

# Surface Speciation of Organoarsenicals on Iron (Oxyhydr)oxides Using As-XANES

Hind A. Al-Abadleh and Tuan Hoang

1

## PRINCIPAL CONTACT:

**H.A. Al-Abadleh**  
Chemistry Department,  
Wilfrid Laurier University  
halabadleh@wlu.ca  
519-884-0710 ext.2873

## Introduction

Arsenic (As) contamination of soils, surface and groundwater is a serious problem in many parts of the world including North America. Sources of this pollution can either be natural or anthropogenic. Anthropogenic sources of arsenic in the environment include the industrial effluents from petrochemical and coal industries, application of organoarsenical pesticides[1] and poultry litter contaminated with arsenic feed additives on agricultural lands[2].

The most common organoarsenical species in the environment contain arsenic in the oxidation states of +III and +V, and can exist in aliphatic and aromatic forms. These compounds include monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), p-arsanilic acid (p-AsA) and roxarsone (ROX) (see Table 1). These compounds are generally thought to be less mobile and toxic than inorganic forms of arsenic. Depending on the level of microbial activity and redox potential in soils, biotransformation processes eventually lead to the formation of the more toxic inorganic forms of arsenic (iAs(V) and iAs(III)). With the implementation of lower maximum contaminant levels of total arsenic in drinking water (10 ppb), there are concerns about the fate of organoarsenicals introduced to the environment.

Compound	Structure	pK <sub>a</sub>
MMA (V)		(1) 3.6 (2) 8.2
DMA (V)		(1) 6.14
p-Arsanilic acid		(-NH <sub>2</sub> ) 1.9 (1) 4.1 (2) 9.2
Roxarsone		(1) 3.5 (-OH) 5.7 (2) 9.1

**Table 1:** Structure and pK<sub>a</sub> of organoarsenicals used in our studies.

## Science

The environmental impact of arsenic compounds is usually quantified through the determination of properties such as mobility, bioavailability and speciation, which depend to a large extent on the surface interactions with geosorbents,

mainly minerals and organic matter. While these interactions are well established for inorganic arsenic, little is known about the surface interactions of organoarsenicals with geosorbents at the molecular level. Adsorption mechanisms (i.e. thermodynamics and surface speciation) are usually determined from batch experiments, infrared and synchrotron X-ray based techniques.

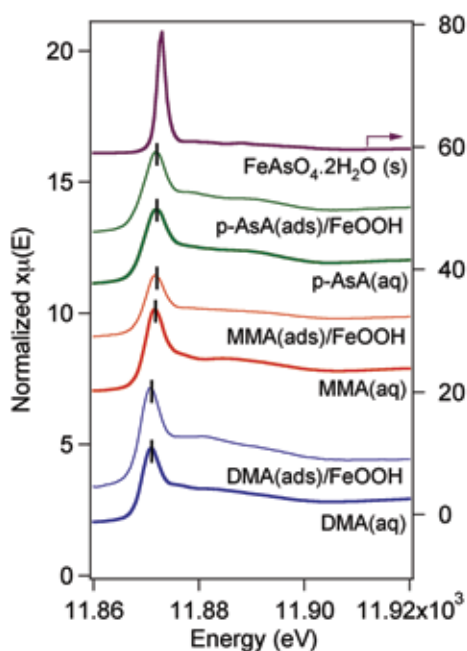
We have recently utilized ATR-FTIR spectroscopy for in-situ identification of surface complexes and measurement of the binding energies of p-AsA adsorption on iron (oxyhydr)oxides[2]. However, in order to fully understand the geometry of organoarsenicals surface complexes, vibrational spectroscopy data should be complemented by X-ray absorption spectroscopy data. Hence, we report herein preliminary As *K*-edge (11.87 keV) EXAFS data collected at the HXMA beamline 06ID-1 for a number of organoarsenicals adsorbed on iron (oxyhydr)oxides.

## Materials and Methods

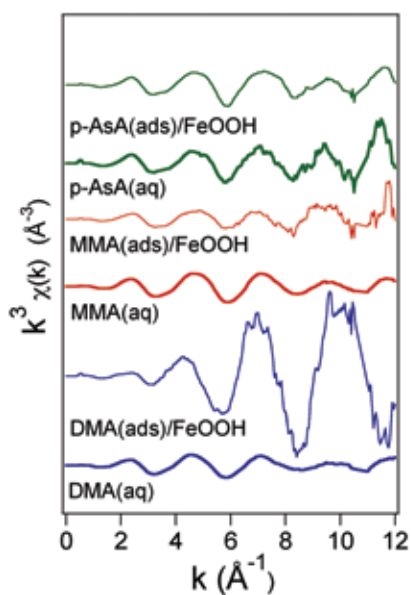
Organoarsenicals adsorption on 24 g/L iron (oxyhydr)oxide samples including hematite, maghemite and goethite was investigated at pH 7, 0.01 M KCl, and initial organoarsenical concentration of 10 mM. After centrifugation, pastes of reacted iron (oxyhydr)oxides were spread over kapton tape for transmission mode XANES measurements at the HXMA beamline. Each final spectrum represents the average of four spectra. Standard samples were also analyzed and they include aqueous solutions of organoarsenicals and scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O).

## Discussion

Figure 1 shows selected preliminary As *K*-edge XANES spectra of organoarsenicals adsorbed on goethite (-FeOOH) along with standard materials. The edge energies of MMA and DMA solutions of 11872 and 11871 eV, respectively are in agreement with previous studies[3]. The edge energy of p-AsA(aq) has not been reported before and its value equals that of MMA, which is not surprising given that the arsonic group in both molecules is monosubstituted with an organic group. Moreover, the values of the energy edge did not change when the above organoarsenicals are adsorbed on goethite. These values are slightly lower than that of arsenic in the scorodite structure. Figure 2 shows the *k*<sup>3</sup> weighted EXAFS spectra of adsorbed organoarsenicals and standard aqueous solutions, which could be used to determine the local coordination environment of organoarsenicals as described in the modelling studies of Jing et al. [3]. This work is currently underway.



**Figure 1:** Selected preliminary As K-edge XANES spectra of organoarsenicals adsorbed on FeOOH. Thicker lines show spectra of standard materials including scorodite and aqueous solutions of DMA (50 mM), MMA (50 mM), and p-AsA (5 mM). All spectra are normalized and offset for clarity.



**Figure 2:** The  $k^3$  weighted observed EXAFS spectra of the As K-edge for organoarsenicals adsorbed on FeOOH and standard aqueous solutions.

## Conclusion

Our studies clearly show that XANES could be used to gather information on the oxidation states, coordination and local structure environments of organoarsenicals (oAs) binding to metal oxide particles. Such data when complemented with results from *in situ* vibrational spectroscopy provide detailed mechanistic and molecular level information that can be used to: (1) enhance the quality of data feeding pollutant transport models, and hence better assessment of organoarsenicals fate in the environment; (2) improve our understanding of surface uptake versus redox chemistry of these arsenic compounds and its overall impact on their bioavailability; and (3) build a solid experimentally-based knowledge about the fundamental properties of interfacial processes between organoarsenicals and common geosorbents that will lead to more cost-effective design of remediation technologies.

## References

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