Environmental Engineering and Management Journal

November 2018, Vol. 17, No. 11, 2645-2656 http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu



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EXPERIMENTAL STUDY OF *IN SITU* REMEDIATION OF LOW PERMEABILITY SOILS BY BIOVENTING

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Abstract

The goal of the present work is to evaluate the efficiency of bioventing on low permeability soils stimulated with hydraulic fractures and polluted by a mixture of semi-volatile and non-volatile hydrocarbons. A synthetic non-aqueous phase liquid (NAPL) composed of 5 hydrocarbons is prepared: 1,2,4-trimethylbenzene (TMB), methylcyclohexane (MCE), n-dodecane (n-C₁₂), n-decane (n-C₁₀), n-eicosane (n-C₂₀). The capacity of indigenous bacteria to degrade high NAPL concentrations is evaluated with bioventing tests on small soil reactors under favorable and unfavorable conditions. Then, soil polluted with synthetic NAPL at an average concentration ~30g/kg-soil is packed in a tank (0.5m x 0.55m x 0.12m) of poly-methyl-methacrylate (PMMA) and two lenses of coarse-grained sand act as inlet and outlet hydraulic fractures. After the completion of bioventing tests, soil samples are collected to measure the NAPL concentration and composition as well as the potential growth of micro-organisms. A simplified numerical model of ventilation is used to estimate the contribution fraction of volatilization to the overall process efficiency. The NAPL concentration is reduced uniformly over the soil, the indigenous bacteria of soil are active even under toxic conditions, whereas biodegradation is enhanced weakly by the presence of nutrients. The contribution fraction of ventilation to the remediation efficiency is significant for the most volatile compounds (MCE), moderate for the less volatile compounds (TMB, n-C₁₀), and negligible for the non-volatile compounds (n-C₁₂, n-C₂₀), and hence biodegradation is responsible of the removal of a respectable percentage of semi-volatile and non-volatile NAPL compounds.

Key words: bioventing, hydraulic fracture, non-aqueous phase liquid, soil remediation, volatilization

Received: March, 2013; Revised final: January, 2015; Accepted: January, 2015; Published in final edited form: November 2018

1. Introduction

Bioventing combines the advantages of soil venting with enhanced biodegradation to costeffectively remove organic pollutants from the vadoze zone of soils (Dupont, 1993; Eweiss et al., 1998; US EPA, 1995). The air injected in the unsaturated soil stimulates the microorganisms to aerobically biodegrade organic compounds (Sims et al., 1990). Air is supplied at low rates (Baker and Moore, 2000), and the minimum oxygen concentration that does not limit pollutant biodegradation is 2-4% (Miller et al., 1991). Bioventing has been proved very efficient for a great variety of organic pollutants. Among the pollutants tested in lab- and field-scale studies are BTEX (Magalhaes et al., 2009), jet fuel (Hinchee et al., 1991), diesel fuel (Aichberger et al., 2005), polycyclic aromatic hydrocarbons (Garcia-Frutos et al., 2010), kerosene (Shabir et al., 2008), etc. Moreover, bioventing seems a well-promising method for the *in situ* soil remediation for a variety of pollutants such as perchlorate, nitrate, uranium, chromium, halogenated solvents, explosives and pesticides (Höhener and Ponsin, 2014). Among the various organic substances, intermediate order linear and branched alkanes (C_{10} - C_{20}) exhibit the highest

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rates of biodegradation, and are more biodegradable than cyclo-alkanes and aromatics. On the other hand, higher order alkanes ($>C_{20}$) exhibit very low solubility in water and low biodegradability (Chaineau et al., 1995).

In general, the rate of biodegradation of petroleum hydrocarbons trapped in soils depends on the interactions of a great variety of factors related to the pollutant properties (e.g. biodegradability), soil characteristics, and local microbiological conditions (Amellal et al., 2001; Banock et al., 2016; Del'Arco and de Franca, 2001; Dupont, 1993; Höhener and Ponsin, 2014; Labud et al., 2007; Leachy and Colwell, 1990; Rathfelder et al., 1995; Scherr et al., 2007; Song et al., 1990; Zhou and Crawford, 1995). For the rational design of a bio-venting experiment on a contaminated site, it is important to know the kinetics of biodegradation processes as functions of prevailing conditions (e.g. temperature, oxygen content, moisture, type and amount of nutrients, etc) in order to maximize the pollutant biodegradation rate (Shewfelt et al., 2005; Zytner et al., 2001). Air-injection can be combined with other systems to reduce the duration of treatment (Magalhaes et al., 2009).

