ScienceDirect

Journal of Hazardous Materials
Volume 417, 5 September 2021, 125883

The effects of hydraulic/pneumatic fracturing-enhanced remediation (FRAC-IN) at a site contaminated by chlorinated ethenes: A case study

Ondřej Lhotský [a b], Jan Kukačka [a], Jan Slunský [c], Kristýna Marková [d], Jan Němeček [d], Vladislav Knytl [a b], Tomáš Cajthaml [b e]

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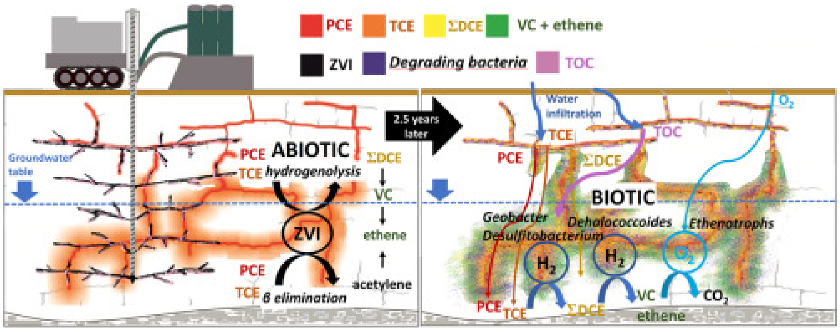
Abstract

A low-permeability locality with heterogeneous geology contaminated primarily by tetrachloroethene (PCE) present partially in the free phase in the unsaturated zone was treated on a pilot scale via direct push pneumatic fracturing combined with the hydraulic delivery of a remediation suspension consisting of milled iron, sulphidated nanosized zerovalent iron and sand in guar gum solution. Afterwards, a whey solution was injected into the fractures as a carbon source for bacteria. The unsaturated and saturated zones were treated. Long-term monitoring of the groundwater revealed that the abiotic reduction of PCE and trichloroethene was the dominant remediation processes for several months after the injections. A complex microbial consortium was developed that was capable of effective, long-term chlorinated ethenes (ClE) dechlorination. The consortium consisted mainly of *Dehalococcoides* but also of other anaerobic bacterial strains capable of partial dechlorination of ClE, including the sulphate-reducing bacteria; *Geobacter* and *Desulfitobacterium*. The average chlorine number in the groundwater decreased from 3.65 to 1.38 within 2.5 years after the injections, while the average ClE concentration increased from 13.5 to 31.5 mg L^{-1} because of the substantial acceleration of the ClE mass-transfer to the groundwater caused by the treatment. The remediation processes remained fully active for 2.5 years.

Graphical Abstract



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Introduction

Contaminated soil continues to be commonly managed using 'traditional' techniques, e.g., excavation and off-site treatment and/or disposal, which accounts for more than 70% of the management practices in Europe (JRC Annual Report 2014, 2015). However, increasing the regulatory control of landfill operations and the associated rising costs, combined with sustainability requirements, are altering the pattern of remediation practices. The use of in situ remediation technologies is steadily increasing, as they are usually connected with lower environmental and economic costs.

Chlorinated ethenes (ClE; tetrachloroethene - PCE; trichloroethene - TCE; *cis*-1,2-dichloroethene – cDCE and vinyl chloride – VC) are among the most abundant pollutants of groundwater and soil because of their frequent use in industrial applications (Němeček et al., 2020). These contaminants can be transformed in situ biologically and chemically, but to do so, direct contact between the remediation agent (either degrading bacteria or a chemical agent) and ClE must be enabled. This condition becomes challenging in low-permeability geologic formations because of the limited mass transport rates of the contaminants and remediation agents. Therefore, the use of in situ remediation technologies remains problematic at sites with low permeability or heterogeneous geological environments. Thus, significant effort has been devoted to the development of techniques for improving soil permeability (Horst et al., 2019) and/or the distribution of remedial agents in such environments (Newell et al., 2014). One of the methods to overcome transport limitations is the application of fracturing, which plays a dual role in increasing formation permeability and delivering remediation agents into geological formations to enhance in situ biodegradation (Venkatraman et al., 1998) or in situ chemical reduction/oxidation (ISCR/ISCO).

