Experimental and numerical investigations of pneumatic venting in unsaturated soils

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INSTITUTE OF ENVIRONMENT & RESOURCES

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Preface

The present report "Experimental and numerical investigations of pneumatic venting in unsaturated soils" has been submitted as a part of the requirements for the Ph.D. degree at the Technical University of Denmark. The study has been taking place at the Institute of Hydrodynamics and Water Resources (ISVA) and at Environment and Resources (E&R) in the period of September 1998 to October 2005. Within this period, the study was halted in approximately 2.5 years due to parental leave. The remainder of the study was performed using part time work weeks only. Professor Karsten Høgh Jensen, Geological Institute, University of Copenhagen, and Senior Scientist Torben Obel Sonnenborg, Geological Survey of Denmark and Greenland (GEUS), acted as primary advisors.

The report is organized in three parts. Part 1is a synopsis summarizing relevant literature including the work presented in this study. Part 2 and Part 3 are drafts of journal papers presenting results from the work carried out during the Ph.D. period. The first draft "Experimental investigation of pneumatic soil vapor extraction" deals with results of laboratory experiments performed during this study. The second draft "Analysis of mechanisms controlling pneumatic soil vapor extraction" deals with numerical simulations of the laboratory experiments and numerical investigation of the pneumatic venting technique.

The laboratory work was performed in corporation with Christian Kortegård and Maher Nasser, who both contributed by performing laboratory experiments in connection with elaboration of their Master Thesis. Performing the laboratory experiments raised many problems and challenges, and both Christian and Maher worked consciously and hard. Also the atmosphere in the laboratory was always pleasant, even when problems arose. I acknowledge Christian and Maher for their work. Associate Professor Hans Mosbæk (E&R) provided support and guidance into the field of analysing gas samples. Characteristic of Hans is his ability to view problems as challenges, which should be addressed with a light spirit. I am very grateful for his involvement in this project.

During performance of the numerical simulations, Dr. Jacob Gudbjerg was always available for comments and discussion. His contributions to this work are greatly acknowledged.

Further I gratefully acknowledge Torben O. Sonnenborg and Karsten H. Jensen for their competent guidance and support, and finally thanks to the rest of my colleagues for creating a pleasant atmosphere.

The study was funded by the Technical University of Denmark. The support is greatly acknowledged.

The papers (Part 2 and Part 3 of this thesis) are not included in this www-version but may be obtained from the Library at the Institute of Environment & Resources, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Kgs. Lyngby (library@er.dtu.dk)

Copenhagen, October 2005
Camilla Kruse Høier

Abstract

Throughout the last century increased production of chemicals has led to numerous accidental spills or leakages of chlorinated solvents and mineral oil products to the soil. These chemicals (NAPLs) are only slightly soluble in water and are transported through soil as a separate phase. When NAPL infiltrates through soil, it leaves behind small volumes of NAPL, residual NAPL, trapped in the soil by capillary forces. When residual NAPL is retained in the unsaturated zone it poses risks of contaminating ground water or health risk to people living in the vicinity of the contaminated area. Hence NAPL contamination needs to be restored. Soil venting is a very common in situ technique used in restoring NAPL spills located in the vadose zone of soils. However popular, the technique of soil venting possesses limitations which result in less efficient performance and prolonged clean up times. One of the reasons for limited performance efficiency is found when dealing with layered soils of variable permeability. In such soils the efficiency of SVE is often reduced due to airflow bypassing areas of relative low permeability. Problems of flow bypassing are the subject of this study.

In the present work a new venting technique, pneumatic venting, is proposed as an alternative to conventional soil venting, when dealing with restoration of layered soils. The technique is based on imposing substantial transient pressure fronts through the vadose zone of soil. These pressure fronts are imposed by repeatedly lowering the gas phase pressure of the soil and subsequently release pressure. In this study pneumatic venting was tested in 2D tank laboratory experiments. The experiments comprised venting experiments on homogenous and heterogeneous sand packs contaminated by Trichloroethylene. Experiments showed that changing pumping schemes from constant flow venting to pneumatic venting resulted in highly improved removal efficiencies. However experiments did not reveal the mechanisms controlling the effect of pneumatic venting. In order to determine the processes responsible for the effect of pneumatic pumping, the results of the laboratory experiments were tested numerically. By use of the numerical model the dominant removal mechanism during pneumatic venting was identified as gas expansion. When pressure is lowered, gas is expanding and thereby gas/VOC fluxes are mobilized within the entire plume area of the low permeable area.

Having identified the mechanism controlling pneumatic pumping, the numerical work was extended to comprise sensitivity analysis of the efficiency of the technique towards selected parameters. The parameters comprised initial NAPL distribution, absolute permeability of the low permeable area and finally the effect of the magnitude of the total pressure drop imposed on the system. Results showed that even though removal efficiency of pneumatic pumping was sensitive towards all of these parameters, the pneumatic venting performed better than constant flow in all scenarios tested. Removal was increased by factors in the range of 2.2 to 4.8 when using pneumatic pumping in preference to constant flow venting. The largest gain was found when reducing permeability of the low permeable area.

In summery the results of the present study suggest that pneumatic venting may be an attractive alternative to constant flow venting, however further research is needed to establish the applicability of the technique to field scenarios.

Resumé

Gennem det sidste århundrede har øget produktion af kemikalier forårsaget talrige spild eller lækager af klorerede opløsningsmidler og olieprodukter til jord. Disse kemikalier (NAPL) er svagt opløselige i vand og transporteres gennem jord som en separat fase. Når NAPL infiltrerer gennem jord efterlades små volumener af stoffet tilbage i jorden (residuel NAPL) fanget af kapilære kræfter. Når residuel NAPL tilbageholdes i den umættede zone af jord, udgør det en forureningstrussel mod grundvandet og er en sundhedsrisiko for mennesker, der bor nær det forurenede område. Derfor er det nødvendigt at fjerne sådanne forureninger. Jord ventilering bliver ofte brugt til at restorere NAPL forureninger i den umættede zone af jord. På trods af at denne teknik er populær besidder jord ventilering begrænsninger, som ofte resulterer i nedsat ydeevne og lange oprensningstider. I lagdelt jord med varierende permeabilitet kan en af grundende til nedsat ydeevne være at luften ikke kommer i kontakt med det forurenede område af jorden. Denne problemstilling ligger til grund for dette studie.

I dette studie præsenteres en ny ventilering teknik, pneumatisk ventilering. Denne teknik er tænkt som et alternativ til konventionel jord ventilering, når forureninger skal fjernes fra lagdelt jord. Teknikken baseres på at den umættede zone i jord påføres store, dynamiske fronter af undertryk. Disse tryk fronter påføres ved cyklisk at sænke trykket i jordens gas fase og derefter at frigive trykket igen. Under dette studie blev metoden testet ved laboratorie forsøg med en 2D rende. Laboratorie arbejdet omfattede ventilerings forsøg på homogene og heterogene sand pakninger forurenet med Trikloretylen (TCE). Forsøgene viste at skift i ventilering teknik fra konventionel ventilering til pneumatisk ventilering forårsagede kraftige stigninger i fjernelsesraten. Derimod afslørede forsøgene ikke årsagen til den forbedrede effekt af pneumatisk ventilering. For at fastlægge mekanismerne bag pneumatisk ventilering opstilledes en numerisk model med baggrund i forsøgsresultaterne. Den numeriske model viste, at den dominerende mekanisme i pneumatisk pumpning er gas udvidelse. Når trykket sænkes, udvides gasfasen, og der mobiliseres stof flux i alle områder af forureningsfanen i det lav permeable område.

Efter at have identificeret årsagen til effekten af pneumatisk ventilering, blev det numeriske arbejde udvidet til at omfatte sensitivitetsanalyser af sammenhængen mellem udvalgte parametre og metodens effektivt. Disse parametre omfattede initial NAPL fordeling, den absolutte permeabilitet af det lavpermeable område og endelig effekten af størrelsen af det påførte undertryk. Resultaterne af sensitivitetsanalysen viste, at på trods af at metoden var sensitiv overfor alle nævnte parametre, var pneumatisk ventilering at foretrække frem for konventionel ventilering i alle undersøgte scenarier. Fjernelsestiden blev reduceret med faktorer i intervallet 2.2 til 4.8, når pneumatisk ventilering blev anvendt frem for konventionel ventilering. Den største fordel ved pneumatisk ventilering blev fundet for scenariet med lavest permeabilitet i det lavpermeable område.

Afslutningsvist blev konkluderet at pneumatisk ventilering virker som et attraktivt alternativ til konventionel ventilering. Men der skal foretages yderligere undersøgelser af teknikken, for at kunne fastslå, om pneumatisk ventilering kan anvendes i felten.

CONTENTS

PART I

PART II
Experimental investigation of pneumatic soil vapor extraction

PART III
Analysis of mechanisms controlling pneumatic soil vapor extraction

1 INTRODUCTION

1.1 Background

Throughout the last century increased production of chemicals has led to numerous accidental spills or leakages of chlorinated solvents and mineral oil products to the soil. These chemicals are only slightly soluble in water and are transported through soil as a separate phase. Contaminants existing as a separate phase within the soil are named non aqueous phase liquids (NAPLs), and are divided into two main groups; those that are lighter than water (LNAPLs) and those that are denser than water (DNAPLs). The main difference between the two groups of NAPLs are that when infiltrating through the soil, DNAPLs will penetrate the water table and spread into the saturated zone, whereas LNAPLs will tend to pool on the water table. Common for DNAPLs and LNAPLs is that when infiltrating through the unsaturated zone of the soil, only part of the NAPL will reach the ground water table. Another part will be retained in the unsaturated zone by capillary forces and immobilization caused by fragmentation. The retained portion of the NAPL is immobile and referred to as residual NAPL. Although being retained in the vadose zone, residual NAPL posses threats to contaminate large portions of groundwater, both by dissolution and transport in infiltrating water, but also by contaminant spreading within the gas phase of the vadose zone. This is possible since many chlorinated solvents and mineral oil products are volatile organic compounds (VOCs). These VOCs are able to spread widely in the gas phase of the soil (Baehr, 1987), both by diffusion and in some cases by density driven gas flow (Falta et al., 1989). Besides being a threat of groundwater contamination, NAPL retained in the vadose zone can be a health risk to people living in the vicinity of the contaminated areas, and therefore such contaminated areas has to be restored. When possible, remediation of spills within the unsaturated zone is often done by excavating the contaminated soil and treating it off site. However at some sites the contaminated area might be too large, or for other reasons not accessible to excavation, and in these cases in-situ remediation is necessary. In the unsaturated zone the choice of in-situ technology often includes Soil Vapor Extraction (SVE), also known as soil venting.

1.2 Conventional soil vapor extraction

The principles behind SVE is very similar to conventional pump and treat methods, only SVE targets the gas phase instead of the water phase, as often is the case when remediating soil contamination. Thus SVE takes advantage of the fact that many NAPLs are highly volatile. During venting operations, flow of clean gas is established through the contaminated zone by pumping from a system of vadose zone wells. The volatile contaminants partition into the clean air as it moves through the contaminated soil towards the extraction wells. From these wells the contaminated vapors are transported to an above ground treatment unit.

The method was developed in the early 1980's, and has since then become widespread. Travis and Macinnis (1992) states that as of 1992, SVE was used at 18% of the U.S. Superfund sites, and the number of SVE applications was increasing. The popularity of the SVE technologies stems from their proven effectiveness for removing large quantities of VOCs from the soil and their relative simple non-intrusive implementation. Whether or not, SVE is considered an attractive remediation technology on a given site depends upon the soil type of the contaminated area and on the type of compound spilled in the area. Wilson and Clarke (1994) list a set of rules of thumbs, which can be used to assess whether the contaminating compound is suitable for SVE remediation. U.S. EPA (1991) lists compounds considered not applicable for remediation using SVE.