Only a few systematic studies have been done to assess bio-venting as an efficient method for the removal of non-aqueous phase liquids (NAPLs) from the unsaturated zone of low-permeability soils. A comparative analysis of bioventing treatment in a gasoline-ethanol and gasoline contaminated undisturbed soil showed that the soil toxicity, associated with high concentrations of pollutants, lasts longer and microbiota recover more slowly when ethanol is present (Osterreicher-Cuncha et al., 2004). A systematic experimental study of bioventing in soil contaminated by a mixture of toluene / n-decane showed that toluene is removed in early times by ventilation whereas the decrease of the concentration of n-decane occurs at late times and is mainly due to biodegradation (Molina et al., 2002). Moreover, the remediation efficiency can be optimized by adjusting the air injection rate during remediation (Malina et al., 2002). In low permeability soils, the flow of the nonwetting fluid (e.g. gas phase, NAPL) is governed by preferential flow paths through the porous matrix (Aggelopoulos and Tsakiroglou, 2009) and/or fracture networks (Slough et al., 1999), both comprising a small percentage of the total porosity. After a long period of contamination, the target NAPL pollutant may accumulate in the low permeability porous matrix which has limited accessibility to the highpermeability paths (Harrar et al., 2007; Totsche et al., 2003). In this manner, the conventional vertical wells installed on low permeable media are expected to be inefficient as long as they do not intersect the natural fractures and preferential flow paths. The mass transfer rates of NAPL species between the gas and liquid phases (e.g. diffusion, dissolution, vaporization, etc.) for porous media that are heterogeneous at the pore-scale are so small (Hønning et al., 2007) that a long duration of soil treatment and a high density of wells are required to achieve an efficient remediation. For this purpose, various stimulation technologies have been suggested with the hydraulic fracturing being the most promising one (Hossain et al., 2000). In the present work, bio-venting experiments are performed in two-scales: (i) in small reactors to assess the activity of indigenous bacteria under toxic conditions; (ii) in a large soil tank to examine the cooperative effects of biodegradation and masstransfer processes on the overall pollutant removal efficiency. The soil is polluted with a 5-component synthetic LNAPL at an average concentration ~30g/kg-soil, and humidified air is injected at a constant flow rate. In the soil tank, two coarse grained regions act as injection and extraction hydraulic fractures. After the completion of the tests, soil samples are analyzed with gas chromatography-flame ionization detection (GC-FID), and soil samples are streaked onto nutrient agar plate to confirm the presence and growth of micro-organisms. An approximate numerical model is used to assess the relative contribution fraction of ventilation and biodegradation to the reduction of the concentration of NAPL compounds.

2. Material and methods

2.1. Material and experimental setups

The soil was collected from the Region of Western Greece (Kato Achaia) and used for bioventing tests in small reactors and a large soil tank (Table 1). The synthetic NAPL was a mixture of n-decane (n- C_{10}), n-dodecane (n- C_{12}), n-eicosane (n- C_{20}), methyl-cyclohexane (MCE) and 1,2,4-trimethylbenzene (TMB) and its total concentration was 30g/kg-soil (Table 2). All substances were of analytical grade and, with the exception of n- C_{20} , are basic components of jet fuel. It is worth mentioning that n- C_{20} was added in NAPL due to its very low volatility and recalcitrance.

Bioventing tests were conducted simultaneously on four 500 mL reactors (glass flasks) containing unsaturated soil under varying conditions (Fig. 1): (i) a mixture of soil, synthetic NAPL, and 3distilled (3D) water (moisture saturation, $S_w=0.14$); (ii) a mixture of soil, synthetic NAPL, and aqueous solution of nutrients (5 g/L KH₂PO₄, 3.22 g/L Na₂HPO₄, 2.0 g/L NH₄Cl, 1g/L MgSO₄.7H₂O and 0.1 g/L KCl); (iii) a mixture of soil, synthetic NAPL at total concentration 30 g/kg-soil, and aqueous solution of 1g/L HgCl₂ (abiotic conditions); (iv) a mixture of soil and water (blank test). The nutrients were added to enhance the activity of indigenous bacteria, whereas HgCl₂ was added to assess the effects of abiotic conditions on bio-venting efficiency. The tests on small reactors were done to: (1) confirm the capacity of bacteria to degrade NAPL at high concentration that might be toxic for their growth; (2) adjust the conditions (e.g. variation of pH, addition of nutrients), if necessary, for improving the biodegradation capacity of bacteria. No parametric study was done to clarify the individual effect of each parameter (e.g.

pH, moisture, NAPL concentration & composition, temperature, bacteria type) on the bioventing efficiency.

With the aid of a peristaltic pump and a humidifier (Fig. 1) air was injected at a rate 2.2 mL/min through a coarse-grained sand (grain sizes~1-1.5 mm) of thickness 2 cm, placed on the bottom of each reactor (Fig. 1). The headspace gas was connected with another smaller flask containing a solution of ~0,029M Ca(OH)₂ that reacts with CO₂ and produces CaCO₃ which gradually precipitates (Fig. 1). In order to prevent the diffusive transfer of atmospheric CO₂, a CO₂ trap composed of NaOH pellets inserted in cotton was used (Fig. 1). The pH, moisture, cultivable bacteria population, and NAPL concentration were measured before the initiation and after the completion (~40 days) of the experiments.

