



Review

Arsenic transfer and biotransformation in a fully characterized freshwater food web



Richard D. Foust Jr.^{a,*}, Anne-Marie Bauer^a, Molly Costanza-Robinson^{a,1}, Dean W. Blinn^b, Roger C. Prince^c, Ingrid J. Pickering^{d,2}, Graham N. George^{d,2}

^a Department of Chemistry and Biochemistry, Northern Arizona University, Flagstaff, AZ 86011-5698, USA

^b Department of Biological Sciences, Northern Arizona University, Flagstaff, AZ 86011-5460, USA

^c ExxonMobil Research and Engineering Company, Route 22 East, Annadale, NJ 08801 USA

^d Stanford Synchrotron Radiation Laboratory, Menlo Park, CA, USA

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ARTICLE INFO

Article history:

Received 1 December 2014

Received in revised form 22 February 2015

Accepted 6 March 2015

Available online 16 March 2015

Keywords:

Arsenic
Biotransformation
Diminution
Food web
Montezuma Well

ABSTRACT

X-ray absorption near edge spectroscopy (XANES) was combined with ICP-MS to understand arsenic transfer and transformation within the freshwater Montezuma Well (central Arizona, USA) food web. Montezuma Well water contains $110 \mu\text{g L}^{-1}$ arsenic (100% H_3AsO_4), which was shown previously to originate from ore deposits approximately 30 km to the west, and transported underground to enter Montezuma Well through vents in the bottom of this collapsed travertine spring. The Montezuma Well food web contains three trophic levels with only five organisms in the top two levels, making it possible to account for the arsenic in >90% of the biomass of the food web. Arsenic diminution generally occurs between trophic levels, with 702 mg kg^{-1} As in the primary producers, 3.4 mg kg^{-1} As in the second trophic level, and $<1.3 \text{ mg kg}^{-1}$ As for the top-tier of the littoral zone food web. A notable exception to the biodiminution trend is the very high total arsenic content (2810 mg kg^{-1}) of *Motobdella montezuma*, an endemic leech and top predator. The biotransformed (sulfur-coordinated) arsenic in *M. montezuma* appears to be present almost entirely on the surface of the organism, possibly suggesting a detoxification mechanism. XANES sample spectra were fit by a linear combination of model arsenic compound spectra and indicated that arsenic enters the food web from the Well water entirely as inorganic As(V) and is transformed within the food web into more reduced and organic arsenic species, including sulfur-coordinated and methylated compounds.

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* Corresponding author. Current address: Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA 22807, USA. Tel.: +1 011 540 568 6800; fax: +1 011 540 568 7938.

E-mail address: foustrd@jmu.edu (R.D. Foust Jr.).

¹ Current address: Program of Environmental Studies and Department of Chemistry and Biochemistry, Middlebury College, Middlebury, VT 05753, USA.

² Current address: Department of Geological Sciences, University of Saskatchewan, Saskatoon, SK S7N 5E2, Canada.

1. Introduction

Arsenic deserves a special place among the chemical elements because of its chemistry and its interesting history. Arsenic has been known as a substance since antiquity and was named “arsenikon” by the Greeks, their name for the yellow mineral orpiment, As_2S_3 . Arsenic was identified as a chemical element by Albertus Magnus in the 1200s [1]. Arsenic is the 20th most abundant element of the Earth’s crust and over 245 arsenic bearing minerals are known [2]. Arsenic trioxide is an important industrial chemical. The United States imported more than 20,000 tons of arsenic trioxide annually during 2001–03. This quantity dropped to 6100 tons when the use of chromated copper arsenate as a wood preservative was banned. High-purity arsenic (99.9999%) is used in the electronics industry to manufacture semi-conductors, solar cells, and specially coated optical materials [3].

Hippocrates (460–357 BC) used orpiment (As_2S_3) and realgar (As_2S_2) as a corrosive salve and to treat ulcers [4]. Pliny the Elder (23–79 AD) described the preparation of an arsenic liniment made with vinegar that was suggested as a remedy for asthma, cough, and several other ailments [1]. Modern medicinal uses of arsenic include using sodium cacodylate and sodium arsenite to treat pellagra, malaria, and sleeping sickness [1,4,5]. In 1909, arsphenamine was proposed by Paul Ehrlich as a treatment for syphilis and trypanosomiasis. This practice continued for nearly 40 years until penicillin became available [4]. Arsphenamine is considered the first chemotherapeutic agent [6].

The toxic properties of arsenic were reported by Aristotle in 340 BC when he wrote that realgar (As_2S_2) kills horses and cattle when put into water [1,7]. Arsenic’s poisonous properties have been used to change the course of history. Nero is reported to have poisoned Britannicus in 55 AD to secure his Roman throne, and Pope Alexander IV, and his son, Cesare Borgia, are legendary for their use of arsenic solutions to kill enemies [4]. The Chinese are credited with using arsenic sulfides as an insecticide as early as 900 AD, and arsenic oxide was reportedly used in ant bait in Europe in 1699 [8].