Although popular the performance of the SVE system is most often less than ideal. During SVE operations, the systems characteristically exhibit large initial contaminant exhaust concentrations followed by rapid drop of and extended periods of low-level removal ("tailing concentrations") (Chai and Miura, (2004), Thomson and Flynn (2000), DiGiulio (1992)). This type of non-ideal performance was also observed in this study (see section 3.3). As a result of deteriorating SVE performance, contaminant levels often remain above clean up targets and increased clean-up cost are incurred from pumping large volumes of gas at low contaminants concentrations (Barnes, 2003).

Diminished removal efficiency and long term tailing behaviour is caused by reduced ability of the VOCs present in the contaminated zone to access the gas flow stream induced during SVE applications. The reason for this reduced ability can roughly be divided into three categories.

Firstly, slow removal can partly reflect the preferential removal of more volatile constituents of multicomponent NAPL spills (i.e. gasoline, Hayden et al., 1994). Secondly long tailing behaviour can be attributed from rate-limiting VOC transfer between the soil gas, the soil water, and the soil grains. These rate-limiting transfer processes was studied extensively by different research teams in the 1990's. Gierke et al. (1992) showed that in moist, aggregated soils, intraaggregate diffusion could cause mass transfer limitations. Based on numerical simulations of experiments on laboratory scale columns packed with natural sand, Croisé et al. (1994) found that rate-limiting mass transfer most likely was attributed to micro-scale diffusion both in soil grains and organic matter. Sorption of VOCs to aquifer particles are depended on water content and content of organic matter (Ong and Lion (1991); Petersen et al. (1995); Wehrle and Brauns (1994)). Petersen et al. (1995) showed that in very dry soil the sorption of Trichloroethylene (TCE) was dominated by sorption to mineral grains (clay) of the soil, whereas the sorption of TCE in wet soils was dominated by sorption to the organic material in the soils. Generally the mentioned types of mass transfer limitations have the largest effect on SVE performance, when the free NAPL phase has been depleted from the contaminated area.

Finally long tailing behaviour can arise during soil venting, even when NAPL still exist as free phase within the contaminated area. This problem arises, when the gas stream is prevented access to areas containing free NAPL, i.e. due to flow by-passing in layered soils (Kearl et al., 1991; Ho and Udell, 1992; Smith et al., 1996). In layered soils variations occur in permeability, water saturation and NAPL distribution. When gas flow is bypassing low permeable areas of the contaminated zone, contaminant removal may be restricted to gas diffusion, which is a very slow process even in air.

Alternative strategies, such as pulsed pumping and injection of steam, have been suggested to increase the efficiency of the venting process in heterogeneous soils. Pulsed pumping involves pumping for a length of time, shutting down for a significant period of time then restarting pumping. The intension is that the contaminated area is flushed by constant pumping until recovery is reduced, due to mass transfer limitations. Then the pump is stopped in order to allow mass transfer to take place and then the pumping is restarted, and so forth. The method was tested numerically by Armstrong et al. (1994) on a system, where diffusive mass transfer in water limited the removal efficiency of the venting process. They showed that pulsed pumping was less efficient than continuous pumping at an equivalent average rate. The reason was that continuous pumping maximizes the diffusive mass transfer of contaminant by maintaining the concentration gradient at a steady maximum state. Also Schulenberg and Reeves (2002) found that pulsed pumping was less efficient compared to constant pumping

Injection of steam seems to be an effective technique in remediation from heterogeneous porous media (i.e. She and Sleep, 1999), although uncontrolled downward migration of contaminant has been a concern using this technique. However, new evidence indicates, that migration could be prevented, if the injected steam is mixed with air (Schmidt et al., 2002).

Though promising, the thermal technologies are expensive and often complicated to perform in the field. In this study a new venting technique, pneumatic venting or pneumatic SVE, is presented as an alternative to the constant flow technique traditionally employed in SVE applications. The pneumatic venting technique is hypothesized to enhance VOC removal from low permeable layers by increasing the magnitude of VOC being transported from zones of low permeability to zones of high permeability.

1.3 Pneumatic venting

The technique of pneumatic venting is based on imposing large transient pressure fronts (e.g. 2 mH_2O) on the contaminated region of the subsurface, as opposed to the constant air pressure field produced during constant flow venting (conventional SVE). The transient pressure fronts are produced by repeatedly increasing the vacuum by periodically reducing the accessibility to the atmosphere. In this manner the method deviates from the pulsed pumping technique in which the pressure fluctuations are obtained by turning the pump on and off. Further, the rate of pulsing and the magnitude of imposed pressure drop is much higher during pneumatic SVE compared to pulsed venting.

Pneumatic venting is hypothesized to take advantage of two simultaneous processes being active when alternating periods of enforcing and releasing partial vacuum are used. Firstly the method utilizes the fact that gas is able to expand. By generating a substantial pressure drop in the unsaturated zone the gas will expand and contaminated air is forced out of low permeable soil units. When pressure conditions close to atmospheric pressure subsequently are established, air will flow back in to the low permeable soil units. If the contaminant forced out of the lens is removed from the adjacent high permeable area before the air re-enters the lens, net transport of contaminant from less permeable to more permeable soil is generated. Also mixing of the contaminated air inside the low permeable areas is hypothesized to contribute to increased VOC removal during pneumatic pumping. Mixing is hypothesized to occur as a consequence of flow fluctuations originating from transient pressure fronts. The third potential effect of pneumatic venting is caused by the generation of non-stationary pressure field. The pressure fronts will continuously move through the contaminated soil and permanent stagnation points, where no flow takes place, will therefore be avoided.

The potential of using pneumatic SVE as a clean-up technology has previously been subject to a numerical analysis on 1D and 2D hypothetical systems (von Christierson, 1997).The numerical model used for the analysis was T2VOC, which was also applied in this study (T2VOC is described in section 4).

The 1D simulations were performed for homogenous soil columns. Initially the soil columns contained air saturated with Trichloroethylene (TCE) vapours at atmospheric pressure. No flow and specified pressure was applied as lower and upper boundary conditions, respectively. Three scenarios were tested using different upper boundary conditions. Firstly removal of TCE was simulated using constant atmospheric pressure as upper boundary, leaving transport processes within the soil column to be controlled solely by diffusion in the gas phase. Secondly a constant pressure of 0.5 atm was applied as upper boundary. Thirdly, to illustrate the effect of pneumatic venting, fluctuating pressure between 1 and 0.5 atm was applied.

Based on results from 1D simulations it was found that a constant pressure drop (0.5 atm) initially enhanced TCE removal compared to removal by pure diffusion. At early stages advective flow through the column was induced, but with time flow would cease and removal of TCE was entirely controlled by diffusion. When fluctuating pressure was applied, stagnation of flow and thereby reduction in TCE removal rates was avoided.

von Christierson (1997) also performed numerical simulations for 2D systems. This analysis was performed to examine the feasibility of pneumatic venting on a more realistic system, where clean air is allowed to enter the subsurface from the atmosphere. The model area of the 2D simulations was 5 meters in depth and 85 meter in length. Matrix was composed of sand and both homogenous and heterogeneous settings were studied. NAPL was not present in any of the simulations. In the homogenous setting contamination was present as VOC spread at the entire pore volume of the model set-up. For this setting results showed that pneumatic venting would do no better than traditional constant flow venting. In the heterogeneous setting a well-defined low permeable lens was inserted into the model area and VOC was confined to the lens area. Sealing of the ground surface was included in the model to prevent clean air to enter the subsurface. Results showed that when applying pneumatic venting to this setting faster removal of VOC was obtained compared to constant flow venting.

von Christierson (1997) also performed simulations introducing a water table into the model domain. The model simulation was ended after 23 hours (model-time). Within this period results showed that upwelling of groundwater was avoided when using pneumatic venting contrarily to results from the constant venting scheme.

2 OBJECTIVES AND METHODOLOGY

The objectives of this study are

1. To investigate pneumatic venting as an alternative technology for remediation of contaminated soils
2. To carry out controlled laboratory experiments for analyzing the effect of applying pneumatic venting
3. To apply a numerical model to the experimental data for identification of the mechanisms responsible for removal of contamination during pneumatic venting
4. To analyze the sensitivity of the effect of pneumatic venting towards selected parameters

In order to meet these objectives, 2D tank venting experiments were performed in the laboratory using both the techniques of constant flow and pneumatic venting on different sand packs. The laboratory experiments were simulated by the multiphase model, T2VOC. The numerical work provided insight into the processes controlling the effects of pneumatic venting. Further the numerical study included a sensitivity analyses, showing the effect of changing factors controlling the efficiency of pneumatic venting.

3 LABORATORY EXPERIMENTS

This section provides a brief summery of laboratory experiments performed in the present study.

3.1 Experimental set-up and procedure

2D-tank soil vapor extraction experiments were performed on homogenous and heterogeneous sand packs contaminated with Trichloroethylene (TCE). The tank dimension was 106 cm x 74 cm x 8 cm. The homogenous packs consisted of coarse sand, whereas the heterogeneous pack consisted of a fine sand lens (80 cm x 20 cm) surrounded by the coarse sand used for the homogenous packs. Figure 1 shows a sketch of the laboratory tank including placement of the fine lens (Figure 1B). Preparing the soil venting experiments, the packs where saturated with water, and then drained for five days. After five days of drainage TCE was injected and left to equilibrate for 36 hours. At this time spreading of TCE ceased in the coarse sand of the homogenous pack. Equal amounts of TCE were injected into the homogeneous and heterogeneous packs. In the heterogeneous packs, however, half of the TCE was injected into the fine lens. Figure 1 shows the placement of the TCE in the homogenous pack (Figure 1A) and in the heterogeneous pack (Figure 1B).

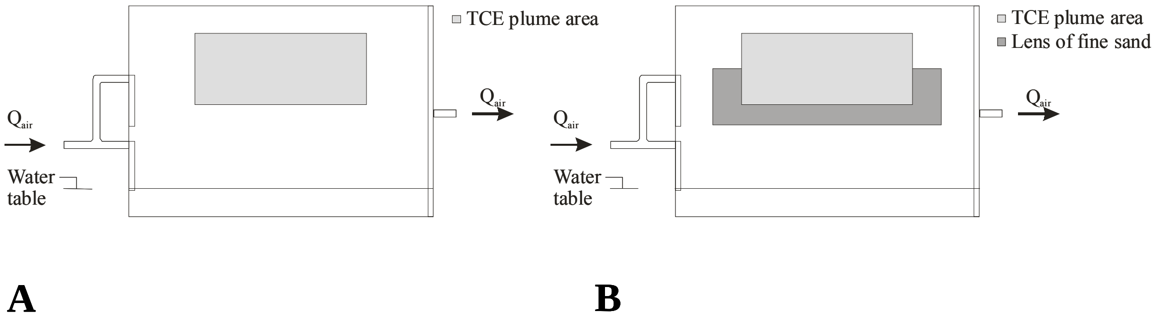


Figure 1 Laboratory set-up of homogenous pack (1A) and heterogeneous pack (1B)

A total of six experiments were carried out and divided into three different groups: (1) Homogenous sand packs (Hom1 and Hom2) were vented using constant air flow (traditional venting), (2) Heterogeneous packs (Het1 and Het2) were vented using constant air flow, and (3) Heterogeneous packs (Pneum1 and Pneum2) were vented using alternating periods of constant flow and pneumatic venting. Pneumatic venting was applied by repeatedly lowering the gas pressure within the pack by closing the air inlet, while an air pump was pumping continuously at the outlet from the pack. The gas pressure was subsequently released by opening the air inlet. The Het1 and Het2 venting experiments were performed on the same pack, such that proceeding termination of the Het1 experiment, TCE was re-injected and a second venting experiment (Het2) was performed on the pack.

