Effects of Peroxydisulfate Oxidation on Biodegradation of Perchlorethene

UCT PRAGUE

Lenka Honetschlägerová, Marek Martinec, Radek Škarohlíd

(Department of Environmental Technology, University of Chemistry and Technology Prague, Prague, Czech Republic)

GROUP 1

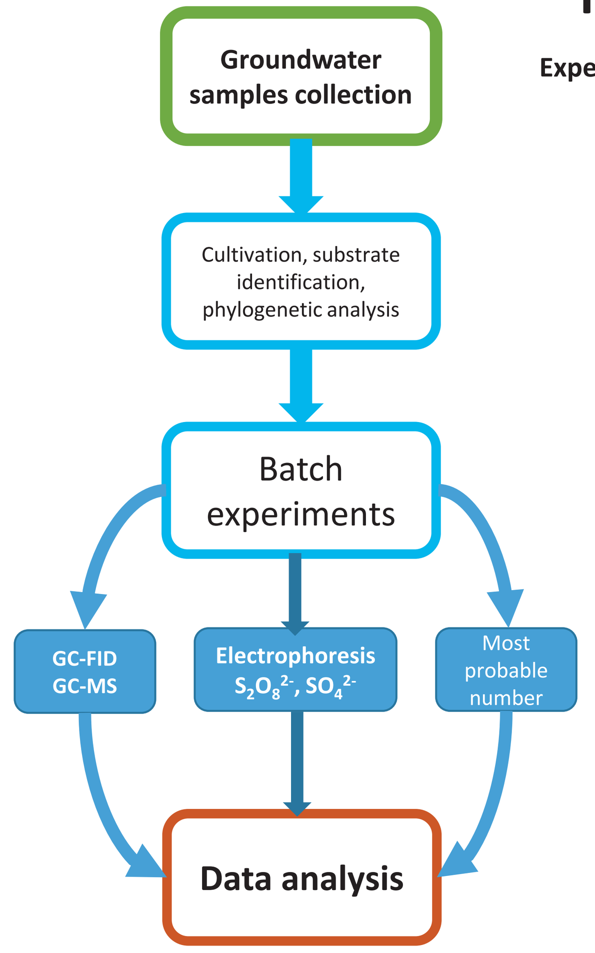
INTRODUCTION

- sites contaminated by chlorinated ethenes are challenging to restore because of their complex contaminant distribution and the timeframes for their remediation, which tend to be long and are indeed often measured in decades
- chlorinated ethenes include chemicals such as PCE (per or tetrachloroethene), TCE (trichloroethene), DCE (dichloroethene), VC (vinylchloride)
- their movement and fate in the environment are determined by their physical, chemical and biological properties and by site hydrogeological characteristics
- chlorinated ethenes undergo the same natural attenuation processes as other groundwater contaminants such as advection, dispersion, sorption, volatilization, and **biodegradation**
- **Abiotic remediation approaches:**
  - In situ Chemical Oxidation (ISCO) using peroxydisulfate (PDS)
  - PDS is a strong, water-soluble oxidant with unique properties that make it a promising ISCO reagent for treating chlorinated solvents contaminated plumes
  - the reactivity of PDS can be significantly enhanced by activating persulfate to generate sulphate radicals
  - sulphate radicals are very powerful non-specific aggressive oxidants
  - **sulphate radical based ISCO (SR-ISCO), when improperly applied may not only degrade the contaminant but also change soil characteristics by reacting with organic matter, and influence microbial community size, structure, and function, thus decreasing remediation sustainability**
- **Bioremediation**
  - natural microbial degradation steps are either metabolic or cometabolic, whereby transformation occurs without producing energy
  - all chlorinated ethenes are slowly cometabolised under anaerobic conditions to lower chlorinated ethenes and ethene
  - the reactions are catalysed by methanogens and acetogenic bacteria, which are microorganisms containing reduced enzyme cofactors

