ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Effect of heterogeneity on enhanced reductive dechlorination: Analysis of remediation efficiency and groundwater acidification

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1. Introduction and motivations

- Enhanced reductive dechlorination is a promising technique to remediate chlorinated solvent contaminated sites.
- The remediation scheme consists in the injection of a fermentable substrate to stimulate the activity of microbial consortia.
- Chlorinated solvents are transformed to ethene by progressively removing 1 atom of Cl, resulting in a net generation of hydrochloridric acid.
- The parallel build up of organic acids (e.g. acetate) further contributes to the pH drop.
- The pH decrease can be however partially mitigated by the alkalinity of the pore water, and minerals in soil (e.g. calcite, iron minerals, etc) (Robinson et al., 2009).
- Microbial activity is sensitive to the pH level, and too low (or too high) values can reduce or stop the biological transformations (Brovelli et al., 2011, Lacroix et al., 2011).
- **The aim of this work was to evaluate how the heterogeneous distribution of subsurface properties (hydraulic conductivity, porosity and mineral phases) influences the dechlorination patterns and groundwater acidification.**

2. Methodology

- Dechlorination was modelled using a two step approach (Robinson et al., 2009, Brovelli et al., 2011),

1. Fermentation: $\mathbf{C_{18}H_{32}O_2 + 16H_2O \rightleftharpoons 9CH_3COOH + 14H_2}$
2. Reductive dechlorination: $\mathbf{R\text{-}Cl + H_2 \rightleftharpoons R\text{-}H + HCl}$

- Both reactions were modelled using simplified Monod kinetics, including pH inhibition
- Reactive transport simulations were run using PHAST (Parkhurst et al., 2004, available from http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phast/)
- Simulated tracer experiments were used to characterize the hydraulic residence time (HRT) each hydraulic conductivity field
- Results were analyzed considering two metrics (Ω is the model domain)

1. Total dechlorination $$D(t) = \int_\Omega \frac{dC_{\mathrm{R\text{-}Cl}}(t)}{dt}\, d\Omega$$
2. Average pH change $$\Delta\,\mathrm{pH}(t) = \frac{1}{A}\int_\Omega (\mathrm{pH}_0 - \mathrm{pH}(t))\, d\Omega$$

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3. Model definition

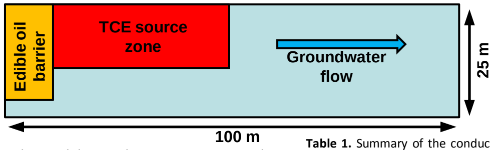

Figure 1. Sketch of the modelled area depicting the location of the contaminant source zone and of the fermentable substrate.

- The model reproduces a contaminated site where enhanced reductive dechlorination treatment was implemented
- The fermentable substrate (edible oil) slowly dissolves and acts as long term source of H_2
- TCE - DNAPL (residual saturation of 1.5%) creates the contaminant source zone

Table 1. Summary of the conductivity fields studied. The mean was always set to 10 m d^{-1}. St dev is the log10 of standard deviation (m d^{-1}), C_H, C_L the horizontal and longitudinal correlation lenghts (m).

Case	St dev	C_H	C_L
A	0.58	40	6.25
B	0.30	40	6.25
C	0.58	25	10
D	0.30	25	10

4. Hydraulic conductivity

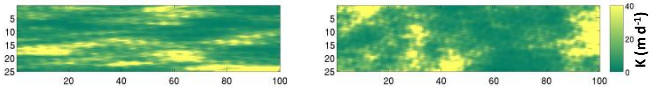

Figure 2. Examples of the hydraulic conductivity random fields. Left panel: $C_L >> C_H$ (such as in Cases A, B). Right panel $C_L \approx C_H$ (such as in Cases C, D). The patterns and connectivity of the high conductivity zones influence the hydraulic residence time (HRT) and therefore the overall degradation efficiency.

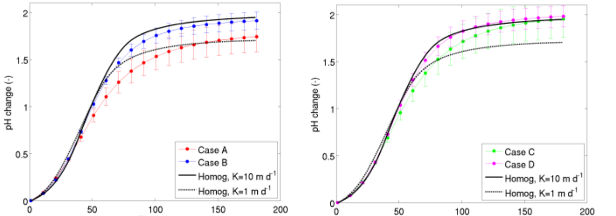

Figure 3. Average pH change in the 4 studied cases. The bullets indicate the mean value of 20 realizations with the same statistics, the error bar 1 standard deviation. The black lines is the pH change with homogeneous conditions. For cases B, C and D the mean is close to the predictions with homogeneous K = 10 md-1, whereas for Case A results are closer to the homogeneous case with smaller K.