3.2 Model contaminant

Trichloroethylene (TCE) was chosen as model compound for this study. TCE was chosen because it is very often encountered at contaminated sites. Through the last century TCE has been one of the most widely used cleaning and degreasing solvents in the United States of America [Doherty, 2000]. As of 1997, TCE was reported as being present at 852 of 1430 National Priority List sites. This makes TCE on of the most commonly encountered contaminants at U.S. Superfund sites [Doherty, 2000]. Also Denmark has often encountered soil and groundwater contamination problems by of chlorinated solvents. In 1987 the county of Copenhagen found traces of chlorinated solvents in 42 of 189 examined groundwater extraction wells (Jensen and Nilsson, 1996, in Danish). TCE was found in the majority of these wells.

3.3 Results of venting experiments

Figure 2 shows measured outlet concentrations from the constant flow experiments on a homogenous pack (Figure 2A) and heterogeneous pack (Figure 2B), respectively. The figure clearly illustrates the problems of non-ideal behavior often met during constant flow venting operations; large initial outflow concentrations are followed by extended periods of low-level removal. Figure 2A shows that tailing behavior was encountered when NAPL phase was depleted from the homogenous laboratory pack. In general, this type of tailing behavior is caused by rate-limiting mass transfer between soil gas, soil water and soil grains (see section 1.2). However, the tailing behavior shown at Figure 2A was probably attributed to some kind of diffusion limited transport within the soil water. Rate-limiting sorption could also explain the observed tailing behavior, but this is considered less likely, since the measured organic carbon content of the coarse sand was zero.

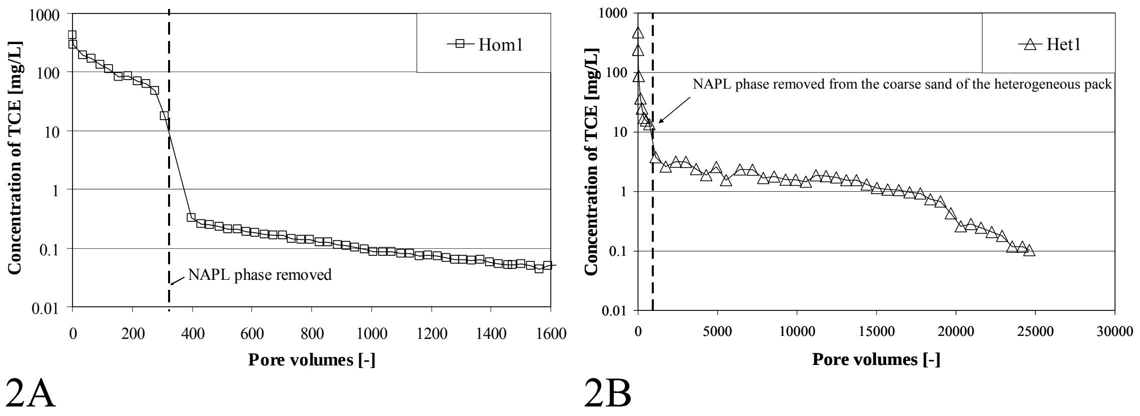


Figure 2   Outlet concentrations from homogenous (2A) and heterogeneous packs (2B)

The heterogeneous pack (Figure 2B) also exhibited non-ideal behavior that clearly was more severe than was encountered for the homogenous pack. The tailing in this case was attributed to flow bypassing, since advective flow through the low permeable lens was significantly reduced compared to that of the coarse sand. In the homogenous pack NAPL-phase was removed after approximately 320 pore volumes, whereas the same amount of NAPL in the heterogeneous pack was removed after 25.000 pore volumes. This clearly illustrates the problems that may be encountered when traditional venting is applied on layered soils.

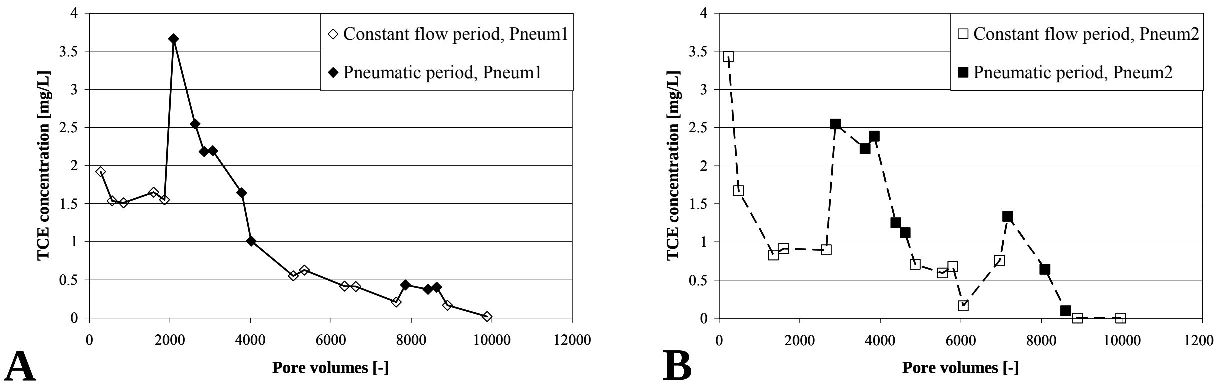


Figure 3   Outlet concentrations from the pneumatic venting experiments

Results of the pneumatic experiments are shown at Figure 3. The figure shows that when constant flow venting was replaced by pneumatic venting, outlet concentrations increased considerably. The initial steep increase was followed by a steep decrease in outlet concentrations. The decrease was steeper than found during the constant flow periods, indicating that the removal efficiency was reduced faster during the pneumatic periods than during constant flow periods. This behavior was an implication of the fast removal leading to a fast reduction in retained mass and an associated reduction in removal rates.

Figure 4 shows the cumulated mass removal from the pneumatic experiments plotted against dimensionless time. Thus the slope of the curves represents removal rates expressed in g pr. pore volume. From the figure is seen that removal rates clearly increased when pneumatic venting was applied.

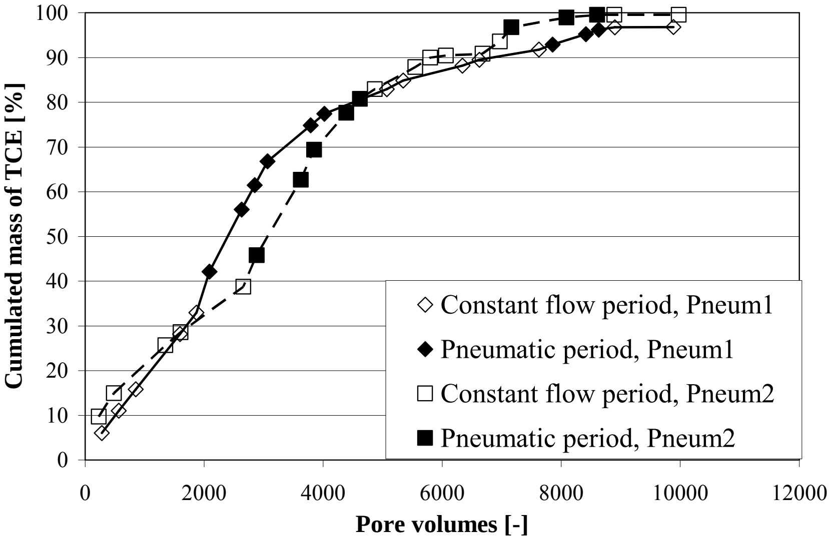


Figure 4 Cumulated mass removals for the pneumatic experiments

In the beginning of the first pneumatic venting period removal rates increased by 60% and 77% for the Pneum1 and Pneum2 experiments, respectively, compared to the preceding constant flow periods. Further, when the pneumatic venting technique was replaced by constant venting, the removal rates decreased by 64% and 54%. These differences in removal rates clearly indicate that using the pneumatic venting technique had a beneficial effect on the remediation process. Although laboratory experiments demonstrated enhanced removal using pneumatic venting, laboratory results did not conclusively reveal the mechanisms controlling the effect of the technique. In order to determine these mechanisms a numerical model analysis was carried out for the laboratory results.

4 NUMERICAL MODELING OF SOIL VENTING AND PNEUMATIC VENTING

This section presents general aspect related to air flow (section 4.1). Further section 4.2 presents the governing equations of T2VOC, which is the numerical model used in this study. The results of the modeling of laboratory experiments are presented in section 4.3, which also includes results of a sensitivity analysis performed on the model set-up.

4.1 Modeling air and water flow

The results of the laboratory experiments were simulated by a numerical model. In these simulations the dominating feature is flow/transport of/within the gas phase. Historically focus of contaminant transport modeling has been on describing flow/transport of/within the water phase. This section provides an overview of the most important differences between modeling water and gas flow.

Four main differences exist between water and gas flow/transport. Firstly, water is most often assumed incompressible, which is, in general, not valid for gas flow. At low gas pressures (<2-3 atm) the dependency of gas density on pressure can be described assuming ideal gas behaviour (Baehr et al., 1989; Falta et al., 1995). Secondly the viscosity of gases is lower than that of water, which means that smaller pressure gradients are required to generate gas flow than corresponding amounts of water flow. Thirdly diffusion coefficients of gas phases are much larger than those of the water phase. (Digiulio et al., 1990; Brusseau, 1991). And finally, the assumption of zero flux at surfaces of solids, which is used for water flow, may not be valid for gas flow. The nonzero fluxes are referred to as the Klinkenberg effect or slip flow (Dullien, 1979; Massmann, 1989). The nonzero fluxes are caused by Knudsen diffusion, which occurs when the mean free path of the gas molecules approaches the dimension of the pores. In these cases significant molecular collisions occurs with the pore wall rather than with other gas molecules (Wakao and Kaguei, 1982; Wu et al., 1998).

According to Fen and Abriola (2004) transport of gases in porous media has traditionally been described by an advective-dispersion formulation combined with a Klinkenberg correction term (“AD-Klinkenberg”-formulation). In this formulation diffusion is described by Fick’s law and slip flow effect caused by Knudsen diffusion has been included by modifying the gas permeability through the Klinkenberg correction term (Webb and Pruess, 2003). Through the last decade, the “AD-Klinkenberg”-approach has been questioned by a number of researchers (see e.g. Fen and Abriola, 2004), and it now seems generally accepted, that use of the dusty-gas model is preferred to describe transport of gases in low permeable soils (Webb and Pruess, 2003). In the dusty gas model porous medium is assumed to consist of large motionless molecules treated as a component of the gas mixture. The kinetic gas theory is then applied to this “dusty gas” mixture. Knudsen diffusion and thereby slip flow effect is inherently included in this model. Webb and Pruess (2003) show that using the “AD-Klinkenberg” formulation for transport of trace gas could result in over prediction of the gas diffusion flux by orders of magnitudes in some types of low permeable soils.

In this study gas flow is modeled by T2VOC, which describes slip flow by the AD-Klinkenberg approach. This means that the model may have some problems to describe the slip flow effects in some low permeable soil types. Fortunately the slip flow effect is assumed negligible in the model simulations presented in this study. The justification of this assumption is based on findings of the following researchers. Massmann (1989) found that slip flow effects are negligible in silts, sand and gravels. Baehr and Hult (1991) showed that omission of the slip flow effect induces errors on the estimated gas permeability of less than 10%, when porous media with an intrinsic permeability larger than 10^{-13} m^2 are considered. In this study SVE experiments are performed on sands having intrinsic permeabilities larger than 10^{-11} m^2. Apart from being a function of pore sizes of the porous media, the magnitude of slip flow effect is also a function of pressure. When gas pressure is reduced the portion of molecule - pore wall collisions are increased compared to molecule-molecule collisions. McWhorter (1990) concludes that the slip flow effect can be ignored when the gas pressure difference is less than 20% of atmospheric pressure, which is the pressure range of practical importance for SVE operations. During pneumatic venting, however, the slip flow effect may possibly be an issue, since the technique is based on imposing large pressure drops to soils. In this study, however, pneumatic venting experiments were performed by repeatedly lowering and releasing gas pressure from 1 atm to 0.8 atm and back. According to McWorther (1990) this pressure drop is considered to be within the limit of the range in which slip flow can be ignored.