In the large-scale bio-venting experiment (Fig. 2), the wet soil (moisture saturation, $S_w=0.14$) was mixed with synthetic NAPL at an average concentration~30 g/kg soil (NAPL saturation, $S_o=0.1$), and packed inside a rectangular tank of polymethyl-methacrylate (PMMA) with height=0.55 m, length=0.5 m and width =0.12 m (Fig. 2). First, the bottom of the tank was packed with a fully water-saturated soil layer of thickness 5 cm. Then, the NAPL-contaminated soil was packed layer by layer in the tank up to a thickness of 40 cm.

During the soil packing, two "hydraulic" fractures of average aperture ~ 2 cm was inserted at depths 10 and 40 cm from the bottom of the tank by replacing the soil with a coarse sand of size 1-1.5 mm.

The polluted soil was covered by a dry layer of soil, and the tank was sealed by tightening two screws on an aluminium plate placed on the PMMA cover plate (Fig. 2).

Humidified air was injected through the lower fracture and exhaust gases escaped through a tube inserted in the middle of the upper hydraulic fracture at an average rate 35 mL/min (Fig. 2). The temperature was recorded continuously at two horizontal positions with the insertion of thermocouples, and the experiment lasted 5 months.

2.2. Analytical procedures

Soil pH was measured with and without the presence of electrolyte (CaCl₂ 0.01 M) at a solid (soil) to liquid (water) ratio 1:1. Weighted quantities of soil and 3D water were added in beakers, stirred strongly and left to settle for 1 hr. Then, they were stirred for 10 s and the pH was measured. After the completion of the tests on the small reactors (Fig. 1), 5 soil samples were collected from each reactor, except for the "blank" one. The concentration of NAPL compounds in soil samples were measured with gas chromatography combined with flame ionization detector (GC-FID). Soon after sampling, the soil samples were precisely weighted $(2.3\pm0.6 \text{ g})$ and placed immediately into 7 mL amber glass vials capped with Teflon-faced silicon septa. In each vial, 4 ml of dichloromethane was added, and the vials were shaken for a couple of hours on an overhead shaker at a speed of 10 rpm.



Fig. 1. Schematic diagram of bioventing tests on small reactors

Table	1.	Soil	properties
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<i>pH</i> (1:1)*	Conductivity (S m ⁻¹)	TOC (% w/w)	Total Porosity (%)	MIP Porosity (D _p <215μm ^{**}) (%)	Pore Diameter Distribution (D _p <215µm)	Permeability (m ²)	Density (kg/m ³)
6.5	0.11	1.4	42.0	32.5	$\langle D_p \rangle = 23 \mu m$ $\langle \sigma_p \rangle = 53 \mu m$	385x10 ⁻¹⁵	1580

*Ratio of soil weight to tri-distilled water weight

**The maximum pore diameter detected with Mercury Intrusion Porosimetry (MIP)



Fig. 2. Schematic diagram of bioventing experiment in soil tank

The organic solution was decanted to a clean vial, desiccated with the addition of Na₂SO₄, and filtered on 0.45-µm PTFE filters with glass syringes. A GC-FID (GC 2014 Shimadzu), equipped with a fused silica capillary column was used to measure the concentrations of the five compounds of synthetic NAPL. After the completion of bio-venting experiment in soil tank, the soil was removed layer by layer, and 54 soil samples were collected from seven horizontal cross-sections and along five vertical directions (Tzovolou et al., 2011). Twenty-seven pairs of samples were collected at distances 3 cm from the front (front side) and back (back side) PMMA plates. Soon after sampling, the soil samples were precisely weighted (1.9±0.4 g) and placed immediately into 7ml amber glass vials capped with Teflon-faced silicon septa. The NAPL extraction procedure as well as their chemical analysis were identical to those applied to small reactors.

After the end of experiments, soil samples were collected from two positions of each small reactor, and seven depths along two vertical positions of the soil tank. An amount of each soil sample weighted precisely (~30 g), was added in flasks containing 100 ml of 3D-sterilized H₂O, and left for 24 h under stirring at room temperature so that micro-organisms were detached from the soil. Then, the suspensions were stirred vigorously and 100 µL of them were transferred to Eppendorfs containing 900 µL of 3Dsterilized H₂O. Afterwards, each suspension was diluted successively five times at ratio 1:10, 100 µL of each new Eppendorf was streaked onto nutrient agar plate, and the plate was placed at the vertical position so that five liquid strips were created by gravity flow. The plates were incubated at 30 °C under aerobic conditions for 24h, and afterwards the microbial colonies of the 3rd dilution were counted (Colony Forming Units - CFU counting). All abovementioned procedures were performed under sterilized conditions after (t=t_{end}) the bio-venting tests. Before the initiation of the bioventing test in soil tank $(t=t_0)$ the microbial colonies were also counted in four soil samples collected from two depths of the front and rear side of the tank (soil+NAPL). CFU counting is used as an additional test to assess the capacity of indigenous bacteria to grow under favourable and unfavourable conditions. It's worth noting that CFU counting is not offered for obtaining quantitative information for the microbial activity kinetics or the real number of cells and can be regarded as a tool for comparative analyses.

