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Journal of Environmental Sciences

www.jesc.ac.cn

A review on completing arsenic biogeochemical cycle: Microbial volatilization of arsines in environment

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ARTICLE INFO

Article history:

Received 06 March 2013

revised 23 May 2013

accepted 08 August 2013

Keywords:

arsenic

methylation

microorganism

volatilization

DOI: 10.1016/S1001-0742(13)60432-5

ABSTRACT

Arsenic (As) is ubiquitous in the environment in the carcinogenic inorganic forms, posing risks to human health in many parts of the world. Many microorganisms have evolved a series of mechanisms to cope with inorganic arsenic in their growth media such as transforming As compounds into volatile derivatives. Bio-volatilization of As has been suggested to play an important role in global As biogeochemical cycling, and can also be explored as a potential method for arsenic bioremediation. This review aims to provide an overview of the quality and quantity of As volatilization by fungi, bacteria, microalga and protozoans. Arsenic bio-volatilization is influenced by both biotic and abiotic factors that can be manipulated/elucidated for the purpose of As bioremediation. Since As bio-volatilization is a resurgent topic for both biogeochemistry and environmental health, our review serves as a concept paper for future research directions.

Introduction

Inorganic arsenic, a class one, non-threshold human carcinogen (IARC, 1980, 1987), is ubiquitous in the natural environment. Arsenic contamination in the environment has been reported worldwide (Sohel et al., 2009; Li et al., 2011). There is increasing concern regarding As-related pollution due to various anthropogenic activities such as ore mining and smelting, use of As-containing fertilizers and pesticides, and fossil fuel burning. Natural sources, such as weathering and erosion of arsenic-containing rocks and soil are also important (Wang and Mulligan, 2006). Arsenic pollution in groundwater has been a serious health threat to the public human in SE, SW and NE USA, Inner Mongolia (China), SW Taiwan coastal regions, Sonora (Mexico), Pamplonian Plain (Argentina), West Bengal (In-

dia), Northern Chile, and Bangladesh (Argos et al., 2010; Valette-Silver et al., 1999). The World Health Organization (WHO) deemed the As in Bangladeshi groundwater to be “the largest mass poisoning of a population in history” (Argos et al., 2010). Inorganic As enters the human through both drinking water and food, and in particular circumstances through respiratory exposure (Li et al., 2011). Inorganic As exposure can lead to a series of health problems including severe gastrointestinal disorders, hepatic and renal failure, cardiovascular disturbances, skin pigmentation, hyperkeratosis, and cancers in many organs such as the lung, bladder, liver, kidney, and skin (Agusa et al., 2010).

Nearly twenty As species can be commonly detected in the environmental and biological systems (Gong et al., 2002). These individual As species differ in their mobility, availability and toxicity. Arsenic exists primarily as inorganic arsenate (As(V)) and arsenite (As(III)) in the natural environment, and these are amongst the most

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toxic arsenic species. Inorganic As can be chemically or biologically methylated into mono-, di- or trimethylarsine. *In vivo*, the toxicity of soluble inorganic and organic As species are dimethylarsenite (DMAs(III)), monomethylarsenite (MMAs(III)) > As(III) > As(V) > dimethylarsenate, (DMAs(V)), monomethylarsenate (MMAs(V)) > trimethylarsine (TMAs), trimethylarsine oxide (TMAsO) (Akter et al., 2005). Inorganic arsine and mono-, di-, and trimethylarsine, denoted as AsH_3 , MeAsH_2 ($(\text{CH}_3)\text{AsH}_2$), Me_2AsH ($(\text{CH}_3)_2\text{AsH}$) and Me_3As ($(\text{CH}_3)_3\text{As}$), termed collectively arsines, are a volatile class of trivalent arsenic compounds and can partition into the atmosphere from aqueous solution due to their low boiling points (Mestrot et al., 2013), as illustrated in **Fig. 1**. Though arsines are released into atmosphere, their concentration is still low due to the dilution of air. Arsine formation could effectively mitigate As poisoning in soils and water toward human or animals. On the other hand, As volatilization may lead to As transfer via the atmosphere (Bentley and Chasteen, 2002). Microorganisms have evolved dynamic mechanisms to cope with the toxicity of As in the environment. It has been estimated that as much as 2.1×10^7 kg As could be lost annually through volatilization from land surfaces to the atmosphere (Srivastava et al., 2011). Some microorganisms have been identified to form arsines for the decrease of intercellular As (Yin et al., 2011a, 2011b), including bacteria, fungi and algae (**Table 1**). Re-

cently, it was reported that the presence of rice stimulated arsine production from paddy soils (mainly as TMAs), presumably through stimulation of microbial activities (Jia et al., 2012). The factors (organic matter amendments) regulating arsines formation from different soil types, sourced throughout the globe, have been reported (Mestrot et al., 2011).

