Use of an Anaerobic Bioreactor to Treat Chlorinated Solvent-Contaminated Soils

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Abstract
Anerobic bioremediation of chlorinated solvent contaminated soil was carried out using a mobile bioreactor. A laboratory-scale treatability study provided critical information as a basis for determining the optimal physico-chemical and microbiological parameters for the remediation of trichloroethylene (TCE)-contaminated soil in a bioreactor. It was found that bacteria present in a sewage sludge mixture are capable of a complete dechlorination of TCE to ethylene (ETH) under anaerobic conditions. The chlorinated solvents contaminated soil bioreactor (CSCS bioreactor) consists of a 6 m^3-reactor vessel, a gas recirculation system, a leachate recirculation system and a data acquisition system. The bioreactor vessel was designed as a continuous gas flow packed bed reactor. Four tons of contaminated soil (containing approximately 350 mg TCE/kg of soil) amended with sewage sludge have been completely remediated under anaerobic conditions over 32 weeks. The obtained results indicate that the stepwise dechlorination of TCE to ETH occurs in the bioreactor. Increasing amounts of chloride in the leachate were correlated with anaerobic dechlorination. This case study demonstrates that microbiological and chemical monitoring parameters should be combined for the comprehensive evaluation of *ex situ* bioremediation evaluation.

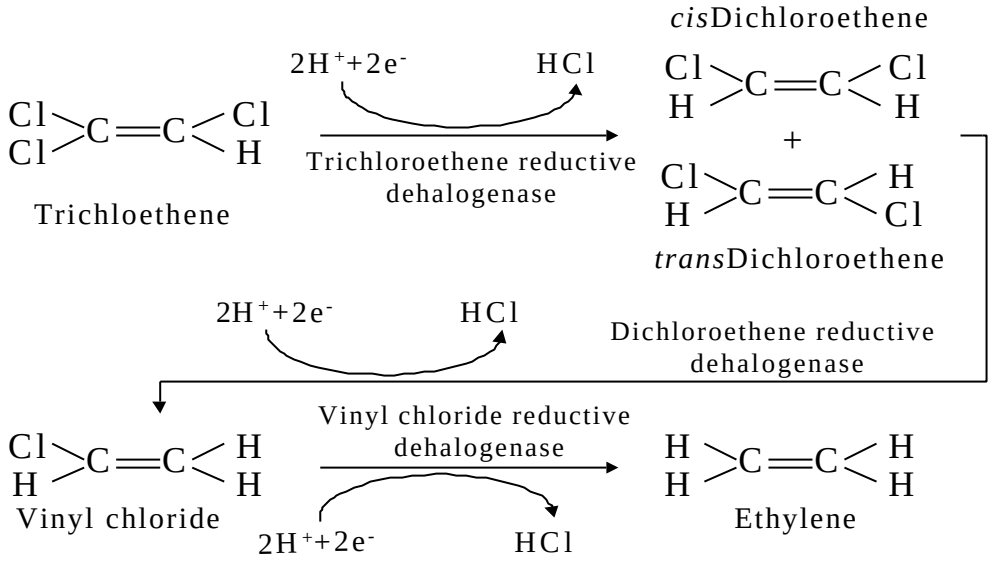
Introduction
One of the most common environmental problems in many European countries as well as in the USA is soil and groundwater contamination with chemical solvents classified as Volatile Organic Compounds (VOCs). Chlorinated solvents such as tetrachloroethene (PCE), trichloroethene (TCE), trichloroethane (TCA) and carbon tetrachloride (CT) commonly are used as degreasing agents in manufacturing, maintenance and service facilities all over the world and are casually released into the environment, particularly into soils and groundwater. While large areas of contaminated soil justify dedicated remedial operations, smaller areas could be addressed with *ex situ*, on-site batch remediation.
Chlorinated solvents can be biodegraded when used as a primary growth substrate or via a co-metabolic pathway in the following reactions:

- reductive dehalogenation (halorespiration) and
- oxidation reactions:
  - aerobic oxidation,
  - anaerobic oxidation.

