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Controlling Factors for Natural Attenuation of Petroleum Vapors in a Layered Subsurface

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CONTROLLING FACTORS FOR NATURAL ATTENUATION OF PETROLEUM VAPORS IN A LAYERED SUBSURFACE

Andreas Houlberg Kristensen

Preface

This dissertation is submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It is based on a study carried out in collaboration between Ramboll Denmark A/S and Section of Environmental Engineering, Department of Biotechnology, Chemistry, and Environmental Engineering, Aalborg University (AAU). Funding was provided by Ramboll and The Danish Agency for Science, Technology and Innovation under the Industrial PhD program.

The dissertation consists of an extended summary and four supporting papers, of which three have been published in international per-reviewed journals and one is in preparation.

The work was carried out in the period May 2007 to April 2010 under the supervision of Professor Per Møldrup (AAU) and Head of department Lars Mortensen (Ramboll). In addition, parts of the study were supervised by Associate Professors Kaj Henriksen and Tjalfe G. Poulsen (AAU). The field work was carried out in Nyborg, Denmark, in collaboration with The Danish Oil Industry's Environmental Fund (Oliebranchens Miljøpulje).

I wish to thank Lars Mortensen for giving me the opportunity to work as an Industrial Ph.D. student in an innovative company such as Ramboll. Thanks are due to everyone at the Ramboll offices in Vejle and Aalborg. Special thanks to my supervisors, and in particular Per Møldrup, for excellent and committed guidance throughout the study. In addition, I acknowledge everyone who provided their assistance during field work, in the laboratory, or by reviewing early drafts of manuscripts or this dissertation, especially Helle Blendstrup, Anne Thorbjørn, Hanna Gerlach, Mette Pedersen, Chisato Hosoi, Anja Kristiansen, Kate M. Scow, Rune R. Andreasen, Kelum Chamindu, Maria P. Jensen, Ben Newton, Mads G. Møller, Lars Bennedsen, Claus Köser, and Kim Olsen. A special thanks to Susan Boriths, who prepared the indispensable coffee at the university every morning. Finally, I would like to thank my awesome office mates Ksawery, Rune, Chamindu, and Sam, all my friends, my brother Kristian, and my parents for their help and support the past three years.

Aalborg, May 1, 2010
Andreas Houlberg Kristensen

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List of supporting papers

I. **Kristensen, A.H.**, Henriksen, K., Mortensen, L., Scow, K.M. and Moldrup, P. 2010. Soil physical constraints on intrinsic biodegradation of petroleum vapors in a layered subsurface. *Vadose Zone Journal* 9:137-147.

II. **Kristensen, A.H.**, Poulsen, T.G., Mortensen, L., and Moldrup, P. 2010. Variability of soil potential for biodegradation of petroleum hydrocarbons in a heterogeneous subsurface. *Journal of Hazardous Materials* 179: 573-580.

III. **Kristensen, A.H.**, Thorbjørn, A., Jensen, M.P., Pedersen, M., and Moldrup, P. 2010. Gas-phase diffusivity and tortuosity of structured soils. *Journal of Contaminant Hydrology* 115:26-33.

IV. **Kristensen, A.H.**, Hosoi, C., Henriksen, K., and Moldrup, P. (*in prep.*). Vadose zone biodegradation rates of benzene vapors in repacked and undisturbed soil cores: Effect of soil structure and gas diffusivity.

Supporting papers will be referred to by their roman numbers, e.g., (Paper I).

Abstract

Since most petroleum constituents are easily degradable in the soil environment, remedial strategies including "monitored natural attenuation" (MNA) are increasingly chosen as a cost-effective and environmental friendly alternative to active remediation approaches. This dissertation addresses effects of soil physical properties, and their variability, on the potential for petroleum vapor diffusion and natural biodegradation, which are generally the dominant attenuation processes in deep and low-organic vadose zones.

In contrast to homogeneous sandy soils, values for gas diffusivity (D_p/D_0) measured in limestone and till materials indicated occurrence of drained macropores, causing a dual-porosity and preferential gas-phase diffusion. As a result, the classical and widely used model by Millington and Quirk (1961) yielded severe underestimation of the gas diffusivity ranging up to $7 \cdot 10^6$ times for low air-filled porosity, at which diffusion occurs essentially through drained macropores. A two-region model, combining the Penman (1940) model and classical non-linearly relationships, was successfully fitted to all data. The soil potential for aerobic biodegradation of petroleum vapors, determined as benzene degradation rates in slurry reactors, was closely linked to the soil potential for gas-exchange, represented by values for air filled porosity and D_p/D_0. In addition, benzene biodegradation in 100-cm^3 soil cores indicated diffusion limitation for values of $D_p/D_0 < 0.02$, independent on soil texture.

Values for gas-phase diffusivity and slurry degradation rates for benzene in a given soil layer were statistically related to geological soil classification ($P < 0.05$). This was also the case for air-filled porosity, presence of petroleum NAPL, total counts of soil microorganisms, water content, and bulk density, clearly suggesting the geological variation and stratification as the controlling factor for fate of petroleum contaminants on the field scale. Directional semivariogram analysis of measured soil parameters showed that spatial continuities were 2-5 times greater in the horizontal than in the vertical direction. Collectively, results from this research suggest considering the potential for soil gas-exchange and microbiological heterogeneity when evaluating feasibility of remedial strategies involving MNA in a petroleum-contaminated vadose zone.

Resumé (In Danish)

Størstedelen af benzin- og oliestoffer er nedbrydelige i jordmiljøet. Som følge heraf bliver "naturlig nedbrydning" i stigende grad betragtet som et effektivt og miljøvenligt alternativ til mere aktive oprensningsstrategier. Denne afhandling omhandler sammenhængen mellem jordfysiske egenskaber i umættet zone og muligheden for diffusiv gastransport og biologisk nedbrydning af flygtige kulbrinter – to processer, som typisk er dominerende i den dybe umættede zone hvor jordens indhold af organisk stof er lavt.

Målinger af gasdiffusivitet (D_p/D_0) i kalk og moræneler viste, at gastransporten her var styret af afdrænede makroporer, mens dette ikke var tilfældet i homogene sandjorde. Som følge heraf gav beregninger med en hyppigt anvendt D_p/D_0-model af Millington og Quirk (1961) værdier der lå op til $7 \cdot 10^6$ gange lavere end dem bestemt eksperimentelt. Dette var især tilfældet ved højt vandindhold, hvor gasdiffusionen hovedsageligt foregik gennem afdrænede makroporer. I disse jorde kunne D_p/D_0-data i stedet simuleres med en ny model for gasdiffusivitet i dobbeltporøse medier. Potentialet for nedbrydning af benzen i batch-flasker var tæt forbundet med luftfyldt porøsitet og D_p/D_0 for den givne jordtype under feltforhold. Nedbrydning af benzen i 100-cm^3 intakte jordprøver antydede desuden, at ilttilførslen var begrænsende for nedbrydningen for $D_p/D_0 <$ 0,02.

Målte værdier af D_p/D_0 og hastigheden af benzennedbrydning i batch-flasker var statistisk korrelerede til geologisk jordtype ($P < 0{,}05$). Det samme var tilfældet for luftfyldt porøsitet, fordelingen af NAPL, bakterietællinger, vandindholdet og jordens densitet. Dette illustrerede med tydelighed den store betydning af geologisk variabilitet og lagfølge for transport og nedbrydning af benzin- og oliestoffer i umættet zone. En semivariogramanalyse viste rumlige korrelationer der var 2-5 gange højere i horisontal retning end i vertikal retning. Samlet set fremhæver dette studie vigtigheden af, at vurdere jordens gastransportegenskaber, samt den rumlige fordeling af potentialet for mikrobiologisk nedbrydning, forud for implementering af "naturlig nedbrydning" som afværgestrategi i en benzinforurenet umættet zone.

1.   Introduction

Soil contamination is generally caused by the introduction of xenobiotic chemicals to the natural soil environment. The extent of contaminated land is well known in North America and Western Europe, with most countries in these areas having a legal framework to indentify and deal with this environmental hazard. In particular the United States (U.S.) has been a leader in defining standards and implementing new methods for investigation and remediation of contaminated sites. Since the Superfund program was enacted by Congress in 1980, the U.S. Environmental Protection Agency (EPA) has dealt with tens of thousands of hazardous waste sites. Also most European countries, including Denmark, have over the past 25 years made an extensive effort to clean up contaminated land. Nonetheless, the Danish Department of Environment in 2003 estimated that additional 14,000 sites are still in need of remediation, due to unacceptable threats posed by soil contaminants to potential receptors. For about 100 of these sites, the estimated expenses for investigation and cleanup exceed DDK 10 million (approx. $1.85 million), classifying them as "megasites" (DKEPA, 2007).

The most common soil pollutants are chlorinated solvents, pesticides, heavy metals, and petroleum hydrocarbons (PHC). In general, petroleum-related spills dwarf all other sites of environmental and health concern due to the numbers of individuals, refineries, service stations, and other facilities managing fuels and petroleum products. In Denmark, around 40 % of polluted soil sites are impacted by PHC contamination, typically arising from the rupture of underground pipelines and storage tanks buried in soil above the groundwater table, termed the "vadose zone" (DKEPA, 2008). Additional anthropogenic sources include leaching from landfills or direct discharge of industrial wastes to the subsurface (Downey et al., 1999).

1.1   *Petroleum vapor movement in the vadose zone*

Presence of PHC contamination in the vadose zone involves generation of a vapor plume of volatile petroleum constituents, such as benzene, toluene, ethylbenzene, and isomers of xylene (BTEX), as shown in Fig. 1. From the source area, these vapors will spread rapidly in the soil gas-phase through unsaturated pores and fractures, while transport with seepage water will generally be of minor importance (Christophersen et al., 2005; Maier and Grathwohl, 2005). The vapor plume may expand in all directions away from the source, as demonstrated in studies of landfill sites showing lateral methane gas migration as far as 90 m from the source zone (Kjeldsen and Fischer, 1995).
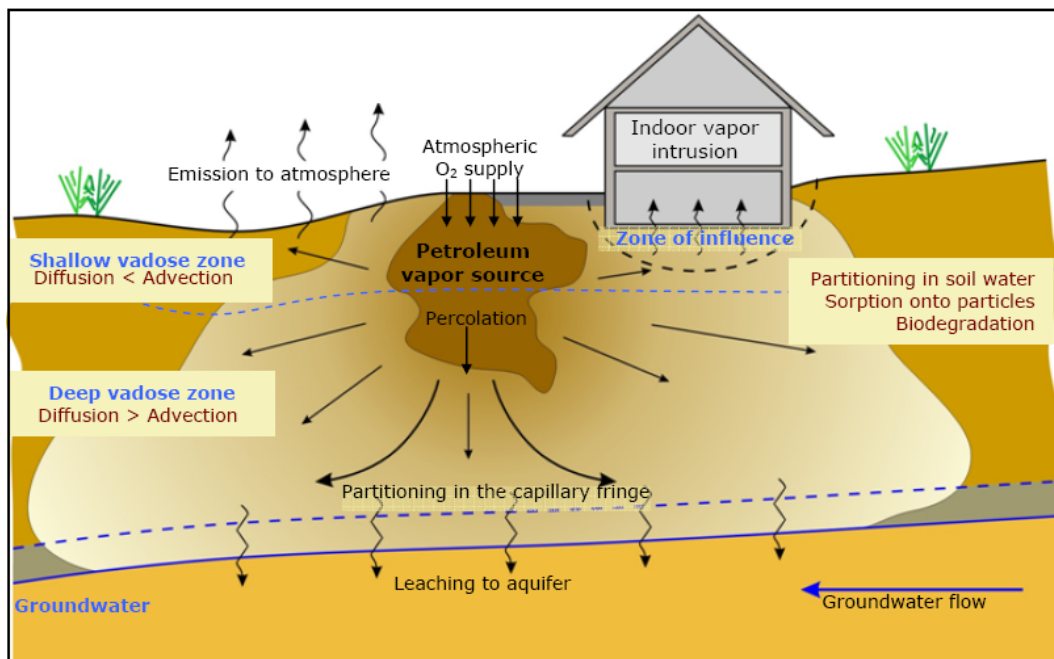
Figure 1. Conceptual model of a petroleum-impacted vadose zone, including a variety of processes and transport pathways affecting the fate of volatile petroleum hydrocarbons (modified from Kjeldsen, 2008).

Contaminant vapor movement in the vadose zone involves risks of (i) migration towards the underlying capillary fringe and aquifer; and (ii) vapor intrusion to built structures above ground (Fig. 1). The former represents an important source of secondary contamination of public water supplies (Baehr et al., 1999; Pasteris et al., 2002) while the latter pose an inhalation health risk to residents or workers at the site (USEPA, 2004b; Patterson and Davis, 2009). For permeable soils (with an air permeability exceeding 10^{-12} m^2), vapor intrusion to indoor air is usually driven by a low air pressure inside the building compared to the soil surrounding it (Johnson and Ettinger, 1991; Abreu and Johnson, 2005). This may generate a zone of influence beneath the building, in which advective air movement transports petroleum and other soil vapors towards the building's substructure and through foundation cracks with fluxes exceeding those achieved by diffusion alone (Nazaroff and Doyle, 1985). The transport mechanisms responsible for contaminant vapor intrusion are identical to those of subsurface radon entry to dwellings, a phenomenon representing a health concern since radon is a leading cause of lung cancer (Nazaroff, 1992).

