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Comparisons of degradation kinetics of chloroethenes in groundwater between microcosms and field scale.

MANGERET A. **(1), ROLLIN C. (2), KERGARAVAT O. (3), ATTEIA O. (1)**

(1) EGID Institute, University of Bordeaux 3, Pessac (France)
(2) INERIS, Parc Technologique ALATA, Verneuil-en-Halatte (France)
(3) ADEME, Angers (France)

Abstract :

Groundwater pollution by chlorinated solvents is a major concern since several years. It has been demonstrated that in specific physicochemical conditions, microbial processes like direct reductive dechlorination allow contamination reduction at several sites. Therefore, determination of biodegradation kinetics of chloroethenes is crucial in applying Natural Attenuation protocols on contaminated sites and assessing the potential risks for human health and natural media. Biodegradation of chlorinated solvents is effective in highly reduced conditions, which rarely concerns the whole contaminant plume.

In this study, direct reductive dechlorination of chloroethenes was studied on two different scales, on microcosms in the laboratory and at the real scale that corresponds to the contaminated site. Microcosms studies were conducted in three different ways: (1) sediments sampled from the site and mixed with groundwater modified or not by a synthetic electron donor (Na propionate, Na lactate, toluene) ; (2) composite sediments coming from several places of the site mixed with groundwater modified or not by a synthetic electron donor ; (3) autoclaved sediments and groundwater modified or not by synthetic organic matter. Studies on the real scale were conducted by the achievement of a synthesis of historical data (hydrogeological, geological and physicochemical data) of a polluted site.

The synthesis of physicochemical data and then modelling the real site revealed the presence of degradation products of chloroethenes in the plume : cis-1,2-DCE and VC. The results of comparisons of degradation kinetics obtained on the laboratory and the field under the same physicochemical conditions showed significant differences. Indeed, biodegradation of chlorinated solvents were faster in lab studies than in the field at the global scale. The existence of chlorinated ethenes biotransformation in microcosms confirmed the presence of a bacterial population able to catalyse reductive dechlorination reaction until CV. It is also likely that the bacterial consortium permitted to degrade other species like electron acceptors ; detection of sulphide ions and Fe(II) and the presence of a black precipitate of FeS are proofs of sulphate reducing, ferro reducing and dechlorinating activities.

The clear difference that there is between kinetics of degradation on microcosms and field scale could be explained by differences in chemical conditions that are not optimal everywhere in the plume of pollutants.

The differences of chemical conditions (electron acceptors, type of natural organic matter, pH, redox potential...) are investigated in details to explain the differences in kinetic constants.

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Keywords :

Natural Attenuation, Chlorinated ethenes, Groundwater, Microcosm, Field Scale.

Problematic :

Chlorinated ethenes are still widely utilized in industry, primarily as degreasing agents or in dry cleaning. Particularly, the compounds which are more concerned by these activities are PCE (tetrachloroethylene) and TCE (trichloroethylene).

Because of transport of these products and eventually leaking of tanks, these substances are found in contact with groundwater and prevent the direct use of this water for the production of drinking water.

Indeed, several chloroethenes are considered as potentially carcinogens, particularly with vinyl chloride (VC), which is quoted in the first category, as a carcinogen substance.

In groundwater, Natural Attenuation is defined as a set of physical, chemical and biological mechanisms allowing to reduce mass, toxicity, mobility and concentration of contaminants in soils or in water table (US-EPA, 1997). Recently, Monitored Natural Attenuation is a strategy more and more used, allowing to promote the bacterial populations capacity of degradation in aquifers ; this by monitoring the contaminated site in a long term.

Among all the mechanisms governing Natural Attenuation, anaerobic reductive dechlorination is the main reaction. This includes a chain of successive reactions where dissolved hydrogen, which is produced by fermentation of organic substrates, reacts with a chlorinated solvent. Thus, in a molecule of chlorinated solvent, a chlorine atom is replaced by a hydrogen atom. These transformations only occur with an adapted dechlorinating bacterial population. Successively, PCE is degraded to TCE, to DCE (dichloroethylene), then to CV and finally to ETH (ethene), which is non-toxic and doesn't affect human beings and the natural media.

