Interactive comment on “Subsurface arsenic removal column tests: from the laboratory to the field” by D. H. Moed et al.

Anonymous Referee #2

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General comments

This is one of several papers Moed and his colleagues have produced on evaluation of an in situ treatment method for removing arsenic from groundwater as drinking water resources. Other researchers also have explored this approach. Basically, it uses aerated water to oxidize dissolved ferrous iron to ferric iron which forms co-precipitates or surface chemical complexes with dissolved arsenic (mainly arsenite) thus decreasing aqueous arsenic concentration. The injection of aerated water (push) and abstraction of treated water (pull) cycles continue until the sorptive capacity of iron oxides becomes exhausted. Many factors can influence the outcome of this approach: reductive capacity of the aquifer materials (the total amount of dissolved oxygen needed to oxidize dissolved ferrous ion and to maintain oxidizing condition may be very high if excess
amounts of reducing chemical species are present in the aquifer such as sulfides), presence of competing anions such as phosphate and silicate and to a less degree bicarbonate, presence of dissolved organic matter, pH (optimum pHs for arsenate and arsenite adsorption by ferric oxides differ but should be in the range of 5 – 8), permeability of soil matrix (soil texture, oxygen diffusion rates), etc. The authors state that “the objective of this study was to investigate the efficiency of SAR, at groundwater pumping stations with a phosphate and nitrate concentration $< 0.1 \text{ mg l}^{-1}$, and a silicate concentration similar to the one in the laboratory (7 mg l$^{-1}$ as Si), using PVC columns filled with virgin sand. This way a comparison between field results and laboratory findings can be made. Also, additional arsenite and ferrous iron were dosed, to investigate whether changing the arsenic and iron concentration would influence the results”. It is doubtful that these objectives were met. For a fair comparison, the laboratory column test should have used the same soil materials collected from the two field sites (not the pure sand) and the sand column could have been used as a control treatment.

Specific comments

The authors only measured total dissolved arsenic using GF-AAS. No arsenic speciation (As(V) and As(III)) was conducted. This is a weak point with respect to evaluating redox transformation of added As(III) in simulated groundwater or preexisting As(III) in real groundwater. Previous studies show As(III) oxidation occurs both biotically by microbes and abiotically by ferric oxides.

The authors do not say whether the solution samples were filtered or not using a membrane with a defined pore size (for example, 0.1 $\mu$m) before analysis for total Fe with AAS and for total As with GF-AAS. The analysis will be biased (with higher values) without filtration than with filtration because the iron oxide colloids will artificially increase both total Fe and As values measured with AAS. This may partly explain why a lower dose of added ferrous iron at 0.65 mg/L resulted in an earlier arsenic breakthrough than at a higher dose at 2.72 mg/L shown in Fig. 3.
Both pH and Eh are important parameters in the experiment and a graph should be provided to show their trend over pore volumes for the sand column test (and soil column test to be undertaken). Electrical conductivity data should also be shown.

Characterization of the sand and iron oxides at the end of column test is lacking. Analytical tools such as TEM, SEM, and XRD could have been used to identify the nature of minerals (discrete phases or surface coatings) formed after injection of aerated water.

Technical corrections
Page 195, line 19. Change “could” to “could be”.