Objective

- to add a new knowledge in the understanding of the relationships between indigenous microorganisms able to perform bioremediation and other compartments creating the contaminated subsurface with SR-ISCO

METHODS



Experimental set up

- batch experimental microcosms for PCE/TCE degradation by PDS and/or microbial inoculum were conducted in 20 mL glass vials under anaerobic conditions
- the vials were capped with PTFE/silicon-aluminium septa
- PCE dehalogenation was examined in aqueous/soil microcosms, triplicates were used for all treatments, each microcosm contained 5 mL of headspace and 15 mL of experimental medium
- to establish conditions similar to those of natural groundwater the microcosms were incubated in darkness, at 13°C for 14/22 days
- the experiments were conducted in artificial groundwater (AGW) that was prepared using demineralized water enriched with 0.5 mM $NaHCO_3$, $KHCO_3$, $MgCl_2.6H_2O$, $CaCl_2.2H_2O$, AGW was sterilized at 121°C for 20 min and then de-aerated by bubbling with pure nitrogen
- microcosms were prepared separately for each sampling day and they were set up in triplicate, control microcosms with only 10 mg.L^{-1} PCE in AGW were included, chlorinated ethenes, PDS and sulfates concentrations, microbial density, pH and oxidation reduction potential (ORP) were measured in the 0, 1, 3, 8, 14, and 22 day of the experiment
- Molar PCE:PDS follows stoichiometry reaction:

$$C_2Cl_4 + 2S_2O_8{}^{2-} + 4H_2O = 4SO_4{}^{2-} + 8H^+ + 4Cl^- + CO_2$$

- metal activation using Fe^{2+} chelated with citric acid (CA) and activation using CaO_2, the molar ratio Fe^{2+}/PDS was 2.5:1, Fe^{2+}/CA was 2:3, and CaO_2/PDS was 4:1

Molar ratio PCE:PDS	PDS [mmol.L^1]	Fe^{2+} [mmol.L^{-1}]	CA [mmol.L^{-1}]	CaO_2 [mmol.L^{-1}]
1:8	0,48	0,1	0,14	1,93
1:16	0,96	0,19	0,29	-
1:32	1,93	0,39	0,58	-

Microcosms composition

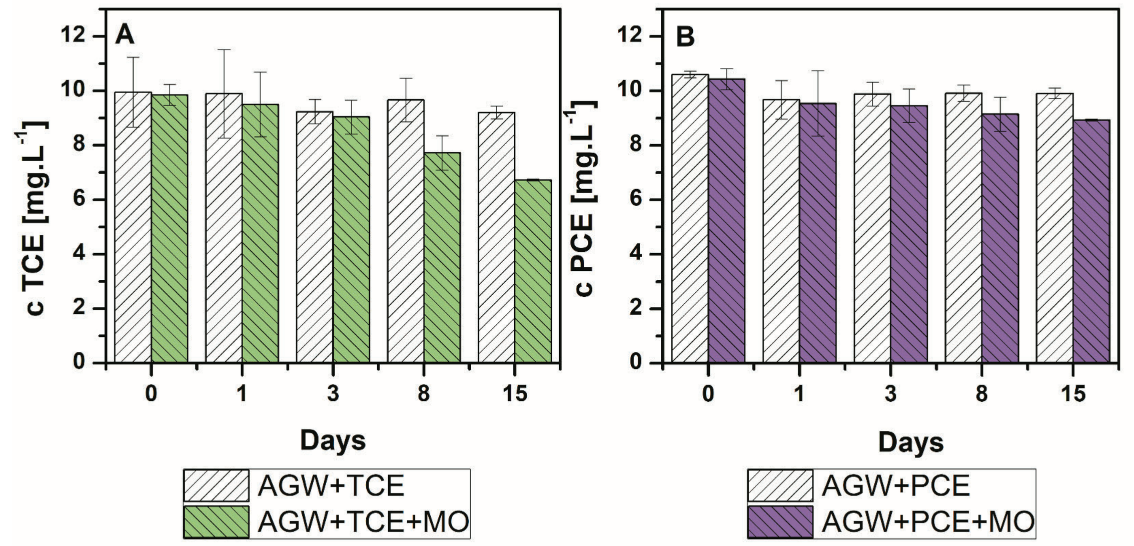
Systems	PCE	AGW	MO	PDS	Fe+CA	CaO_2
A	+	+	-	-	-	-
B	+	+	-	+	-	-
C	+	+	+	-	-	-
D	+	+	+	+	-	-
E	+	+	-	+	+	-
F	+	+	+	-	+	-
G	+	+	+	+	+	-
H	+	+	-	+	-	+
I	+	+	+	+	-	+
J	+	+	+	-	-	+
K	-	+	-	+	-	-
L	-	+	-	+	+	-