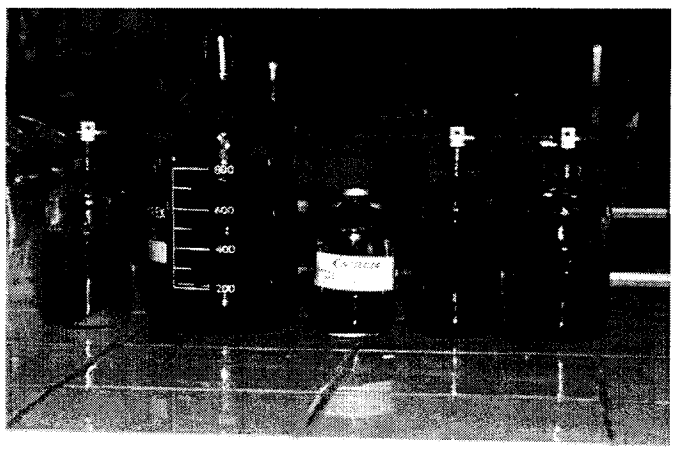
However, at the real scale, it is very common that biodegradation stops at cDCE or CV. Indeed, reductive dechlorination is effective in highly reduced conditions ; which is rarely the case at all the extend of the site.

The aim of this work is to compare degradation kinetics measured on a laboratory scale, with microcosm, and on a real scale ; all theses experiments being carried out in the same physicochemical conditions.

Methodology :

Several microcosm studies have been performed with a commercial bacterial population named KB-1. This bacterial consortia was isolated and enriched from soil groundwater obtained from a TCE-contaminated site in Ontario (Canada). This bacterial population KB-1 is composed of a large number of bacterial species that can catalyse several reactions like denitrification, sulphate reduction, reductive dechlorination or methanogenesis. Complete reductive dechlorination of TCE to ETH is possible with the strain KB-1 ; it has been used for the purposes of bioaugmentation in a lot of sites contaminated by chlorinated solvents.

Two kinds of experimental designs were used for studying the laboratory scale. The first is made up with a glass bottle which is surmounted by a Mininert valve. The second device consisted in applying headspace vials closed with a magnetic rubber and equipped with a butyl septa. The first design is illustrated by this photo below.



Microcosm design with Mininert valves

Several physicochemical conditions were applied in this batch reactors ; the influence of several factors were estimated, like the amount of fermentable organic matter, concentrations of electron acceptors (nitrate, Fe(III), sulphate) and the composition of the culture medium.

Four different organic compounds were tested in these studies : two electron donors often detected on sites contaminated by organic chemicals such as methanol or ethanol, a substrate which is quickly degraded (sodium lactate) and a slowly fermented substance : sodium propionate.
Variable quantities of electron acceptors are present in groundwater: nitrate, sulphate, Fe(III)... These species can disrupt degradation kinetics of chloroethenes. Reductive dechlorination could occur when several electron acceptors were consumed. Thus, competition between different types of micro-organisms will occur between the different types de micro-organisms for the fixation of hydrogen produced by fermentation of organic matter. So, minimizing activity of micro-organisms other than those dechlorinating chloroethenes is necessary. Depending on the amount of hydrogen in the environment, activity of several populations prevail over others. Then, choice of the appropriate fermentation substrate is crucial.
In this study, the composition of the nutritive media has also been varied. Indeed, the growth of a dechlorinating population depends on the type, the quantity of bioavailable nutrients and organic substrates. Generally, at the field scale, the distribution of the species are mostly heterogeneous and optimum growth zones of dechlorinating populations are relatively reduced. Thus, determining optimum growth conditions necessary for obtaining highest biodegradation kinetics of chloroethenes constitute an important issue.
The finality of this work was to carry out microcosm studies with real samples from the polluted site and using the same methodology quoted previously.
The field scale has also been developed. The fist step consisted in collecting physicochemical data which were measured since the discovery of the contamination source, and several studies about the site. All the data of the site were then synthesized as graphs of evolution of concentrations in time. It can give us a first indication about the extent of the pollution and the potential formation of daughters products of biodegradation.
Synthesis of all the physicochemical data enables us in the future to purpose several complementary measures designed to understand more degradation mechanisms occurring on the site and identify a potential Natural Attenuation.
After, results of campaigns of measures were utilized for the estimation of degradation kinetics on the site with the help of the model developed at the Institute EGID : VisualRFlow.