For the detection of CO_2 produced during biodegradation, the exhaust gas from each reactor (Fig. 1) passed through a Ca(OH)₂ solution, and any potential turbidity was attributed to the formation of CaCO₃ (white crystals), according to the Eq. (1):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O \tag{1}$$

The formation of $CaCO_3$ was indicative of CO_2 production in the flasks. By weighting the amount of precipitate formed during 48 hrs, and accounting for the reaction stoichiometry and $Ca(OH)_2$ concentration, an average CO_2 production rate was estimated.

2.3. Interphase mass-transfer processes and numerical modeling

For the interpretation of experimental results, the dynamics of biodegradation must be combined with the rates of mass-transfer mechanisms taking place between the three coexisting phases (gas, water, NAPL). The main mechanisms of NAPL removal are illustrated in Fig.3 and are described in detail below. (a) The convective flow of air through a generally heterogeneous porous medium follows high conductivity preferential flow paths, and the intrinsic velocity vector u_g is governed by the gas effective permeability, $k_{g.eff}=kk_{rg}$, of the porous medium, according to Darcy law (Eq. 2).



Fig. 3. Mass-transfer processes in micro-porous matrix during bio-venting

$$\mathbf{u}_g = -\frac{kk_{rg}}{\phi\mu_g}\nabla P_g \tag{2}$$

where k is the absolute permeability, k_{rg} is the gas relative permeability, Φ is the porosity, μ_g is the gas viscosity and P_g is the gas pressure. Due to the uniform distribution of air across the inlet hydraulic fracture, the gas flow can be approximated by a onedimensional upward flow with an average pore velocity, $\langle u_g \rangle$, given by the Eq. (3):

$$\langle u_g \rangle = -\frac{Q_g}{\phi A (1 - S_o - S_w)} \tag{3}$$

where Q_g is the gas flow rate, **A** is the cross-sectional area perpendicular to the flow, and S_o , S_w are the NAPL and water saturation, respectively.

(b) The potential biodegradation of NAPL compounds (either dissolved in aqueous phase or as free phase) by indigenous bacteria consumes oxygen and induces a concentration gradient that enhances the diffusion of oxygen from preferential flow paths to the interior of micro-porous matrix according to the Fick law (Eq. 4):

$$\mathbf{j}_{O_2} = -\rho_g D_{O_2,g}^{eff} \nabla \omega_{O_2} \tag{4}$$

where \mathbf{j}_{O_2} is the mass flux of oxygen, ρ_g is the gas density, ω_{O_2} is the local oxygen mass fraction, and $D_{O_2,g}^{eff}$ is the effective oxygen-air diffusion coefficient given by Eq. (5):

$$D_{O_2,g}^{eff} = D_{O_2,g}^m \frac{1}{F\phi(1-S_g)}$$
(5)

where $D_{O_{2,g}}^{m}$ is the bulk diffusion coefficient of oxygen, *F* is the electrical formation factor Φ is the porosity, and S_{g} is the gas phase saturation. The formation factor, *F*, was determined as the slope of a

line obtained with linear regression to measurements of the electrical resistance of a soil column fully saturated by an aqueous solution of NaCl vs the electrical resistance of the same space fully occupied by the solution, at varying NaCl concentration.

(c) The volatilization rate of NAPL compounds (mass per unit volume per unit time) is controlled by the diffusion of organic pollutant vapors from microporous matrix toward the high conductivity flow paths and is enhanced by the gas concentration gradient, due to the "venting" effect of air flow. Considering that NAPL is an ideal liquid mixture and Raoult law is valid, the transfer rate of a compound, *i*, from NAPL (*o*) to gas (*g*) phase (volatilization rate), $E_{og,i}$, is described by the relation (Rahbeh and Mohtar, 2007) (Eq. 6):

$$E_{og,i} = K_{og,i} \left[\left(\frac{P_i^{sat} M_i}{RT} \right) x_{o,i} - C_{g,i} \right]$$
(6)

where P_i^{sat} , M_i , $x_{o,i}$, $C_{g,i}$ are the vapor pressure, molecular weight, NAPL mole fraction, and gas concentration for compound *i*, *T* is the absolute temperature, *R* is the universal gas constant, and $K_{go,i}$ is the volatilization mass-transfer coefficient. An empirical equation for the calculation of $K_{go,i}$ is Eq. (7) (Anwar et al., 2003):

$$K_{go,i} = 10^{-4.0} \theta_o^{-1.42} D_{i,g}^{-0.35} u_g^{-1.35} \langle d_g \rangle^{-0.65}$$
(7)

where θ_o is the NAPL volumetric content $(=\phi S_o)$, $D_{i,g}$ is the bulk diffusion coefficient of *i* in gas phase, and $\langle d_g \rangle$ is the mean grain size.