4.2 Governing equations of T2VOC

The numerical code used in this study, T2VOC (Falta et al., 1995), is a member of the TOUGH family of codes developed to simulate non-isothermal transport of contaminants in multiphase systems (Preuss, 1987; Preuss, 1991). The code was partly designed to be able to simulate SVE applications. In this section the governing equations of T2VOC is briefly described. Further the constitutive relations between phase saturation, capillary pressure and relative permeability used in this study are presented.

4.2.1 Mass balances and fluxes

The description of the governing equations of the model is based on the T2VOC User's guide (Falta et al., 1995).

T2VOC considers water, NAPL and gas as separate phases. These phases consist of the three components air, water and chemical. In reality air consist of different components, such as nitrogen, oxygen, etc., but in T2VOC the air component is described as a single "psuedo-component" with averaged properties. This means that for example the gas phase may be a mixture of water (as a component), chemical and air "pseudo-component".

In this study T2VOC is used exclusively in isothermal mode. In this case three mass balance equations, one for each component, are needed to describe the system:

$$\frac{d}{dt}\int_{V_n} M^{\kappa} dV_n = \int_{A_n} F^{\kappa} \cdot n \; dA_n + \int_{V_n} q^{\kappa} dV_n \qquad (1)$$

where M^{κ} is the mass of component κ (water, chemical or air) per unit porous medium volume (V_n), F^{κ} is the mass flux of the component into V_n, n is the inward unit normal vector, and q^{κ} is the rate of mass generation of component κ per unit volume. The mass term is calculated as the sum of the contributions from the three phases

$$M^{\kappa} = \phi \sum_{\beta} S_{\beta} \rho_{\beta} X_{\beta}^{\kappa} \tag{2}$$

where ϕ is porosity, S_β is the saturation occupied by phase β, ρ_β is the β phase density, and X_β^κ is the mass fraction of component κ in phase β. For the mass accumulation term calculated for the chemical an additional term may be added to include sorption (linear equilibrium adsorption, see Falta et al., 1995).

The mass flux terms, F^κ (equation (1)), of the three components water, air and chemical is calculated as a sum of contributions from the three phases water, gas and NAPL.

$$F^{\kappa} = \sum_{\beta} F_{\beta}^{\kappa} \tag{3}$$

In the NAPL and water phases only advective transport is considered (Falta et al., 1995), and the mass flux due to this mechanism is calculated according to the multiphase extension of Darcy's law.

$$F_{\beta} = -k \frac{k_{r\beta} \rho_{\beta}}{\mu_{\beta}} \left(\nabla P_{\beta} - \rho_{\beta} g \right) X_{\beta}^{\kappa} \tag{4}$$

Where k is the absolute permeability, $k_{r\beta}$ is the relative permeability of the phase β, μ_β is the dynamic viscosity of phase β, P_β is the fluid pressure of phase β, and g is the gravitational acceleration.

In the gas phase the component transport mechanisms include both advection and diffusion.

$$F_{g} = -k_{slipflow} k \frac{k_{rg} \rho_{g}}{\mu_{g}} \left(\nabla P_{g} - \rho_{g} g \right) X_{g}^{\kappa} + J_{g}^{\kappa} \tag{5}$$

where J_g^κ is the diffusive mass flux of the component κ in the gas phase, which is described by Ficks law. The tortuosity of the porous media is described by the Millington and Quirk model (see Falta et al., 1995).

Apart from the diffusive mass flux, equation (5) deviates from equation (4) by the factor $k_{slip\ flow}$, which is a correction term, which accounts for the possible slip flow effect in gasses. As mentioned in section 4.1 slip flow effects are ignored in this study, however it is noted that the slip flow factor is a function of gas pressure and absolute permeability of soils. Several correlations exist relating the slip flow factor to permeability, see e.g. Heid et al. (1950), Baehr and Hult (1991), Thorstenson and Pollock (1989) and Jones and Owens (1980).

In T2VOC the mass transfer of the chemical is simulated by equilibrium partitioning between the gas, aqueous and solid phases. This approach is not entirely correct for a rigorous simulation of the soil vapor extraction experiments performed in this study, because it has been widely documented, that mass transfers limitations often control transfer of partitioning between phases. In this study, however, equilibrium partitioning is assumed to sufficiently describe the process in focus, since the errors introduced by assuming equilibrium mass transfer are most severe, when free NAPL phase is removed from the system. Generally this process is not the focus of the simulations in this study. Errors can be expected particularly when modeling periods where NAPL has just been depleted from the coarse sand of the heterogeneous packs. These periods are characterized by outlet concentrations that are reduced from a relatively high level, controlled by NAPL-phase removal in the coarse sand, to relative low concentrations, controlled by NAPL-phase removal in the fine lens. In this “transition” period TCE dissolved in the water-phase of the coarse matrix could be removed too fast in the model. In T2VOC also the mass transfer between NAPL and gas-phases is simulated by equilibrium partitioning. This approach is probably adequate for use in this study (Bloes et al., 1992; Hayden et al., 1994).

Dispersion of the gas phase is neglected in T2VOC, which causes an underestimation of the spreading of VOC. Generally speaking the larger the transport distances of VOC the larger errors are induced when neglecting dispersion. Also errors become larger, when gas flow is high. The precise effect of neglecting gas dispersion during the simulations performed in this study is difficult to assess. On one hand transport distances are relatively small in the laboratory packs, on the other hand gas velocities are very high in the coarse sand immediately after the gas pressure is released (i.e. the air inlet is opened) during pneumatic venting. Thereby the largest effect on neglecting dispersion is probably found for transport of VOC from the coarse sand to the outlet during periods of releasing pressure. Therefore it cannot be out ruled that the amount of VOC reaching the outlet during these periods may be slightly overestimated.

4.2.2 Constitutive relations for pressure-saturation-permeability

Specification of constitutive relations for pressure-saturation-permeability (p-S-k relations) is required for modeling multiphase systems, and their formulation has been subject to extensive investigations (Miller et al., 1998). In this section the focus is on describing the p-S-k-relations used in the numerical modeling of this study.

The individual phase pressures are related through the capillary pressures between the phases:

$$P_{gas} = P_{NAPL} + P_{c,gas-NAPL} = P_{water} + P_{c,gas-water} \qquad (6)$$

where P_c is the capillary pressure between two phases defined as

$$P_{c,gas-water} = P_{gas} - P_{water};\, P_{c,gas-NAPL} = P_{gas} - P_{NAPL};\, P_{c,NAPL-water} = P_{NAPL} - P_{water} \qquad (7)$$

Water is normally the wetting phase, NAPL the intermediate wetting phase and gas the non-wetting phase, and this wettability order was adapted in this study. Thereby the pressures of each phase decrease in following $P_{gas} > P_{NAPL} > P_{water}$, which makes the capillary pressure positive.

Capillary pressure-saturation

The capillary pressure is a function of phase-saturation. Thus in order to determine the individual phase pressures these functions have to be described. Further these functions are needed for describing relative permeabilities for the individual phases. For environmental applications the most commonly used parametric models for describing the capillary pressure-saturations relationship are the van Genuchten (1980) and the Brooks and Corey (1966) models. These models were originally formulated for two-phase systems. Parker et al. (1987) suggested a scaling procedure that extended the model applications to three-phase systems. The van Genuchten model is used in this study (Parker et al, 1987):

$$P_{c,gas-NAPL} = \frac{\rho_w g}{\beta_{gn}\alpha}\left(\bar{S}_l^{-\frac{1}{m}} - 1\right)^{\frac{1}{n}}; \quad P_{c,NAPL-water} = \frac{\rho_w g}{\beta_{nw}\alpha}\left(\bar{S}_w^{\frac{-1}{m}} - 1\right)^{\frac{1}{n}} \qquad (8)$$

Where α, n and m are parameters which can be found by fitting the van Genuchten two phase expression to data obtained from displacement experiment from a two-phase system (usually displacement of water by air). Certain restrictions can be put on m, depended on which type of S-k relations is used during modeling. The effective saturations of equation (8) are defined as follows:

$$\bar{S}_w = \frac{S_w - S_{wr}}{1 - S_{wr}}; \quad \bar{S}_l = \frac{S_w + S_n - S_{wr}}{1 - S_{wr}} \qquad (9)$$

Where S_w and S_n is the wetting fluid and intermediate wetting fluid saturations, respectively and S_{wr} is the residual wetting fluid saturation. The scaling procedure proposed by Parker et al. (1987) involves application of so called "scaling parameters". Employing two phase air-water system as reference, these scaling parameters are calculated as (Lenhard and Parker, 1987)

$$\beta_{nw} = \frac{\sigma_{gw}}{\sigma_{nw}}; \quad \beta_{gn} = \frac{\sigma_{gw}}{\sigma_{gn}} \qquad (10)$$

where σ is the interfacial tension between the phases water (w), NAPL (n) and gas (g). In absence of NAPL phase the gas-water capillary pressure is calculated from

$$P_{c,\,gas-water} = P_{c,gas-NAPL} + P_{c,\,NAPL-water} \qquad (11)$$

For this to correctly reduce to the two-phase capillary pressure it is required that (cf. equation (8))

$$\frac{1}{\beta_{gn}} + \frac{1}{\beta_{nw}} = 1 \qquad (12)$$

Keeping this constraint, discontinuous jumps in saturations are avoided when multiphase flow models changes between two and three-phased systems (Wipfler and van der Zee, 2001, Lenhard and Parker, 1987).

In the described model the capillary pressure is a function of saturation and fluid-dependent scaling parameter. As shown in equation (10) the scaling parameter is a constant based on the interfacial tensions. It is well known however, that interfacial tension may vary with concentrations of dissolved contaminants. Oostrom et al. (2003) shows that the presence of tetrachloride (CCl_4) vapors in an unsaturated sand column results in considerable drop in the water-air interfacial tension, due to partitioning of CCl_4 vapor into the aqueous phase. The drop in interfacial tension causes drainage to occur in the columns. Oostrom et al. (2003) suggest the use of a scaling factor to convert between water saturation-capillary pressure data of “clean” and “contaminated” systems. In this study however, scaling parameters defined by equation (10) has been used.

Relative permeability-saturation

In environmental applications the two most commonly used relative permeability models are those of Burdine (1953) and that of Mualem (1976). The Burdine model, which was used in this study, tends to predict lower relative permeabilities than the Mualem model (Oostrom and Lenhard, 1998). The Burdine relative permeability is described as (Burdine, 1953):

$$k_{rw}\left(\bar{S}_w\right) = \bar{S}_w^2 \frac{\int_0^{\bar{S}_w} \frac{1}{P_c^2(x)} dx}{\int_0^{1_w} \frac{1}{P_c^2(x)} dx} \qquad (13)$$

When combining the Burdine relative permeability model with the van Genuchten (1980) capillary pressure-saturation relationship closed form expressions can be derived for the relative permeability curves. van Genuchten (1980) developed a water relative permeability expression for a two phase water/air system using the Burdine model based on the assumption that m = 2-1/n and n>2 ($m \in [0, 1]$). van Genuchten (1980) also derived a similar expression, using the Mualem relative permeability model, however this expression is based on the assumption that m=1-1/n and n>1. Thereby the factor m in the van Genuchten expression describing capillary pressure-saturation relationship is defined by the type of relative permeability model is being used. Parker et al. (1987) extended the two-phase relations to three phases resulting in the following Burdine expressions (see e.g. White and Oostrom, 1996)

$$k_{rw} = \overline{S}_w^{\,2}\left(1-\left(1-\overline{S}_w^{\frac{1}{m}}\right)^m\right),\ k_{rn} = \overline{S}_n^{\,2}\left(\left(1-\overline{S}_w^{\frac{1}{m}}\right)^m-\left(1-\overline{S}_l^{\frac{1}{m}}\right)^m\right),\ k_{rg} = \overline{S}_g^{\,2}\left(1-\overline{S}_l^{\frac{1}{m}}\right)^m \quad (14)$$

where the effective phase saturations for water ($\overline{S}_w$) and total liquid ($\overline{S}_l$) is calculated from equation (9) and the effective NAPL and gas saturations are given by

$$\overline{S}_n = \frac{S_n}{1-S_{wr}}; \quad \overline{S}_g = \frac{S_g}{1-S_{wr}} \qquad (15)$$

