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Litteraturgennemgang af strategier til dokumentation af nedbrydning af oliestoffer i den umættede zone

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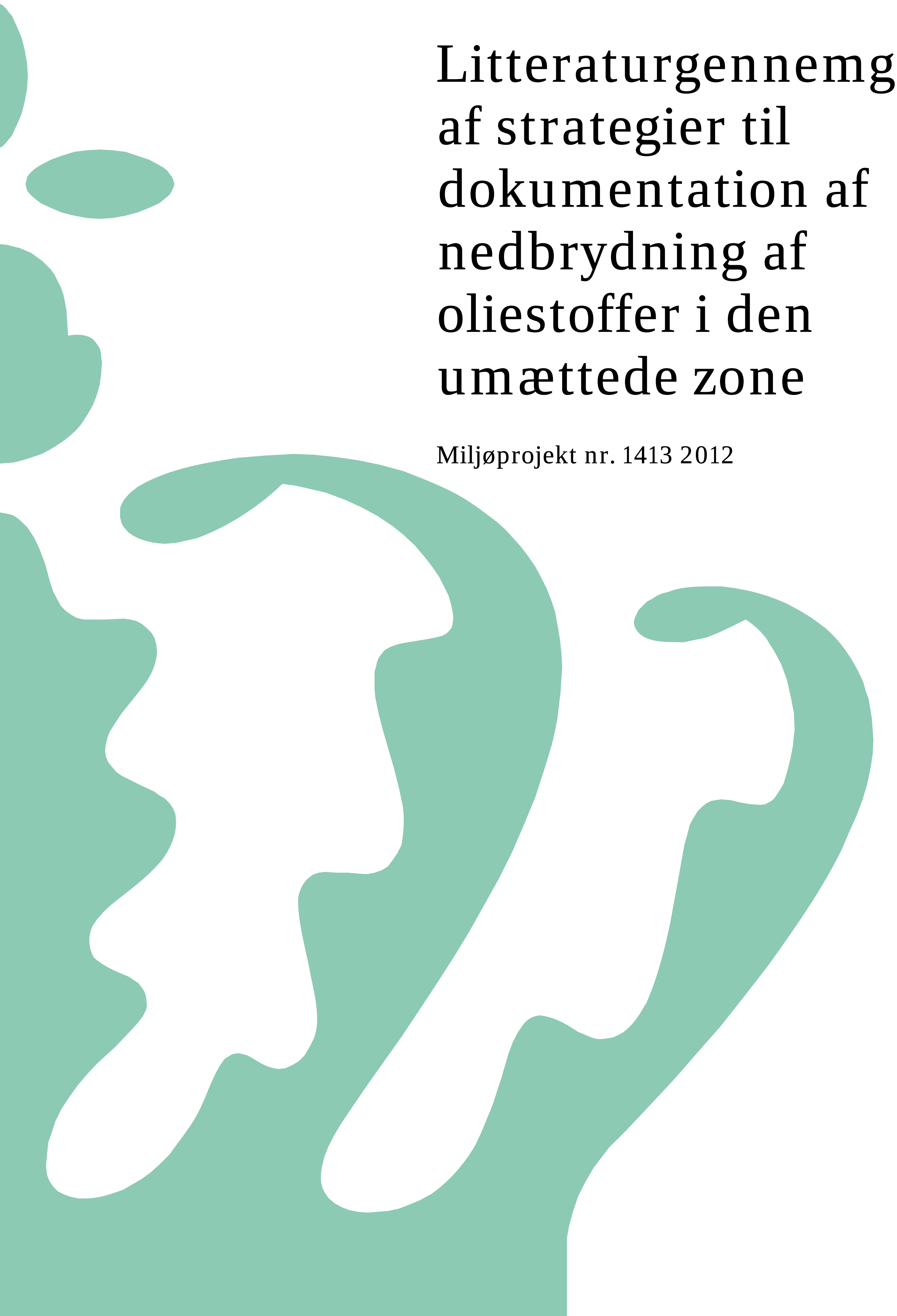

Titel:

Litteraturgennemgang af strategier til dokumentation af nedbrydning af oliestoffer i den umættede zone

Redaktion:

Nanna Muchitsch og Anders G. Christensen
NIRAS A/S

Per Loll og Andreas Houlberg Kristensen
Dansk Miljørådgivning A/S

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Ansvarsfraskrivelse:

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Indhold

Forord

Denne rapport har til formål at beskrive og vurdere forskellige strategier der har været anvendt, eller vurderes at kunne bringes i anvendelse, i forhold til at dokumentere nedbrydning af oliestoffer i jordens umættede zone. Herunder er det hensigten, at strategigennemgangen skal rettes imod anvendelse i den risikovurderingskontekst der opstilles i JAGG 2.0.