Systems	PCE	AGW	MO	PDS	Fe+CA	sand
AA	+	+	-	-	-	-
BB	+	+	-	+	-	+
CC	+	+	+	-	-	+
DD	+	+	+	+	-	+
EE	+	+	-	+	+	+
FF	+	+	+	-	+	+
GG	+	+	+	+	+	+
HH	+	+	-	+	-	+
II	+	+	-	-	-	+

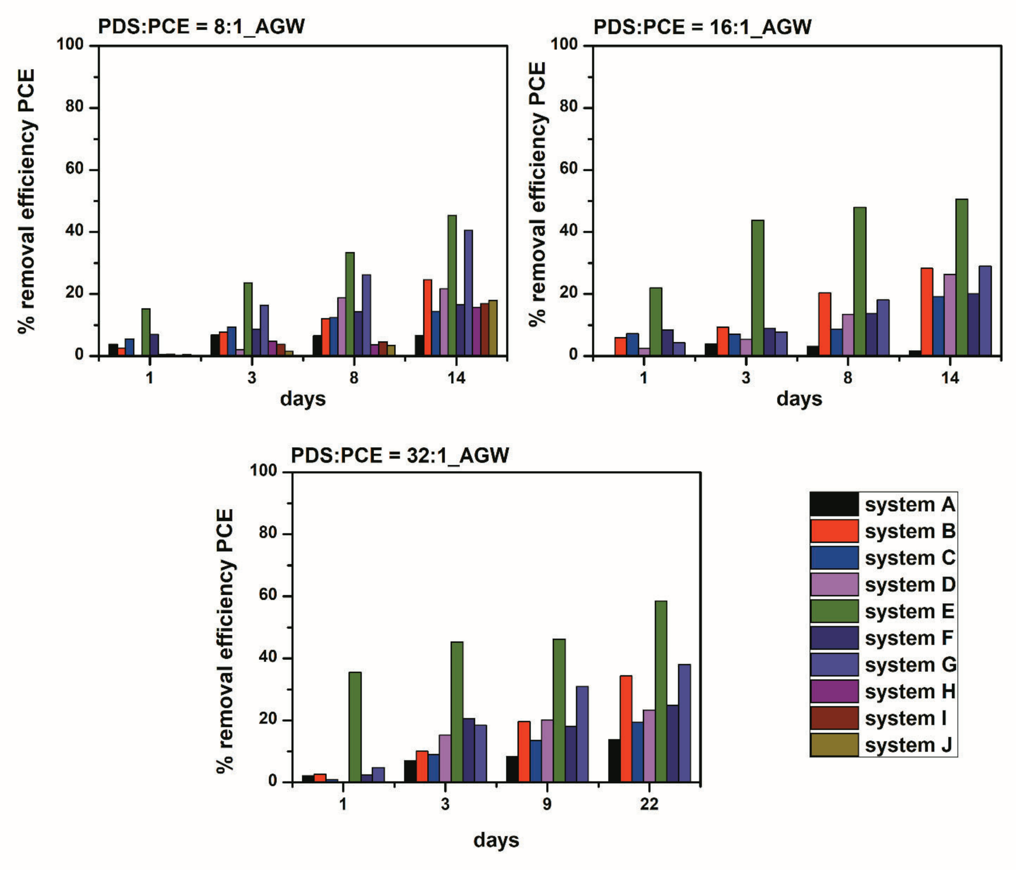
RESULTS

- **Groundwater samples collection**
  - Samples were collected from a selected well within the site contaminated with chlorinated ethenes Na Vrtálně (Pardubice, Czech Republic)
  - the selected well was contaminated with VC and 1,2-cis-DCE which indicated the potential for chlorethenes degradation

