Sulfur-arsenic interactions and formation of thioarsenic complexes in the environment

I. Herath¹, J. Bundschuh¹ & P. Bhattacharya²

¹Faculty of Health, Engineering and Sciences, University of Southern Queensland,
Toowoomba, Queensland, Australia

²KTH-International Groundwater Arsenic Research Group, Department of Sustainable Development, Environmental
Science and Engineering, KTH Royal Institute of Technology, Stockholm, Sweden, and International Center for
Applied Climate Science, The University of Southern Queensland, Toowoomba, Queensland, Australia

ABSTRACT: Thiolated arsenic compounds are the sulfur analogous substructures of oxo-arsenicals as the arsinoyl (As=O) is substituted by an arsinothioyl (As=S) group. Relatively brief history of thioarsenic research, mostly in the current decade has endeavored to understand their consequences in the natural environment. However, thioarsenic related aspects have by far not attached much research concern on global scale compared to other arsenic species. This paper provides a critical overview on formation mechanisms of thioarsenicals and their chemistry aiming to direct future research towards thioarsenic mitigation strategies. Sulfur-arsenite/arsenate interactions and dissolution of arsenic sulfide minerals are the main mechanisms that involve in the formation of different thioarsenic species in the natural environment. The formation and chemical analysis of thioarsenicals in soil and sediments are highly unknown. Future research needs to be more inclined towards in determining the molecular structure of unknown thioarsenic complexes in various environmental suites.

1 INTRODUCTION

Arsenic (As) and sulfur (S) commonly co-exist in the environment due to their strong interrelationship in the biogeochemical cycles. Arsenic species where the oxygen-bonded As is substituted by sulfur, thereby forming As-SH and/or As=S substructures are known as thioarsenic compounds (Guo *et al.*, 2017). Occurrence of thioarsenic species has been identified as a vital parameter to better understand the geologic and geochemical mechanisms of As enrichment in sulfidic waters. Therefore, a holistic understanding of the formation, speciation and chemical analysis of thioarsenic species is crucial for investigating the fate of As in different environmental, geological, and biological systems. However, the definite chemical nature of many thioarsenic compounds still remains a subject of debate and hence, it is urgently necessary to develop proper analytical protocols for resolving this dispute in order to understand mechanisms of As speciation, geochemistry, and mobility in the natural environment. The present paper provides an overview of the formation mechanisms of thiolated As complexes and their chemistry in order to direct future research towards thioarsenic mitigation strategies.

2 DISCUSSION

2.1 Formation of thioarsenic species

Thioarsenic species are formed as a result of geochemical interactions between As and sulfur-bearing compounds (sulfides; S²⁻/HS⁻) in favorably reducing

or anoxic environments (Härtig & Planer-Friedrich 2012). Laboratory as well as field scale studies have demonstrated the formation pathways of thioarsenic complexes in sulfidic water containing both inorganic arsenate and arsenite. Oxidation of arsenite in sulfidic environments and dissolution of arsenic sulfide minerals have been recognized as the most significant geochemical triggers for the formation of thioarsenic species in the environment.

2.2 Formation of thioarsenic species by sulfur-arsenite interactions

Thioarsenic complexes in the form of thioarsenate are formed through a series of redox reactions between arsenite and sulfur while donating non-bonding electron pair of arsenite to sulfur atom. The formation of thioarsenate takes place through the deprotonation of arsenite in the presence of aqueous sulphide (H₂S), where arsenite is partially oxidized to monothioarsenate (reaction 1).

In natural environments, such as some ground water and geothermal fluids, this reaction occurs due to presence of electron acceptors such as sulfate and sulfur which are produced from H₂S by bacterial activities. The monothioarsenate produced from reaction (1) is further converted to dithioarsenate in the presence of excess sulfide (reaction 2).

Microbial activities of sulfate-reducing bacteria, such as *Desulfotomaculum* can strongly influence the formation of thioarsenate from the oxidation of arsenite in sulfidic geothermal water (Wu *et al.*, 2017). In sulfidic aquifers under anoxic conditions, *Desulfotomaculum* bacterium can oxidize arsenite to arsenate which can react with S^{2-}/HS^- , thereby producing thioarsenates ($AsO_{4-x}S_x^{2-}$ with $x = 1-4$) along with mono-, di-, and tri-thioarsenate as dominant species (reaction 3).