(d) The dissolution rate of NAPL compounds in water is controlled by their solubility in water, the dissolution coefficient, and the extent of the area of water/NAPL interphase. In the present problem, the NAPL dissolution coefficient is low, due to the lack of relative motion between NAPL and aqueous phase $(u_w \cong 0, u_o \cong 0)$, low solubility of NAPL compounds in water (Table 2), and limited NAPL/water contact area since the gas phase occupies the largest fraction of porosity. Due to the limited solubility of NAPL compounds in water, the stripping of dissolved NAPL compounds from aqueous to gas phase can be ignored.

Assuming that the advective gas flow is sufficiently high for the rapid sweeping of NAPL vapors $(C_{g,i} \approx 0)$, Eqs. (6) and (7) can be used to estimate approximately the volatilization rates. By ignoring any axial or lateral NAPL and gas concentration gradients over the soil, mass balances for the five compounds in NAPL phase yield (Eq. 8):

$$\frac{dC_{o,i}}{dt} = -K_{og,i} \frac{P_i^{sat} M_i}{RT} x_{o,i}$$
(8)

where the mole fraction, $x_{o,i}$, are converted to mass fractions, $\omega_{o,i}$, through the relations (Eqs. 9-10):

$$x_{o,i} = \frac{\omega_{o,i}/M_i}{\sum_i \omega_{o,i}/M_i}$$
(9)

and

$$\omega_{o,i} = \frac{C_{o,i}}{\sum\limits_{i} C_{o,i}} \tag{10}$$

The NAPL volumetric content, θ_o , can be updated by using the relationship (Eq. 11):

$$\theta_o = \frac{C_t}{\rho_o} \tag{11}$$

where C_t is the total NAPL concentration defined by Eq. (12):

$$C_t = \sum_i C_{o,i} \tag{12}$$

and ρ_0 is the NAPL density defined by Eq. (13):

$$\rho_o = \sum_i \omega_i M_i \tag{13}$$

By defining the dimensionless variables (Eq. 14):

$$c_{o,i} = \frac{C_{o,i}}{C_{t0}}, \ \tau = \frac{t \langle u_g \rangle}{H}$$
(14)

where $C_{t0} = C_t(t=0)$, and *H* is the height of the porous medium, Eqs. (8) and (10) are transformed to the dimensionless ordinary differential equations (ODEs) (Eqs. 15, 16).

$$\frac{dc_{o,i}}{d\tau} = -\frac{\langle u_g \rangle}{HRT} \left(\frac{K_{og,i} P_i^{sat} \omega_{o,i}}{\sum_i \omega_{o,i} / M_i} \right)$$
(15)

and

$$\theta_o = \frac{C_{t0}}{\sum_{i} \omega_i M_i} \sum_{i} C_{o,i} \tag{16}$$

3. Results and discussion

3.1. Bio-venting tests on small reactors

After the end of the small-scale bioventing tests, the microbial enumeration tests revealed the presence of active microbial population even under unfavourable conditions (Fig. 4). It was observed that a respectable concentration of microbial colonies was counted in all cases including the "Abiotic" case (Fig. 4, Table 3). Evidently, the quantity of HgCl₂ added in the soil was not sufficient to prevent entirely the growth of bacteria. Initially, the microbial activity was suppressed given that the rate of CO₂ production was nil (Fig. 5). When the amount of Hg²⁺ (toxic factor) was adsorbed in the soil, the growth of bacteria was reactivated and this is reflected in the increase of CO₂ production rate after the 27th day (Fig. 5).

Moreover, HgCl₂ is not toxic for all microorganisms, and the growth of some microbial populations might be suppressed while some other microbial populations remained unaffected. It is worth mentioning that differences were observed not only with respect to the number of microbial colonies per sample, but also with respect to the type of microbial colonies, although no identification was done.