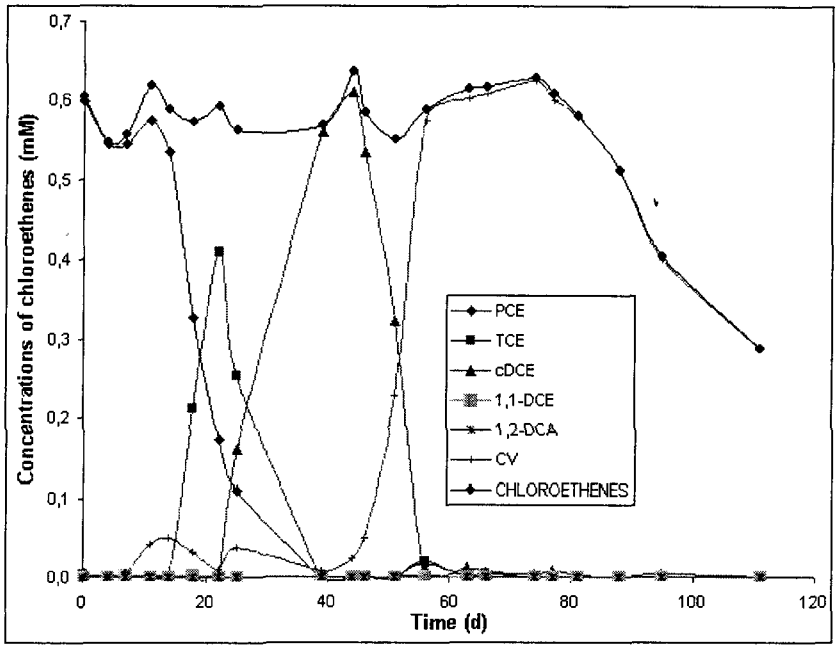
Results :

With concentrations of sulphate greater than 250 mg/L, a decrease of the degradation kinetics of TCE with KB-1 occurred. This reduction is probably due to an intense sulphate-reducing activity. Indeed, the production of a black precipitate of iron sulphide FeS confirms this hypothesis.
However, results are different, depending on the electron donor used. Quickly fermented substrates such as methanol, ethanol or lactate promote the production of a high dissolved hydrogen concentration in the media.

Dissolved hydrogen concentrations for reduction processes (Lovley et al. (1994), Chapelle et al. (1995))

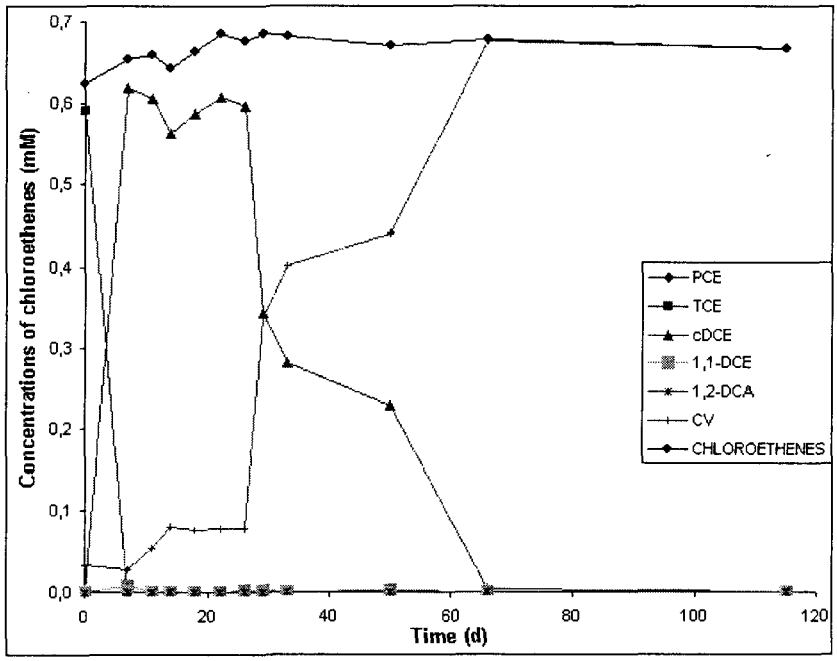
Process	Dissolved hydrogen concentration		
	nM	atm	$\mu g.L^{-1}$
Denitrification	< 0,1	$< 1,3\times10^{-7}$	$0,4\text{-}1,6\times10^{-3}$
Fe(III) reduction	0,2-0,8	$0,26\text{-}1,0\times10^{-6}$	$0,4\text{-}1,6\times10^{-3}$
Sulfate reduction	1-4	$1,3\text{-}5,0\times10^{-6}$	$2,0\text{-}8,0\times10^{-3}$
Methanogenesis	5-20	$63\text{-}250\times10^{-6}$	$10\text{-}40\times10^{-3}$