It is worth noting that not all chlorinated solvents can be degraded via all of these reactions. Vinyl chloride (VC), for example, is known to degrade via all of these pathways, while trichloroethene (TCE) as a primary substrate can be degraded to dichloroethenes via halorespiration only (Wiedemeier et al. 1999).
There are many reports in the literature on reductive dechlorination of perchloroethene (PCE) and TCE to ethane or ethene by anaerobic mixed cultures of bacteria both in the laboratory and in the field. Many studies have also indicated that selection of an appropriate electron donor may be the most important design parameter for developing a healthy population of microorganisms capable of dechlorinating PCE and TCE (Smatlak et al., 1996, Fennel et al., 1997, Yang and McCarty, 1998).
A typical TCE reductive dechlorination process is presented in Figure 1.
The goal of this project was to develop a technology for bioremediation of chlorinated solvent contaminated soil using a small, mobile bioreactor. The system was intended to treat trichloroethylene (TCE) contaminated soils but could be used to treat other organic contaminated soils as well. Laboratory tests and bioremediation in the bioreactor were carried out under anaerobic conditions,

although the bioreactor has the ability to operate aerobically or anaerobically in batch mode. The project includes the following tasks:
(1) treatability study to define optimal parameters for TCE biodegradation;
(2) bioreactor design and construction; and
(3) bioremediation test of TCE contaminated soil in the bioreactor.

Figure 1 Anaerobic Trichloroethene Graphic Pathway Map



Data from the treatability study (Plaza *et al*., 2003) provided information, which served as a basis for determining the physico-chemical and microbiological parameters for the remediation of TCE-contaminated soil in a bioreactor. It was found that bacteria present in the sludge mixture are capable of complete dechlorination of TCE to ethylene (ETH) in anaerobic conditions.

The bioreactor system construction

The chlorinated solvents contaminated soil bioreactor (CSCS bioreactor) consists of a 6 m^3-reactor vessel made of carbon steel, gas recirculation system, a leachate recirculation system and a data acquisition system The bioreactor vessel was designed as a continuous gas flow packed bed reactor. A false floor was mounted inside the reactor to support the soil bed and connections were made for gas recirculation, leachate recirculation and data monitoring. In order to prevent the bioreactor soil bed from freezing during winter, a light and easy to remove enclosure made of wood and 15 cm thick pressed polystyrene foam sheets was built around the bioreactor. Inside the enclosure two heaters, 2 kW each were installed for heating the reactor if required.

The leachate recirculation system consists of a tank, a pump, valves, perforated hoses and process piping. This system has one influent and one effluent connection to the reactor vessel. The effluent process piping, equipped with a shutoff valve, is connected to a tank vessel located beneath the bottom of the bioreactor vessel. Nitrogen from a gas cylinder can be blown through the tank vessel to prevent ambient airflow into the system, if necessary. Leachate from the tank is pumped through a system of parallel, perforated hoses located at the inlet to the reactor, allowing the leachate to be spread uniformly on the upper surface of the soil bed to control soil moisture and allow the addition of nutrients, etc. as needed.

The gas recirculation system consists of a blower equipped with an inlet gas filter, a bypass pipe equipped with a control valve and an inlet gas nozzle. The bypass pipe allows the introduction of inert gas (e.g., nitrogen) or substrate gas (e.g., methane) into the bioreactor.

The monitoring system is designed to collect data, support the control of the bioreactor working parameters and evaluate the bioremediation rate. As reductive conditions have to be maintained in the reactor, there is no opportunity for taking soil samples from the reactor when the bioremediation test is in progress. Information on how bioremediation proceeds has to be obtained from changes in the composition of leachate and soil gases. The gas sampling system consists of 5 probes distributed

evenly along the main axis of the reactor vessel, about 30 cm below the surface of the soil bed. Each probe has a separate connection to the point where soil gas samples are taken using a B&K Multi-gas Monitoring device. Leachate samples are taken from the leachate tank. Soil redox potential is measured using five platinum electrodes, each one coupled with one of two silver-silver chloride reference electrodes. Each redox electrode is located near one of the soil gas probes. Before installation, the electrodes were calibrated using standard solutions. Checking callibration will be performed after the CSCS bioreactor test is completed.
Temperature is measured at three locations in the soil bed and at one point above the soil, in the vicinity of the gas outlet to the circulation system.
Humidity of the gas phase is measured at the same point as gas temperature.
The data acquisition system was build using Advantech Inc. ADAM 4000 series modules and a PC computer running MS Windows NT 4.0 workstation. The data acquisition process is fully controlled by IETU created software working in Advantech VisiDaq environment.

