Implementation of Auxiliary-Substrates to enhance the Degradation of Chlorinated Hydrocarbons in anaerobic Systems (Experiences with ARDEC based on a Case Study)

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About INTERGEO

INTERGEO is an independent company represented on four continents (in more than 20 countries) offering engineering and consulting services for environment and planning. We work for a number of clients in both the public and private sectors and provide our clients with goal-oriented, sustainable, economic and innovative answers to their questions. INTERGEO offers expert knowledge and expertise in a number of areas, including the Investigation and Remediation of Soil and Groundwater, Engineering Geology, Environmental Protection and Work Safety as well as Waste Management.

INTERGEO has performed over 10,000 soil and groundwater investigations in Europe and overseas since being founded in Salzburg (Austria) in 1983. We provide a single source for all services – from the investigation to the detailed remediation action plan.
Structure of Talk

• Occurrence and Application, Characteristics and Behaviour of Chlorinated Hydrocarbons (CHC)

• DNAPL characterisation and remediation

• Concept of in-situ Bioremediation

• Enhanced Natural Attenuation (ENA) by implementing Auxiliary-Substrates (Case Study)
Chlorinated Hydrocarbons (CHC)

- organochloride, organochlorine compound, chlorocarbon, chlorinated hydrocarbon
- organic compounds containing at least one covalently bonded atom of chlorine that has an effect on the chemical behavior of the molecule
- volatile chlorinated hydrocarbons (VOC): e.g. PCE, TCE, DCE, VC
- non-Volatile chlorinated hydrocarbons: e.g. insecticides (HCH, DDT), fungicide (HCB, PCP), PCB etc.

![Figure 1: chemical structure of Trichloroethene (TCE)](image1)

![Figure 2: chemical structure of Dichlorodiphenyltrichloroethane (DDT)](image2)
Occurrence and Application of CHC

- solvents and cleaning agents
- starting products in the chemical and pharmaceutical industry
- manufacture of plastics

CHC applications are divided into 4 groups (after Munz and Häner, 2009)

1. cleaning and solvents (degreasing, dry cleaning)
2. Solvents in chemical production
3. Solvents in products (e.g., paints, adhesives)
4. Production of plastics such as PVdC (polyvinylidene chloride) and in particular PVC (polyvinyl chloride)
Behaviour of CHC

- the range of CHC compounds and their use is very broad
- CHC are among the most dangerous organic chemicals
- low solubility in water and can appear in the subsurface as a separate fluid phase immiscible with water
- CHC are DNAPLs (dense non-aqueous phase liquids)
- once released into the aquatic environment, CHC bear the potential to migrate into deeper aquifer-systems
- DNAPL source zones can persist for thousand of years
- several compounds are highly toxic and very low concentrations pose unacceptable high risk to human health
DNAPL characterization challenges

- limited information about source/release
- complex migration patterns
- small volumes (which can create persistent dissolved plumes) are difficult to delineate
- “needle in haystack” problem
- high risk of mobilization by intrusive characterization activities
- composition and physical properties can change with age
- residual DNAPL serve as a long term source of dissolved phase groundwater contamination
- re-mobilization of residuals DNAPL (e.g. blobs and ganglia) requires extremely steep hydraulic gradients

Figure 3: schematic propagation pattern of DNAPL in the subsoil (Pope et al., 1999)
DNA PL characterization challenges

- DNA PL migration will always proceed along the path of least capillary resistance

- complex DNA PL distribution can lead to highly stratified dissolved plume concentrations

- as DNA PL will not migrate to a well it is difficult to detect them

- presence of DNA PL can be assessed by checking the concentration of CHC in water samples

- CHC-concentrations between 1% and 10% of the actual water solubility of one of the substances are considered as a probable indication for the presence of DNA PL

- CHC-concentrations >10% of the solubility in water are considered to be a practically safe indicator for the presence of DNA PL

Figure 4: spreading of CHC (DNA PL) in the subsoil (Beal and Faircloth, 2002)
Remediation Methods

- in-situ chemical reduction (ISCR) e.g. ZVI and ZVM
- in-situ chemical oxidation (ISCO) e.g. permanganate, Fenton’s reagent, persulphate etc.
- in-situ biological reduction (ISBR) supply of electron donors (e.g. from organic carbon sources)
- in-situ biological oxidation (ISBO) supply of electron acceptors (O₂) and nutrients
- in-situ thermal desorption (ISTD) e.g. Thermal Conduction Heating (TCH)