Fremadrettet er det hensigten, at der på baggrund af anbefalingerne fra dette projekt skal foretages en afprøvning af en eller flere strategier/-metoder på danske feltlokaliteter.

Projektet er udført af NIRAS og DMR A/S og projektforløbet er blevet fulgt af en følgegruppe bestående af:

Ole Kiilerich, Miljøstyrelsen.
Arne Rokkjær, Region Hovedstaden.
Henrik Aktor, AKTOR Innovation.

Målgruppen for projektrapporten er ikke miljøsagsbehandlere i bred forstand, men dem der måtte have en speciel interesse for fagområdet risikovurdering med fokus på nedbrydning i den umættede zone, samt i at følge processen frem til afprøvning og anvendelse af strategier på feltsager i en dansk risikovurderingskontekst.

Projektgruppen vil gerne takke Professor Peter Kjeldsen, DTU Miljø, Anne Lausten Hansen studerende ved Københavns Universitet samt chefkonsulent Mads G. Møller, RAMBØLL, og seniorforsker Vibeke Ernstsen, GEUS,for assistance i forbindelse med litteraturstudiet.

Resumé

Baggrund

Miljøstyrelsen har i 2006 iværksat "Projekt om opgradering af JAGG til version 2.0", hvorunder der i tre delprojekter udarbejdes nye beregningsmoduler til indarbejdelse i JAGG-modellen. I det ene delprojekt er der præsenteret et nyt koncept til beregning af stoftransporten igennem den umættede zone og til det førstkommende underliggende grundvandsmagasin /260/.

Formål

Det overordnede formål med projektet er, på baggrund af et litteraturstudium, at beskrive, hvilke strategier der findes til at dokumentere og kvantificere naturlig nedbrydning af oliestoffer i jordens umættede zone, samt at få belyst, om der findes eller kan udvikles (simple) feltstrategier, der kan sandsynliggøre, at nedbrydning foregår og er tilstrækkelig – og evt. muliggør, at der kan estimeres lokalitetsspecifikke nedbrydningsrater. Endvidere gives der anbefalinger til afprøvning og implementering af metoder/procedurer/måleprogrammer ift. anvendelsen af givne metoder/strategier sammen med JAGG 2.0. Desuden er der i henhold til kommissoriet for projektet, parallelt med litteratursøgningen på strategier/metoder for den umættede zone, indsamlet tilgængelig litteratur for push-pull test i den mættede zone og tilgængelige erfaringsværdier for styrende parametre (næringssalte og ilt) fra den dybere umættede zone på danske lokaliteter.

Inddragede strategier og metoder

De identificerede overordnede strategier og metoder til dokumentation af nedbrydning i den umættede zone eller, som kan benyttes til en decideret estimering af nedbrydningsrater er følgende:

- Indirekte kvantitative metoder
- Fanemodellering i umættet zone (1D, 2D og 3D)
- Isotopteknikker
- Gas fase push-pull test
- Diffusiv emitter test
- Dual Point Degradation test (DPD-testen)
- Kildestyrkekarakterisering og -dokumentation

Sammenfatning af strategier og metoder

De enkelte strategier og metoder er diskuteret og sammenlignet i forhold til dels bestemmelse af nedbrydningsrater og teknologistadium, økonomi og praktisk anvendelighed. Endvidere er metodernes anvendelighed i forhold til andre miljøfremmede stoffer groft skitseret.

Dokumentation af nedbrydningen over tid

I forlængelse af gennemgangen af de konkrete strategier er det gennemgået, hvordan strategierne skal anvendes sammen med risikovurderingskonceptet indeholdt i JAGG 2.0. Herunder er der opstillet overordnede retningslinjer/anbefalinger til den dokumentation, der på konkrete sager bør indgå ved dokumentation af naturlig nedbrydning. Denne dokumentation indeholder overvejelser om kildens forventede levetid og den tidslige udvikling i balancen imellem kildestyrken og nedbrydning i den afskærende zone imellem kilden og grundvandet, samt dokumentation og monitering ift. de overordnede massebalancer for næringssalte og ilt.

Anbefalinger til feltafprøvning af metoder

Med udgangspunkt i den eksisterende viden anbefales det, at der igangsættes ét eller flere feltprojekter, hvor isotopmetoden (C og H) til bestemmelse af nedbrydningsrater testes på én eller flere lokaliteter, hvor der allerede er gennemført monitering over en længere årrække. Endvidere anbefales det at videreudvikle og dokumentere en ny in-situ test (DPD-testen) til kvalitativ og kvantitativ dokumentation, som sideløbende med dette projekt er blevet testet på et indledende stadium med støtte fra Miljøstyrelsens Teknologiudviklingsprogram. Endelig anbefales det, at AMETIS-systemet til måling af kildestyrken/porevandskoncentrationer under kilden testes på en enkelt af disse lokaliteter.