The widespread global use of arsenical insecticides over the past 150 years represents one of society’s major environmental catastrophes. Copper acetoarsenite, commonly known as Paris Green, was first used in 1867 on the Colorado potato beetle in the USA. Paris Green sprays were soon used by fruit growers to control the codling moth (*Cydia pomonella*), an insect pest capable of destroying up to 98% of a farmer’s apple production [8,9]. Paris Green was also used internationally in mosquito abatement programs for which it was applied directly to water bodies as a powder. Lead arsenate was first used as an insecticide against the gypsy moth (*Lymantria dispar*) in 1892 in Massachusetts, USA. Lead arsenate proved to be more effective than Paris Green sprays for the gypsy moth because of its lower solubility in water and its tendency to adhere to the surfaces of plants. Lead arsenate became the insecticide of choice for many agricultural crops including apples, cherries, cotton and many vegetables [8–10]. Lead arsenate use increased steadily in the United States, peaking in 1944 at 86.4 million pounds annually. Sophisticated sprayers were designed to apply lead arsenate over large areas of farmland and orchards. Adding lead arsenate to irrigation water became a common practice in some locations [9].

The discovery of DDT’s insecticidal properties in 1947 provided a convenient alternative to lead arsenate. Lead arsenate insecticides were quickly replaced by DDT, largely because the insect pests had built up resistance to lead arsenate and DDT was more effective at lower doses. All insecticidal uses of lead arsenate in the United States were officially banned in 1988 [8].

Unfortunately, hundreds of thousands of hectares of contaminated soil are the legacy that remains from a century of relying on arsenic-based insecticides. Elevated levels of arsenic and lead

Table 1

Chemical forms of arsenic substances found in aquatic environments, their formulas and abbreviations [22,23].

	Name	Formula	Abbreviation
1	Arsenous acid or arsenite	H_3AsO_3	As(III)
2	Arsenic acid or arsenate	H_3AsO_4	As(V)
3	Monomethylarsonous acid	$\text{CH}_3\text{As}(\text{OH})_2$	MMA(III)
4	Monomethylarsonic acid	$\text{CH}_3\text{AsO}(\text{OH})_2$	MMA(V)
5	Dimethylarsinous acid	$(\text{CH}_3)_2\text{As}(\text{OH})$	DMA(III)
6	Dimethylarsinic acid	$(\text{CH}_3)_2\text{AsO}(\text{OH})$	DMA(V)
7	Trimethylarsine	$(\text{CH}_3)_3\text{As}$	TMA
8	Trimethylarsine oxide	$(\text{CH}_3)_3\text{AsO}$	TMAO
9	Arsenocholine	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{OH}$	AsC
10	Arsenobetaine	$(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CO}_2^-$	AsB
11	Arsenosugars	$(\text{CH}_3)_2\text{AsOCH}_2\text{C}_4\text{H}_4\text{O}-\text{R}^a$	AsS
12	Arsenic glutathione complex	$(\text{GS})_3\text{As}(\text{III})^b$	$(\text{GS})_3\text{As}(\text{III})$

^a R can be an alcohol, phosphate, sulfate, sulfite, carboxylic acid or a heterocycle.

^b GS represents the glutathione anion.

were discovered in apples as early as 1919 when experiments were begun to identify washing procedures to eliminate the toxic residues. Although lead remains in the top 5–20 cm of soil, the arsenic may be transported through runoff or through groundwater because of its higher solubility. In soluble forms, arsenic can be transported through the root system into plants or to wells where they can be ingested through drinking water. Transport via groundwater has resulted in millions of people living in the Bengal Delta Plain in Bangladesh and the West Bengal area of India to acquire arsenic poisoning from their drinking water, although in this case the underlying source of arsenic in the water is geologic, rather than human activity [11–13].

Rice accumulates arsenic at higher levels than other terrestrial plants. Indeed, dietary arsenic from rice grown in contaminated fields is known to be a contributing factor for arsenic poisoning in the Bengal Delta [14,15]. The American Chemical Society addressed this concern in a recent symposium on arsenic contamination in food and water [16], and the U.S. Department of Agriculture has a program to measure the arsenic content of rice grown in the United States [17].

It is essential to understand the environmental chemistry of arsenic in order to develop methods for remediating contaminated arsenic soil and water. The solubility of arsenic, and therefore its ability to be transported in an aqueous environment, is governed by the oxidation state of arsenic, the presence of other metals in the soil or aquifer material and their oxidation states [2,18–20]. The toxicity of arsenic also depends on the oxidation state and on the ligands that surround the arsenic atom, making the chemical form of the arsenic as important as the amount of arsenic when assessing environmental hazards [21]. Until recently, the literature on environmental arsenic has emphasized arsenic quantity present in environmental samples and has paid less attention to its chemical form.

1.1. Environmental transformations of arsenic

More than 50 organoarsenic compounds are found in nature [22,23]. Table 1 lists the most common arsenic substances found in aquatic environments. Inorganic arsenic species predominate in aqueous environments, and depending upon the redox properties of the system, the arsenic may be present in the +5 oxidation state as arsenic acid (H_3AsO_4) or in the +3 oxidation state as arsenous acid (H_3AsO_3) [20,21]. Most arsenic compounds isolated from biological organisms are organic species that are produced through metabolic processes in phytoplankton, bacteria or in the organs of vertebrates [21,24,25]. Two recent review articles document arsenic concentrations in an extensive list of organisms and the species of arsenic that have been identified in these organisms

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