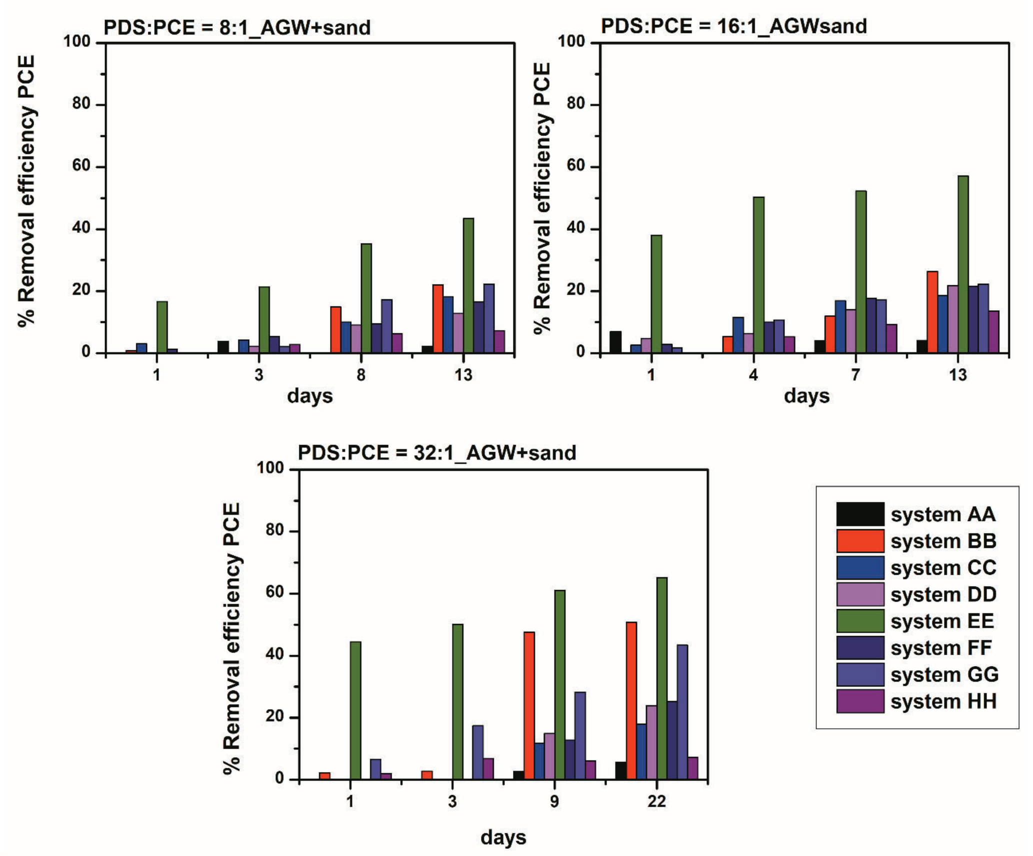
TCE/PCE removal by microbial consortioum