- “traditional” remediation techniques (e.g. pump & treat) are not effective
Choice of Remediation Method

- remediation goal
- site specific (hydro-)geological conditions
- site specific bio- and hydro-geochemical boundary conditions
- site specific laboratory testing results (to assess potential solutions)
- site-specific process understanding
- site specific pilot testing results of chosen remediation method
- economic proportionality
Expectations for in-situ biological methods at DNAPL source zones (ENA)

- destruction of contaminants mass
- reduction of contaminant mass starts within month of implementation
- increase of rate of dissolution and desorption
- treatment of multiple chlorinated compounds
- low maintenance
- start-up costs may be lower compared to other techniques
- timeframe is uncertain
Degradation pathways of chlorinated ethanes and ethenes (reductive degradation)

Theoretical anaerobic degradation pathways

- pathway 3: Dehydrochlorination (abiotic)
- pathway 1A: Hydrogenolysis
- pathway 1B: Hydrogenolysis and Dichloroelimination
- pathway 2: Dichloroelimination
- pathway 1 and pathway 2 require certain boundary conditions provided by microbiological activity

anaerobic degradation of PCE

- reductive dechlorination (halorespiration)
- productive biodegradation
- sequential transformation PCE --> Ethen
- anaerobic oxidation is difficult to detect
Concept of in-situ Bioremediation (Biodegradation Reaction)

- Biodegradation = Redox Reaction

Figure 6: concept of redox-reaction (Source: Pearson Education, Inc., publishing as Benjamin Cummings)
Potential anaerobic degradation processes

anaerobic halorespiration ("productive degradation")

- contaminant (CHC) acts as Electron-Acceptor
- contaminant is primary energy source for microbiological growth
- Microorganisms produce enzymes that act as catalysts in the course of redox reactions taking place by reducing the threshold energy
- productive degradation is initiated in which the organisms acquire energy for their metabolism and their growth

cometabolic dechlorination

- cometabolic reactions are caused by an enzyme which is produced during microbial metabolism of another compound
- no direct gain of energy for the organisms involved
- reaction happens fortuitously
Anaerobic Reductive Dechlorination

anaerobic halorespiration

\[
PCE \rightarrow TCE \rightarrow cDCE \rightarrow VC
\]

• increased concentration of dehalogenase genes during metabolism

cometabolic dechlorination

\[
PCE \rightarrow TCE \rightarrow cDCE \rightarrow VC
\]

• fortuitous sequential hydrogenolysis

Degradation rate differs by several orders of magnitude
Appropriate conditions for microbiological induced degradation processes of CHC

- the amount of H₂ formed under anaerobic conditions depends on the kind of available aux-substrates
- other biochemical reactions occur as competitive reactions and consume H₂
- optimum range in which dechlorinating bacteria are compatible against sulfate reducing and methanogenic bacteria is 0.4 to 2 nM H₂

Figure 7: Sequence of the main reduction processes and corresponding classification of the reductive CHC-dechlorination (left figure).
Suitable H₂-utilization ranges of the respective degradation reaction (right figure).
(Grandel and Dahmke, 2008)
Reducive Dechlorination of chlorinated Ethenes

Bacteria (Microbes)

Transformation PCE --> cDCE

- Desulfitobacterium
- Clostridium
- Dehalobacter
- Desulfuromonas
- Dehalospirillum
- Sulfurospirillum
- Dehalococcoides

Transformation cDCE --> Ethen

- Dehalococcoides

Electron Donor Substrates

- H₂, lactate, formiate, ethanol
- Glucose
- H₂
- acetate, pyruvate
- H₂, lactate, formiate, ethanol
- Lactate
- H₂
Problem Summary

Problem

• tens of thousands DNAPL sites worldwide (in every country)
• low maximum contaminant levels (MCL) in most cases
• long half-lives
• contaminant-specific properties (e.g. denser than water)

Solution approach

• in-situ Bioremediation of chlorinated Ethanes/Ethenes DNAPL-source zones
  • efficient
  • cost-effective
Case Study: CHC contamination at a pharmaceutical industry site