As described, e.g., by Brown et al. (2009), two reductive processes are generally used to remove chlorinated volatile organic solvents (CVOCs) and other halogenated compounds from contaminated environments: (i) biologically mediated reductive dechlorination/enhanced reductive dechlorination (ERD) and (ii) in situ abiotic chemical reduction (ISCR). Although both processes ultimately involve the transfer of electrons to the chlorinated solvent, resulting in dechlorination, the pathways and the mechanisms are quite different (Mueller and Booth, 2016).

ERD relies on reductive dechlorination/hydrogenolysis, wherein ClE serves as the electron acceptor and molecular hydrogen and acetate, both released as byproducts of organic substrate fermentation reactions, are used by dehalorespiring bacteria as electron donors and carbon sources, respectively (Stroo et al., 2014). In this process, the C-Cl bonds in ClE are sequentially replaced by C-H bonds to form Cl^- and a less chlorinated ClE. β-Elimination of ClE dominates during ISCR, wherein triple bonds are created between the carbon atoms (producing highly reactive chlorinated acetylenes and acetylene) and halogens are simultaneously removed from the molecules in the form of Cl^- (Černík and Zeman, 2020), while hydrogenolysis represents a minor pathway of ClE degradation via ISCR.

Currently, the combination of ERD and ISCR is often exploited because it provides better results than ERD or ISCR alone, and numerous remediation products based on combinations of these technologies are commercially available (e.g., EHC® ISCR reagent from Peroxychem and BOS 100® from Remediation Products, Inc.). Recently, Fan et al. (2017) found that iron-based materials (especially micro- and nanosized zerovalent iron, µZVI and nZVI, respectively) used in water treatment and groundwater remediation are more effective in their sulphidated forms, i.e., modified with lower-valent forms of sulphur (SµZVI and SnZVI).

This work addresses direct push pneumatic fracturing combined with the hydraulic delivery of remediation agents, called Frac-In, for the treatment of low-permeability localities contaminated by ClE. The site is characterised by heterogeneous geological conditions with contamination fixed to low-permeability sandy clays in the saturated and unsaturated zones. The site was treated earlier via pump and treat methods and whey injections that could remove the contamination from the preferential pathways, but after the end of pumping, a substantial rebound of contamination occurred. Soil near the pilot locality was partially excavated previously. These works revealed the presence of a PCE-free phase (in form of so called dense non-aqueous phase liquid, DNAPL) in the existing fractured system in the unsaturated zone. These naturally occurring fractures were probably created via shrinkage and expansion of soil caused by changes in moisture content. ISCR combined with ERD was used as the remediation technology in the pilot test.

This work focuses on the elucidation of processes that were enhanced by the tested Frac-In technology and contributed to the accelerated removal of ClE contamination in a complex heterogeneous, low-permeability environment using hydrochemical and biological methods and high-resolution site characterisation tools. One of the aims was to investigate whether the injections using direct push pneumatic fracturing combined with hydraulic delivery of a mixture of sand, ZVI and SnZVI in guar gum followed by the injection of dry whey solution with a pH adjustment could trigger abiotic and biotic remediation processes in the heterogenous site with a low permeability. Another aim of the study was whether the processes could enhance mass transfer of ClE at the site with low permeability and whether the process is active for longer period (2.5 years). To the best of our knowledge, this is the first paper that provides a comprehensive field assessment of direct push pneumatic fracturing combined with the hydraulic delivery of remediation agents.

Section snippets

Test site

The tested site is located on the premises of an old, demolished metalworks contaminated with chlorinated ethenes in the unsaturated and saturated zones located in western Czechia. PCE was the primary contaminant at the site, having been used in the past as a degreasing agent. The pilot test occurred at one of the most contaminated spots in the site. The aquifer is developed in Quaternary deposits formed by a mixture of loamy to sandy clays with a substantial number of existing preferential…

Tracer test, MIP site survey and other investigations

The results of the tracer tests confirmed the change in the porosity of the aquifer after the Frac-In injections. A substantial increase in the calculated pore volume (2- to 3-fold) of the aquifer at the pilot site was observed (see SM Tracer tests). Based on the obtained tracer test results and the observations during the small-scale excavation, we assume that the injected nitrogen and the slurry of the remediation agents and sand preferentially migrated into the pre-existing preferential flow …

Conclusions

The results of this case study can be summarised as follows:

- So-called Frac-In injections using direct push pneumatic fracturing combined with the hydraulic delivery of a mixture of sand, ZVI and SnZVI in guar gum, followed by the injection of dry whey solution with a pH adjustment, triggered abiotic and biotic remediation processes in the heterogeneous site with a low permeability.…