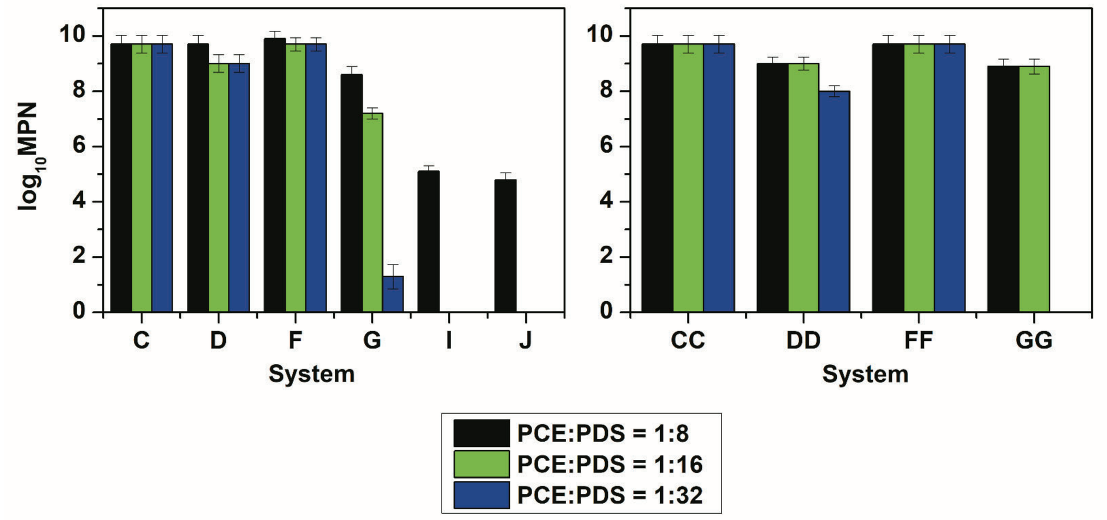
PCE removal efficiency for different molar ratios in the presence of AGW



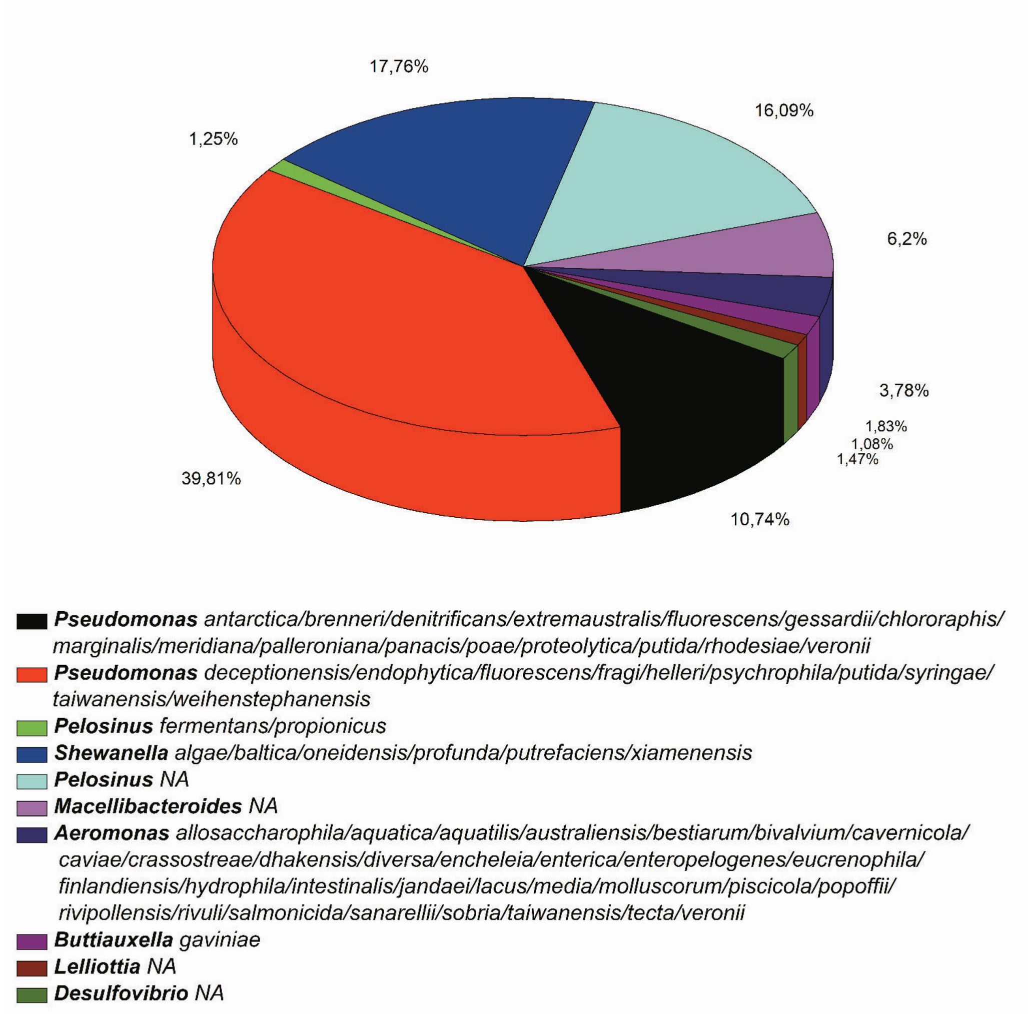
PCE removal efficiency for different molar ratios in the presence of AGW and sand