The scaling procedure deduced by Parker et al. (1987) is based on the assumption that NAPL as the intermediate wetting fluid, when present, spreads over the water phase as a NAPL film (the so-called Lewerett assumption). This means that disconnected NAPL (residual NAPL) is not accounted for in the relative permeability expressions, and using the Parker et al. (1987) scaling procedure as presented above does not allow for the presence of residual NAPL in the unsaturated zone. As a result NAPL injected into the unsaturated zone will be fully mobile and migrate through the zone without leaving behind “tracks” of residual NAPL saturations. All though formation of residual, discontinuous NAPL saturations are not yet well understood (Oostrom et al, 2003) it is generally accepted that non-spreading NAPLs can be retained in the vadose zone (i.e. Oostrom et al., 2003; Wipfler and van der Zee, 2001). The experiments performed in this study also showed that TCE was retained at low saturation within the sand packs. Using the relative permeability expression described above (equation 14) in combination with the effective saturations defined by equation (9) and equation (15) results in model simulations, where injected NAPL migrates through the pack, and spread at the bottom of the tank (below the water table). Therefore residual NAPL needed to be incorporated into the effective NAPL saturation (equation (15)). The method proposed by Schmidt et al. (2002) and Gudbjerg (2003) was used in which effective NAPL saturation is expressed as

$$\bar{S}_n = \frac{S_n - S_{nr}}{1 - S_{wr}} \qquad (16)$$

In this manner the releative permeability for NAPL approaches zero, when the actual NAPL saturation (S_n) approaches a prescribed value for NAPL residual saturation (S_{nr}).

As mentioned above using the van Genuchten-Burdine relative permeability model (VGB-model) puts constraints on the fitting parameter m originating from the van Genuchten capillary pressure-saturation relationship ($m=1-2/n$, $m \in [0,1]$). During simulation of the laboratory experiments, however, the constraint on m had to be relaxed for the coarse sand of the laboratory packs. In order to obtain acceptable fits between simulated and observed results, m was considered as a fitting parameter.

4.3 Modeling results

T2VOC was used to simulate results of the laboratory experiments performed during this study (section 4.3.1) and further to perform a study on the sensitivity of the efficiency of pneumatic venting towards changing selected parameters (section 4.3.2).

4.3.1 Modeling laboratory experiments

During modeling of laboratory experiments, the experiments were divided into two groups: constant flow experiments and pneumatic venting experiments. The first group of experiments was utilized for calibration of the model, whereas the second group was used for model testing and evaluation of the processes responsible for the effect of pneumatic venting.

Modeling of the homogenous packs appeared to be rather straight forward, since NAPL distribution and matrix permeability as a whole was relatively homogenously distributed. In contrast it was not possible to simulate the heterogeneous packs (traditional venting) to the same degree of accuracy mainly because of heterogeneities in NAPL distribution within the fine lens. These heterogeneities was observed visually in the laboratory experiments, but were not included in the model, due to their arbitrary nature. Instead two different model parameterizations were tested in an attempt to match the laboratory results. In these two simulations two different parameters for the absolute vertical permeability of the lens ($k_{z\ lens}$) were used, $k_{z\ lens}= 1.6\cdot 10^{-11} m^2$ and $k_{z\ lens}= 5.0\cdot 10^{-11} m^2$, respectively. Since the Het1 and Het2 venting experiments were performed on the same pack, deviations in obtained vertical lens permeability should not occur. Thus the "true" vertical lens permeability is assumed to lie within this permeability range, and failing to determine this "true" value is assumed to be caused by inadequate description of NAPL distribution within the lens of the model pack.

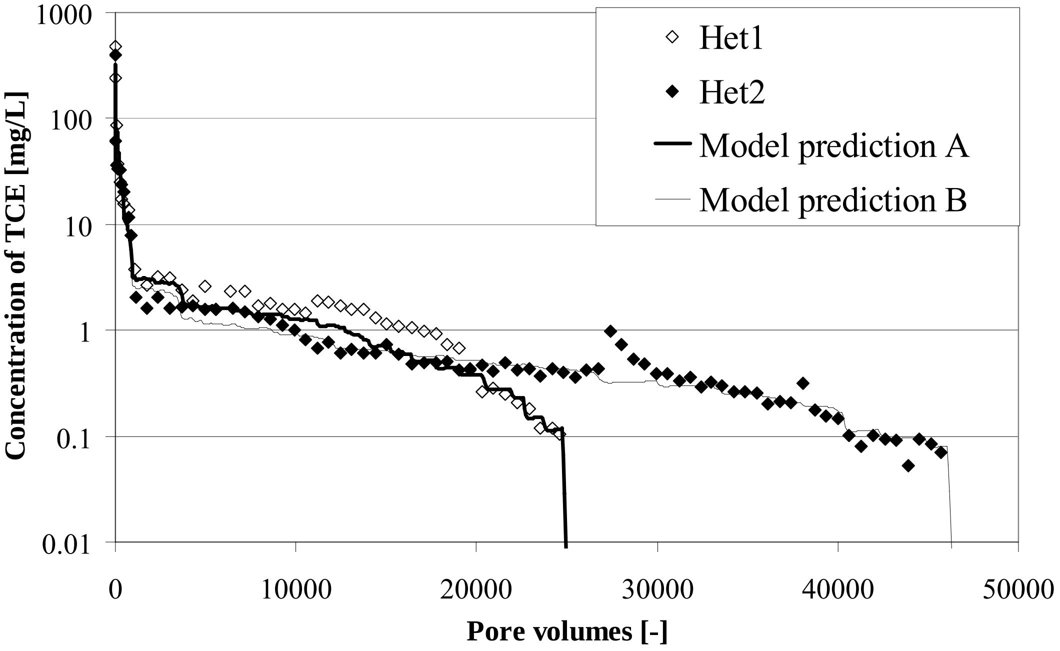


Figure 5 Outlet concentration and model predictions from the heterogeneous packs. Two model are applied, one using $k_{z,lens}$= 5.0 $\cdot 10^{-11} m^2$ (Model prediction A) and one using $k_{z,lens}$= $1.6\cdot 10^{-11} m^2$ (Model prediction B)

Figure 5 shows the outlet concentrations from the Het1 and Het2 experiments plotted along with the results of the two model predictions. From the figure is seen that when using $k_{z\ lens}= 1.6\cdot10^{-11}m^2$ the outlet concentrations of the Het2 experiments are matched, whereas when using $k_{z\ lens}= 5.0\cdot10^{-11}m^2$ the outlet concentrations of the Het1 experiments are matched.

The two parameterizations obtained by calibration were subsequently applied to the pneumatic venting experiments. Pneumatic venting was introduced in the model by specifying the following boundary conditions: The closed inlet period was modeled by a no flow boundary condition at the inlet end and a prescribed measured pressure boundary condition at the outlet end. The open inlet period was modeled by specifying constant atmospheric pressure at the inlet and a prescribed gas flow at the outlet. Figure 6 shows the outlet concentrations from the pneumatic experiments. The figure shows that in general the match between model and laboratory results were satisfactorily with a slight tendency of the model to overestimate the TCE removal during pneumatic venting. Possible explanations for this discrepancy include inaccurate specification of the NAPL distribution within the fine lens and neglect of dispersion in the gas phase.

The modeling of the Pneum1 and Pneum2 experiments revealed that gas expansion is the most important mechanism for enhanced removal of the pneumatic venting technique. In the "low pressure" periods, gas expands within the pack, pulling out large amounts of VOC from the fine lens. Gas expansion mobilizes VOC fluxes at every single point of the plume area. Only relative small amounts of the VOC being pulled out reaches the outlet during the low pressure period, and large amounts stays within the coarse sand of the pack. When gas pressure is released by opening the inlet valve, the majority of the VOC residing in the coarse sand is transported to the outlet, and only a smaller part flow back into the lens as a consequence of gas compression.

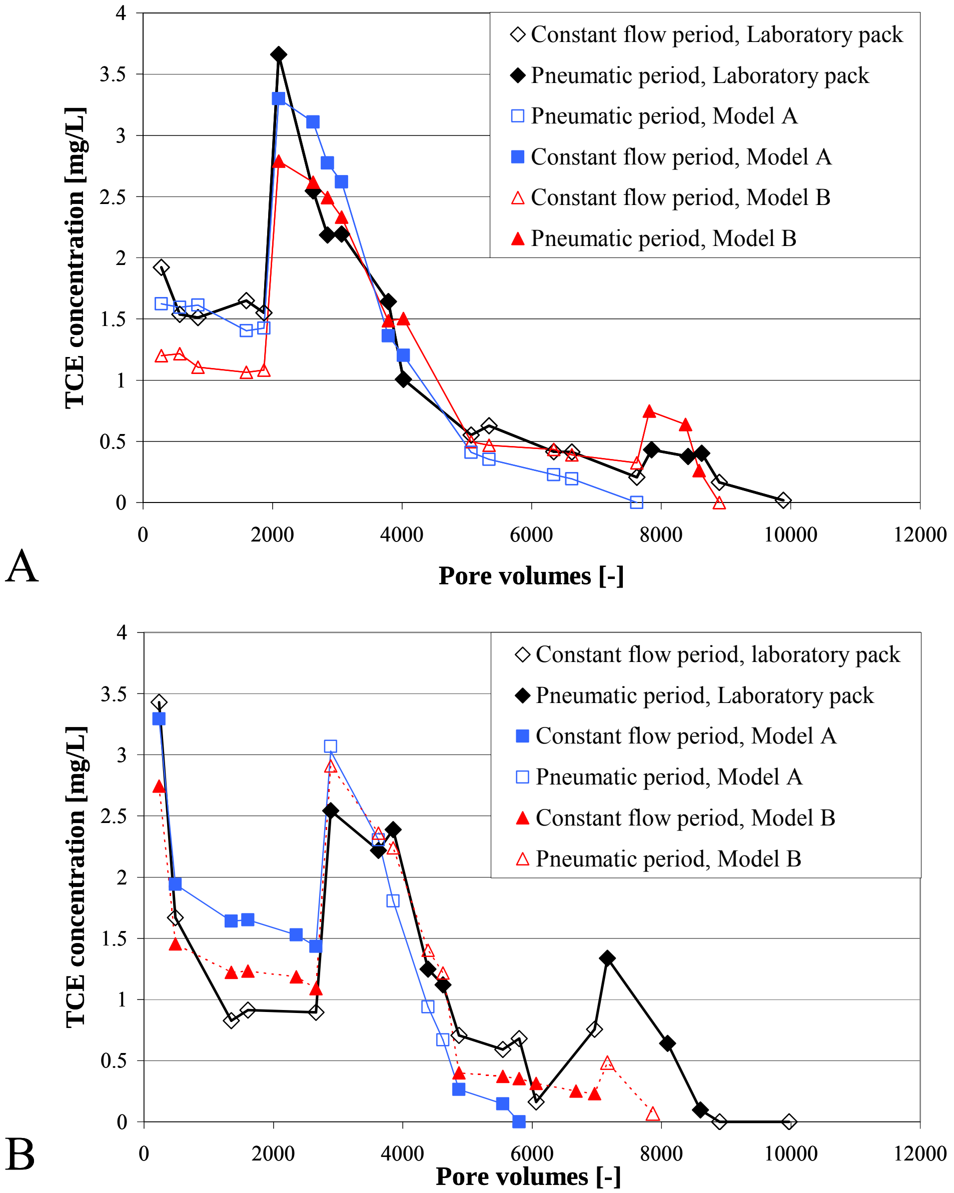


Figure 6 Observed and predicted outlet concentrations from the Pneum1 pack (A), and observed and predicted outlet concentrations from the Pneum2 pack (B). Simulations are performed for two different values of absolute vertical permeability of the fine lens: $k_{z,lens}=1.6\cdot10^{-11}$ m^2(Model B) and one using $k_{z,lens}=5.0\cdot10^{-11}$ m^2 (Model A).