According to the above table, high levels of dissolved hydrogen favour in the first place methanogenesis while for reductive dechlorination of TCE, this value is closed to 0,7 nM (Hoelen et Reinhart, 2004). Thus, the use of a slowly fermenting substrate would be more adapted for competing with sulphate reducing micro-organisms.
The experiments carried out with sodium propionate confirm the previous hypothesis because sulphate reduction doesn't occur with 0,5 mM of sodium propionate and 250 mg/L of sulphate. However, the formation of FeS occurs just when TCE has been totally transformed into cis-1,2-DCE. The following figure describes the results of a study conducted with PCE, sodium lactate and KB-1.



Evolution of concentrations of chloroethenes with PCE, sodium lactate and KB-1

Globally, reductive dechlorination of chloroethenes is higher with sodium propionate than the other electron donors cited previously. Therefore, our choice was turned to the use of sodium propionate as electron donor. The following figure represents the results of the reductive dechlorination with TCE, sodium propionate and KB-1.



Evolution of concentrations of chloroethenes with TCE, sodium propionate and KB-1

In these microcosm studies, the composition of the natural media was modified. In the first time, no nutritive media has been added to the bacterial population. This hasn't disrupted the growth of KB-1. Several transfers of this consortium to other batch reactors devoided of nutrients can't still avoid their growth.

On all the studies, degradation kinetics of chloroethenes are proved to be faster with a nutritive media ; this result is logical because the higher the concentration of nutrients are, the more the growth of the bacterial population will be favoured.
We also observed elevated lag times on several tests, involving that reductive dechlorination of chloroethenes occurs only between 10 and 20 days after the beginning of the experiment. It is manly due to two factors :

- adaptation of bacterial populations to their new growth conditions,
- inhibition of dechlorinating activity by other reactions.

In the case where the bacterial population is taken in contact with a compound, it needs that this bacterial consortium get used to this new environment ; a kind of evolution will occur.
Inhibition of reductive dechlorination can be linked to mechanisms of competition between different types of bacteria, particularly sulphate-reducing and methanogenic.
Field studies were conducted on an industrial site still active and close to areas of ecological interest. Abnormally high concentrations of chloroethenes in groundwater were detected ; the contamination source was highlighted as an old washing machine of metallic pieces by PCE.
Several soil and groundwater analysis sampled on the source zone showed occurrence of degradation byproducts, as TCE, cis-1,2-DCE and CV.
Knowing that only PCE was used for cleaning metallic pieces, reductive dechlorination might occur at the source of contamination. A plume modelling of the various sub-degradation products will be described in the scientific poster of this congress.

Conclusion :

Kinetics of degradation of chlorinated solvents obtained with the bacterial population KB-1 were very different according to physicochemical conditions. However, these results are specific to the bacterial population used of bioaugmentation. So, they aren't applicable to general cases.
The influence of the other types of micro-organisms like sulphate reducing and methanogenic bacteria is very important : it is necessary to minimize their activity by producing small quantities of hydrogen.
The field scale study demonstrated the occurrence of several daughters products of biodegradation of chlorinated ethylenes, a Natural Attenuation mechanism probably occurs at the contaminated site.
An extra scale will be developed in the coming months ; thus, a comparison of degradation kinetics of chloroethenes on three different scales (microcosms, columns and the real site) will be carried out.
Molecular biology methods will also be applied in order to characterize qualitatively and quantitatively the bacterial population active on the polluted site.

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