2.3 Formation of thioarsenicals by dissolution of arsenic sulfide minerals

Arsenic bearing sulfide minerals, specifically orpiment (As_2S_3), enargite (Cu_3AsS_4) and arsenopyrite ($As-Fe-S$) are important sources of the formation of various thioarsenic species in the environment. Dissolution of these mineral phases may trigger the release and formation of thioarsenic compounds which play a crucial role in As cycle in aqueous sulfidic systems.

Orpiment dissolution

The dissolution of amorphous As_2S_3 in sulfide deficient and sulfide rich solutions has been investigated at $pH\ 4.4 \pm 0.4$ and a range of temperature from 25 to 90°C. In sulfide-deficient solutions ($H_2S < 10^{-3}$ M), H_3AsO_3 is the main product of the dissolution of As_2S_3 and the dissolution reaction can be expressed as:

In sulfide rich solutions ($H_2S > 10^{-3.8}$ M), the solubility of As_2S_3 is controlled by the concentration of H_2S and the dissolution As_2S_3 may result $H_2As_3S_6^-$ as the dominant species of As (reaction 5). This trimeric thioarsenite is the solubility controlling species of amorphous or crystalline orpiment in sulfur rich solutions.

Arsenopyrite dissolution

The oxidative dissolution of arsenopyrite in alkaline media produces dominantly monothioarsenates at ($\Sigma As/\Sigma S$) of 0.8–1.3 (reaction 6) (Suess & Planer-Friedrich 2012).

The formation of monothioarsenate from arsenopyrite dissolution is governed by a physisorption mechanism of hydroxide under both oxic and anoxic conditions. First, arsenopyrite reacts with dissolved oxygen and subsequently hydroxyl group is adsorbed via a physisorption mechanism (reaction 7–9).

As a result of these electron transfer reactions, a complex of $As-OH-S$ is formed and thereby resulting in a surface complex of monothioarsenate (reaction 10).

Apart from the occurrence of thioarsenicals in environmental and geological systems, various thioarsenic complexes have also been detected in biological systems. Micro-biota living in human and animal gut can enhance the production of inorganic as well as methylated thioarsenate compounds due to complexation reactions between thiol groups and ingested arsenates in the gut. The replacement of OH^- groups of methylated arsenic species by SH^- (thiolation) can occur in H_2S producing gut microbiota within the distal gastrointestinal tract. For instance, highly toxic dimethylmonothioarsenate ($LC50 = 10.7$ in cultured A431 human epidermoid carcinoma cells) is formed by the thiolation of dimethylarsenate during the metabolism of dimethylarsenate in human urine.

3 CONCLUSIONS

This review focuses on the existing knowledge in relation to the formation mechanisms of thioarsenic species in the natural systems. Sulfur-arsenite/arsenate interactions and dissolution of arsenic sulfide minerals are the main mechanisms that involve in the formation of different thioarsenic species in the natural environment. The formation of thioarsenic complexes may lead to increase the solubility, mobility and bioavailability of As in the environment. More future researches are essential on thioarsenic related aspects in clarifying formation mechanisms, and developing upgraded analytical instrumentation to establish a sustainable arsenic mitigation on a global scale.

REFERENCES

- Guo, Q., Planer-Friedrich, B., Liu, M., Li, J., Zhou, C. & Wang, Y. 2017. Arsenic and thioarsenic species in the hot springs of the Rehai magmatic geothermal system, Tengchong volcanic region, China. *Chem. Geol.* 453: 12–20.
- Härtig, C. & Planer-Friedrich, B. 2012. Thioarsenate Transformation by Filamentous Microbial Mats Thriving in an Alkaline, Sulfidic Hot Spring. *Environ. Sci. Technol.* 46(8): 4348–4356.
- Suess, E. & Planer-Friedrich, B. 2012. Thioarsenate formation upon dissolution of orpiment and arsenopyrite. *Chemosphere* 89(11): 1390–1398.
- Wu, G., Huang, L., Jiang, H., Peng, Y., Guo, W., Chen, Z., She, W., Guo, Q. & Dong, H. 2017. Thioarsenate Formation Coupled with Anaerobic Arsenite Oxidation by a Sulfate-Reducing Bacterium Isolated from a Hot Spring. *Front. Microbiol.* 8(1336).