- cocktail of various CHC (chlorinated ethanes and ethenes)
- primary-contaminants
  - 1,1,2,2 TeCA
  - TCE
  - all possible biotic and abiotic derivates are present
- secondary-contaminants
  - aliphatic and (monocyclic) aromatic HCs (BTEX)
- spatial extent of residual DNAPL zones ca. 1 ha
- DNAPL source-architecture indicates onetime spill (1950s)
- potable water supply network (water work) in the neighboring
- highly mobile CHC (cDCE and VC) threaten water supply wells
- TeCA-concentration close to the revealed residual DNAPL zones up to 1-3 millions µg/l

Figure 8: TeCA damage pattern in shallow aquifer (A2)
Case Study: CHC contamination at a pharmaceutical industry site

- DNAPL accumulate on top and within aquitards
- relatively small lateral spread of contaminants in aquifers
- vertical-dominated migration pattern
- aquifer-system is subdivided into 3 GW-storeys including 12 aquifers
- vertical base of contamination in a depth of 56 m bgl (A6)
- still contaminants are only detected in 1. GW-Storey

Figure 9: contaminant-concentration vs. depth
Case Study: CHC contamination at a pharmaceutical industry site

Tasks performed by INTERGEO

- geological investigation
- hydrogeological investigation
- Cone Penetration Testing (CPT)
- sampling and analytics
- isotope-hydrological investigation
- batch-microcosm tests (aux-substrates)
- Polymerase Chain Reaction (PCR)
- Compound-Specific Isotope Analysis (CSIA)
- numerical transport-modelling (reactive multi-species)
Case Study: CHC contamination at a pharmaceutical industry site

In-situ bioremediation design (ISBR)

- execution of comparative laboratory batch-microcosm test (ca. 500)
  - evaluation of endemic bacteria-consortium for it’s capability to mineralize all CHC by reductive microbiological processes
  - evaluation of effectiveness of several auxiliary-substrates (“nutrient amendments”)
  - evaluation of effectivity and feasibility

- execution of pilot tests
Case Study: CHC contamination at a pharmaceutical industry site

- Comparative efficiency of lactate application

**Figure 12:** result control - microcosms

**Figure 13:** result microcosms amended with lactate
Case Study: CHC contamination at a pharmaceutical industry site

- Comparative efficiency of **ARDEC** application

Figure 14: result control - microcosms

Figure 15: result microcosm amended with **AREDC**
Case Study: CHC contamination at a pharmaceutical industry site

• Comparative efficiency of EHC application

Figure 16: result control - microcosms

Figure 17: result microcosm amended with EHC
Case Study: CHC contamination at a pharmaceutical industry site

- Comparative efficiency of EHC application

Figure 18: result control - microcosms
Figure 19: result microcosm amended with ARDEC
Case Study: CHC contamination at a pharmaceutical industry site

- approximated degradation rate constants (1st order kinetic model)
  - yellow columns: incubated at 22 °C
  - blue columns: incubated at 12 °C

![Graph 1: approx. rate constants for 1,1,2,2-TeCA](chart1.png)

![Graph 2: approx. rate constants for cis 1,2-DCE](chart2.png)

- amendment of lactate and EHC decreases degradation rate
- amendment of ARDEC increases degradation rate by two orders of magnitude
Case Study: CHC contamination at a pharmaceutical industry site

Performance of Pilot Tests

• preparing of a mixture (ARDEC and ZVI) at the site

• injection of mixture into underground in the center of DNAPL plume (29 m - 35 m bgl)

• injection with Primawawe (Wavefront Technology Solutions Inc.)

• soil sampling in injection-area to evaluate results and zone of influence

• storing of microcosms for 595 d at 12 °C

![Figure 22: approx. rate constants for 1,1,2,2, TeCA](image)

![Figure 23: preparation of ARDEC mixture on site](image)
Case Study: CHC contamination at a pharmaceutical industry site

Results of **ARDEC** – injection

- significant decrease of contaminant-concentration

![Figure 24: cis 1,2 DCE concentration in injection-area](image)

![Figure 25: VC concentration in injection-area](image)

- 65 [d]
- 234 [d]
- 595 [d]
Conclusion

• site-specific process understanding is very important

• several auxiliary-substrates contribute the degradation of CHC

• application of ARDEC revealed best results (complete mineralisation of CHC)

• comparison and implementation of laboratory scale on field conditions is possible

• application of in-situ biological reduction (ISBR) and ENA can be an useful option
Thank you for your Attention!