Anbefalinger til dokumentation af nedbrydningen over tid

På baggrund af litteraturstudiet af tilgængelige standardværdier for indhold af næringssalte og ilt i den dybe umættede zone på danske lokaliteter er det dokumenteret, at der pt. kun eksisterer et meget sparsomt datamateriale på dette område. Derfor anbefales det, at der på en række sager – fremadrettet – indsamles erfaringstal for typiske værdier under danske forhold, således at disse evt. fremadrettet kan indbygges som velunderbyggede standardværdier i JAGG 2.0 modellens database. I forlængelse heraf anbefales det, at der gennemføres ét til to feltprojekter, hvor de opstillede anbefalinger til dokumentation af moniteringsstrategi og grundlaget for dokumentationen på langt sigt kan afprøves og illustreres.

Anbefalinger videreudvikling af JAGG 2.0

Endelig bør det undersøges, om der kan udarbejdes en simpel massebalancemodel til 1D-modellen i JAGG 2.0, der kobler kildestyrken og iltindholdet, for at kunne foretage en vurdering af den langsigtede holdbarhed af det aerobe nedbrydningspotentiale.

Summary

Background

In 2006, the Danish EPA launched a series of projects as part of an effort to upgrade the existing risk assessment software JAGG 1.5. In one of these sub-projects, a new computational module for simulating transport processes through the unsaturated zone was developed and included in the upgraded version of the model, JAGG 2.0 /260/.

Scope

The overall objective of the project is to perform a literature review in order to identify existing strategies directed toward documenting and quantitifying natural degradation of petroleum hydrocarboons in the unsaturated zone, and to evaluate whether existing or developmental field strategies exist or could be developed, that allows estimation of site specific degradation rates. Recommendations are presented for further testing and implementation of methods/procedures/measurement programs that can be used in connection with practical risk assessment using JAGG 2.0. In parallel with the literature search on strategies, available literature on the use of push-pull tests in the saturated zone and the available empirical values for controlling parameters (nutrients and oxygen) from the deeper unsaturated zone at Danish sites has been collected.

Identified strategies and methods

The identified main strategies and methods for documentation of degradation in the unsaturated zone, or that can be used specifically to estimate site specific degradation rates, are as follows:

- Indirect quantitative methods
- Inverse numerical modelling (1D, 2D and 3D)
- Isotope Techniques
- Gas phase push-pull test
- Diffusive emitter test
- Dual Point Degradation test (DPD) test
- Source characterization and documentation

Summary of strategies and methods

The different strategies and methods are discussed and compared in relation to the ability to determine degradation rates, the maturity of the technology, economy, and ease of practical use. Moreover, the applicability of the methods to describe and quantify the fate of other organic substances are roughly outlined.

Documentation of degradation activity over time

Following the discussion of the specific strategies, it is examined how these strategies should be used in conjunction with the risk assessment concept presented in JAGG 2.0. Specific recommendations and guidelines for the practical documentation at typical field sites are proposed. This include considerations on the source longevity and the temporal evolution in the balance between mass discharge from the source and the degradation in the intercepting zone between the source and the underlying groundwater, as well as documentation of the overall mass balances of nutrients and oxygen.

Recommendations of methods to be tested in the field

Based on the existing knowledge, it is recommended that field projects be initiated and the isotope methods (C and H) to measure the degradation rates tested – potentially at one or more existing locations already monitored for a number of years. Furthermore, it is recommended to further develop and demonstrate a new in-situ test (DPD) for qualitative and quantitative documentation of degradation rates that, in parallel with this project, has been tested at a preliminary stage, with support from the Dansih Environmental Protection Agency's Technology Development Program. Finally, it is recommended to test the AMETIS-system for measuring source strength/porewater concentrations under the source at one of these sites.

Recommendations of methods to document the degradation over longer time spans

Based on the literature study of values for content of nutrients and oxygen in the deep unsaturated zone at Danish sites, it is found that at present there exist only a very sparse data set. It is therefore recommended that supplementary data are collected at future sites, to support the determination of default values in the JAGG 2.0 model database. It is recommended that one or two field projects are selected for testing and demonstrating the established recommendations for documentation of the monitoring strategy - and to illustrate and visualize the use of the strategy.

Recommendations for the further development of JAGG 2.0

Finally, it should be considered to develop framework for a simple mass balance module to be used with the 1D model in JAGG 2.0. The module should calculate and couple the mass discharge from the source and the oxygen consumption in the soil in order to make an assessment and verification of the long-term sustainability of the aerobic degradation potential.

