# Monodentate inner–sphere coordination of arsenate and phosphate anions, stabilized by hydrogen bonding, at the goethite/water interface

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We have previously described adsorption of arsenate to goethite (α-FeOOH) using a simplified surface complexation model including two surface complexes with arsenate anions [1]. ATR-FTIR studies have, however, shown that more than two complexes are formed [2,3]. Supported by this information new models are presented for surface complexation of arsenate and phosphate. Based on data from potentiometric titrations and batch adsorption experiments, combinations of complexes were tested. Different stoichiometries with corresponding charge distributions according to Pauling's valence bond theory were tested. A coordination mode considering monodentate inner-sphere binding to singly coordinated surface hydroxyl groups with hydrogen bonding to neighbouring triply coordinated surface oxygen were assumed. The resulting model consists of six ternary surface species which match data from both wet chemistry and spectroscopy. Four of the complexes involve a hydrogen bond between the arsenate (or phosphate) anion and a neighbouring surface site. In one complex the ligand acts as a hydrogen bond acceptor and in the other three as a hydrogen bond donator. Species with the same overall charge can be regarded as surface isomers.

[1] Nelson *et al*.. (2013) *Appl. Geochem*. In press.[2] Loring *et al*.. (2009) *Chemistry- a European Journal* **15**, 5063-5072. [3] Persson *et al*.. (2012) *J. Colloid Interface Sci*. **386**, 350-358.

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# Use of mobile laser-based methane analysers to target plume sampling for high-precision isotopic analysis

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Laser-based analysers are capable of very high precision methane concentration measurements, but are not yet close to matching the precision for isotopic measurement of methane by isotope ratio mass spectrometry. The challenge is even bigger for mobile platforms, such as aircraft, where a plume of methane may be encountered for as little as 5-seconds.

Real-time methane measurements have been made using mobile laser-based spectrometers on land, sea and air platforms, while steel flask and Tedlar bag sampling systems have been used to grab air samples from the identified plumes for later high precision isotopic analysis by IRMS. The rapid-response (1Hz or better) of the methane concentration measurements combined with fast-flow sampling pumps allows narrow plumes to be targeted for sample collection.

A 4WD vehicle is used to detect plumes from landfill sites, gas processing and distribution systems in the UK. A ship-based system is detecting emissions of methane near hydrate dissociation zones in the Arctic and outflow of biological plumes from South America into the Atlantic. The aircraft-based system has been used to target emission plumes from leaking gas rigs, wetlands and forest fires.

The IRMS systems at RHUL are capable of ±0.05‰ precision or better on triplicates using 75cc of air per analysis. Methane sources have very distinctive $\delta^{13}C$ signatures around -20‰ to -40‰ for combustion sources down to -60 to -80‰ for biological sources. The further away from the source that a plume is encountered the more diluted toward atmospheric background of -47‰ is the plume signal. This requires high-precision isotopic measurement to identify the source of the methane increment over background.

Although laser-based isotopic systems are starting to provide useful data at static ground-sites close to source emissions, the combination of laser-based concentration measurements and IRMS provides the best method to identify unknown methane sources, to understand distribution of sources at the regional scale and to tightly constrain the source isotopic signature of known sources.

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