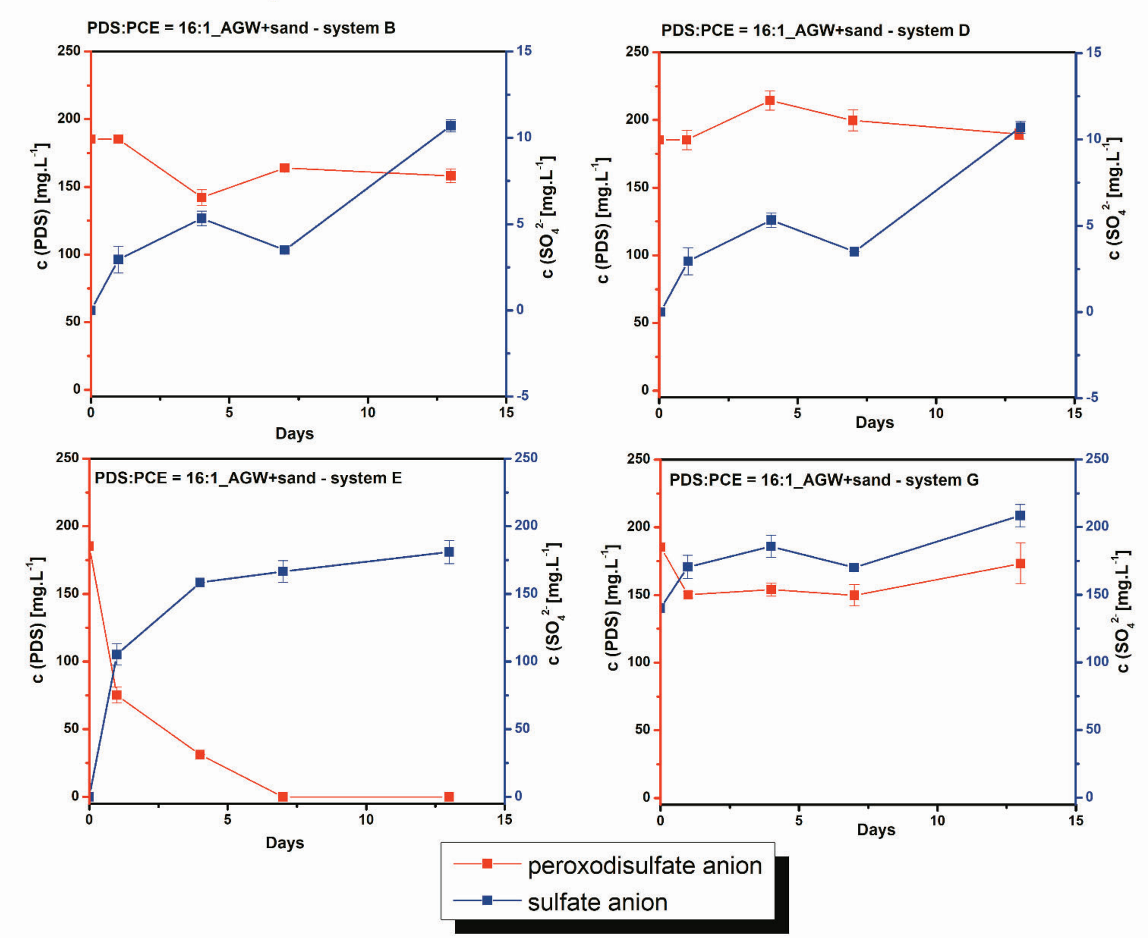
The effect of SR-ISCO on microbial growth