4.3.2 Results of sensitivity analysis

A sensitivity analysis was performed in order to examine how the efficiency of the pneumatic venting technique changes with selected parameters. The parameters selected for sensitivity analysis comprised initial NAPL distribution, absolute lens permeability and the magnitude of the total pressure drop imposed on the system. Figure 7 shows the outlet gas pressure conditions and the initial NAPL distributions used for the sensitivity study. The outlet gas pressures were obtained by prescribing gas flow as the outlet boundary.

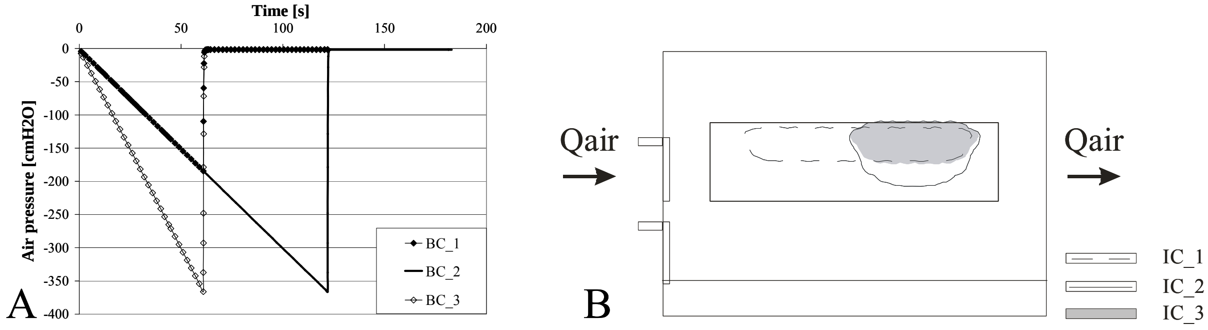


Figure 7 Outlet gas pressure (A) and initial NAPL spreading (B) used in simulations of the sensitivity study.

The results of the sensitivity simulations were compared to a reference simulation, which was performed using initial NAPL distribution named "IC_1" and the boundary condition named "BC_1" (see Figure 7). In addition to the described simulations, constant flow venting simulations were performed using initial NAPL distributions and outlet air flows corresponding to the pneumatic scenarios. These simulations were performed in order to be able to compare performances of the pneumatic and constant venting for the different scenarios. Tables 1 and 2 provide an overview of the simulations performed during the sensitivity study, whereas Figure 8 presents the outlet concentrations for the simulations performed using pneumatic venting (Figure 8A) and constant flow venting (Figure 8B).

Table 1 Pneumatic simulations performed during sensitivity study. “Original lens permeability” refers to the absolute lens permeability obtained by calibration of the laboratory packs ($k_{z,lens}$=5.0·10^{-11}m^{2}).

Simulation	Outlet boundary	Initial TCE distribution	Lens permeability
P_A1	BC_1	IC_1	Original lens permeability
P_A2	BC_1	IC_2	Original lens permeability
P_A3	BC_1	IC_3	Original lens permeability
P_B1	BC_2	IC_1	Original lens permeability
P_B2	BC_3	IC_1	Original lens permeability
P_C1	BC_1	IC_1	Lens permeability is reduced by a factor of 10 in x-and z-directions

Table 2 Constant flow simulations performed during sensitivity study. “Original lens permeability” refers to the absolute lens permeability obtained by calibration of the laboratory packs ($k_{z,lens}$=5.0·10^{-11}m^{2}).

Simulation	Outlet boundary	Initial TCE distribution	Lens permeability
C_A1	BC_1	IC_1	Original lens permeability
C_A2	BC_1	IC_2	Original lens permeability
C_A3	BC_1	IC_3	Original lens permeability
C_B1*	BC_1	IC_1	Original lens permeability
C_C1	BC_1	IC_1	Lens permeability is reduced by a factor of 10 in x-and z-directions

*Outlet flow corresponds to P_B1 and P_B2 simulations

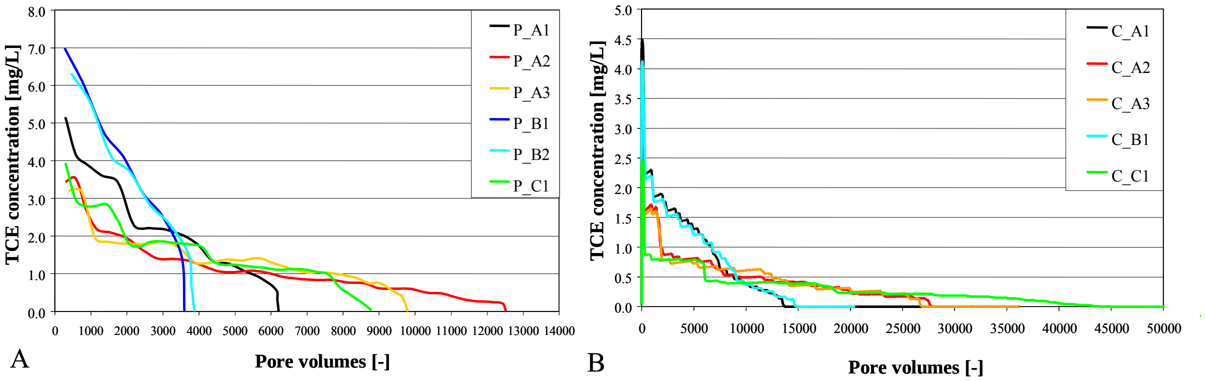


Figure 8 Outlet concentrations from pneumatic simulations (A) and constant flow simulations (B).

Changing the initial NAPL distribution revealed that pneumatic venting was sensitive towards both horizontal and vertical NAPL spreading, as opposed to the technique of constant venting, which showed to be relative insensitive towards the vertical spreading of NAPL. Using both pneumatic and constant venting, the results revealed that the fastest removal time was found for the simulation having large initial horizontal spreading. The reason is that during both pneumatic and constant venting flow paths through the lens is orientated largely from the bottom to the top of the lens. Thereby the cross sectional area for flow through the TCE plume is larger, the larger the horizontal spreading. Larger cross sectional area results in larger removal. Using pneumatic venting the slowest removal was found for the simulation having large vertical spreading, whereas simulations performed using constant venting revealed that the result was largely insensitive to the vertical spreading of NAPL.

Although the removal efficiency of the pneumatic venting was reduced when changing initial NAPL distribution, the pneumatic venting technique in all cases performed considerably better than constant flow venting. For the different initial NAPL distributions, the removal time was increased by a factor of 2.2 to 2.8 when pneumatic venting was applied.

Changing the magnitude of the total gas pressure confirmed that the removal efficiency of pneumatic venting technique was sensitive toward the total pressure drop imposed on the system. Two different approaches were tested. Firstly the pressure drop was doubled by doubling the rate of pressure decrease (i.e. doubling gas flow at the outlet of the pack). This pressure decrease was named “BC_3” at Figure 7. Secondly the pressure drop was doubled simply by extending the “low pressure” period from one to two minutes (See “BC_2” on Figure 7). Results showed that doubling the pressure drop during the “low pressure”-periods resulted in decreased removal times. When pressure drop increased, so did the gas expansion, which ultimately resulted in increased mass fluxes of VOC being pulled out from the fine lens of the pack. Simulations revealed that in terms of volumes of air removed from the system (i.e. volume of air to be treated), the system was largely insensitive to the rate at which the total pressure drop was obtained. In terms of absolute time, however, removing VOC by imposing the larger rates of pressure decreases should be preferred. Simulations showed that doubling the rate of pressure decrease resulted in reduction of the removal time by a factor of 2, whereas doubling the “low pressure” time period resulted in a reduction by a factor of 1.4.

Reducing lens permeability by a factor of 10 resulted in increased removal times for both pneumatic and constant flow venting. For the case of constant flow, the reduction in removal efficiency was solely attributed to reductions in advective flow through the lens. Reduction in advective flow also contributed greatly to the reduced removal of VOC during the “released pressure”-periods (or open inlet period) of the pneumatic cycles, since relative small reductions were found in the amount of VOC being pulled out of the lens during “low pressure”-periods (closed inlet periods). All though removal efficiency of the pneumatic venting technique was reduced when lowering the lens permeability, the removal efficiency of constant flow venting was reduced even further. Thereby pneumatic venting performed even better compared to constant venting, when lens permeability was lowered. Prior to lowering of the permeability the removal time was a factor of 2.2 lower for pneumatic venting, when permeability was reduced this factor increased to 4.8. The reason for this relative increase in performance efficiency was, that in constant flow venting VOC removal depended solely on the magnitude of advective flow through the lens, and therefore the sensitivity towards reductions in lens permeability was far greater using constant flow venting.

In summery the presented simulations showed that using pneumatic venting reduced removal times by a factor in the range of 2.2 to 4.8 as compared to traditional venting. In principle this should make the pneumatic venting technique a promising alternative to constant flow venting in scenarios, where NAPL is to be removed from low permeable areas. Whether or not pneumatic venting can be used in practice is another matter. This issue is addressed in section 6.

5 SUMMERY AND CONCLUSIONS

The background for the presented work is that performance efficiency of conventional soil venting is reduced, when used on soils comprising layers of variable permeability. Conventional soil venting, or constant flow venting, is a standard technique for remediating VOC from the vadose zone soils by enhancing advective transport through a contaminated area. When the contaminated area involves areas of variable permeability, the advective flow through relative low permeable areas is reduced due to flow by-passing. Thereby remediation becomes slow and restoration is delayed considerably. In this study the method of pneumatic venting is proposed as an alternative to constant flow venting of complex subsurface settings. To our knowledge pneumatic venting has not previously been presented in the literature. The technique is based on imposing large transient pressure fronts through the soil, as opposed to the stagnant pressure distribution obtained using constant flow venting. The transient pressure fronts are induced by generating substantial pressure drops in the gas phase of soil and subsequently release pressure.

The pneumatic venting technique was hypothesis to improve venting efficiency for several reasons: Firstly when large pressure drops are imposed on the system, gas will expand and VOC fluxes will be mobilized from within low permeable areas towards the higher permeable areas. When air pressure subsequently is released large gas fluxes and thereby large amounts of advective flow will be generated within the high permeable area, resulting in increased VOC removal from the system. One side effect of releasing pressure was however foreseen; when pressure is released gas compression takes place and backflow of VOC from the coarse sand to the fine lens will occur. The efficiency of pneumatic venting thus relies on the amount of VOC removed due to advective flow through the coarse sand to be larger than the amount being pulled back into the lens.

Secondly shifting flow directions originating from expansion/compression of gas was expected to induce mixing of VOC within the gas phase of the low permeable lens. The induced mixing was hypothesized to contribute to increased VOC removal during pneumatic venting.

Thirdly a potential effect of pneumatic pumping is caused by the generation of non-stationary pressure field. The pressure fronts will continuously move through the contaminated soil and .permanent stagnation points, where no flow takes place, will therefore be avoided. This point of the hypothesis was not tested in this study, since permanent stagnation points were not present in the model set-up.

The main objective of this work was to test if the use of pneumatic venting increases removal efficiencies compared to constant flow venting, and if so, to pinpoint the principle mechanisms responsible for the improved removal efficiency.

In order to meet these objectives, soil venting operations were performed in 2D-tank laboratory experiments. Two different techniques were tested; the technique of constant flow venting and the technique of pneumatic venting. Results from constant flow laboratory experiments clearly demonstrated the limitations of the constant flow technique, when dealing with removal of NAPL from low permeable layers of the soil. When half of the TCE plume was placed within a low permeable layer, the removal time was increased by two orders of magnitudes. The laboratory experiments also revealed that when changing remediation technique from constant flow to pneumatic venting, removal rates increased by up to 77%.

