Complexation of As(III) by organic matter: Model highlights thiol groups implications

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It is well known that arsenic (As) poisoning via the contamination of groundwaters has become a major public health issue. When the oxidized form of As - As(V) - substitutes for phosphorus in DNA, As(III) is complexed to cystein unit of protein via sulfhydryl (SH^-) functional group, which strongly impairs the protein or enzymatic funtion. Organic matter (OM)-mediated As(III) complexation was studied by several authors [1-3]. However, these studies were performed under variable conditions and none unambiguous binding mechanisms can be assessed from their results. Recent spectroscopy records suggested that As(III) could be bound with OM sulfhydryl groups as monodentate or tridentate complexes [2] [3].

Through a coupled experimental and modelling approach, the aim of this study was therefore, to point out the role played by the sulfhydryl groups on the As(III) binding by humic acids (HA). Isotherm experiments of As(III) binding with pure or SH-spiked HA were conducted in an anoxic glovebox. As(III) binding to HA remains limited. Humic acids were described as carboxylic, phenolic and thiol sites using PHREEQC-Model VI. The protonation constant of each sites were determined from titrations and data fitting using PHREEPLOT-Model VI for the HA and S(-II)-HA. In a second step the As(III) binding parameter was fitted from the experimental As(III)-HA binding dataset. Two hypotheses were tested: (i) As(III)-OM binding through monodentate complexes with HA sulfhydryl group and, (ii) As(III)-OM binding through tridentate complexes with HA sulfhydryl group. Finally, both hypotheses were tested on datasets available in the litterature. The only monodentate hypothesis was able to reproduce the whole investigated datasets, confirming that As(III) is able to bind directly to HA via monodentate complexes through sulphydryl groups. Indeed, by contrast to flexible proteins, sulfhydryl groups are rather isolated in the rigider OM not allowing the formation of tridentates complexes.

[1] Buschmann et al. (2006) *Env. Sci. Tech.* **40**, 6015-6020. [2] Hoffmann et al. (2012) *Env. Sci. Tech* **21**, 11788-11797. [3] Langner et al. (2011) *Nat. Geo.* **5**, 66-73.