Phylogenetic affiliation of the most abundant enriched bacterial sequence variants



Mass balance of peroxidisulfate anion and sulfate anion concentration PDS:PCE = 16:1



CONCLUSIONS AND DISCUSSION

- Microbial consortium isolated from a site contaminated by chlorinated ethenes demonstrated efficient removal of PCE and TCE, however, the removal efficiency was lower in the case of PCE compared to TCE.
- The microbial consortium comprised of known dechlorinating bacteria.
- GC showed that the main product of PCE biodegradation was TCE that together with the composition of microbial consortium, thus suggesting that the mechanisms of PCE biodegradation was anaerobic cometabolism.
- PDS:PCE in molar ratios 8:1 and 16:1 did not have any negative effect on microbial growth as expected, on the other hand, it was observed inhibited PDS reduction and decrease in PCE removal efficiency in the systems containing both PDS and microbial consortium.
- Activation using Fe^{2+} chelated with citric acid showed negligible impact on microbial consortium as well as a higher effect on PCE removal efficiency by PDS compared to CaO_2 activation.
- The main product of SR-ICSO PCE degradation was chloroacetone.
- Chloroacetone was not detected in the systems containing microbial consortium.

Biodegradation is a sensitive natural process depending mainly on the innate microbial capacity to process the pollutants. The microbial consortium may be irretrievably damaged when an abiotic remediation agent is applied improperly. Missing knowledge of specific interactions between the abiotic remediation agents and the subsurface ecosystems already affected by chlorinated solvents is the basic knowledge gap, which limits results of every remediation. The results indicates that high concentrations of PDS inhibit microbial growth, however, the ubiquitous microorganisms on the other hand can affect the efficiency of one of the most commonly applied abiotic remediation technique by inhibiting its chemistry.

Acknowledgments

This work was conducted within the project TRAIN (**Train technology development for the removal of chlorinated ethylenes from the subsurface**) founded by Technological Agency of the Czech Republic.

References

- Henschler, D., *Toxicity of Chlorinated Organic Compounds: Effects of the Introduction of Chlorine in Organic Molecules.* Angewandte Chemie International Edition in English, 1994. **33**(19): p. 1920-1935.
- Arp, D.J. , Yeager, C.M., Hyman, M.R. , *Molecular and cellular fundamentals of aerobic cometabolism of trichloroethylene*, Biodegradation, 12 (2001) 81-103.
- Suttinun, O., Luepromchai, E. , Müller, R., *Cometabolism of trichloroethylene: concepts, limitations and available strategies for sustained biodegradation*, Reviews in Environmental Science and Bio/Technology, 12 (2013) 99-114.
- M. Kotik, A. Davidová, J. Voříšková, P. Baldrian, Bacterial communities in tetrachloroethene-polluted groundwaters: A case study, Sci Total Environ, 454-455 (2013) 517-527.
- Honetschlägerová, L., et al., *Interactions of nanoscale zero valent iron and iron reducing bacteria in remediation of trichloroethene.* International Biodeterioration & Biodegradation, 2018. **127**: p. 241-246.

Contact: lenka.hokrova@vscht.cz