For newly introduced spills of volatile contaminants, an overpressure is reported to arise within the source area, causing advective vapor migration to the adjacent soil until the pressure gradient has dampened (Gaganis et al., 2004). However, in the deep vadose zone, often defined as unsaturated soil > 2 m below ground, gas-phase diffusion will generally be dominant over advection, since building underpressurization and wind gusts have little impact in such depths (Garbesi and Sextro, 1989; Garbesi et al., 1993; Riley et al., 1996; CSRIO, 2004; USEPA, 2004b; Choi and Smith, 2005; Maier and Grathwohl, 2005).

1.2   *Attenuation processes in petroleum-contaminated soil*

Physical, chemical and biological processes that are at work in Fig. 1, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil (Downey et al., 1999; Boulding and Ginn, 2003). Attenuation processes include dilution by diffusion, emission to the atmosphere, and partitioning into soil water. In addition, dissolved PHC constituents may sorp onto soil organic surfaces and/or undergo biodegradation related to respiration of naturally occurring microorganisms (CSRIO, 2004).

Sorption of petroleum constituents is reported to cause significant retardation in (i) organic rich soils (> 1 %), as organic chemicals mainly adsorp onto the large surface area associated with natural organic matter; and (ii) dry soils with water saturation < 30 %, as organic vapors can be sorbed directly from the vapor phase onto soil minerals (e.g., Petersen et al., 1994; Batterman et al., 1995; Petersen et al., 1995; Chiou, 2002). However, since the deep vadose zone is typically associated with natural water saturations above 30 % and an organic matter content as low as 0.1-0.2 % w/w, sorption of PHC vapors is often considered to be negligible under such conditions (Chiou, 2002).

Biodegradation, however, has been shown to represent a key attenuation process in petroleum-contaminated soil independent on depth, although microbiological populations found in deep-lying soils tend to be lower in density and less diverse than those found in surface soils (Bone and Balkwill, 1988; Konopka and Turco, 1991; Zhou et al., 2004). Since PHC biodegradation occurs mainly under aerobic conditions, the natural biodegradation rate in deeper soils will typically depend on the diffusive supply rate of atmospheric oxygen (Huesemann and Truex, 1996; Lundegard et al., 2008; Davis et al., 2009).

1.3   *Monitored natural attenuation*

Through the past two decades, "monitored natural attenuation" (MNA) has been introduced as a remedial strategy, in particular at sites affected with easily degradable petroleum constituents. The U.S. Environmental Protection Agency defines MNA as the:

> "Reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods." (USEPA, 2004a).

A remedial strategy for the vadose zone involving MNA will typically be chosen in conjunction with, or as a follow-up to, more active remediation measures such as excavation, soil vapor extraction (SVE), or enhanced biodegradation (e.g., bioventing or application of nutrients). Based on a literature study, the decision-tree in Fig. 2 summarizes a variety of conditions that generally need to be met before employing MNA in petroleum-polluted and unsaturated soil. Such guidelines are useful for evaluating feasibility of MNA from available site data. However, "blind" application may involve risk of misinterpretation related to two specific issues:

- Do the approaches (empirical or experimental) applied for determining site-specific transport properties and biodegradation rates yield values that are representative for in-situ conditions?

- What are the variability and/or uncertainty of data within the site?

These questions should indeed be asked and answered during the site characterization to avoid any need for costly and time-consuming supplementary field investigations (Sturman et al., 1995; Höhener et al., 1998; Aichberger et al., 2005).

1.4 *Objectives*

This dissertation addresses factors controlling natural attenuation processes in a petroleum-contaminated vadose zone. The main focus is the effect of the soil physical properties (and their variability) on the potential for: (i) gas-phase diffusion and (ii) natural biodegradation of volatile petroleum constituents in low-organic deposits below 2 m (i.e., the deep vadose zone soils). The content of the dissertation is based on results presented in **Paper I-IV** and examples from a study site in Nyborg, Denmark, although data from other sites are included for comparison. The study site is a former service station and has a 16-m-thick vadose zone polluted with around 8000 kg of PHC of which BTEX constitutes 25 %. The following chapters describe and discuss:

(i) Prediction of gas diffusivity in variably structured vadose zone materials, including till and limestone

(ii) Soil physical factors affecting intrinsic biodegradation rates in the deep vadose zone; and

(iii) Field-scale variation of geological and soil physical factors controlling gas-phase diffusion and biodegradation in the deep vadose zone.
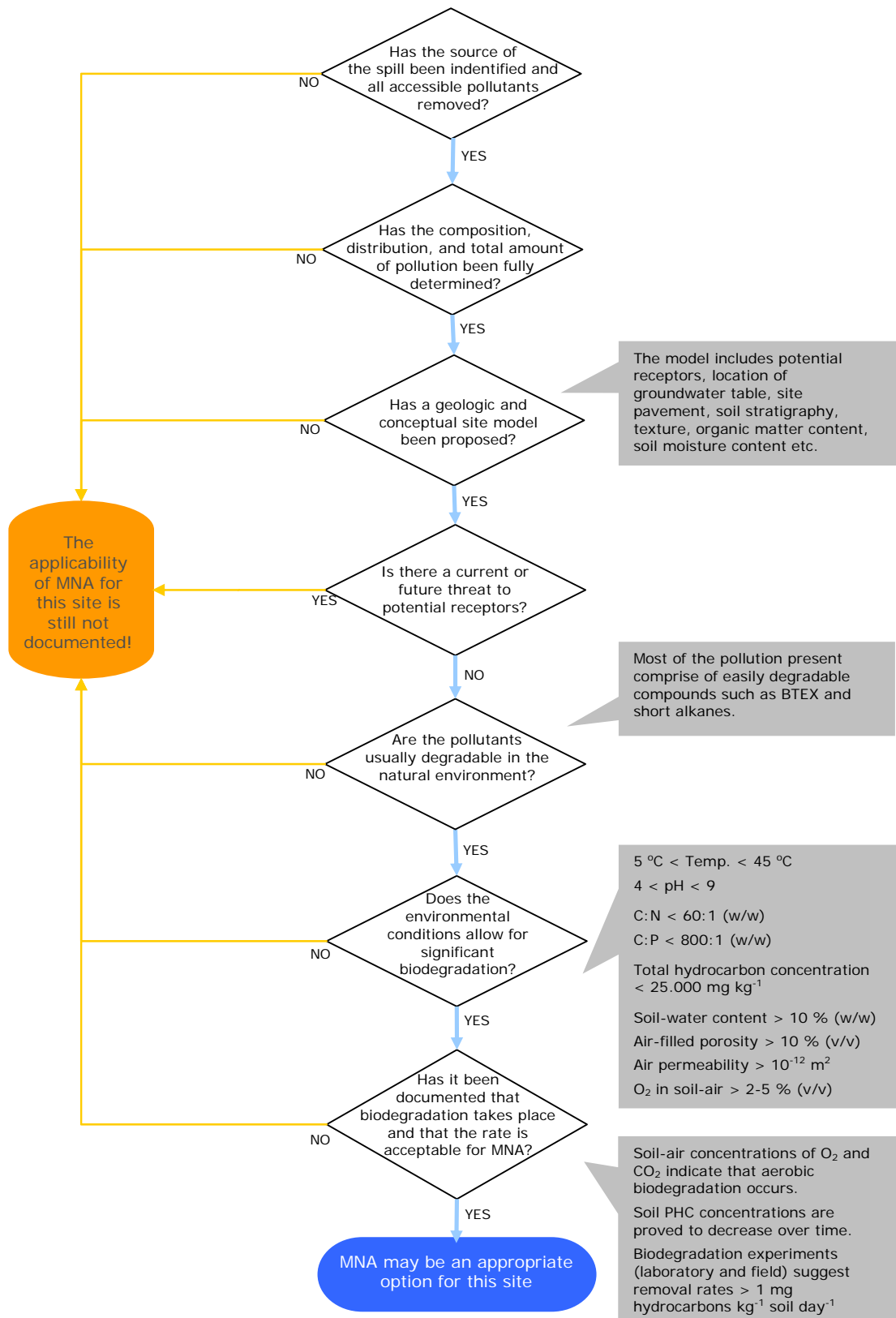
Figure 2. Decision-tree for evaluating MNA effectiveness in petroleum-impacted vadose zone soils (based on Dibble and Bartha, 1979; Troeh et al., 1982; USEPA, 1991; USEPA, 1996; Downey et al., 1999; DKEPA, 2002; Boulding and Ginn, 2003; USEPA, 2004a).

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2.   Diffusion of petroleum hydrocarbon vapors

In the absence of a pressure gradient, gasses present in unsaturated soil move by gas diffusion, driven by a gradient of vapor concentrations (i.e., partial pressures). Diffusion velocities of gas mixtures, such as petroleum vapors, are related to each other in a complex manner dependent on the mole fraction, molar mass and density of each gas. If gravity effects are ignored, the well-known Stefan-Maxwell equations provide the theoretical framework for diffusion of gasses in soils (Rolston and Moldrup, 2002). Fick's first law for one-dimensional diffusion, as given in Eq. 1, is a restrictive case of the Stefan-Maxwell equations, applicable only for cases where the total mole fraction of volatile organic vapors in the air does not exceed about 0.05 (Amali and Rolston, 1993):

$$\frac{M}{A \cdot t} = -D_p \cdot \frac{\partial C_a}{\partial z} \qquad (1)$$

where M is the amount of gas diffusing (g), A is the cross-sectional area of the soil (cm^2 soil), t is the time (s), C_a is the concentration in the gaseous phase (g gas cm^{-3}), z is the distance (cm soil), and D_p is the gas diffusion coefficient (cm^3 gas cm^{-1} soil s^{-1}). For unsteady diffusion in soils, Eq. 1 can be introduced into the equation of continuity leading to Fick's second law of diffusion (Eq. 2).

$$\frac{\partial C_a}{\partial t} = \frac{D_p}{\varepsilon R_g} \cdot \frac{\partial^2 C_a}{\partial z^2} - S(z,t) \qquad (2)$$

To account for non-conservative gasses in Eq. 2, a sink term $S(z,t)$ and a gas-phase retardation factor R_g are included. The former accounts for degradation processes occurring during transport (with a rate variable with depth and with time), while the latter accounts for partitioning into soil water and sorption onto soil particles (assuming instantaneous equilibrium and a constant temperature) (Eq. 3) (Grathwohl, 1998; Olesen et al., 2001):

$$R_g = 1 + \frac{\rho_b}{\varepsilon} \frac{K_d}{K_H} + \frac{\theta}{\varepsilon K_H} \qquad (3)$$

where ρ_b is the dry bulk density (g soil cm^{-3} soil), θ is the water-filled porosity (cm^3 water cm^{-3} soil), ε is the air-filled porosity (cm^3 air cm^{-3} soil), and K_d (cm^{-3} water g^{-1} soil) and K_H (cm^{-3} water cm^{-3} air) are the soil/particle and air/water partition coefficients, respectively. As given by Eq. 1 and 2, the effective mass transfer of a diffusing gas is proportional to the negative concentration gradient measured normal to the surface through which diffusion is taking place.

2.1 *Controlling factors for gas-phase diffusivity*

For steady-state transport of diluted gasses according to Fick's laws, the potential for gas-phase diffusion in a porous media is described in terms of the gas diffusivity (D_p/D_0), where D_0 refers to gas diffusion in a standard media, usually free air without any solid or liquid present (e.g., Troeh et al., 1982). Values of D_p/D_0 can be determined experimentally using tracer gas in intact soil columns (Currie, 1960; Rolston and Moldrup, 2002) or from large-scale field experiments (Werner and Höhener, 2003; Werner et al., 2005; Tick et al., 2007; De Steene and Hohener, 2009).

(a) Parrallel straight tubes	(b) Dry porous media	(c) Wet media	(d) Wet and fractured media (dual-porosity)
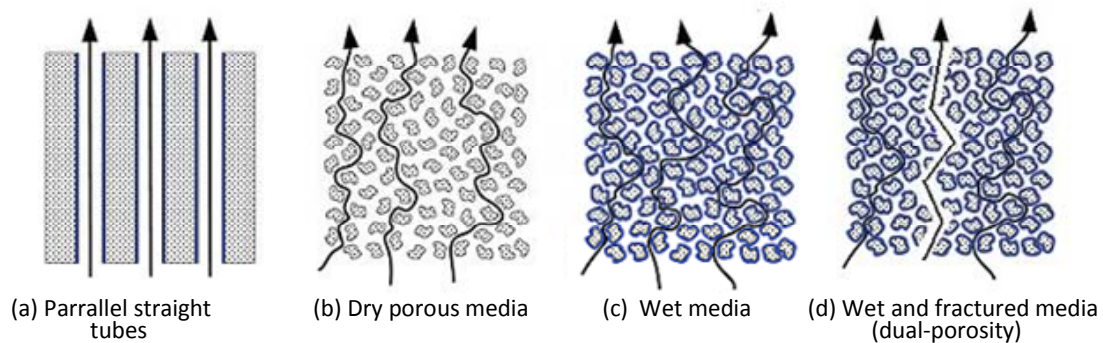
Figure 3. Conceptual model of gas-phase diffusion in porous media with various tortuosity (modified from Thorbjorn et al., 2008).