The laboratory experiments were modeled using the numerical model T2VOC. As a whole T2VOC was able to reproduce laboratory experiments satisfactorily, which suggest that T2VOC is a useful tool in future research on pneumatic venting technique. By use of the numerical model the dominant removal mechanism during pneumatic venting was identified as gas expansion. When pressure is lowered, air is expanding, and thereby gas/VOC fluxes are mobilized within the entire plume area of the low permeable area. Parts of the mobilized VOC are transferred into the coarse layer, whereas parts stay inside the lens during the low pressure period. When pressure subsequently is released VOC within the coarse sand is removed from the system by means of advective flow in the high permeable layer. Some of the VOC, however, re-enters the low permeable layer due to backflow caused by gas compression.

As mentioned above increased mixing was hypothesized to take place within the gas phase of the lens, due to flow directions are repeatedly changed during periods of low pressure and periods of releasing pressure. This effect was not directly quantified in this study, mainly because the effect is difficult to isolate from other processes taking place during pneumatic pumping. However, the effect of mixing is assumed to be of minor importance at least for the scenarios considered in this study. This assumption is based on the following arguments. Firstly the effect of mixing is larger, if directions of flow in low pressure periods deviate considerably from directions of flow during the greater part of periods of releasing pressure (i.e. “constant flow” periods). In such cases VOC that has spread in the lens due to mixing may be transported directly from the lens to the coarse sand. In this study however, directions of flow paths did not deviate significantly. Both during low pressure periods and the greater part of periods of releasing pressure, flow within the fine lens was directed mainly from the bottom of the lens towards the top of the lens. Thereby VOC which had been transported to areas beneath the plume during backflow was transported back into the plume area, when backflow ceased.

Secondly mixing may contribute to a raise in VOC concentrations between the plume area and the upper lens/coarse sand border. Thereby diffusion from the lens could be enhanced by mixing. The effect of increased diffusion is however expected to be greatly overruled by the effect of gas expansion. Thereby when applying pump schemes in which lowering of pressure is imposed with high frequency, the effect of increased diffusion is assumed to be small. Mixing may still be important when the NAPL plume to be removed has spread deeply into the low permeable areas. However, this work only comprised studies of relatively shallow plume spreading within the low permeable area.

Results of the numerical study revealed that the performance of the pneumatic venting technique was sensitive to parameters such as initial NAPL spreading, lens permeability and total pressure drop. Decreasing lens permeability resulted in reduced performance of the pneumatic venting technique. This reduction was for a great part attributed to reduced advective flow through the lens during periods of releasing pressure, and to a lesser degree caused by reduced VOC fluxes from the lens to the coarse sand during “low pressure” periods. Thereby compared to the technique of constant venting, the pneumatic venting technique performed even better at low lens permeabilities.

Changing initial NAPL distribution revealed that the better performance for both pneumatic venting and constant venting was found when NAPL was distributed in such a way that the cross sectional area of flow through the NAPL plume was large. Model runs for other initial NAPL distributions revealed that the technique of pneumatic venting was sensitive to the vertical depth of the plume spreading within the low permeable layer. Simulations showed that the deeper the spreading, the slower the removal. Regardless of initial NAPL spreading, however, the pneumatic venting technique performed better than the technique of constant flow venting. The removal rate of NAPL was more than doubled when using pneumatic venting in preference to constant flow venting.

Finally sensitivity tests on the effect of the magnitude of the total pressure confirmed that the larger the pressure drop, the more effective the pneumatic venting technique becomes. At large pressure drops gas expansion increases, and thereby larger amounts of VOC is transferred from low permeable areas to high permeable areas. Simulations also revealed that the faster removal was found for systems imposed to larger rates of pressure decrease. In other words this means that the bigger the pump capacity of the system is, the faster the removal becomes.

In summery the work presented in this thesis suggest that the pneumatic venting technique may be an attractive alternative to use in preference to constant flow venting, when dealing with removal of NAPL from low permeable areas of layered soil. However, the work presented has tested the technique of pneumatic venting both experimentally and numerically on laboratory scale. Further work is needed to evaluate if pneumatic venting is applicable in the field.

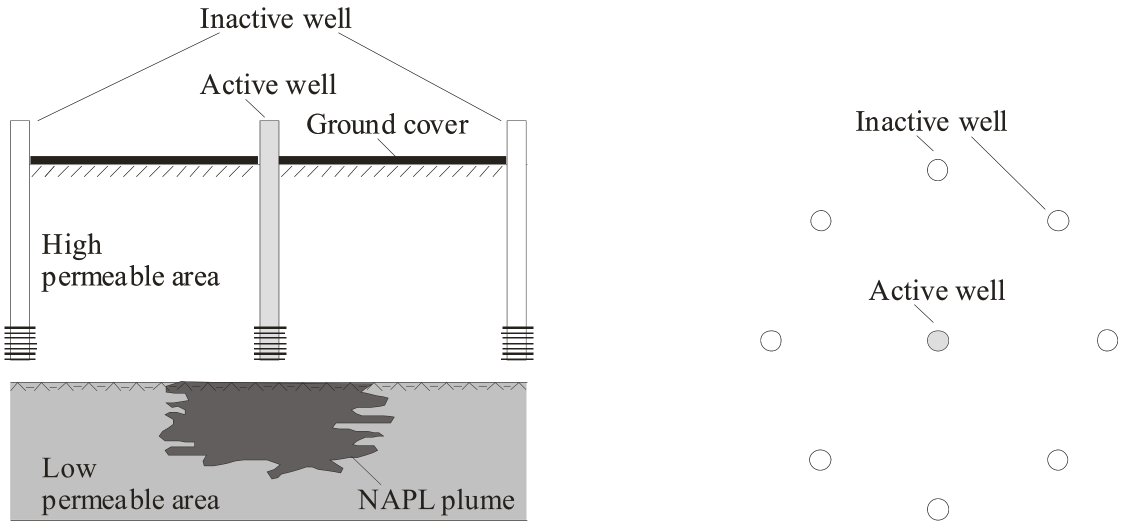
6 PERSPECTIVE

The work performed in this study focused on testing the pneumatic venting technique in a 2D laboratory tank. Though pneumatic venting seemed promising at laboratory scale, chances still are that the performance of the technique could be less ideal in natural soil formations. Thereby to access if pneumatic venting is feasible in natural soils, there are still problems to be addressed. Perhaps the most obvious question is, if it is possible to obtain the relative large pressure drops needed for the pneumatic venting technique to be effective. And secondly; how should the field set-up be constructed in order to perform pneumatic venting?

The answer to the first question is that in some cases implementing pneumatic venting is not straight forward. For instance, problems obtaining the necessary pressure drop will probably arise in field scenarios, where stratified soil posses sequences of high permeable soils overlaying layers of low permeable soil. Problems can be foreseen, if air is allowed to enter freely from the atmosphere to the upper high permeable layer. In these scenarios air short cutting could be expected, resulting in difficulties obtaining the necessary pressure drops. Even if substantial pressure drops is obtained, air short cutting could considerably reduce area of influence of pneumatic pumping. In these situations ground cover may improve the applicability of pneumatic venting. On the other hand, many NAPL spill sites are located in urban or/and industrial areas, in which a large portion of the ground surface is already ceiled by roads, buildings, parking lots, etc.

Other problems of obtaining the necessary pressure drops could stem from horizontal air flow. If the coarse layer overlying a fine layer is too permeable, problems could also arise obtaining the necessary pressure drops. In some scenarios this may be the case; however, numerical tests of different field scenarios would provide a closer insight into this problem. Such tests are needed to assess whether pneumatic venting is an attractive alternative to constant flow venting during field applications, and may very well show, that in some cases pneumatic venting is possible and in some it is not.

In the laboratory, pneumatic venting was implemented by opening and closing the inlet of the tank. At the current stage, how to implement pneumatic venting in the field is nearly a line of thoughts, which of cause should be tested both numerically and in the field. However some ideas are presented in the following; a series of wells should be established, in which an extraction well is located at the center of a circle of “inactive” wells (see Figure 9). The screening of the wells should be located in the high permeable soil layer as close as possible to the low permeable layer. If the horizontal spreading of the plume within the low permeable area is known, the extraction well should preferably be located near the center of plume. The pump at the extraction well should be left running at all times, whereas the rest of the “inactive” wells should be opened and closed using predetermined time intervals, adapting the principle of the open and closed valve interval from the laboratory set-up. Alternatively pumps could be installed at the “inactive wells” if horizontal airflow is high and problems arise achieving the necessary pressure drop. In this case pumping in the surrounding wells could be turned on in the low pressure periods and access to the atmosphere could be allowed in the high pressure periods.



9A

9B

Figure 9 Vertical profile (A) and horizontal profile (B) of field set-up proposed for application of pneumatic pumping

In the previous discussion it has been assumed that geology and plume spreading is relatively well defined at a specific site. However, soil venting is often used on field sites in which limited knowledge exist related to location of low permeable areas and plume spreading. This may results in wells, which are established at less optimal locations. Thus in order to draw firm conclusions on applicability of pneumatic venting, numerical studies should be performed on the sensitivity of the performance efficiency towards well locations.

7 REFERENCES

Armstrong, J.E., Frind, E.O. and McClennan, R.D., 1994. Nonequilibrium mass transfer between vapor, aqueous, and solid phases in unsaturated soils during vapor extraction.Water Resour. Res., 30(2), 355-368.

Baehr, A.L., 1987.Selective transport of hydrocarbons in the unsaturated zone due to aqueous and vapour phase partitioning.Water Resour. Res. 23 (10), 1926-1938.

Baehr, A.L., Hoag, G.E. and Marley, M.C., 1989.Removing volatile contaminants from the unsaturated zone by inducing advective air-phase transport.J. Contam. Hydrol., 4: 1 26.

Baehr, A.L. and Hult, M.F., 1991.Evaluation of insaturated zone air permeability through pneumatic tests.Water Resour. Res., 27 (10), 2605-2617.

Barnes, D.L., 2003.Estimation of Operation Time for soil Vapor Extraction Systems.J. Environ. Eng., 129(9), 873-878.

Burdine, N.T., 1953.Relative permeability calculations from pore-size distribution data. Petroleum Transactions of the American Institute of Mining Engineering, 198, 71-77.

Bloes, M.B., Rathfelder, K.M. and MacKay, D.M., 1992.Laboratory studies of vapour extraction for remediation of contaminated soil. Subsurface Contaminations by Immiscible Fluids, Weyer (ed.), Balkema, Rotterdam. ISBN 90 6191 175 3.

Brusseau, M.L., 1991. Transport of Organic Chemicals By Gas Advection in Structured or Heterogeneous Porous Media: Development of a Model and Aplication to Column Experiments. Water. Resour. Rev., 27 (12), 3189-3199.

Brooks, R.H. and Corey, A.T., 1966. Properties of porous media affecting fluid flow. J. Irrigation Drainage Division, ASCE 92(IR2), 61-88.

Chai, J.-C. amd Miura, N., 2004. Field vapor extractin test and long-term monitoring at PCE contaminated site. J. Haz. Mat. 110, 85-92.

Croisé, J., Armstrong, J.E. and Kaleris, V., 1994. Numerical simulation of rate-limited vapour extraction of volatile organic compounds in wet sands. Transport and Reactive Processes in aquifers, Dracos and Stauffer (eds), Balkema, Rotterdam. ISBN 90 54 10 368 X.

DiGiulio, D.C., Cho, J.S., Dupont R.R., and Kemblowski, M.W., 1990. Conducting field tests for evaluation of soil vacuum extraction application. Proceedings of 4th National Outdoor Action Conference on Aquifer Restoration, Groundwater Monitoring, and Geophysical Methods , NWWA, Las Vegas, NV.

DiGiulio, D.C. 1992. Evaluation of soil venting.U.S. EPA, EPA/540/s-92/004.