Property	Methyl- cyclohexane	1,2,4- Trimethyl benzene	n-C10	n-C12	n-C20
Mole fraction in NAPL	0.2	0.2	0.2	0.2	0.2
Molecular formula	C7H14	C9H12	C10H22	C12H26	$C_{20}H_{42}$
Molar mass, g/mol	98.2	120.2	142.3	170.3	282.5
Density (T=25°C) kg/m ³	774	880	730	750	1260
Viscosity (T=20°C) (mPa s)	0.735	1.01	0.921	1.49	3.28 (T=50°C)
Normal boiling point (°C)	101	169	174.1	216.2	345.1
Vapour pressure at 25 °C (Pa)	6133	267	182	17	0.4 (T=71°C)
Solubility in water at 25°C (mg/L)	14.6 (25°C)	56.5 (25°C)	0.015 (25°C)	0.0037 (25°C)	n.a.

Table 2. Physical and chemical properties of NAPL compounds

The indigenous microbial colonies are able to grow at the selected moisture value under varying conditions (Table 3). The optimal soil pH value for the growth of bacteria is close to 7.0 whereas the pH range that ensures effective bio-venting ranges from 5.5 to 8.5. Therefore, the conditions in the small reactors were adequate for bioventing (Table 4). The reduction of NAPL concentration is shown in Fig. 6. For the various compounds of NAPL, the removal efficiency follows their volatility, and ventilation seems to become the dominant mechanism of remediation



(c)

under abiotic conditions (Fig. 6). For the non-volatile compounds (n- C_{12} , n- C_{20}), the removal efficiency is more sensitive to the environmental conditions, which may favour (presence of nutrients) or inhibit (abiotic conditions) the growth of bacteria (Fig. 6). Microorganisms were active and a significant reduction of n- C_{12} , and n- C_{20} concentration might be attributed to biodegradation. The reduction of the concentration of n- C_{20} , a non-volatile and recalcitrant compound, in combination with the existence of active microbial population confirmed that biodegradation occurred.



Fig. 4. Stereoscopic images of the growth of microbial colonies after the completion of bioventing tests on small reactors: (a) "NAPL", (b) "Nutrients", (c) "Abiotic" and, (d) "Blank"



Fig. 5. Estimates of the CO₂ production rate in small reactors under varying conditions of bioventing. The production rates were estimated by measuring the amount of CaCO₃ precipitated during a period of 48hrs



Fig. 6. Reduction of the NAPL compound concentration in soil samples of small reactors under different bioventing conditions

Table 3. Soil moisture (% w/w) and microbial colonies counts after bioventing tests in small reactors

Small reactor	Moisture (% w/w)	CFU/kg-soil
(i) "NAPL"	13.2	66x10 ⁹
(ii) "Nutrients"	14.0	72x10 ⁹
(iii) "Abiotic"	14.4	62x10 ⁹
(iv) "Blank"	14.2	8.3x10 ⁹

Samula	pH (T=22.5 °C)	pH (T=25.3 °C)
Sample	$t=t_0$	$t=t_{end}$
Soil: H ₂ O (1:1)	5.8	-
Soil: CaCl ₂ 0.01 M (1:1)	5.7	-
Soil-NAPL: H ₂ O (1:1)	6.3	-
Soil-NAPL: CaCl ₂ 0.01 M (1:1)	6.0	-
"NAPL" (1:1)	-	7.5
"NAPL" (CaCl ₂ 0.01 M) (1:1)	-	6.7
"Nutrients" (1:1)	-	7.0
"Nutrients" (CaCl ₂ 0.01 M) (1:1)	-	6.1
"Abiotic" (1:1)	-	6.9
"Abiotic" (CaCl ₂ 0.01 M) (1:1)	-	6.4
"Blank" (1:1)	-	5.6
"Blank" (CaCl ₂ 0.01 M) (1:1)	-	6.2

Table 4. pH values before and after bioventing experiments in small reactors

From bio-venting tests on small reactors, it becomes clear that the indigenous bacteria of soils were active, the high concentration of NAPL was not toxic for bacteria, the presence of nutrients was of secondary importance for biodegradation, whereas the experimental conditions (temperature, pH, moisture) were suitable for biodegradation to proceed.

3.2. Soil tank bio-venting experiment

The experimental conditions at the beginning and end of experiment (Table 5) were favourable for biodegradation to occur. The GC/FID analyses of the 54 soil samples revealed a significant concentration reduction for the majority of NAPL compounds.

The most volatile compounds MCE and TMB were removed totally from the soil (Table 6). The concentration of $n-C_{10}$ and $n-C_{12}$ was reduced substantially (98-100%) and uniformly over the entire

soil (Table 6), whereas the removal efficiency of n-C₂₀ ranged from 60% to 90% (Table 6, Fig.7a,b). The highest removal efficiencies of n-C₂₀ (>95%) were detected beneath the injection hydraulic fracture and the lowest ones (<40%) were detected in the back side and above the injection hydraulic fracture (Fig. 7a,b). The reduction of n-C₂₀ concentration, which is a nonvolatile and weakly biodegradable compound, is expected to increase at locations where the air flow velocity and therefore the supply of oxygen is maximized. It seems that, because of pore space heterogeneities generated during soil packing in the tank, the gas flow rate is quite high below the injection fracture and this is reflected in higher n-C20 biodegradation rate) compared to that observed in upper layer (Fig. 7). Unfortunately, a limited number of datasets with the CO₂ concentration in effluents was collected and it was unable to do any mass balance of the residual NAPL and released CO₂.