Whilst air permeability is closely related to the diameter of drained pores, gas diffusivity in porous media depends mainly on the mean air-filled porosity and the tortuosity of drained matrix pores through which gasses can diffuse (illustrated in Fig. 3) (Buckingham, 1904; Troeh et al., 1982; Hunt, 2005). Additional factors influencing values for D_p/D_0 are soil texture, total soil porosity, the soil water potential, and soil structure (i.e., occurrence and connectivity of macropores, fractures, fissures, and cracks), all of which are related to the geological soil classification and grain size distribution (demonstrated in Fig. 4) (Millington and Quirk, 1961; Troeh et al., 1982; Moldrup et al., 2000; Moldrup et al., 2001; Allaire et al., 2008). These factors collectively determine whether a geologic formation facilitates effective vapor diffusion or represents a near-impermeable barrier. As a result, occurrence of lower diffusivity layers only few centimeters thick have been reported to reduce petroleum vapor diffusion fluxes by several orders of magnitude (Fischer et al., 1996; Davis et al., 2005; Bozkurt et al., 2009). On the other hand, presence of drained macropores caused by (i) fracturing of clay or limestone materials or (ii) a heterogeneous particle size distribution, can open such impermeable soil layers and cause significant preferential gas-phase diffusion, even for near-saturated conditions (Fig. 3d) (Allaire et al., 2008; **Paper III**). At present, little is known about the significance of vapor transport in soil macropores and fractures (Allaire et al., 2008; Kjeldsen, 2008).
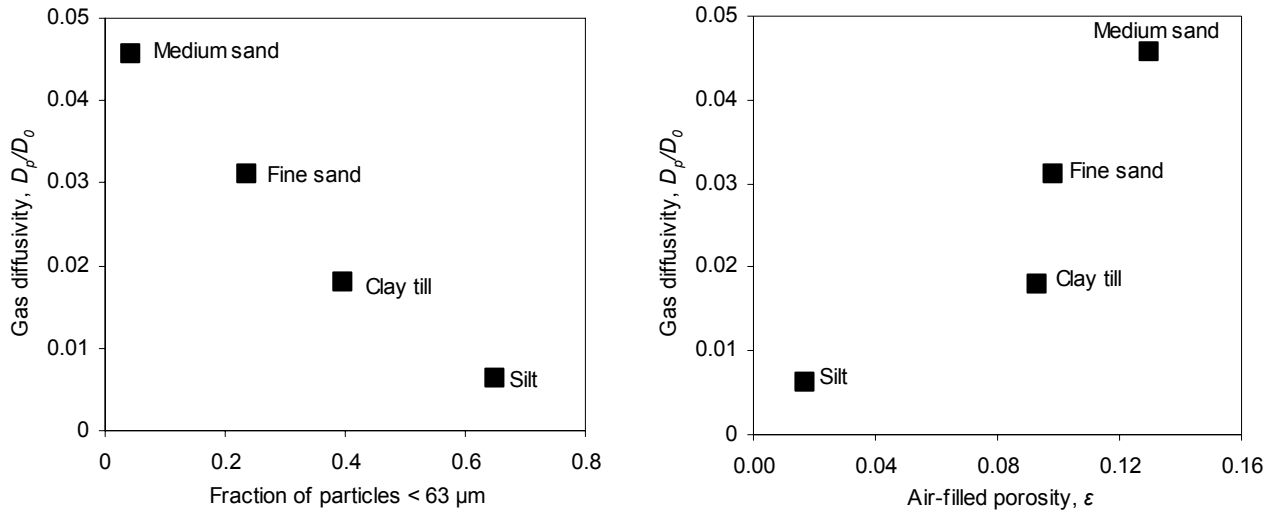
Figure 4. Examples of D_p/D_0 data in variably textured undisturbed soil cores collected in the study site (3-15 m below ground level). All samples were drained to a water potential of -10 kPa, corresponding to the natural water-holding capacity (modified from Paper IV).

2.2 *Predicting gas diffusivity of homogeneous soils*

Estimations of D_p/D_0 have traditionally been obtained from simple semi-empirical or theoretical relationships developed for relatively homogeneous and structureless porous materials (Table 1). In early models such as Buckingham (1904) and Penman (1940), the value of D_p/D_0 is given as a function of the air-filled porosity (ε) of the soil. Models in next generation, such as Millington and Quirk (1961) and Moldrup et al. (2000), consider soil texture and moisture effects by including the total soil porosity (Φ).

Table 1. Commonly used relationships for prediction of soil gas-phase diffusivity (D_p/D_0). The unit is cm^3 air cm^{-3} soil for the air-filled porosity (ε) and cm^3 pore space cm^{-3} soil for the total soil porosity (Φ).

Eq.	Model	Originally developed for:	Reference
(4)	$\dfrac{D_p}{D_0} = \varepsilon^2$	Variably textured, natural soils (repacked and intact)	Buckingham (1904)
(5)	$\dfrac{D_p}{D_0} = 0.66\varepsilon$	Dry porous materials (repacked)	Penman (1940)
(6)	$\dfrac{D_p}{D_0} = \dfrac{\varepsilon^{10/3}}{\Phi^2}$	Relative air permeability of coarse and structureless material with particles of uniform size (derived theoretically)	Millington and Quirk (1961)
(7)	$\dfrac{D_p}{D_0} = \varepsilon^{1.5}\dfrac{\varepsilon}{\Phi}$	Structureless, natural soils (repacked)	Moldrup et al. (2000)

In particular the model by Millington and Quirk (1961), hereon denoted as the MQ(1961) equation, has been widely used to predict D_p values as part of risk assessment modeling of contaminated sites (USEPA, 1996; DKEPA, 2002; Abreu and Johnson, 2005). However, the equation is reported to underestimate gas diffusivity for most soils under typically occurring water potentials (Petersen et

al., 1994; Jin and Jury, 1996; Bartelt-Hunt and Smith, 2002; Werner et al., 2004). The Moldrup relationship (Eq. 7) was originally developed for sieved and repacked samples, but a number researchers have suggested it to provide overall a more accurate and conservative prediction of D_p/D_0 than the MQ(1961) equation (Bartelt-Hunt and Smith, 2002; Wang, 2003; Werner et al., 2004). Both the MQ(1961) and Moldrup relationships can be written in the general form of Eq. 8,

$$\frac{D_p}{D_0} = (\varepsilon)^{X_{dry}} \left(\frac{\varepsilon}{\phi}\right)^N \qquad (8)$$

where X_{dry} is a pore tortuosity factor for $\varepsilon \approx \Phi$ and N is a water blockage factor. Consequently the first term of Eq. 8 accounts for the tortuosity of the dry media while the second term accounts for water blockages reducing the gas-phase diffusivity (Thorbjorn et al., 2008; Hamamoto et al., 2009).

Figure 5 shows measured D_p/D_0 data for 15 undisturbed soil cores consisting of structureless fine sand from two Danish sites **(Paper III)**. In such materials, values of D_p/D_0 plotted against ε generally follow a power function, showing no evidence of dual-porosity. No major difference was observed between data from soil cores taken in the vertical and horizontal direction (except for very dry conditions), suggesting that anisotropy in this example is unlikely to play a role for soil gas diffusivity.
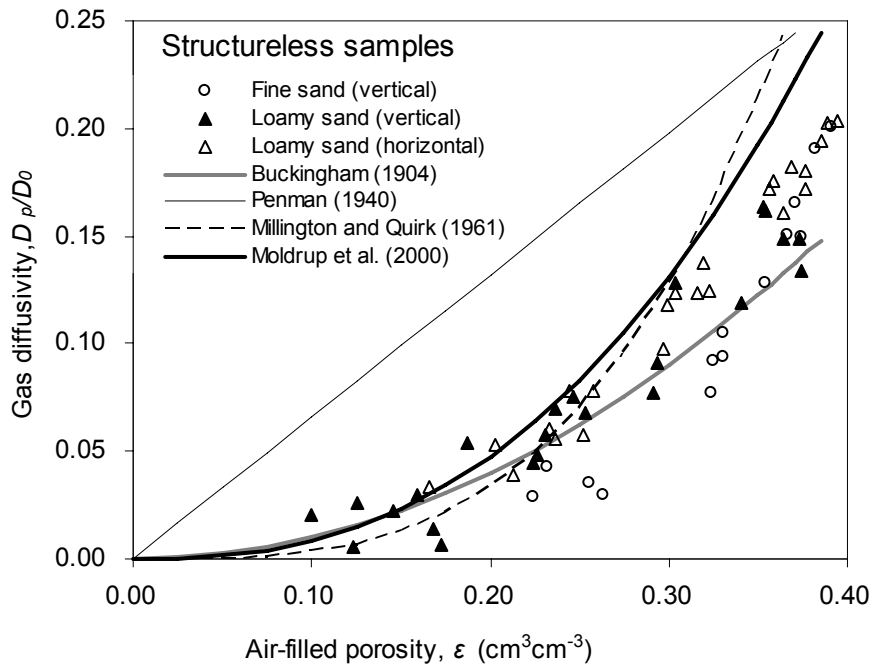

Figure 5. Measured gas diffusivity (D_p/D_0) in soil cores of structureless sandy materials (Paper III).

In line with previous studies, the linear Penman model overestimates D_p/D_0 in Fig. 5 throughout the measured range of ε (Petersen et al., 1994; Jin and Jury, 1996; Werner and Höhener, 2003; Werner et al., 2004). The Buckingham model provides the best overall fit, a finding also reported by Cannavo and coworkers (2006). The Moldrup relationship represents an approximate upper limit for most measuring points, while the MQ(1961) model tends to underestimate some data for low ε (**Paper III**). In a review by Werner and coworkers (2004), it was concluded that the Moldrup relationship is generally useful for conservative prediction of soil-gas diffusivity of relatively homogenous and non-structured natural deposits.

2.3   *Predicting gas diffusivity of materials with dual-porosity*

As shown in Table 1, most gas diffusivity studies have been based on repacked and structureless soil columns, which suffer from the flaw of not reflecting preferential transport through macropores (Allaire et al., 2008). While a number of studies have determined D_p/D_0 relationships for aggregated soils (e.g., Gimmi et al., 1993; Resurreccion et al., 2008), there is lack of studies addressing gas-phase diffusion in possibly fractured and heterogeneous materials (Bartelt-Hunt and Smith, 2002; Werner et al., 2004; Allaire et al., 2008).

Figure 6 shows results of D_p/D_0 measurements performed on 27 undisturbed soil cores of structured clay till, silt, and limestone (**Paper III**). The classical diffusivity models (Eq. 4-7) overall provide a poor fit of these data, which were exhibiting a two-region behavior. The error was most evident for low air-filled porosity where the ratio between measurements and values predicted using the MQ(1961) equation ranged up to $7 \cdot 10^6$.

Under wet conditions, values for D_p/D_0 increased linearly with ε, similar to the Penman model, while measurements at high ε values followed the shape of a power function. This suggests dual-porosity with a presence of readily drained macropores surrounded by porous matrix with lower diffusivity (i.e., higher tortuosity). Macropores are traditionally defined as pores > 30 μm (Hillel, 1998), but the D_p/D_0 data do not reveal details on the type and origin of macropores in the core samples. The clay till did not have any major cracks and openings and dual porosity is possibly a result of a considerable range of particle sizes (from clay to gravel and stones) (Allaire et al., 2008). For limestone, however, the dual-porosity effect is likely due to fractures in the fine-textured limestone matrix (Price et al., 1993). The term "macropore" heron refers to both types of dual-porosity.
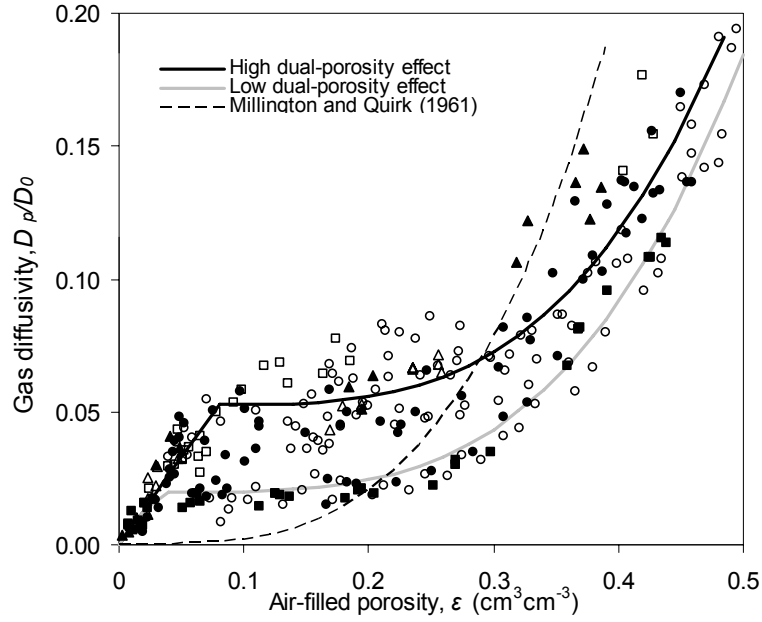
Figure 6. Measured gas diffusivity (D_p/D_0) in 100-cm³ soil cores taken from 6 different geologic formations. Curves represent previously suggested models for gas diffusivity in materials with a low and high dual-porosity effect, respectively (Paper III).