TCE-contaminated soil bioremediation test

Soil pretreatment

About 4 Mg of soil from the IETU site, were sieved and mixed with 200 L fresh hard-wood chips. Selected sewage sludges were used as a source of innocula based on data from treatability study. Soil was mixed with approximately 200 kg of each of dewatered sewage. Then the mixture was delivered to the bioreactor

Bioreactor startup

The bioreactor was closed tightly and the inside air was replaced by nitrogen to obtain a reductive atmosphere. Then 1 L of TCE (about 400 mg/kg) and 3 L of methanol were mixed with 20 L of water and applied to the bioreactor using the leachate circulation system. After a 3-day stabilization period, gas recirculation and the registration of measurement parameters were initiated.

Bioreactor operation

The soil gas was circulated through the bioreactor in closed circuit for 8 hours a day with a flow rate of about 1 m^3/hr. Leachate was circulated daily for about 8 hours with a flow rate of about 10 L/hr. Bioreactor pressure was controlled through a U-tube manometer fixed to one of the gas outlets. Gas cylinder nitrogen was attached to the gas circulation system and the bioreactor can be flushed, if necessary.

Sampling and data monitoring

Gas samples for TCE, DCE, VC, ethylene and ethane analyses were taken from the gas space above the contaminated soil using a B&K multi-gas monitor. The gas samplers are flushed several times with the gas before the sample is taken and delivered to the IETU laboratory. Gas that flushes the gas samplers is circulated back to the bioreactor.
The sampling cycle was adjusted to reflect intensity in changes in sample composition. During the first week of the test, gas samples were collected daily but, because their composition did not differ considerably, a biweekly, and, in the final process stage, a weekly air sampling cycle was found adequate to monitor biodegradation rates.
A sampling port was used to collect leachate samples from the leachate recirculation system. Both the soil and the sludge were analyzed before and after finishing the soil clean-up process. The leachate pH, TCE, DCE, VC, TPH, COD, nutrients, and chloride were monitored on a weekly basis.
Redox potential and temperature in the soil bed as well as humidity, temperature and pressure in the gas above the soil bed were measured continuously.

Results

Measurement results of the physico-chemical parameters and the data on the changes of gas composition in the bioreactor are presented in Figures 2-5.

