Speciation matters – from mobility in groundwater to effects on human health

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Arsenic is *the* classical groundwater contaminant and its mobilization as arsenite or arsenate by reductive dissolution of iron (oxyhxyro)xides has received great attention. Arsenic mobilization by dissimilatory sulfate reduction has received muss less attention despite sulfate-reducing microorganisms being ubiquitous in anoxic aquifers. Additionally, regional geology and an increasing pressure on water resources will increase future use of aquifers in which sulfate reduction is important such as coastal floodplain or organic-rich sediments.

Traditional speciation analysis only resolves the inorganic species arsenite and arsenate. In sulfate-reducing environments, however, thioarsenates ($[HAs^{V}S^{-II}_{n}O_{4-n}]^{2-}$, n=1-4) form spontaneously from arsenite, sulfide, and S^0 and can dominate arsenic speciation. Routine sample preservation by acidification leads to precipitation of all thioarsenates, except monothioarsenate. To avoid the risk of incorrect species identification and underestimation of total arsenic, anoxic or flash-frozen storage and chromatographic separation at high pH are required. In groundwaters, thioarsenate formation causes arsenic mobilization due to less sorption than the oxyanions to iron (oxyhydr)oxides, iron sulfides, and likely also to organic matter. The lower sorption also makes simple de-centralized treatments, e.g. with Kolshi or SONO filters, less effective. Oxidation would be an obvious solution, but upon aeration, higher thiolated arsenates transform slowly (trithioarsenate half life 170 min) to the more mobile arsenite, not to arsenate. Monothioarsenate is kinetically stable, showing no transformation over 24 hours of aeration, and could thus enter the human body directly via drinking water.

Consideration of thioarsenates is also important with regard to human health. Even if drinking water contains no thioarsenates but arsenite, the presence of free sulfide in the human gut lumen can lead to their spontaneous formation *in vivo*. Surprisingly, only methylated, but not inorganic thioarsenic species have been investigated so far. We recently showed that thioarsenates survive passage through human intestinal cells and that acute toxicity of thioarsenates to bladder and liver cells is higher than that of arsenate, but lower than that of arsenite. Being able to measure all relevant species correctly is the basis for determining the true risk of arsenic (and other elements) in the environment or for human health.