2.3.1 Conceptual understanding and model development

To obtain a general model for prediction of gas diffusivity in soils with dual-porosity we assume that the relationship between air-filled porosity and D_p/D_0 can be described by two regions: (i) a "wet region" in which transport occurs only in drained and isolated macropores with a low tortuosity and D_p/D_0 values increasing linearly with the air-filled porosity, similar to the Penman model; and (ii) a "dry" region in which some small and tortuous matrix pores are drained and contribute non-linearly to D_p/D_0, similar to the Buckingham, MQ(1961) and Moldrup relationships. Furthermore, we consider gas-phase diffusion in drained macropores and matrix pores to be independent and additive. This conceptual understanding leads to the semi-empirical dual-porosity model described as Eq. 9, which combines the Penman model with Eq. 8.

$$
\frac{D_p}{D_0} = H\varepsilon, \quad \text{if } \varepsilon \leq \varepsilon^*
$$

$$
\frac{D_p}{D_0} = H\varepsilon^* + \left(\varepsilon - \varepsilon^*\right)^{X_m}\left(\frac{\varepsilon - \varepsilon^*}{\phi - \varepsilon^*}\right), \quad \text{if } \varepsilon > \varepsilon^*
$$

(9)

where H is the macropore tortuosity factor, X_m is the matrix tortuosity factor, and ε^* is the (effective) macropore porosity. The model parameters were fitted to individual data sets to reach a minimum root mean squared error (RMSE) (e.g., Hamamoto et al., 2009). Table 2 includes a range and mean values for model parameters determined for the data in Fig. 6.

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Table 2. Model parameters determined for D_p/D_0 data presented in Paper III.

Site	Total soil porosity, Φ	Macropore porosity, ε^*	Matrix porosity, Φ-ε^*	Macropore tortuosity factor, H	Matrix tortuosity factor, X_m	Macropore effect, $H\times\varepsilon^*$
	(cm^3 cm^{-3})	(cm^3 cm^{-3})	(cm^3 cm^{-3})	(-)	(-)	(-)
Mean	0.44	0.08	0.35	0.60	2.16	0.04
Min.	0.26	0.02	0.20	0.17	1.80	0.01
Max.	0.56	0.23	0.43	1.00	2.57	0.08
Model for low dual-porosity	-	0.03	-	0.66	2.5	0.022
Model for high dual-porosity	-	0.08	-	0.66	2.2	0.053

As the soil stratigraphy found in the vadose zone often includes texturally and structurally different layers, it is common to have different levels of dual-porosity within a single soil profile, as also seen in a study by Cannavo and coworkers (2006). In Fig. 6 and Table 2 are included two model expressions representing "low" and "high" dual-porosity effects on gas diffusivity **(Paper III)**. Both models are based on Eq. 9 and suggest the Penman model to sufficiently describe gas diffusivity for $\varepsilon < \varepsilon^*$, while gas diffusion in drained matrix pores can be described using model expressions approximating the MQ(1961), Moldrup, or Buckingham (1904) equation.

2.3.2 Tortuosity of macropores

The pore tortuosity (T) is commonly defined as the relationship between the average transport path length (L_e) and the length of the porous media (L) along the major flow axis as given in Eq. 10:

$$T = \frac{L_e}{L} \qquad (10)$$

Values of T can be estimated based on D_p/D_0 as shown in Eq. 11 (Troeh et al., 1982; Moldrup et al., 2001):

$$T = \sqrt{\frac{\Psi_T}{D_p / D_0}} \qquad (11)$$

where D_p/D_0 can be either measured or predicted values and Ψ_T is the phase in which diffusion takes place, i.e., water or air-filled porosity. Figure 7 shows tortuosity of the macropore porosity at completely dry conditions for dual-porosity materials studied in **Paper III**. The macropore tortuosity is plotted against total soil porosity (Φ), where T is calculated from Eq. 11 and the value of $D_p/D_0(\varepsilon^*)$, determined for each sample. It is seen that T values tend to be highest for $\Phi > 0.40$ cm^3 cm^{-3}, suggesting compacted till and limestone ($\Phi < 0.40$ cm^3 cm^{-3}) will more frequently provide

macropores with low tortuosity as compared to more porous media. The conclusion that soil compaction can have an increasing effect on soil gas diffusivity is in line with previous laboratory studies on repacked soils, suggesting the proportion of the effective pore space for gas diffusion relatively increases during compaction (Shimamura, 1992; Fujikawa and Miyazaki, 2005).
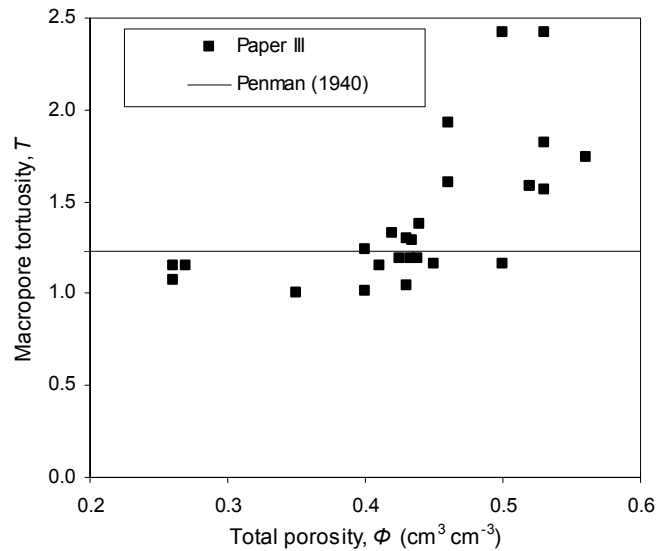
Figure 7. Gas-phase tortuosity of macropores in dual-porosity materials as a function of total soil porosity (Φ) (Paper III).

2.4   *Scale issues*

Scale issues associated with transport in porous media are often discussed in terms of the "representative elementary volume" (REV) (e.g., Miyazaki, 2006). The concept of REV was developed in recognition of the variability of natural sample materials at the pore scale, and has been interpreted to be the minimum volume for which statistical treatments of transport properties should apply (Hunt, 2005). For air permeability in soil systems, the scale dependency and REV have been reported to be substantial due to spatial variability or occurrence of a network of macropores (Garbesi et al., 1999; Iversen et al., 2001). Thus studies by Garbesi and coworkers (1999) showed that a scale-increase from 0.05 to 1 m increased the air permeability 14 times. For soil gas-phase diffusion, however, the REV is traditionally considered to be much less, assuming this process depend on the mean air-filled porosity rather than the connectivity and size of macropores (Moldrup et al., 2001; Hunt, 2005). Therefore, for homogeneous soils, a sample-volume of 100 cm^3 is generally considered sufficient for characterizing gas diffusivity (discussed in Sato and Tokunaga, 1976; Moldrup et al., 2003b; Moldrup et al., 2003a).

Data shown in Fig. 6 suggest a percolation threshold for some sample materials (typically limestone). In these fine-textured materials, a relatively large volume of voids is needed to ensure connectivity of drained macropores or fractures (e.g., Hunt, 2005). This likely cause a sample

volume of 100 cm^3 to be insufficient for accurate description of gas-phase diffusion and percolation thresholds at low air-filled porosity (Werner et al., 2004; Hunt, 2005) and estimated values for H and ε^* may be associated with uncertainty. However, a sample volume of 100 cm^3 is believed to be adequate when the air-filled porosity exceeds the macropore porosity ($\varepsilon > \varepsilon^*$ in Eq. 9). Likewise, estimates of the resulting effect of macropores on D_p/D_0 in each sample (equal to $H \times \varepsilon^*$) can be held with greater confidence **(Paper III)**. A solution to scale issues in laboratory D_p/D_0 measurements may be in-situ testing using tracer gas as proposed by Werner and Höhener (2003) and Tick and coworkers (2007). However, similar to laboratory experiments, field tests may face problems with mass conservation in heterogeneous systems (Allaire et al., 2008).

2.5 *Summary and recommendations*

- Evaluating gas-phase diffusion in the vadose zone should be based on measurements of total soil porosity and moisture conditions in every major geologic formation. In addition, the geological characterization of sample materials obtained during drilling activities should include an evaluation of possible dual-porosity. For example: are any cracks or fractures observed? Do precipitated iron oxides indicate macropores? And; are gravel and stones present in the sample materials?

- For structureless materials, gas diffusivity relationships suggested by Moldrup and coworkers (2000) and Buckingham (1904) provide acceptable estimations, while the widely used model by Millington and Quirk may underestimate values for naturally occurring moisture conditions.

- For dual-porosity materials such as clay till and limestone, a combination of the Penman (1940) model and the classical relationships proposed by Millington and Quirk (1961), Moldrup et al. (2000), or Buckingham (1904) provide accurate predictions. This approach is based on an estimated effective macropore porosity (ε^*), which was shown to approximate 0.08 cm^3 cm^{-3} for most soil cores included in this study.

- The significant underestimations of D_p/D_0 values associated in the use of the Millington and Quirk (1961) model in structured materials can be a valuable warning sign for "blind" application of the classical gas diffusivity models.

3.   Biodegradation of petroleum hydrocarbon vapors

Almost all fuel-related hydrocarbons are degradable by microorganisms naturally growing in the terrestrial environment, for which reason natural biodegradation is generally considered a critical process in petroleum-polluted sites (e.g., Gaganis et al., 2004; Christophersen et al., 2005; Abreu and Johnson, 2006). Hydrocarbon degraders in pristine ecosystems may constitute < 0.1% of total organisms, but up to 100 % in contaminated systems, illustrating the potential impact of PHC pollution on indigenous microorganisms (Atlas, 1981). The gasoline additive methyl *tert*-butyl ether (MTBE) is one important exception showing little biodegradation potential in the environment (e.g., Höhener et al., 2003), although significant aerobic rates for this compound have been observed in soils taken from older source zones at petroleum-contaminated sites (Loll et al., 2007).

Figure 8 shows results of unsaturated soil column experiments in which MTBE and benzene vapors migrate by gas-phase diffusion through a sandy soil from a non-constant source beneath the soil column (about 40 mg of benzene diluted to a total volume of 4 L). Whilst the MTBE vapor concentration increased over time and eventually reached equilibrium, benzene vapors were no longer detectable in the soil column after 55 hrs (Fig. 8). Two additional benzene amendments, performed successively to the soil column, each reduced the distance that benzene could be detected away from the source (eventually to less than 8 cm) (unpublished data). In line with other studies, these results illustrate unsaturated soil under aerobic conditions may function as an effective biological air filter in which naturally occurring microorganisms can (i) adapt to environmental conditions; (ii) grow in numbers; and (iii) rapidly degrade non-persistent hydrocarbons such as benzene, with a rate that potentially restricts the vapor migration to centimeters (Jin et al., 1994; Abreu and Johnson, 2006; Höhener et al., 2006; Devaull, 2007).
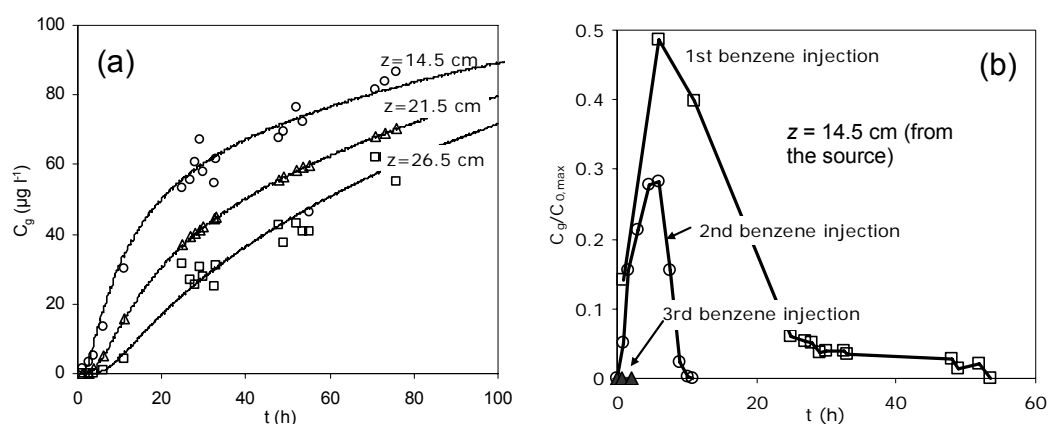
Figure 8. Results from soil column experiments (25 °C). (a) MTBE soil gas concentrations measured in different depth (z); and (b) benzene vapor concentrations (C_g) relative to the maximum source vapor concentration ($C_{0,max}$) during 3 successive benzene applications beneath a repacked soil column of fine sand. Concentration data in Fig. 8b are measured 14.5 cm above the source (unpublished data).