This review summarizes the species of volatile As, and provides an overview of their formation by microorganisms such as fungi, bacteria, microalgae and protozoans. We discuss biotic and abiotic factors influencing As bio-volatilization, also provide examples of genetically engineered microbes for enhanced As volatilization, both of which can be manipulated/elucidated for the purpose of As bioremediation and understating the global As cycling.

1 Volatile arsenic species

Volatile arsenicals are defined as those As species with a boiling point (bp) below 150°C . They can be formed either biotically, as intermediates or end products of the As bio-transformation pathway by microorganisms, or abiotically (**Fig. 1**). With a boiling point of -62.5°C (Planer-Friedrich et al., 2006), AsH_3 is the most volatile As gas. MeAsH_2 has a boiling point of -2°C and Me_2AsH $+36^\circ\text{C}$ (Planer-

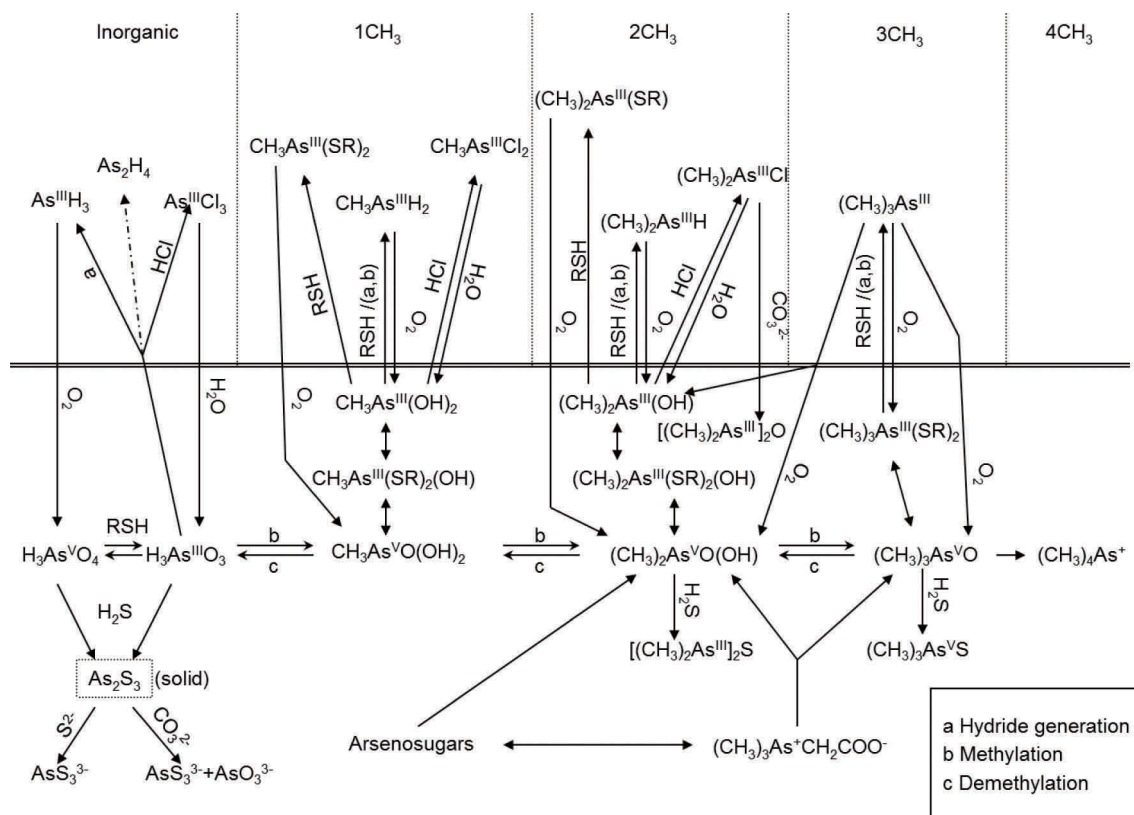


Fig. 1 Mutual transformation scheme of the more common inorganic and organic arsenic compounds in the hydrosphere and atmosphere.

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