Figure 2. Temperatures and pressure in bioreactor

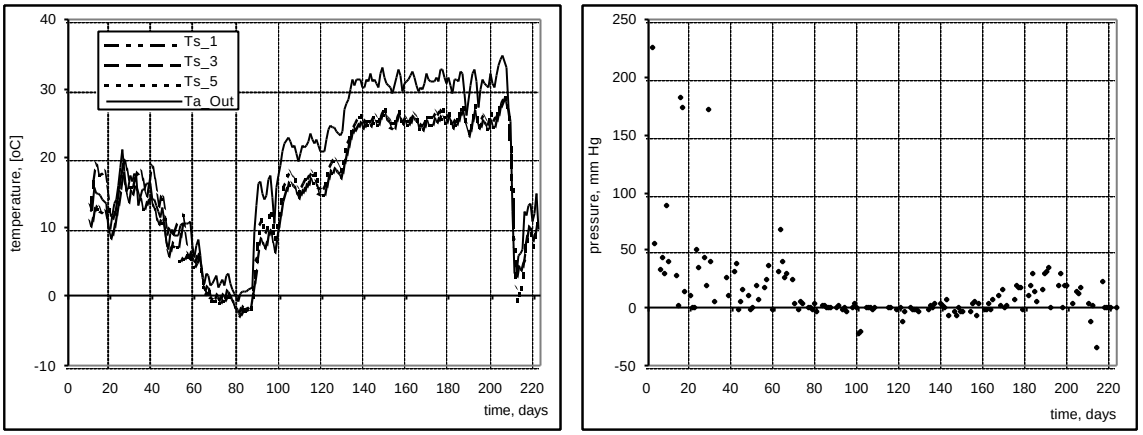


Figure 3. Redox potentials recorded by 5 electrodes placed in bioreactor soil

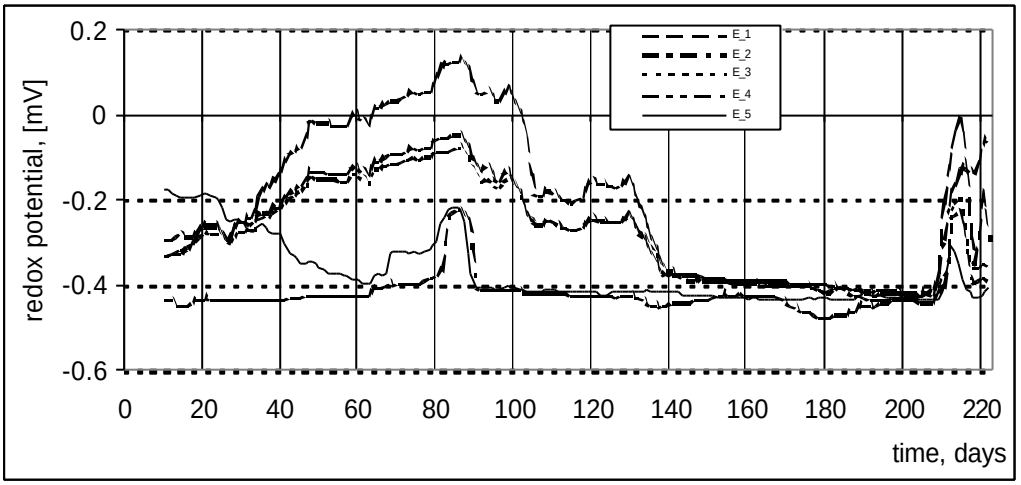
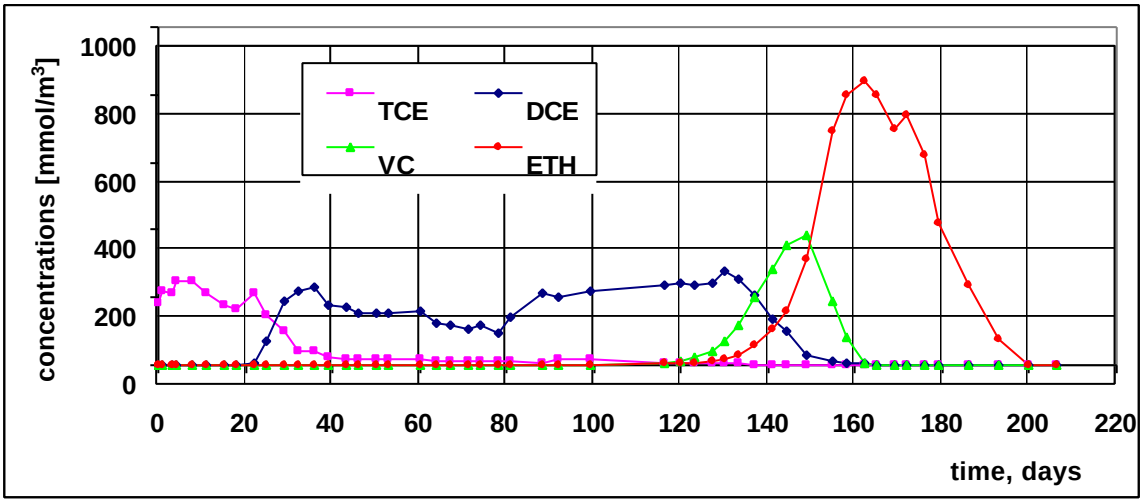


Figure 4. Average TCE, DCE, VC and ETH mean concentrations in soil gas (mmol/m^3)



The reductive biodegradation of TCE to ETH in the bioreactor was successfully completed. Final analyses of bioreactor soil showed very low concentrations of TCE and its dechlorination products. The obtained results are presented in Table 1.

Table 1. Results of soil analysis after the completion of bioremediation process [?g/kg]

TCE	1,1-DCE	Trans-1,2-DCE	cis-1,2-DCE	VC
82	55	<25	148	<30

The microbial consortium present in the wastewater treatment sludge, chosen as the inoculum in the bioreactor test, contains microorganisms capable of VC reductive dechlorination to ETH.
Traditional remediation methods typically monitor only when contaminant concentrations have met regulatory limits, while this evaluation verifies that the VOCs are completely mineralized. From this demonstration it is evident that the bioreactor approach can be applied successfully at small sites where remediation can be accomplished through biodegradation of organic contaminants.

Acknowledgements
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