Similar to the above example, biodegradation generally reduces risks posed by PHC vapors at contaminated sites. McHugh and coworkers reported a lack of correlation between groundwater concentrations of petroleum constituents and indoor air values measured in overlying structures at 31 polluted sites in the U.S., while a clear and increasing correlation was observed for chlorinated solvents (McHugh et al., 2004). The latter is likely a consequence of chlorinated solvents, such as trichloroethylene (TCE) and tetrachloroethylene (PCE) being slowly biodegradable in the vadose zone (like MTBE) and in time will reach and possibly enter built structures above ground. On the contrary, most petroleum constituents such as BTEX are easily degraded aerobically by a large number of naturally occurring bacterial species (Atlas, 1981). This causes the final entry of BTEX vapors to built structures to depend on soil properties affecting transport and biodegradation processes in the vadose zone rather than the concentration in the underlying source.

3.1 *Estimating biodegradation rates at contaminated sites*

Laboratory studies of hydrocarbon biodegradation have traditionally been based on microcosms. In most cases, the experiments are carried out using slurry systems, where optimal mixing, aeration, and improved substrate bioavailability is achieved (e.g., Karlson and Frankenberger, 1989; Nielsen and Christensen, 1994; Davis et al., 2003). In addition, a number of studies have applied unsaturated soil columns and lysimeter experiments to simulate biodegradation during gas transport under relatively well-defined conditions (Jin et al., 1994; Baehr and Baker, 1995; Møller et al., 1996; Pasteris et al., 2002; Davis et al., 2003; Höhener et al., 2003). Field-scale feasibility studies prior to bioventing of petroleum-impacted soil have traditionally involved in-situ respiration tests, measuring the O_2 consumption and/or CO_2 production upon intensive soil aeration (Hinchee et al., 1991; Davis et al., 1998; Aichberger et al., 2005; **Paper I**). Furthermore, a number of researchers have studied vadose zone biodegradation of petroleum contaminants by measuring and modeling gas profiles of O_2, CO_2, and contaminant concentrations (Ostendorf and Kampbell, 1991; Lahvis and Baehr, 1996; Hers et al., 2000; Davis et al., 2005; Höhener et al., 2006; Davis et al., 2009). Lastly, stable carbon isotope fractionation in vadose zone vapor samples is increasingly used in order to provide evidence for natural degradation (Conrad et al., 1999; Bouchard et al., 2008; Coffin et al., 2008). Table 3 summarizes various biodegradation tests according to the scale at which the test is applied.

Table 3 laboratory and field methods for quantifying or documenting intrinsic biodegradation of petroleum constituents in the vadose zone. General comments to different methods are based on (Møller et al., 1996; Davis et al., 2003; Aichberger et al., 2005; Kristensen, 2006; Paper I, IV)

	Microscale	Mesoscale	Macroscale
Experimental system /method	Slurry reactor **(Paper I)**	Unsaturated soil column	In-situ respiration test **(Paper I)**
	Unsaturated batch reactor	Lysimeter experiments	Gas profile analysis of O_2, CO_2, and specific compound conc.
		Unsaturated soil cores (new method presented in **Paper IV**)	Stable isotope analysis in the field
Questions to be answered	Does mineralization of contaminants occur?	What is the rate under semi-natural transport conditions?	Does biodegradation occur under in-situ conditions?
	Is the potential high/low?	Is there a risk of diffusion limitation within the soil matrix?	What is the rate at field-scale and under in-situ conditions?
	Can the rate be enhanced?		Can site-specific clean-up criteria be met?
	What is the residual mass of contaminants?		
Costs	Low (standard equipment)	Medium (a suitable experimental setup are needed)	High (installations on-site, field equipment)
Duration	1-4 weeks	1-15 weeks	In-situ respiration: 1 week
			Other field investigations: > 4 weeks
Representativeness	Low	Low-medium	High
Other factors	Sensitive to variability at field-scale	Somewhat sensitive to field-scale variability	Hard to distinguish between different attenuation processes
	Does not represent natural transport conditions (diffusive limitation)		No prediction of residual concentrations possible

3.2   *Controlling factors for intrinsic biodegradation*

Abundance, diversity, and functions of soil microorganisms are governed by factors that control microbiological growth and activity in general, i.e. bioavailability of water, substrate, terminal electron acceptors, nutrients, and environmental factors such as pH, salinity, toxic compounds, and temperature (Kaufmann et al., 2004; Holden and Fierer, 2005). In the soil environment, these factors are closely related to the physical soil formation, defined by the arrangement of particles, water, and voids (Smiles, 1988; Young and Crawford, 2004; Or et al., 2007b). Thus, the potential for biodegradation of contaminants in the vadose zone reflects the extremely heterogeneous and highly dynamic aquatic and chemical environments formed within soil pore spaces (Or et al., 2007b). In contrast to gas diffusivity, no general empirical relationships are available for prediction of in-situ biodegradation rates from soil parameters. This is due to the large number of transient factors influencing biodegradation processes under in-situ conditions, including chemical composition of the contamination, fluctuating redox conditions, growth of microbiological populations, nutrient bioavailability, and meteorological conditions, just to name a few (Kaufmann

et al., 2004; Holden and Fierer, 2005). Even so, the soil physical parameters have been reported to provide some indication of the aerobic biodegradation potential of unsaturated soil in situations where nutrient deficiency is not a major limiting factor (**Paper I and II**).

3.3 *Effect of soil texture*

Fine textured soils tend to harbor larger microbiological populations than coarser soils, as organic matter and nutrients can attach to the significantly higher surface area associated with clay and silt particles (Taylor et al., 2002; Young and Crawford, 2004). Figure 9 illustrates the texture and soil class effect on first-order rate constants (k_1) of benzene biodegradation determined for differently textured soils from the study site using a slurry reactor setup (**Paper I**). Sterile controls, as the one included in Fig. 9a, indicated that sorption in clay till and fine sand from the study site did not play a significant role, in line with natural organic matter contents < 0.2 %.

Despite high variation, a Mann-Whitney one-sided test (Mann and Whitney, 1947) showed that soil class averages of k_1 for benzene, determined in slurries, were statistically different ($P < 0.05$) in the order: clay till > fine sand > limestone (Fig. 9b). Similarly, as seen in Fig. 10, oxygen consumption rates during in-situ respiration tests performed at the study site were higher in clay till than in fine sand, although the difference was less significant than in the slurries (**Paper I**). Zero-order rates determined in the laboratory and in-situ generally agreed well and suggested a significant potential for aerobic biodegradation with aerobic rates around 0.8-1.7 mg PHC kg^{-1} d^{-1} (10°C). Lastly, direct counts of bacteria were found the highest in clay till and in the order of 10^{8} cells g^{-1}, in line with previously reported counts from pristine subsoil samples (Konopka and Turco, 1991; Taylor et al., 2002; Kaufmann et al., 2004).
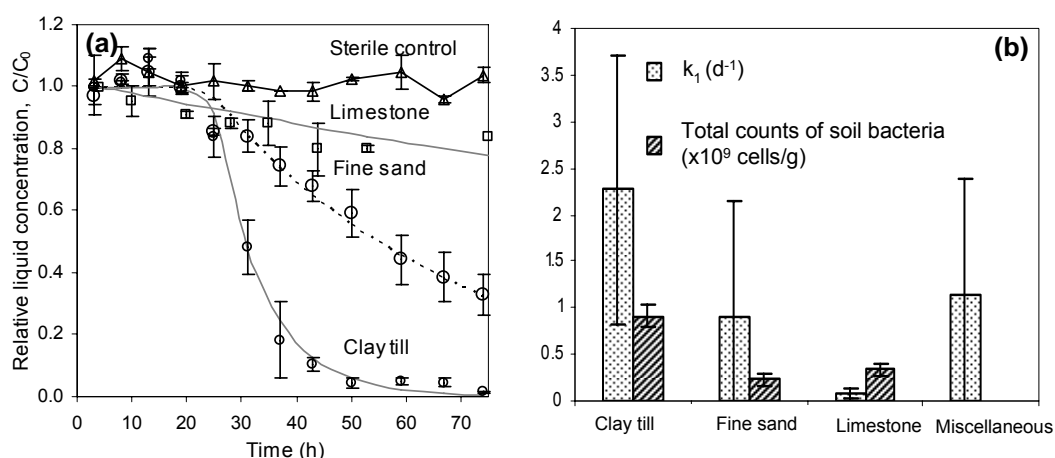
Figure 9 (a) Examples of benzene degradation curves from slurry reactor experiments; and (b) soil class averages of first-order rate constants (k_1). Error bars represent the standard deviation (Paper I).

Above results support the general assumption that fine textured soils have greater microbiological populations and higher aerobic activity than coarser soils as long as the air-filled porosity provides sufficient exchange of oxygen and gaseous substrate (**Paper I**). This is not the case for the fine-textured limestone samples in Fig. 9, as these were near water-saturated ($\varepsilon < 6$ %), thus effectively restricting aerobic biodegradation and growth of soil microorganisms.
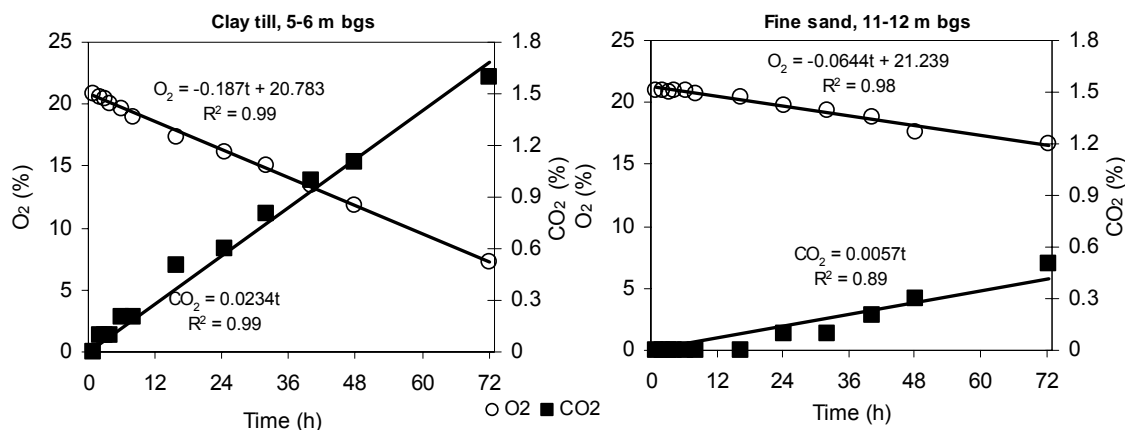
Figure 10. O$_2$ and CO$_2$ concentrations vs. time during in-situ respiration tests in a layer of clay till and fine sand at the study site. Bgs: below ground surface (Paper I).

3.4 *Effect of water and air-filled porosity*

The soil water content is reported to be a major factor affecting PHC biodegradation in soil, because (i) soil bacteria grow and degrade substrates dissolved in water films; and (ii) the soil water content controls the air-filled porosity and the potential gas-exchange (Skopp et al., 1990; Stark and Firestone, 1995; Hers et al., 2000; Holden et al., 2001; Davis et al., 2005). Skopp and coworkers (1990) suggested a conceptual model with a condition of "optimal" water saturation from where additional water will limit the gaseous oxygen supply, while loss of water will limit substrate liquid diffusion to the bacteria attached in water films. The optimal water saturation is typically assumed to range from 30-70 % of the total soil porosity, depending on the soil texture (Greaves and Carter, 1920; Atlas, 1981; Schjonning et al., 2003). Under in-situ conditions, the optimal water saturation will often approximate the natural water-holding capacity around -10 kPa (Boulding and Ginn, 2003). For water potentials lower than -600 kPa, physiological effects associated with dehydration will prevent most microbiological activity (Stark and Firestone, 1995).

In **Paper II**, linear correlation coefficients (R) were determined for soil parameters measured for clay till. The most evident correlation ($R = 0.84$) was observed between values for ε and k_l (Fig. 11), showing that the potential for aerobic biodegradation increased when the air-filled porosity increased from 1 to 17 % (corresponding to water saturations (θ/Φ) ranging from about 95 to 55 %). In agreement with the conceptual understanding provided by Skopp and coworkers (1990), this suggests local diffusion limitation of oxygen and petroleum vapors in these sediments due to

inhibited growth of aerobic soil microorganisms. As a result, a vadose zone including deposits with high natural water saturation will likely generate large-scale microbiological heterogeneity. Above findings are in line with results of previous field studies suggesting biodegradation of petroleum vapors beneath built structures to depend on the extent to which oxygen is capable of migrating beneath the foundation (Franzmann et al., 2002; Abreu and Johnson, 2006; Lundegard et al., 2008; Davis et al., 2009).
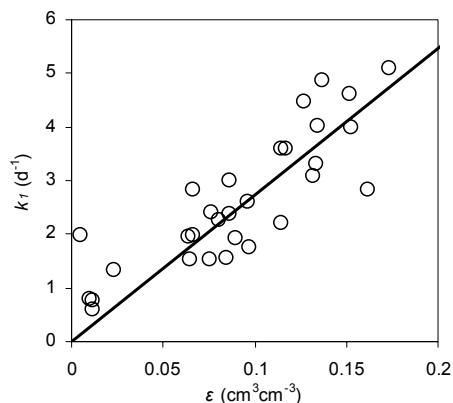
Figure 11. First-order rate constants for benzene degradation in slurry experiments using samples of clay till. The values are related to the antecedent air-filled porosity in the soil layer from where the sample is taken (Paper II).