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Table 5. Moisture, pH and microbia	l concentration in soil befo	ore and after the end of bio	o-venting experiment in soil tank
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Parameter	Initial value	Final value
Moisture (%, w/w)	10.7	15.9
pH (1:1)	5.8 (T=21 °C)	6.3 (T=28 °C)
Microbial concentration (cfu/kg soil)	Soil+H2O (15.6±6.0)x10 ⁹ Soil+NAPL (15.2±0.7) x 10 ⁹	(30.1±10.7)x 10 ⁹

Table 6. Spatial distribution of NAPL compound removal efficiency (%)

	Weight	Front s	Front side of soil		Back side of soil		Entire soil	
NAPL compound	fraction	Mean value	Standard Deviation	Mean value	Standard Deviation	Mean value	Standard Deviation	
MCE	0.2	100	-	100	-	100	-	
TMB	0.2	100	-	100	-	100	-	
n-C ₁₀	0.2	99.9	0.11	99.9	0.09	99.9	0.1	
n-C ₁₂	0.2	98.2	1.9	98.4	2.3	98.3	2.1	
n-C ₂₀	0.2	72.8	13.9	75.0	18.1	73.9	16.1	
NAPL	1.0	94.2	3.1	94.7	4.1	94.4	3.6	



Fig. 7. Equi-percentage contours of n-C₂₀ removal from the (a) front and (b) back side of soil tank (the position of hydraulic fractures is illustrated)

Table 7. Physicochemical	parameters and	initial conditions	used in simulations
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Property	Value
Н	0.55 m
Qg	0.58x10 ⁻⁶ m ³ /s
А	0.06 m ²
R	8314 N m ⁻¹ Kmol ⁻¹ K ⁻¹
Т	298 K
Ct0	47.4 kg/m^3
$\omega_{o,MCE}(t=0)$	0.1207
$\omega_{o,TMB}(t=0)$	0.1478
$\omega_{o,n-C10}(t=0)$	0.1749
$\omega_{o,n-C12}(t=0)$	0.2093
$\omega_{o,n-C20}(t=0)$	0.3473
D _{g,O2-air}	$2.2 \times 10^{-5} \text{ m}^2/\text{s}$
D _{g,MCE-air}	7.86x10 ⁻⁶ m ² /s
Dg,TMB-air	6.87x10 ⁻⁶ m ² /s
D _{g,n-C10-air}	5.82x10 ⁻⁶ m ² /s
Dg,n-C12-air	5.19x10 ⁻⁶ m ² /s
Dg,n-C20-air	3.79x10 ⁻⁶ m ² /s

3.3. Numerical modeling of volatilization

The gas phase molecular diffusion coefficients for the various NAPL compounds, $D_{g,i}$, appearing in Eq. (7) were calculated by using the Wilke-Lee modification of the Hirschfelder-Bird-Spotz method (Table 7) which is recommended for mixtures of gases, and more details of the method are reported in Treybal (1981). The ODEs, Eq. (15) along with Eqs. (7), (9), and (16) were solved numerically with Athena Visual Studio software package (Stewart and Associates, Inc., USA). The input parameter values are given in Table 7, whereas the numerical results are shown in Fig. 8. It is evident that over the time scale of soil tank experiment $(t_{end} \cong 5 \text{ months or }$ equivalently $\tau_{end} \cong 700$), the volatilization coupled with advective gas flow (venting) may lead to the complete removal of MCE and might be responsible of a significant reduction of TMB and n-C10 concentrations (Fig.8). On the other hand, the simulation indicates that only a small percentage of n-C₁₂ concentration reduction could be attributed to ventilation, whereas the n-C₂₀ concentration remains almost unaltered (Fig. 8).

Subsequently, ventilation by itself seems unable to explain the experimentally observed significant reduction of $n-C_{12}$ concentration along with a respectable reduction of $n-C_{20}$ concentration (Table 6, Fig. 7).