Doherty, R.E., 2000. A History of the Production and Use of Carbon Tetrechloride, Tetrachloroethylene, Trichloroethylene and 1,1,1-Trichloroethane in the United States: Part 2- Trichloroethylene and 1,1,1-Trichloroethane. Journal of Environmental Forensics 1, 83-93.

Dullien, F.A.L., 1979. Porous Media: Fluid transport and pore structure. Academic Press, New York, , NY, 396 pp.

Falta, R.W., Pruess, K., Finsterle, S. and Batistelli, A., 1995. T2VOC User's Guide. Lawrence Berkeley Laboratory Report, LBL-36400 University of California, Berkeley.

Falta, R.W., Javandal, I., Pruess, K. and Witherspoon, P.A. Density-driven flow of gas in the unsaturated zone due to the evaporation of volatile organic compounds. Water Resour. Res. 25(10), 2159-2169.

Fen, C.S. and Abriola, L.M., 2004. A comparison of mathematical model formulations for organic vapor transport in porous media. Adv. Water Resour., 27, 1005-1016.

Gierke, J.S., Hutzler, N.J. and McKenzie, D.B., 1992. Vapor transport in unsaturated soil columns: Implications for vapor extraction. Water Resour. Res. 28 (2), 323-335.
Gudbjerg, J., 2003. Remediation by steam injection. Ph.D. Thesis, Environment and Resources, Technical University of Denmark, 2003.

Ho, C.K. and Udell, K.S., 1992. An experimental investigation of air venting of volatile liquid hydrocarbon mixture from homogenous and heterogeneous porous media. Journal of Contaminant Hydrology, 11, 291-316, 1992.

Hayden, N.J., Voice, T.C., Annable, M.D. and Wallace, R.B., 1994. Change in gasoline constituent mass transfer during soil venting. J. Environ. Eng., 120 (6).

Jensen, B.K. and Nilsson, B., 1996. Chlorerede opløsningsmidler i den mættede zone. Miljøprojekt nr. 330, Miljøstyrelsen. (Danish EPA)

Jones, F.O. and Owens, W.W., 1980. A laboratory study of low-permeable gas sands. J.Petrol.Technol., 1631-1640.

Kearl, P.M., Korte, N.E., Gleason, T.A., and Beale, J.S., 1991. Vapor extraction experiments with laboratory soil columns: Implication for Field Programs. Waste Management, 11, 231-239.

Klinkenberg, L.J., 1941. The permeability of porous media to liquids and gases. Drilling and Production Practices, Am. Petrol. Inst., 200-213.

Lenhard, R.J. and Parker, J.C., 1987. Measurement and prediction of saturation-pressure relationships in three-phase porous media systems. J. Cont. Hyd., 1, 407-424.

Massmann, J.W., 1989. Applying groundwater flow models in vapor extraction system design. J. Environ. Eng., ASCE , 115, 129-149.

McWhorter, D.B., 1990. Unsteady radial flow of gas in the vadose zone.
J. Contam. Hydrol., 5, 297-314

Miller, C.T., Chirtakos, G., Imhoff, P.T., McBride, J.F., Pedit, J.A., and Trangenstein, J.A., 1998. Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches. Adv. Wat. Res., 21 (2), 77-120.

Mualem, Y., 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. Wat. Resour. Res., 12, 513-522.

Ong, S.K. and Lion, L.W., 1991. Effects of soil properties and moisture on the sorption of trichloroethylene vapour. Water Research, 25(1), 29-36.

Oostrom, M. and Lenhard, R.J., 1998. Comparison of relative permeability-saturation-pressure parametric models for infiltration and redistribution of the light nonaqueous-phase liquid in sandy porous media. Adv. in water resour., 12, 145-157.

Oostrom, M., Hofstee, C., Lenshard, R.J. and Weitsma, T.W., 2003. Flow behaviour and residual saturation of liquid carbon tetrachloride in unsaturated heterogeneous porous media. J.Cont.Hyd. 64, 93-112.

Parker, J.C., R.J. Lenhard, and T. Kuppusamy., 1987. A parametric model for constitutive properties governing multiphase flow in porous media. Water Resour. Res., 23, 618-624.

Petersen, L.W., Moldrup, P., El-Farhan, Y.H., Jacobsen, O.H., Yamaguchi, T. and Rolston, D.E., 1995. The Effect of Moisture and Soil Texture on the Adsorption of Organic Vapors. J. Environ. Qual., 24, 752 -759.

Preuss, K., 1987. THOUGH User's Guide. Lawrence Berkeley Laboratory Report, LBL-20700 University of California, Berkeley.

Preuss, K., 1991. THOUGH2 – A general purpose numerical simulator for multiphase fluid and heat flow. Lawrence Berkeley Laboratory Report, LBL-29400 University of California, Berkeley.

Schmidt, R., Gudbjerg, J., Sonnenborg, T.O. and Jensen, K.H., 2002. Removal of NAPLs from the unsaturated zone using steam: prevention of downward migration by injection mixtures of steam and air. J. Cont. Hyd., 55, 233-260.

Schulenberg, J.W. and Reeves, H.W., 2002 Axi-symmetric simulation of soil vapor extraction influenced by soil fracturing. Journal of Contaminant Hydrology 57, 189-222.

She, H.Y. and Sleep, B.E., 1999. Removal of Perchloroethylene from Layered Soil system by Steam Flushing. Ground Water Monitoring and Remediation 19, Vol. 2, 70-77.

Smith, J.L., Reible, D.D., Koo, Y.S. and Cheah, E.P.S., 1996. Vacuum extraction of nonaqueous phase residual in heterogeneous vadose zone. J. Haz. Mat., 49, 247-265.

Thorstenson, D.C. and Pollock, D.W., 1989. Gas transport in unsaturated zones: Multicomponent systems and the adequacy of Ficks laws. Water Resour. Res. 25 (3), 477-507.

Thomson, N.R. and Flynn, D.J., 2000. Soil Vacuum Extration of Perchloroethylene from the Borden Aquifer. Ground Water 38, no. 5, 673-688.

Travis, C.C. and Macinnis, J.M., 1992Vapor Extraction of organics from subsurface soils – is it effective? Environ. Sci. Technol., 26(10), 1885-1887.

U.S. EPA, 1991.Innovative Treatment Technologies – Overview and Guide to Information Sources, EPA/540/9-91/002, 1991. U.S. Environmental Protection Agency.

van Genuchten, M.T., 1980.A closed-form equation for predicting the hydraulic conductivity of unsaturated soils.Soil Science Society of America Journal, 44, 892-898.

von Christierson, B, 1997.Soil Vapour Extraction in Heterogeneous Porous Media. M.Sc.Thesis. Department of Hydrodynamics and Water Resources, Technical University of Denmark.

Wakao, N. and Kaguei, S., 1982. Heat and mass transfer in packed beds. Gordon and Breach Science Publishers Inc. ISBN 0-677-05860-8.

Webb, S.W. and Pruess, K., 2003. The use of Ficks law for modelling trace gas diffusion in porous media. Transport in Porous Media, 51, 327 – 341.

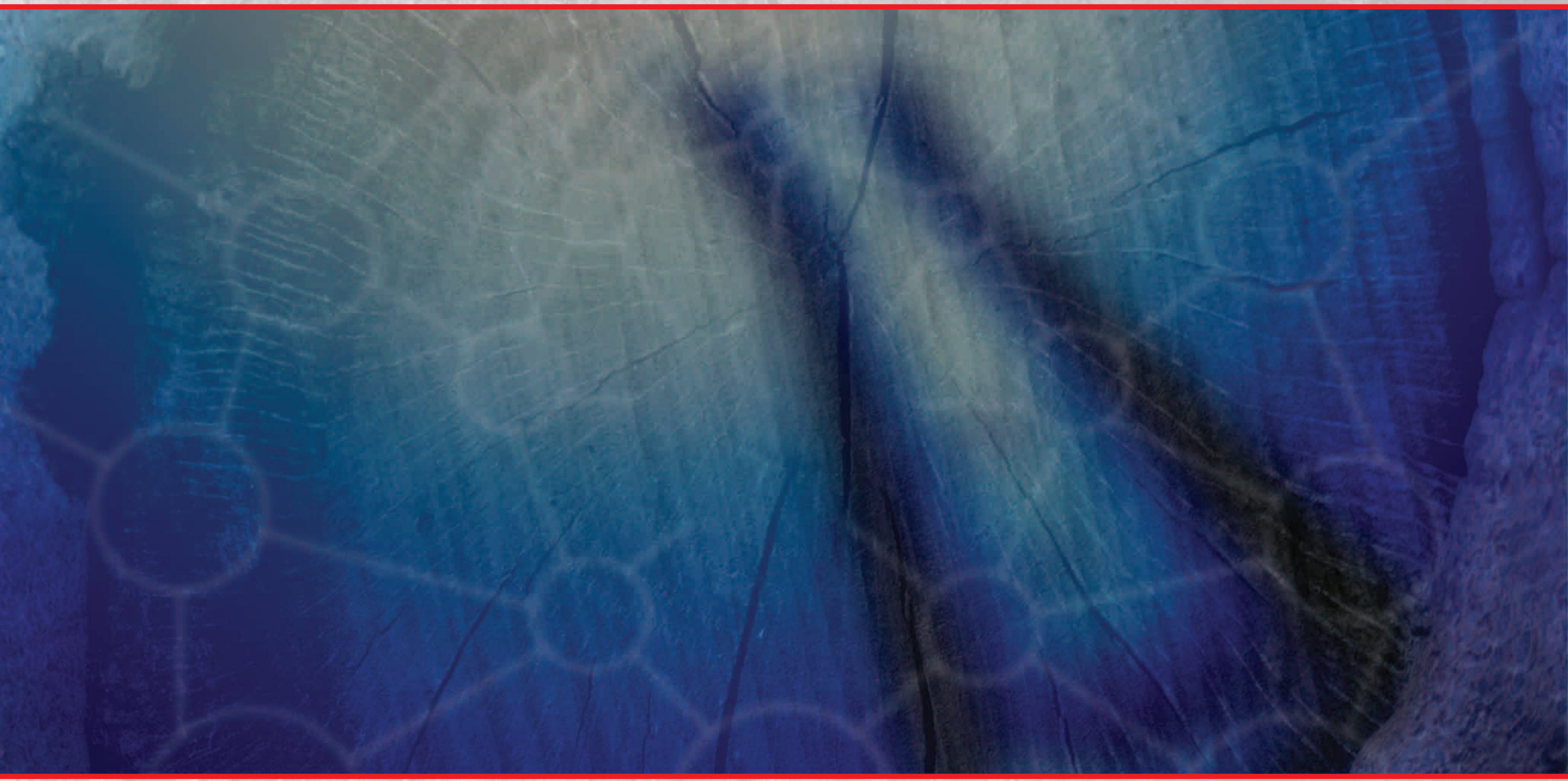
Wehrle, K. and Brauns, J., 1994. Column experiments concerning rate limited vapour extraction of volatile organic compounds from wet sand.Transport and Reactive Processes in Aquifers, Dracos and Stauffer (Eds.), 1994 Balkema, Rotterdam, ISBN 90 54 10 368 X.

Wilson, D.J. and Clarke A. N., 1994. Hazardous waste site soil remediation: Theory and application of innovative technologies. Marcel Dekker, Inc., New York. Editors: Wilson, D.J. and Clarke, A.N.

White, M.D. and Oostrom, M., 1996. Subsurface Transport Over Multiple Phases. Theory Guide, Pacific Northwest National Laboratory, Richland, Washington.

Wipfler, E.L. and van der Zee, S.E.A.T.M., 2001.A set of constitutive relationships accounting for residual NAPL in the unsaturated zone.J. Cont. Hyd. 50, 53-77.

Wu, Y.S., Pruess, K. and Persoff, P., 1998.Gas flow in Porous Media with Klinkenberg Effects.Transport in Porous Media 32, 117-137.



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