3.5   *Linking biodegradation and gas diffusivity*

Experimental and theoretical evidence suggests that surface attachment is the prevailing lifestyle of soil bacteria, whilst planktonian free swimming microbes are rarely seen under most unsaturated conditions (Or et al., 2007b). Soil bacterial cells are often found embedded in biosynthesized "extracellular polymeric substances" (EPS) forming biofilms or stationary colonies attached to solid surfaces (Holden and Fierer, 2005; Or et al., 2007a). The EPS matrix serves as the interface with the environment and it affects diffusion pathways in the immediate vicinity of microbiological cells. In addition, it dampens effects of highly transient fluctuations in water and nutrient fluxes. The distribution of biofilms and bacterial colonies are linked to the arrangement of macropores and transport properties of the soil (Nunan et al., 2003). Hence, diffusive mass transfer is reported to be a main limiting factor for metabolism in soil (Holden et al., 1997; Höhener et al., 2003).

3.5.1   **Effect of soil structure**

Figure 12 shows an experimental setup used for determining benzene vapor biodegradation in (i) undisturbed and (ii) sieved (2mm) and repacked 100-cm^3 core samples taken in the vadose zone of two sandy sites **(Paper IV)**. Comparison of the rates showed statistically similar results ($P < 0.05$) (Fig. 13), indicating that sieving and breaking the physical mm-scale structure of the soil cores does not markedly affect the functions of benzene-degrading biofilms growing on grain surfaces, as long as an intact soil structure is restored afterwards. Also, repacking of the relatively structureless sand

in this example is not likely to alter transport properties and the gas-exchange occurring within the soil cores. On the contrary, the transition of intact soil cores into well-mixed soil slurries significantly changed the degradation kinetics (85 and 210 % as seen in Fig. 13), suggesting the drastic change of transport conditions obtained in a slurry system to have a large potential impact on functions of soil microbes (positive or negative) as their living conditions within soil biofilms are disrupted **(Paper IV)**.
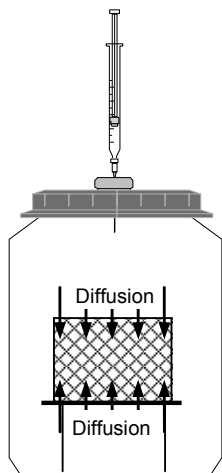
Figure 12. Experimental setup used for measuring benzene biodegradation in intact soil cores (100-cm³ repacked or undisturbed soil cores) using 480-mL glass reactors. The soil core was placed on a permeable plate in the centre of the reactor to allow for diffusion of O₂ and benzene vapors into the soil core from both sides.
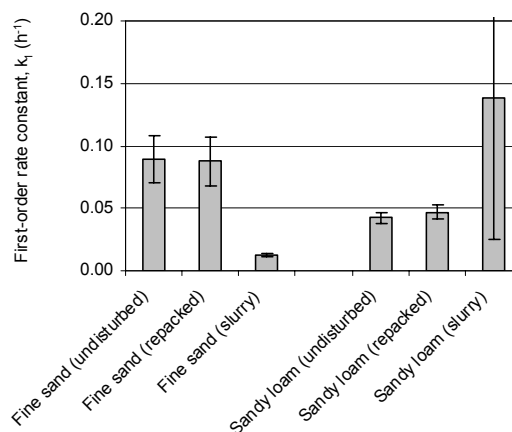
Figure 13. Mean first-order rate constants of benzene biodegradation determined for undisturbed soil cores, repacked soil cores, and soil slurries, respectively, using two sandy soils. Error bars correspond to the standard deviation. All soil cores were wetted to saturation in a sand box and drained to a water potential of -10 kPa.

3.5.2 Effect of gas diffusivity

Figure 14 shows the relation between D_p/D_0 and first-order rate constants in variably textured soil cores **(Paper IV)**. For the low-diffusivity materials, the extent of biodegradation is limited, while soils of higher gas diffusivity exhibit higher and similar biodegradation potentials. This confirms gas diffusivity as a controlling factor for aerobic biodegradation processes in unsaturated soil. Diffusion of oxygen and benzene in the liquid phase will be of minor importance in unsaturated soils since gas-phase diffusion rates are generally orders of magnitude higher. Previous studies suggest a sharp decline in the oxygen diffusion rate in variously textured soils for values of D_p/D_0 lower than 0.005-0.02 (Stepniewski, 1980; Stepniewski, 1981). Also, some studies showed a D_p/D_0 threshold for nitrification in unsaturated soil cores ranging from 0.004 to approximately 0.03 (Schjonning et al., 2003). In consistence with these findings, our results suggest a value of D_p/D_0 around 0.02 to represent a critical aeration limit in variably textured soils affected with petroleum vapors in a situation where gas-phase diffusion is the main transport mechanism. Beneath this limit, the soil water potential, and the resulting gas-phase diffusivity, will likely control the biodegradation rate under in-situ conditions. It is noticed that the latter conclusion presumes that (i)

oxygen is abundant in the adjacent soil layers and (ii) no extreme environmental conditions occur (e.g., occurrence of toxic chemicals).
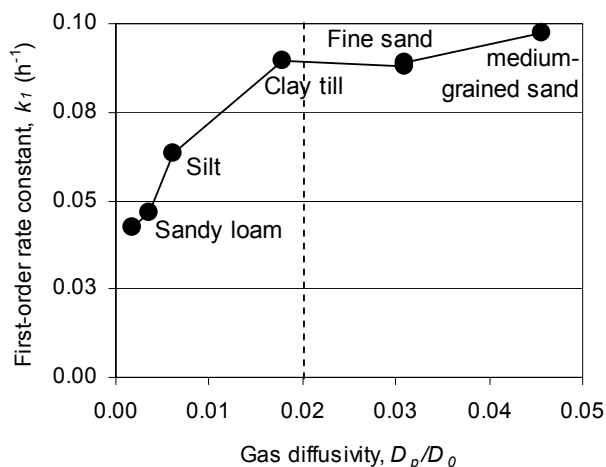
Figure 14. Mean first-order rate constants determined for benzene biodegradation as function of D_p/D_0 values in variably textured soil cores (Paper IV). The dotted line represents the critical limit for sufficient aeration according to previous studies (Grable and Siemer, 1968; Stepniewski, 1980; Stepniewski, 1981).

3.6 *Scale issues*

Estimating biodegradation rates in petroleum-contaminated sites is often associated with uncertainties related to up-scaling and soil heterogeneity effects. The latter includes (i) preferential transport of oxygen, nutrients, and contaminants; (ii) patchy moisture distribution; (iii) occurrence of micro-redox zones; and (iv) complex distribution of non-aqueous phase liquids (NAPL) (Seagren et al., 1994; Rogers and Logan, 2000; Davis et al., 2003). Even with these phenomena frequently occurring in the vadose zone, rates determined from bench scale experiments, using relatively small and homogenized soil samples, are often applied at hydrocarbon spill sites to screen for possible limitations of bioremediation, including nutrient deficiency and insufficient populations of degrading bacteria (Downey et al., 1999; Boulding and Ginn, 2003). Bench scale experiments generally provide substantial data variability, even among samples taken from the same soil layer (Davis et al., 2003; **Paper I**).

In addition, Davis and coworkers (2003) showed that biodegradation rates determined in batch or small-scale column systems are enhanced by more efficient diffusion of substrate and electron acceptors. They found that, as the experimental scale increases, the measured biodegradation rate slow down, since large-scale tests incorporate heterogeneity effects and diffusion limitation. This is in line with the a study by Aichberger and coworkers (2005), suggesting biodegradation rates in petroleum-contaminated soil to vary with the experimental approach used, in the order: batch experiments > soil column experiments > lysimeter experiment > in-situ respiration test. In contrast, a study described in **Paper I** found similar zero-order degradation rates in slurry reactor

experiments and in-situ respiration tests. It is noticed that in-situ respiration tests describes biodegradation activity under aerated condition only (e.g., during bioventing), for which reason it may not be appropriate for evaluating MNA feasibility. Lastly, Hohener and coworkers (2006) reported contradictory results for biodegradation kinetics obtained from microcosms, soil columns and from a field study. In summary, it can be concluded that although large-scale and/or in-situ experiments are usually recommended, general rules for scale effects on biodegradation experiments may not exist, since the outcome of all experiments mainly depends on soil and site-specific factors. This is illustrated in Table 4, showing a literature study of first-order rate constants for benzene biodegradation in different soils and using a variety of experimental approaches. For estimating in-situ biodegradation rates, it is generally recommended to combine experiments performed on different scales (Höhener et al., 1998).

Table 4. Studies of benzene biodegradation in various experimental systems. The tabulated summery is based on reviewed references. The literature data yield an arithmetic mean of k_1 = 1.0 d^{-1} (n=19) (Paper IV).

k_1 (d^{-1})	Reference	Sample description	Method description
Batch (microcosm) experiments:			
2.27	**Paper I**	Clay till	Aerobic slurry reactors, 25 ^{o}C
0.89	**Paper I**	Fine sand	Aerobic slurry reactors, 25 ^{o}C
0.08	**Paper I**	Limestone	Aerobic slurry reactors, 25 ^{o}C
0.004-0.06	(Franzmann et al., 1999)	Shallow sandy unsaturated soil	Aerobic unsaturated microcosms, 22 ^{o}C
0.0057	(Watwood et al., 1991)	Surface soil, sandy, calcareous aridisol.	Aerobic unsaturated microcosms, 25 ^{o}C, water added to reach half of the water-holding capacity
0.023	(Watwood et al., 1991)	Surface soil, calcareous, clay-rich riparian soil	Aerobic unsaturated microcosms, 25 ^{o}C water added to reach half of the water-holding capacity
2.8	(Kristensen, 2006)	Unsaturated fine sand from 4.5 m bgs	Aerobic slurry reactors, 25 ^{o}C
0.20	(Nielsen and Christensen, 1994)	Contaminated sandy aquifer material	Aerobic slurry microcosms, 10 ^{o}C, natural groundwater was used
1.2	(Karlson and Frankenberger, 1989)	Contaminated groundwater	Aerobic, slurry microcosms
Soil column (mesocosm) experiments:			
1.07	**Paper IV**	Sandy loam	Unsaturated intact soil cores (100 cm^3), 25 ^{o}C
1.52	**Paper IV**	Silt	Unsaturated intact soil cores (100 cm^3), 25 ^{o}C
2.12	**Paper IV**	Fine sand	Unsaturated intact soil cores (100 cm^3), 25 ^{o}C
2.15	**Paper IV**	Clay till	Unsaturated intact soil cores (100 cm^3), 25 ^{o}C
2.33	**Paper IV**	Medium-grained sand	Unsaturated intact soil cores (100 cm^3), 25 ^{o}C
0.21	(Höhener et al., 2006)	Unsaturated sand from shallow sandy vadose zone	Aerobic soil column experiment on VOC gas diffusion and biodegradation, 22 ^{o}C
In-situ (macrocosm) experiments:			
1.95	(Höhener et al., 2006)	Shallow sandy vadose zone with emplaced VOC source	Gas profile analysis and modelling
0.07-0.31	(Lahvis et al., 1999)	Capillary fringe at petroleum-contaminated site	Gas profile analysis and modelling

3.7   *Summary and recommendations*

- Documenting and quantifying natural biodegradation will benefit from a combination of small-scale and large-scale experimental approaches. Field or laboratory tests should be conducted in all major contaminated soil layers of the vadose zone.

- Evaluating potential biodegradation in the vadose zone should include in-situ measurements of pore-air concentrations of oxygen and carbon dioxide in major soil layers, since the redox conditions may vary concurrently with the stratigraphy.

- Lastly, estimating values for D_p/D_0 will reveal the potential gas-exchange of oxygen and contaminant vapors, i.e., the distribution and bioavailability of gasses within contaminated deposits. Values greater than 0.02 may indicate that gasses are effectively distributed to microorganisms within the soil formation where biodegradation can occur.

4. Vadose zone variability of controlling factors

The vadose zone of most sites typically includes a number of different geologic soil formations, which then again can have minor lenses. In particular till is known to contain a heterogeneous mixture of stones, gravel, sand, silt, clay, and limestone that have been incorporated in the glacier as it passed over the land surface (Boulding and Ginn, 2003). Glacial materials, transported and deposited elsewhere when the ice melts, typically generate a stratified vadose zone. Characterizing contaminated sites with such a stratified subsurface is critical, since each layer is associated with a set of distinct soil physical and geochemical characteristics, ultimately affecting the gas-phase migration and biodegradation of petroleum vapors (Kristensen et al., 2008; **Paper II**). This chapter describes vadose zone heterogeneity and geostatistical variability of a range of factors affecting gas-phase diffusion and microbiological activity in the vadose zone at the study site **(Paper I, II)**.

