Robust statistical differentiation of redox in arsenic affected Pleistocene and Holocene sediments based on iron mineralogy

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Arsenic (As) sorbed onto Fe (III) (oxyhydr)oxides is typically presumed to be released into groundwater when Fe (III) (oxyhydr)oxides act as electron acceptors in microbial reductive dissolution. In South and Southeast Asia, aquifers containing orange-color sediment are assumed indicative of more oxidized Fe (III) minerals and stronger As retention, and is used as an indicator of As-safe groundwater. In contrast, younger Holocene-aged aquifers are usually gray sands and are often As contaminated [1]. Here we apply X-ray absorption spectroscopy (XAS) to differentiate contaminated and uncontaminated Holocene and Pleistocene aquifers based on their sediment Fe mineralogy in a well-studied field area to the south of Hanoi, Vietnam where Fe reduction is extensive and influencing water quality.

Robust statistical analysis on XAS spectra from a large collection of over 20 sediment cores identify distinct mineralogical based differences between pristine Pleistocene, transitioning to contaminated Pleistocene and contaminated Holocene sediments. From principal component analysis, the first two principal components were useful to distinguish sediment oxidation state. Orange Pleistocene sediments were most oxidized (>70% Fe(III)), Holocene sediments still contained 20-40% Fe(III), and transitional Pleistocene sediments fell directly in between pristine and contaminated sediments in oxidation state but with complex mineralogies. Comparing field reflectance measurements with linear combination fitting of XAS spectra, we quantitatively relate color to reduction. Moreover, unsupervised hierarchical cluster analysis detects distinct changes between the contaminated and pristine aquifers and can further separate aquifers with mineralogy similar to those that may be threatened by arsenic contamination. We highlight the distinct differences in the active redox cycle reflected in Fe mineralogy, especially in transitional zones, that may affect water quality of millions in this region.

[1] Fendorf, Michael, & van Geen (2010), Science 328(5982), 1123–7.