Fig. 8. Numerically simulated transient responses of dimensionless NAPL compound concentrations

Therefore, it is reasonable to assume that biodegradation was the main mechanism for the removal of $n-C_{12}$ and $n-C_{20}$, and their differences with respect to residual concentrations (Table 6) are associated with the higher biodegradability of $n-C_{12}$ compared to that of $n-C_{20}$. In addition, the removal of a substantial percentage of $n-C_{10}$ and TMB might be attributed to biodegradation since the model predictions (Fig. 8) ignore any topological limitations associated with pore space accessibility effects and overestimate their residual concentration. In an earlier

3.4. Assessment of bioventing efficiency

The supply of air through high permability hydraulic fractures seems an efficient method for the remediation of low permeability soils polluted by jet fuel which is a mixture of semi-volatile, and nonvolatile hydrocarbons. Bioventing tests in small reactors confirm that the supply of oxygen in soil is sufficient for the growth of indigenous bacteria and the efficient biodegradation of NAPL even for recalcitrant pollutants and under adverse conditions. Bioventing in soil tank was proved efficient, and a high percentage of semi-volatile (MCE, TMB, n-C₁₀), and non-volatile (n-C₁₂, n-C₂₀) compounds was removed (Table 6, Fig. 7).

The presence of inlet hydraulic fracture ensures (i) the uniform distribution of injected air over a large area, and (ii) the advective flow of air through a high number of preferential flow paths of the porous medium. In this manner, NAPL vapors are swept rapidly by the air flow (ventilation), and the volatilization rate of semi-volatile NAPL compounds (MCE, TMB, n-C₁₀) increases (Fig. 9) thus facilitating the bioaccessibility. Numerical simulation of the soil tank experiment, based on a simplified model of ventilation, revealed that NAPL volatilization, which is the main mechanism of mass-transfer from NAPL to gas phase, is unable to explain the relatively low residual concentration of the non-volatile compounds (n-C₁₂, n-C₂₀) (Fig. 8). Therefore, the highest percentage of the concentration reduction for these compounds is attributed to biodegradation which is maximized along the preferential flow paths.

4. Conclusions

Bioventing was coupled with hydraulic fractures in two-scale tests to assess the in situ remediation of low permeable soils polluted by a synthetic NAPL of semi-volatile and non-volatile compounds. The NAPL concentration is reduced uniformly over the soil, the indigenous bacteria of soil are active even under adverse conditions, whereas the biodegradation is enhanced weakly by the presence of nutrients. The removal of the most volatile compounds (MCE, TMB) is almost complete, the concentration of n-C10 and n-C12 is reduced significantly, and a respectable percentage of the mass of the most recalcitrant and non-volatile compound, n-C₂₀, is also CFU counting confirmed removed. that biodegradation is active even under unfavorable conditions.

Numerical simulation reveals that, under ideal conditions of complete NAPL accessibility to the flowing gas phase, the contribution of volatilization to

NAPL remediation might be significant for MCE, moderate for TMB and $n-C_{10}$, and negligible for $n-C_{12}$ and $n-C_{20}$. Therefore, a significant fraction of the NAPL compounds is removed by biodegradation.

Bio-venting combined with hydraulic fracturing can be applied to the unsaturated zone of low-permeability soils for the efficient removal of pollutants containing semi-volatile and nonvolatile hydrocarbons (e.g. jet-fuel). The air injection has a dual role on the process: on the one hand, it accelerates the volatilization of semi-volatile compounds; on the other hand, it stimulates the biodegradation of semivolatile and non-volatile compounds even under adverse conditions.

The duration of bio-venting is long, and the consumption of energy is low, compared to other energy-expensive methods (e.g. steam injection), presuming that biodegradation is the dominant mechanism. Otherwise, the post-treatment of released vapors may increase profoundly the operation cost of the process. The efficiency of bio-venting as a remediation technology of the vadose zone of soils may be high, presuming that the injected air will be able to vent a significant fraction of porosity, and supplied oxygen will be able to reach the heavily polluted areas (e.g. microporous matrix) of soil. However, the aforementioned conditions are not always satisfied in highly heterogeneous soils (e.g. fractured soils) where air flow may bypass some regions, and bioaccessibility may be limited by the large length-scales and low rates of oxygen diffusion. Under such conditions, the NAPL removal efficiency with bio-venting may be not quite high.

The bioventing / hydraulic fracturing test in soil tank was designed and conducted to examine the process efficiency in a low permeability vadose zone for NAPLs composed of semi-volatile and nonvolatile species (e.g. jet fuel). It was a preliminary step before applying the technology to the field-scale and testing its applicability to the vadose zone of a heterogeneous site polluted by jet fuel (Tzovolou et al., 2009). Because of the different conditions between lab-scale and field-scale tests (e.g. multi-scale soil heterogeneities, microbial populations), we are unable to extrapolate directly the datasets from the lab- to the field-scale and more detailed NAPL biodegradation studies are required. The implementation of in situ bio-venting coupled with hydraulic fractures on pilot cells of Kluczewo site (abandoned military airport in Northwestern Poland) will be presented in a forthcoming publication.

Acknowledgments

This work was performed under Global Change and Ecosystems contract number SSPI-CT-2003-004017-STRESOIL (2004-2007) supported by the European Commission.

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