Depth (m bgs)	PHC (mg kg^{-1})	Field observations
0.0	n/a	Flagstones, gravel
0.3	n/a	Fill material, coarse sand
2.3	0	Clay till, light brown, gravel and sand also present
3.5	0	Fine-medium sand, brown, moist, gravel also present
4.0	4	Clay till, light brown or gray, gravel and limestone present
6.0	3.1	Limestone, white, soft, water-bearing
8.5	0	Clay till, calcareous, gray, dry, gravel also present
10.0	81	Fine sand, yellow, dry
12.8	6400	Coarse sand, strong oil smell, NAPL present
12.9	11	Silt/loam, brown
14.1	0	Loamy limestone, water-bearing, silt is present
15.1	n/a	Fine sand, gray/brown, dry
15.6	0	Aquifer material, medium sand, gray, water saturated
18.0		

Sand	Clay till	Limestone

Figure 15. Example of soil stratigraphy from a borehole in the source area at the study site. The profile includes field observations and concentration of total petroleum hydrocarbons (PHC). n/a: not analyzed.

4.1 *Variations among soil classes*

4.1.1 **Soil physical parameters**

Key soil physical parameters in the vadose zone include (i) compaction (i.e., total soil porosity); (ii) texture and surface area; (iii) water potential; and (iv) soil structure. These parameters are generally static in subsoils, except for the soil water potential, which may show significant temporal variations in cases of open-ground or fluctuating groundwater table (Davis et al., 2005). In addition, constructions at ground potentially cause compaction and reduced moisture conditions in the underlying soil compared to soil external to the building (Tillman and Weaver, 2007).

Table 5 Examples of mean soil properties found in major soil layers within the vadose zone of the study site (Paper I). Numbers in brackets represent standard deviations. n/a: not analyzed.

General information		Clay till	Fine sand	Limestone	Other deposits
No. of soil samples	-	45	17	18	20
Depth range	m bgs	2- 10	10 -13	5 - 9 and 13 -15	2 -16
Maximum soil PHC conc.	mg kg^{-1}	4500	6400	450	81
Maximum vapor PHC conc.	mg m^{-3}	5700	1700	n/a	n/a
Oxygen conc.	%	0-1.5	4-5	n/a	n/a
Carbon dioxide conc.	%	9-12	12-13	n/a	n/a
Physical soil characteristics					
Clay (< 2 μm)	kg kg^{-1}	0.176 (0.0042)	0.05 (0.0056)	n/a	n/a
Silt (2-20 μm)	kg kg^{-1}	0.154 (0.034)	0.025 (0.0049)	n/a	n/a
Fine Sand (20-200 μm)	kg kg^{-1}	0.372 (0.109)	0.868 (0.081)	n/a	n/a
Coarse Sand (200-2000 μm)	kg kg^{-1}	0.297 (0.071)	0.057 (0.079)	n/a	n/a
Gravel and stones (> 2000 μm) †	kg kg^{-1}	~0.100	~0.020	~0	n/a
CaCO$_3$†	kg kg^{-1}	0.249 (0.05)	0.130 (0.029)	>0.800	n/a
Soil organic matter †	kg kg^{-1}	0.0019 (0.0021)	0.0012 (0.00093)	n/a	n/a
Dry bulk density ‡	kg L^{-1}	1.75	1.59	1.71	1.65
Total soil porosity ‡	L L^{-1}	0.34	0.40	0.35	0.36
Water-filled porosity, θ §	L L^{-1}	0.24 (0.052)	0.19 (0.055)	0.31 (0.068)	0.21 (0.11)
Air-filled porosity, ε §	L L^{-1}	0.093 (0.046)	0.21 (0.055)	0.04 (0.068)	0.15 (0.10)
Water saturation	-	0.71 (0.12)	0.45 (0.15)	0.88 (0.20)	0.65 (0.19)
Gas diffusivity (D_p/D_0)	-	0.021 (0.025)	0.031 (0.071)	0.007 (0.017)	0.009 (0.035)

† Contents of gravel, CaCO$_3$ and organic matter are per kg of total dry matter.

‡ Dry bulk density, total soil porosity, and D_p/D_0 are estimated based on 19 intact 100 cm^3 soil cores.

§ Water and air-filled porosity are based on the total soil porosity of the soil class and measurements of the gravimetric water content.

Table 5 shows selected soil parameters and properties measured for major geologic units in depths ranging from 2 to 16 m below ground (**Paper I**). Sample materials of clay till had high contents of gravel and coarse sand, while layers of fine sand and limestone were relatively homogeneous. The total soil porosity varied from about 0.34 cm^3 cm^{-3} in clay till to 0.40 cm^3 cm^{-3} in fine sand. Estimated air-filled porosities of 0.04 cm^3 cm^{-3} in limestone (water-bearing) and 0.21 cm^3 cm^{-3} in fine sand suggested varying potential for gas transport across different soil layers. In clay till, the average air-filled porosity was 0.093 cm^3 cm^{-3}, which is around the critical limit generally indicating an interconnected soil pore network (Troeh et al., 1982). Measurements of D_p/D_0 at in-situ water contents showed values of 0.007 for limestone, 0.021 for clay till, and 0.031 for fine sand.

These results infer that gas diffusion fluxes of oxygen and petroleum vapors will be negligible in layers of limestone, while vapor transport to some extent is possible through layers of clay till. In addition, high air-filled porosity and D_p/D_0 values for fine sand demonstrate favorable transport conditions. This was supported by oxygen gas concentrations at 4-5 % measured in the layer of fine sand, while it was below 1.5 % in clay till (Table 5). As the layer of limestone represented an effective barrier for vertical gas-phase diffusion of oxygen from the atmosphere, it is believed that oxygen diffused horizontally from less contaminated soil zones where oxygen was abundant, through the sand layer, and into the contaminated soil zones where it became available for aerobic biodegradation of petroleum constituents.

4.1.2 Geochemical parameters

The soil pH was generally above 8, reflecting calcareous conditions. Values above 9 in water-bearing limestone may have inhibited microbiological activity, which was supported by laboratory experiments on pH effects on biodegradation activity in soils from the study site **(Paper I)**. Low contents of natural organic matter (< 0.2 % w/w) and nitrogen (< 20 mg total N kg^{-1} and $N_{total}:P_{total}$ ratios around 1:20) illustrated typical subsurface conditions. This has two consequences within the contaminated soil zones where PHC-related carbon was abundant: (i) PHC contamination is likely to represent the main substrate for the microbiological populations and (ii) nitrogen limitation of microbial growth is possible. However, laboratory experiments and geostatistical state-space analyses indicated that nutrient concentrations, although they were low, did not significantly control biodegradation in the study site **(Paper I, II)**.

4.1.3 Distribution of petroleum NAPL and vapors

Figure 15 and 16 show examples of a borehole profile and drill cores collected in the study site. They both suggest the distribution of PHC contamination to be closely connected to the stratigraphy. Presence of NAPL (> 1000 mg PHC kg^{-1}) were associated with sandy lenses on top of water-bearing sediments of silt and limestone, an observation also reported for a number previous studies (Dawe et al., 1992; Smith et al., 1996; Phillips et al., 2007). Concentrations ranging up to 1000 mg PHC kg^{-1} were randomly distributed in deposits of fine sand and limestone, while no NAPL was present in the clay till, generally containing < 10 mg PHC kg^{-1}. However, field measurements showed vapor concentrations ranging up to 5700 μg PHC L^{-1} soil air in geologic formations of clay till **(Paper I)**. Even with the majority of pollution accumulated in coarse lenses, these results illustrate that petroleum vapors spread in fine-textured clay till deposits as well,

possibly due to preferential macropore transport **(Paper III).** In summary, the complex geology of the vadose zone at the study site played an essential role for the distribution of contamination "hot spots" and for the gas-phase migration pathways of petroleum vapors **(Paper I, II)**.

Figure 16. Examples of drill cores taken at the study site. The cores contain limestone (to the left) and various clay till materials. Red squares denote a contaminated sandy lens (Paper II).

4.2 *Variations within soil classes*

Table 6 shows the results of statistical analyses of first-order benzene rate constants (k_1), soil air-filled porosity (ε), available nitrogen (N_{inorg}), and available phosphorous (P_{avail}) measured for 100 sample locations in the study site. Benzene degradation in laboratory slurries occurred with k_1 values ranging up to 5 d^{-1} and with an arithmetic mean of 1.5 d^{-1}. Also, k_1 was the parameter exhibiting the highest coefficient of variation (CV) at 118 % with a number of samples showing no evidence of biodegradation within the timeframe of the experiments (i.e. 75 h). This reflects major sample-scale variability of the microbiological potential for natural degradation of petroleum contaminants. Values of ε were also related to soil class, but less variable than k_1 (CV = 69 %).

Figure 17 shows the density functions for all data together as well as for individual soil classes. Values for P_{avail} and N_{inorg} were generally log-normally distributed with a positive skew (Table 6), in line with findings of Onsoy et al. (2005). The Lilliefors test ($P < 0.05$) showed that values for k_1 and ε were normally distributed within deposits of clay till and limestone.

Table 6. Statistical analysis of first order rate constants (k_1), air-filled porosity (ε), available phosphorous (P_{avail}), and inorganic nitrogen (N_{inorg}). [a]Best fit of the normal or log-normal distribution confirmed by the Lilliefors test ($P < 0.05$) (Paper II).

Variable	Soil class	N	Mean	Min.	Max.	Median	Skewness	SD	CV (%)	Prob. Dist.[a]
k_1 (d^{-1})	All data	97	1.50	0.00	5.09	0.67	1.53	1.76	118	-
	Clay till	40	2.25	0.00	5.09	2.10	0.23	1.52	68	Norm.
	Fine sand	17	0.90	0.02	4.43	0.33	2.07	1.26	140	Log-norm.
	Limestone	18	0.083	0.00	0.54	0.049	2.81	0.131	157	Norm.
ε (cm^3 cm^{-3})	All data	77	0.11	0.00	0.31	0.11	0.23	0.08	69	Norm.
	Clay till	39	0.094	0.01	0.17	0.10	-0.49	0.04	46	Norm.
	Fine sand	15	0.19	0.09	0.27	0.20	-0.14	0.06	29	Log-norm.
	Limestone	16	0.058	0.00	0.16	0.0052	0.49	0.070	120	-
P_{avail} (mg kg^{-1})	All data	98	4.34	0.53	43.37	3.38	6.23	4.69	108	Log-norm.
	Clay till	39	3.61	0.87	12.46	3.30	2.35	2.02	56	Log-norm.
	Fine sand	17	2.14	0.53	4.17	1.97	0.38	0.93	44	Log-norm.
	Limestone	20	6.39	2.46	13.51	6.24	0.94	2.72	43	Log-norm.
N_{inorg} (mg kg^{-1})	All data	100	1.11	0.56	2.75	1.06	1.23	0.43	38	Log-norm.
	Clay till	46	1.09	0.56	2.29	0.99	1.02	0.41	37	Log-norm.
	Fine sand	15	1.13	0.58	2.31	1.09	1.44	0.42	37	Norm.
	Limestone	20	1.16	0.61	1.53	1.33	-0.66	0.32	27	Log-norm.
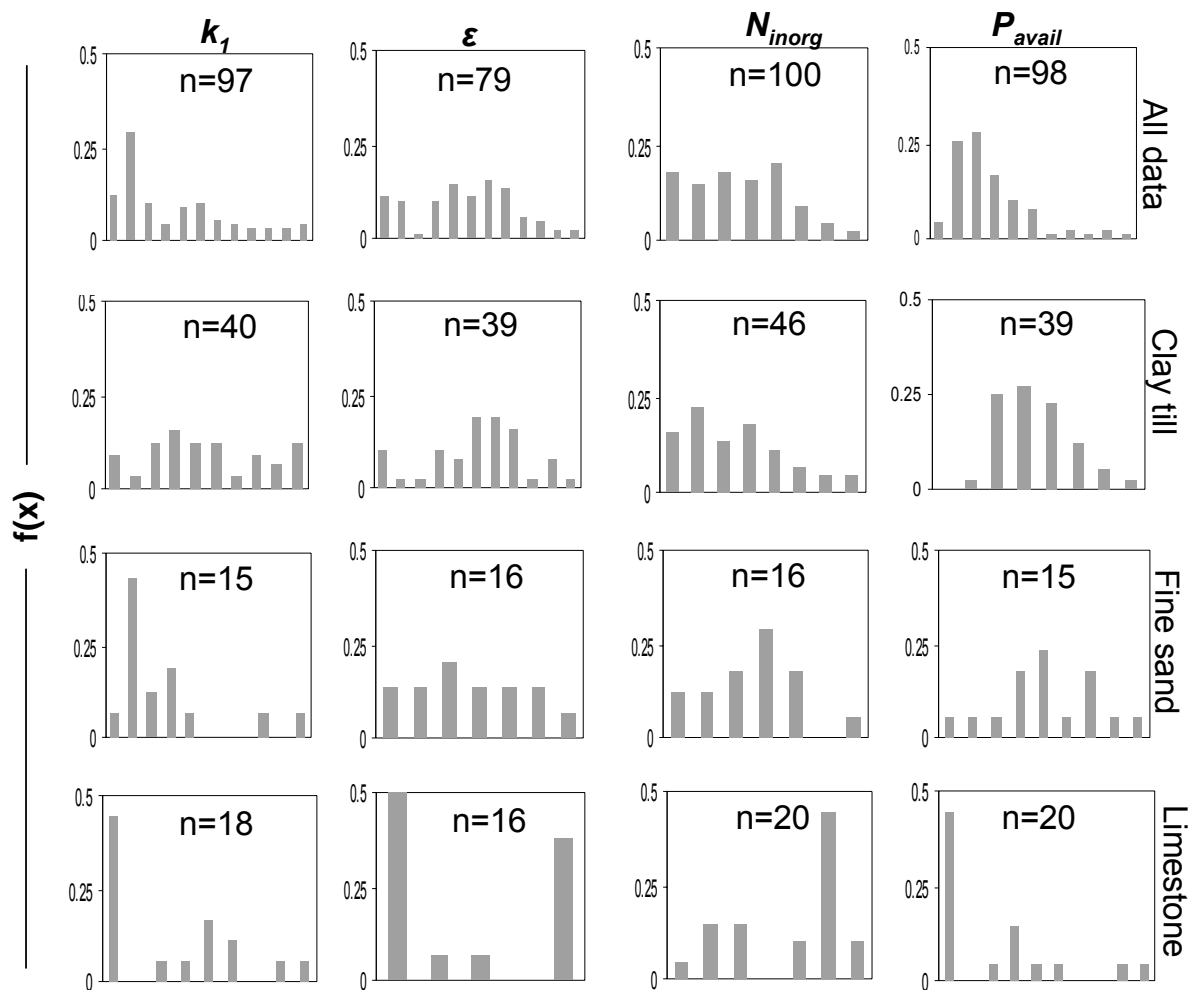
Figure 17. Density functions for first-order rate constants (k_1), air-filled porosity (ε), inorganic nitrogen (N_{inorg}), and available phosphorous (P_{avail}). Plots are shown for all data together as well as for individual soil classes. The x-axes correspond to the range (i.e., min. and max. values) listed in Table 6 (Paper II).

