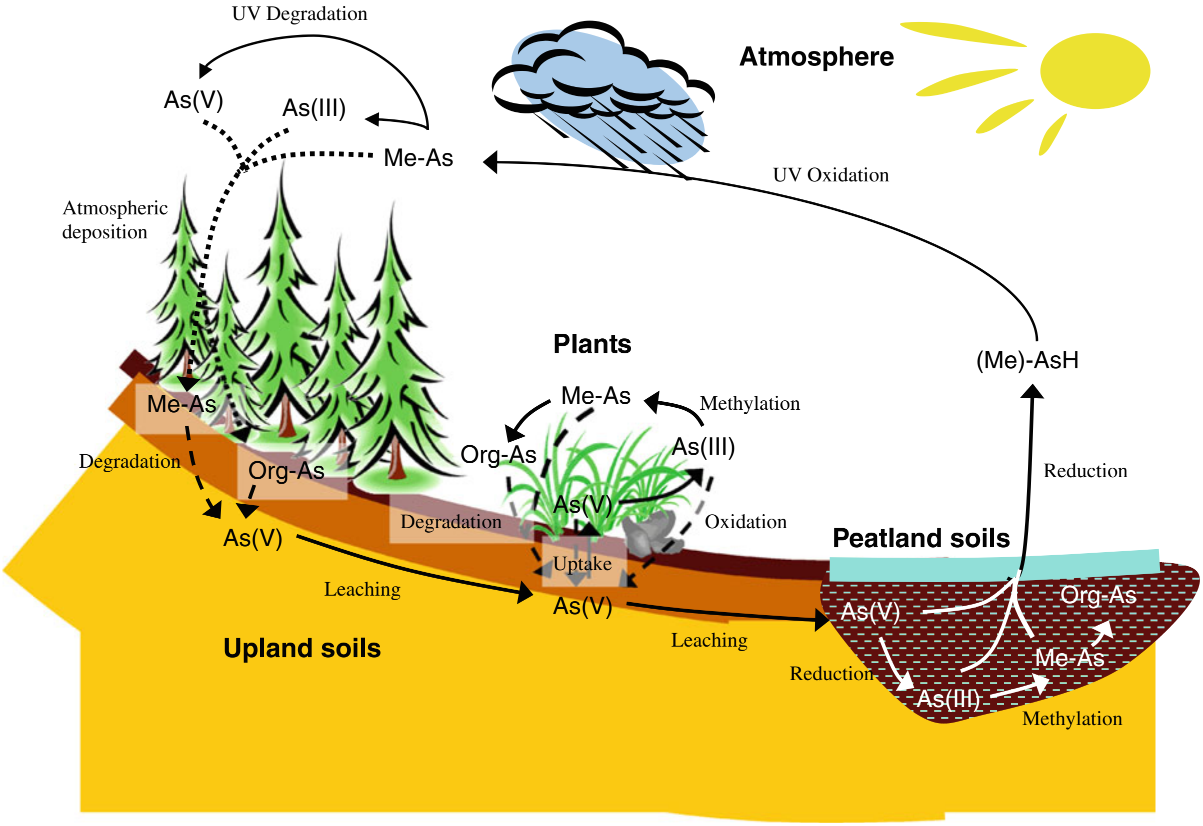

Fig. 4 Schematic presentation of biogeochemical cycles of organic arsenic compounds in the soil environment. *As(III)* arsenite, *As(V)* arsenate, *Me-As* mono-, di-, tri-, and tetra-methyl arsenic, *Org-As* recalcitrant organic arsenic (e.g., arsenobetaine, arsenocholin, and arsenosugars), *(Me)-AsH* (methyl) arsine

remediation of As-polluted soils. However, knowledge about organic As is much less than inorganic As. Still, numerous unknown As were not identified with ESI-MS due to low concentrations. To explore more about organic As in soils, more efforts should be given for more advanced analytical techniques or better pretreatment techniques. High resolution nuclear magnetic resonance spectroscopy on As metabolic models could help understand the interconversion among As species and predict unidentified As compounds (Delnomdedieu et al. 1995).

The terrestrial plants and animals are hot spots of organic As probably due to using methylation as detoxification. However, the relevance of organic As in biological tissues to soil organic As pool is not clear. The limited information from the literature indicated that organic As in biological tissues seems to degrade to inorganic As in aerobic soils (Castlehouse et al. 2003). This is reasonable when comparing to the information that due to the rapid degradation of organic As in aerobic and anaerobic soils (Huang et al. 2007). Since transformation of organic to inorganic As stands for an increase of As toxicity, more research should be addressed the transformation kinetics and quantify the fluxes of organic As from plants and animals to soils to complete the knowledge of As cycle in terrestrial ecosystems.

To date, the occurrence of trivalent methyl As has been evidenced in lake water (Sohrin et al. 1997), but not yet in the soil environment. It is not expected to know the potential MMAA(III) and DMAA(III) and their potential hazards toward the soil ecosystem. Aside from trivalent methyl As, (methyl) thioarsenate and thioarsenite in the environment have drawn more and more attention recently (Planer-Friedrich et al. 2007). However, the findings of these compounds are still limited in specific environment, e.g., geothermal environments (Planer-Friedrich et al. 2007). Unlike MMAA(III) and DMAA(III), the toxicity of these compounds is not clear. Overall, to understand the role of dissolved As-S in As biogeochemical cycle in the terrestrial environment, many efforts are still required.

Recently, XAS was taken for As speciation in hyperaccumulating and hypertolerant plants (Huang et al. 2008). XAS provides detailed information on the speciation and coordination environment of As in solid samples. Moreover, XAS overcomes the typical problem from chromatographic methods that the solvent extraction recoveries from solid phases are usually low. It is believed that more and more applications of XAS for As speciation in soils, plant, and animal tissues will be given in the future (e.g., Moriarty et al. 2009). Information in more depth about As biotransformation in the soil environment may be thus expected, which helps to understand the As ecotoxicity and cycling of As in food chains and the transfer between soils and living creatures.

Acknowledgments Financial support of JHH comes from Swiss National Science Foundation Ambizione fellowship (PZ00P2_122212). KNH is supported by a fellowship from the Intramural Research Program of the National Institute of Diabetes and Digestive and Kidney Diseases of the National Institutes of Health.

Appendix

Abbreviations of different arsenic compounds

Abbreviation	Name	Formula
As(III)	Arsenous acid	H_3AsO_3
As(V)	Arsenic acid	H_3AsO_4
MMAA(V)	Monomethylarsonic acid	$CH_3AsO(OH)_2$
MMAA(III)	Monomethylarsonous acid	$CH_3As(OH)_2$
DMAA(V)	Dimethylarsinic acid	$(CH_3)_2AsO(OH)$
DMAA(III)	Dimethylarsinous acid	$(CH_3)_2As\ (OH)$
TMAO(V)	Trimethylarsine oxide	$(CH_3)_3AsO$
TETRA	Tetramethylarsonium ion	$(CH_3)_4As^+$
AsB	Arsenobetaine	$(CH_3)_3As^+CH_2COO^-$
AsC	Arsenocholine	$(CH_3)_3As^+CH_2CH_2OH$
–	Arsine	AsH_3
MMA(-III)	Monomethylarsine	CH_3AsH_2
DMA(-III)	Dimethylarsine	$(CH_3)_2AsH$
TMA(-III)	Trimethylarsine	$(CH_3)_3As$

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