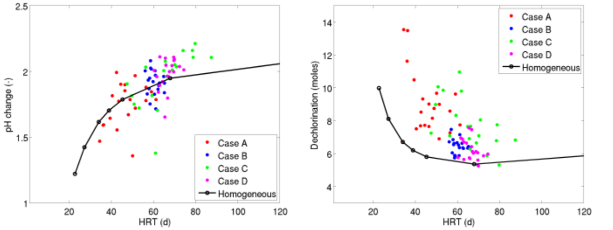

Figure 4. Average pH change and total dechlorination (after 180d) as a function of the HRT. HRT was characterized using simulated tracer experiments. The black line shows the same metrics for homogeneous conditions.

5. Hydraulic conductivity and mineral disstribution

- The effect of cross-correlated hydraulic conductivity and calcite spatial distributions was also studied. Case CA: $C_L >> C_H$, Case CB: $C_{L >>} C_H$.
- It was assumed that K followes a log-normal distribution, while $CaCO_3$ has gaussian distribution.
- The average $CaCO_3$ concentration was 10^{-2} mol kgw^{-1} in all cases. This amount is able to buffer only about 30% of the acidity produced if dechlorination completes.

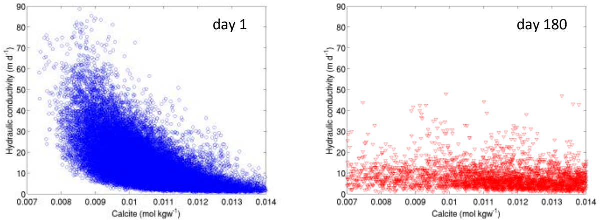

Figure 5. Correlation between calcite distribution and hydraulic conductivity. Left panel: initially, a negative relationship (with correlation coefficient around 0.6) was assumed. Right panel: at the end of the simulation, the relationship between calcite content and conductivity was completely changed, as $CaCO_3$ was preferentially dissolved in highly conductive zones.

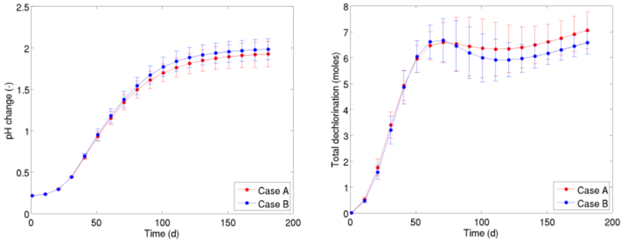

Figure 6. Average pH change and dechlorination extent for the two cases considered. The bullets indicate the mean of 20 realizations, the error bar is 1 standard deviation. The different spatial distributions of K and $CaCO_3$ have a limited effect on the total pH changes, probably because calcite is entirely consumed in both cases. The effect is slightly more marked on the extent of dechlorination, possibly due to the differences in HRT.

6. pH and calcite temporal evolution

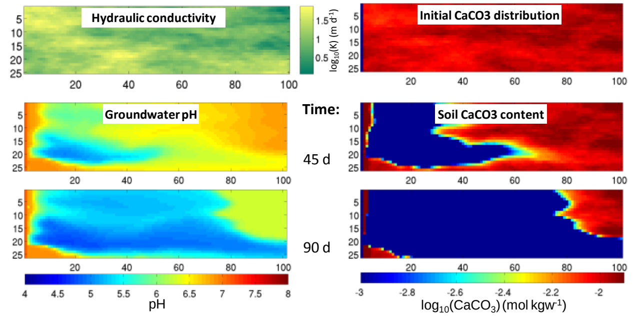

Figure 7. Evolution of groundwater pH (left column) and soil calcite concentration for one of the realizations considered. The observed patters are controlled by the location of the edible oil barrier, TCE source zone and hydraulic conductivity distribution. Note that the largest pH change is NOTobserved downstream the source zone.

7. Conclusions

- Substrate heterogeneity controls the spatial patterns of dechlorination and pH decrease.
- The HRT correlates with the dechlorination extent and pH change better than the average hydraulic conductivity.
- The soil buffering capacity is preferentially consumed in the zones with high hydraulic conductivity. In the design of dechlorination treatments, zones with high K should be used to estimate the expected natural buffering capacity of the site.

8. References and acknowledgements

- Brovelli, A., D.A. Barry, C. Robinson and J. Gerhard (2011) Analysis of acidity production during enhanced reductive dechlorination using a simplified reactive transport model. *Submitted*.
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- Robinson, C., D. A. Barry, P. L. McCarty, J. I. Gerhard, and I. Kouznetsova (2009). pH control for enhanced reductive bioremediation of chlorinated solvent source zones. *Science of the Total Environment, 407*(16), 4560-4573, doi:10.1016/j.scitotenv.2009.03.029.

This work was funded by the Swiss National Science Foundation (SNSF) (200021-120160/1).