

Formation of highly toxic As species by thiolation from dimethylarsinic acid under sulfidic condition

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Dimethylarsinic acid (DMA^V) is a less toxic organo-As species and occurring as trace in surface and subsurface environments. It was classified as possibly carcinogen despite its low toxicity because highly toxic dimethylmonothioarsinic acid (DMMTA^V) could be formed during its metabolic process [1]. DMA^V is formed by biomethylation from inorganic As species in subsurface environments [2] and its thiolated analogues, DMMTA^V and dimethyldithioarsinic acid (DMDTA^V), were detected in a reducing aquifer [3]. Therefore our study aimed to examine DMA^V thiolation kinetics and to understand the environmental conditions responsible for forming DMMTA^V.

The result of our examination showed that the thiolation of DMA^V is pH-dependent, and consists of two consecutive first-order reactions under excess sulfide conditions. DMMTA^V occurred as an intermediate in pH 5-7 and was stable in pH 2.5. The first reaction forming DMMTA^V is first order in H₂S and the overall reaction is second order ($k=0.0780 \text{ M}^{-1}\cdot\text{s}^{-1}$ at pH 6.0 and 20 °C). The reaction rate significantly decreases at pH 8.0 indicating that H₂S(aq) triggers the thiolation of DMA^V. The transformation of DMDTA^V to DMMTA^V is catalyzed in the presence of ferric iron.

DMMTA^V is formed by chemical reaction when H₂S is present, therefore the sulfidic or sulfate reducing conditions posed by arsenic can be considered as possibly condition occurring DMMTA^V.

[1] IARC (2012) IARC Monographs Volume 100C

[2] Maguffin et. al. (2015) *Nat. Geosci.* **8**, 290-293.

[3] Wallschläger & London (2008) *Environ. Sci. Technol.* **42**, 228-234.