4.3 *Spatial continuity*

A large number of past studies have analyzed the spatial variability of geochemical and soil physical conditions. Some soil properties, including texture and volumetric water content, show considerable spatial structure in the horizontal direction, while variables such as bulk density (ρ_b) and total soil porosity (Φ) do not show much spatial correlation in the vadose zone (Duffera et al., 2007). Botros and coworkers (2009) investigated the spatial variability of hydraulic properties in a 16-m-deep vadose zone. They concluded that the spatial continuity of within-lithofacies variability was about 5-8 m in the horizontal direction and approximately an order of magnitude less in the vertical direction.
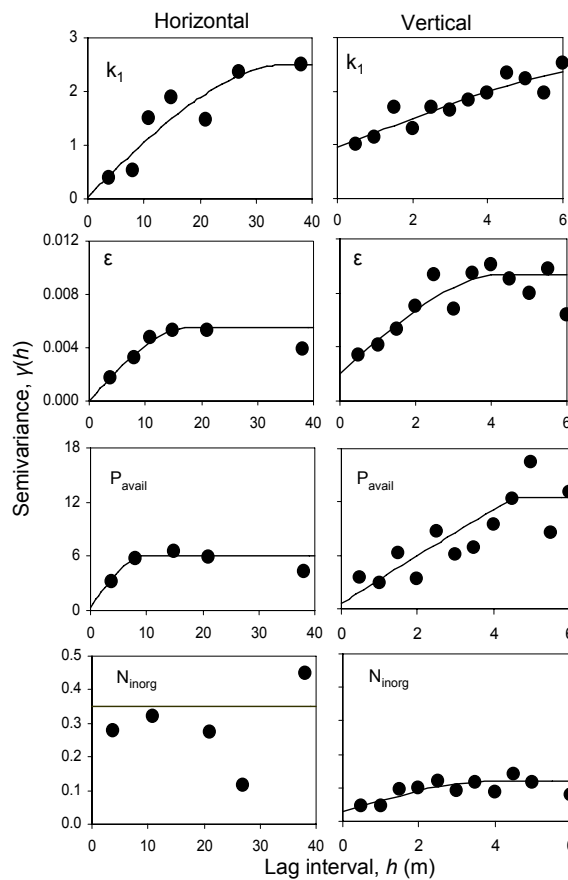
Figure 18. Experimental semivariograms and best-fits of the spherical model (Paper II).

In **Paper II** the spatial continuity of profile data for first-order slurry rates for benzene (k_1), air-filled porosity (ε), inorganic nitrogen (N_{inorg}), and available phosphorous (P_{avail}) in the 16-m-thick vadose zone was determined (Fig. 18). A classical semivariogram analysis was used, which is suitable for irregularly-spaced data (Botros et al., 2009). The experimental semivariograms were fitted to the spherical model with the model parameters given in Table 7 (Nielsen and Wendroth, 2003). The model generally provided a reasonable fit, except for N_{inorg} data in the horizontal direction, where a pure nugget effect was observed. This corresponds to the total absence of auto-

correlation on the scale used in this study (3.75 m < h < 38 m). Other semivariograms showed a low nugget compared to sill, indicating a strong spatial correlation and an adequate sampling frequency (Iqbal et al., 2005). Generally, the sill of the vertical semivariograms was similar or close to that of the horizontal direction. The geostatistical range, however, was 2-4 times greater in the horizontal direction than that in the vertical direction, suggesting anisotropy related to horizontal soil layering. This suggests a need for extensive sampling in the vertical direction during site investigation in a layered subsurface.

Table 7. Best-fit parameters determined with the spherical semivariogram model. (Paper II).

Variable		Nugget	Sill	Range, m	Cross validation R	Nugget/sill
k_1	Vertically	0.94	2.56	8.6	0.92	0.37
	Horizontally	0.04	2.50	35.8	0.92	0.06
ε	Vertically	0.0021	0.0095	4.4	0.84	0.22
	Horizontally	0	0.0055	17.8	0.91	0.00
P_{avail}	Vertically	0.55	9.1	4.7	0.83	0.06
	Horizontally	0	6.1	9.8	0.59	0.06
N_{inorg}	Vertically	0.028	0.12	4.0	0.74	0.24
	Horizontally	0.35	-	-	-	-

Strongest spatial dependence was estimated for k_1 that had a vertical range of 8.6 m and a horizontal one of 35.8 m. As these values were close to or exceeded the maximum lag intervals used, biodegradation potentials measured in samples from any two locations in the study site were likely to be geostatistically related, despite considerable variability. The spatial continuity for the biodegradation potential is stronger than previously observed for hydraulic properties in deep subsurface alluvial soils (Botros et al., 2009). This illustrates that long-term contamination with volatile petroleum compounds most likely has a profound effect on the abundance and activity of soil bacteria on the whole site, while hydraulic and soil physical properties of any given geologic formation will generally be static and unlikely to change over time. The latter is particularly the case when the surface pavement prevents noteworthy infiltration through the vadose zone as was the case at the study site.

4.4 *Summary and recommendations*

- Distributions of petroleum NAPL and vapors are closely linked to stratigraphy, in particular presence of impermeable or water-bearing soil layers.

- Results illustrate that zones of high and no potential for gas transport and intrinsic biodegradation can occur within centimeters from each other, depending on geologic and soil physical conditions. Biodegradation first-order kinetics was the parameter displaying the highest variability among the soil parameters investigated.

- Relatively consistent values for total soil porosity and particle size distribution within main geological soil classes (visually characterized); suggest a few measurements of these parameters to be sufficient for site characterization.

- Data from this study indicated anisotropic variations of most parameters in the vadose zone, with a high variability in the vertical direction compared to the horizontal direction. The geostatistical range in the horizontal direction was about 18 m for air-filled porosity and about 36 m for the benzene biodegradation rate.

5.   Conclusions

The previous chapters have provided a conceptual understanding and discussed experimental and semi-empirical approaches for determining gas-phase diffusion coefficients and biodegradation rates in the vadose zone. Moreover, using different experimental approaches and scales, it was demonstrated how a variety of soil physical conditions, and the variability of these, affect the potential for natural attenuation of volatile petroleum hydrocarbons in deep and unsaturated deposits. Experiences and results presented add new information to the general guidelines for MNA applicability in the vadose zone (previously summarized in Fig. 2, Chapter 1). The main conclusions of this Ph.D. dissertation are:

(i)   Occurrence of drained macropores and fractures was shown to cause dual-porosity and preferential gas-phase diffusion in clay till and limestone. For these materials, the classical and widely used model by Millington and Quirk (1961) yielded underestimations of the gas diffusivity ranging up to $7 \cdot 10^6$ times for low air-filled porosity, at which diffusion occurs essentially through drained macropores. For dual-porosity materials, a two-region model combining the Penman (1940) model and classical non-linearly relationships provided accurate predictions. The tortuosity of macropores and fractures appeared to depend on the total soil porosity, as the macropore tortuosity was low for compacted soil cores ($\Phi < 40$ %). Lastly, it was suggested that choice of prediction model for D_p/D_0 should be grounded on a detailed characterization of the site geology and stratigraphy, since differently textured deposits may exhibit distinct gas diffusivity behavior. The results of this study can be a valuable warning sign for "blind" application of the classical gas diffusivity models across all soil types.

(ii)   Slurry experiments on benzene biodegradation and total counts of soil microorganisms suggested fine textured material possess a greater microbiological potential for biodegradation of petroleum hydrocarbons than more coarse materials. However, for benzene biodegradation in 100-cm^3 soil cores, limitation related to diffusion of oxygen and benzene vapors was observed for D_p/D_0 values lower than about 0.02 independent on soil texture. Therefore, predicted or measured gas diffusivity values may provide some indication whether diffusion limitation is likely to occur during MNA or enhanced biodegradation (e.g., bioventing) in the vadose zone. However, determining gas-phase diffusivity of subsurface deposits does not substitute the need for in-situ measurement of oxygen concentrations to ensure that the redox conditions allow for aerobic biodegradation.

(iii)   Values for gas diffusivity and benzene slurry degradation rates in a given soil layer were statistically related to geological soil classification ($P < 0.05$). This was also the case for air-filled porosity, presence of petroleum NAPL, total counts of soil microorganisms, water content, and bulk density, clearly demonstrating the geological variation and stratification as the controlling factor for fate of petroleum contaminants on the field scale. Likewise, the vadose zone is likely to contain zones with high as well as nearly absent potential for biodegradation and gas-phase diffusion of petroleum vapors, suggesting substantial microbiological heterogeneity and large-scale preferential vapor migration. Directional semivariogram analysis of measured soil parameters (macronutrients, slurry benzene biodegradation rates, and air-filled porosity) showed that spatial continuities were 2-5 times greater in the horizontal than in the vertical direction, demonstrating that site characterization in layered subsurface calls for frequent soil sampling in the vertical direction.

6. Perspectives and application

In contrast to most western countries, the current knowledge on contaminated land in developing and newly industrialized countries may well be just the tip of the iceberg. In China extremely rapid growth over the past 25 years has had enormous environmental impacts on terrestrial environments with the extent of soil contamination reported to be worsening and already representing a threat to food safety and sustainable agriculture (Xu, 2006). This demonstrates that management and remediation of contaminated land outside the western world is likely to represent a major environmental challenge for the future.

Monitored natural attenuation (MNA) is an important remedial option at sites contaminated with fuels and other petroleum products, since it offers a cost-effective and environmental friendly alternative to conventional active remediation at sites where the immediate threats posed by the contamination are low (Balba et al., 1998; Boopathy, 2000). Results from this Ph.D. research provide new insight into soil physical factors determining whether MNA is likely to be successful. In particular, it was suggested that soil ability for gas-exchange of oxygen and petroleum vapors provide important indications of MNA feasibility in petroleum-contaminated vadose zone soils. With these parameters, and their variability, in mind the following two-step strategy is proposed for site characterization and evaluation of MNA feasibility:

Step 1:
Establishing a geological model
1. Distance between boreholes: ~10-20 m
2. Detailed geological characterization of borehole materials
3. Analyses for PHC constituents: 1-5 from each geologic formation/layer dependent on visual inspection.
4. Water content measurements: 1-5 from each geologic formation/layer
5. Texture analyses (grain size distribution): 1 from each dominant soil formation.
6. Total soil porosity measurements: 1 from each dominant soil formation.
7. Estimating D_p/D_0 in major geologic formations based on the geological characterization, water content data, and total soil porosity data.

Step 2:
Documenting biodegradation potential
8. Analyses of O_2/CO_2 in pore air samples taken from major geologic formations
9. Analyses of pH, total nitrogen and total phosphorous contents in soil from major geologic formations
10. Biodegradation experiments using soil from major geologic formations (combining different methods from Table 3)

Figure 19. Recommended strategy for investigations and analyses conducted in each borehole. With a sufficient number of boreholes, the ten steps will provide the basis for evaluating the potential for natural biodegradation in a petroleum-contaminated vadose zone. The approach is based on the statistical and geostatistical variations found in Paper II.

7.   References

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