- The injections caused a substantial increase in the pore volume of the aquifer.…

- The results show the clear effects…

…

CRediT authorship contribution statement

Ondřej Lhotský: Investigation, Writing - original draft, Data Curation, Funding acquisition, Conceptualization. **Jan Kukačka:** Investigation, Data Curation. **Jan Slunský:** Methodology, Data Curation. **Kristýna Marková:** Investigation, Data Curation. **Jan Němeček:** Funding acquisition, Methodology, Conceptualization, Writing - review & editing. **Vladislav Knytl:** Methodology, Data Curation. **Tomáš Cajthaml:** Funding acquisition, Supervision, Methodology, Conceptualization, Writing - review & editing.…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

Acknowledgment

This research was funded by the Eurostars Frac-In project (E!10083) and the Technology Agency of the Czech Republic, grant number TH04030225. The authors acknowledge the assistance provided by Research Infrastructure NanoEnviCz (Project no. LM2015073), supported by the Ministry of Education, Youth and Sports of the Czech Republic. The research was also supported by Technology Agency of the Czech Republic, project No. SS02030008, programme: Prostředí pro život.…

References (55)

A. Brovelli *et al.*

Analysis of acidity production during enhanced reductive dechlorination using a simplified reactive transport model

Adv. Water Resour. (2012)

H. Dong *et al.*

Integration of nanoscale zero-valent iron and functional anaerobic bacteria for groundwater remediation: a review

Environ. Int. (2019)

A.K. Friis
Temperature dependence of anaerobic TCE-dechlorination in a highly enriched *Dehalococcoides*-containing culture
Water Res. (2007)

J.P. Hnatko *et al.*
Bioenhanced back diffusion and population dynamics of *Dehalococcoides mccartyi* strains in heterogeneous porous media
Chemosphere (2020)

O. Lhotský *et al.*
Assessment of biodegradation potential at a site contaminated by a mixture of BTEX, chlorinated pollutants and pharmaceuticals using passive sampling methods - case study
Sci. Total Environ. (2017)

Z. Li *et al.*
A shift in pathway of iron-mediated perchloroethylene reduction in the presence of sorbed surfactant—a column study
Water Res (2006)

J. Němeček *et al.*
Combined abiotic and biotic in-situ reduction of hexavalent chromium in groundwater using nZVI and whey: a remedial pilot test
J. Hazard. Mater. (2015)

J. Němeček *et al.*
Combined nano-biotechnology for in-situ remediation of mixed contamination of groundwater by hexavalent chromium and chlorinated solvents
Sci. Total Environ. (2016)

J. Němeček *et al.*
Thermally enhanced in situ bioremediation of groundwater contaminated with chlorinated solvents – a field test
Sci. Total Environ. (2018)

P.M. Richards *et al.*
Cryogenic soil coring reveals coexistence of aerobic and anaerobic vinyl chloride degrading bacteria in a chlorinated ethene contaminated aquifer
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>
> …% of Fe, 87 % of which was present in the zero-valent form (the rest was in a trivalent form in the form of oxides). The other elements present were carbon (in the form of graphite), oxygen, hydrogen, aluminum and silica; no toxic metals were present (Lhotský et al., 2021). Grass cuttings from grass maintenance were used as the only carbon source for the anaerobic bacteria.…

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> …The results indicated that pneumatic fracturing can alternatively be used to directly deliver bio-supplements (e.g., nutrients, buffers, microorganisms) into fractured formations to enhance in-situ bioremediation. Lhotsk et al. (2021) recently investigated the effectiveness of abiotic and biotic remediation by pneumatic fracturing in a low-permeability area contaminated with PCE. Although direct advanced pneumatic fracturing combined with hydro-suspension remediation may be a suitable method for the in-situ remediation of low-permeability fields, it is insufficient for practical on-site applications.…

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> …Several physicochemical methods have been employed to treat these CVOCs (Dai et al., 2018). Nanosized zerovalent iron (nZVI, Fe0) has been widely applied for the in-situ treatment of sites contaminated with CVOCs owing to its ease of use, low-cost, and eco-friendly characteristics (Lhotský et al., 2021; Mdlovu et al., 2018; Zhang et al., 2019, 2022). However, rapid aggregation and corrosion of nZVI leads to technical difficulties for application in soil and groundwater remediation (Ahmed et al., 2017; Bae et al., 2018; Han et al., 2018; X. Yang et al., 2021).…

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