1 Indledning

1.1 Baggrund

Revision af JAGG-modellen

Miljøstyrelsen har i 2006 iværksat "Projekt om opgradering af JAGG til version 2.0", hvorunder der i tre delprojekter udarbejdes nye beregningsmoduler, til indarbejdelse i JAGG-modellen.

Nedbrydning under vertikal transport

I det ene delprojekt har NIRAS i samarbejde med DTU leveret et nyt koncept til beregning af stoftransporten igennem den umættede zone og til det førstkommende underliggende grundvandsmagasin /260/. For at kunne udnytte det nye koncept, der inkluderer den biologiske nedbrydning i konkrete risikovurderinger, kræves imidlertid, at der vælges en nedbrydningsrate.

Strategier til dokumentation af nedbrydning

Der er således behov for at få belyst, om der findes eller kan udvikles (simple) feltstrategier, der kan sandsynliggøre, at nedbrydning foregår og er tilstrækkelig – og evt. muliggør, at der kan estimeres lokalitetsspecifikke nedbrydningsrater.

1.2 Formål

Litteraturstudium til metodekortlægning

Det overordnede formål med projektet er, på baggrund af et litteraturstudium, at beskrive hvilke strategier der findes til at dokumentere og kvantificere naturlig nedbrydning af oliestoffer i jordens umættede zone. Der fokuseres primært på strategier til dokumentation af opløst/gasformig forurening; dvs. at fokus ligger på den zone, der befinder sig imellem et decideret hot-spot og en given receptor – her det førstkommende grundvandsmagasin.

Opdatering af nedbrydningsrater

Projektet har desuden til formål at belyse, hvorvidt der er grundlag for en opdatering af de nedbrydningsrater, der er fundet i litteraturen i forbindelse med opdateringen af JAGG til version 2.0 /260/.

Litteraturværdier for næringssalte og ilt i dyb umættet zone

I projektet fastslås det, at indholdet af næringssalte og ilt i zonen, der ligger imellem kilden og grundvandet, er kritiske ift. om der i kildens forventede levetid vil være balance imellem kildestyrke og nedbrydning. Derfor gennemføres et litteraturstudium af tilgængelige værdier for indhold af næringssalte ig ilt under danske forhold.

Anbefalinger til afprøvning og implementering

På baggrund af litteraturstudiet kommes med anbefalinger til afprøvning og implementering af metoder/procedurer/måleprogrammer i en dansk risikovurderingskontekst, herunder ifht. anvendelsen af JAGG 2.0.

Perspektiver

Perspektiverne for projektet er, at der foretages en afprøvning af de metoder, der anbefales; herunder kan der blive tale om at foretage en laboratorie- og/eller feltafprøvning af identificerede metoder til estimering af in-situ nedbrydningsrater i den umættede zone.

2 Problemafgrænsning

2.1 Konceptuelt framework – den danske risikovurderingsmodel (JAGG 2.0)

Den umættede zone indgår ikke i JAGG 1.5

I den senest opdaterede version af JAGG - version 1.5, er der i modulet omkring risikovurdering ifht. grundvandsforurening mulighed for at regne på to situationer; én hvor kilden og forureningen er beliggende i den umættede zone og én hvor den maksimale forureningskoncentration har nået grundvandet og hvor der er målt på en grundvandsprøve.

I førstnævnte tilfælde (trin Ia og IIa) inddrages den umættede zone kun i det omfang, at kildegeometrien (areal og bredde), samt kildestyrkekoncentrationen skal karakteriseres. For risikovurderingen er det principielt ligegyldigt om der er 1 eller 50 meter fra bunden af forureningen til grundvandet (transportafstanden fra kilde til grundvand), ligesom aflejringstypen i den umættede zone (hhv. i jordforureningen og imellem jordforureningen og grundvandet) ikke har betydning for resultatet. Man kan sige at den tidsmæssige dynamik, samt de processer der måtte foregå under transporten fra kilde til grundvand, er trukket ud af risikovurderingen.

I sidstnævnte tilfælde (trin Ib og IIb) er der ikke direkte behov for at have kendskab til den umættede zone, udover at der principielt skal foretages en argumentation for, at den maksimale koncentration må forventes at have nået grundvandet, hvilket kan kræve nogle dynamiske betragtninger omkring kildens alder ifht. forventede transporthastigheder og –tider fra kilde til grundvand.

Den umættede zone inddrages i JAGG 2.0

I forslaget til JAGG 2.0 åbnes der i /260/ op for at inddrage den umættede zone mere direkte i risikovurderingen for benzin- og oliestoffer, idet risikovurderingen anbefales opdelt i tre faser:

<u>Fase 1:</u> Der udføres en 1D transient beregning af forureningens dybdemæssige udbredelse til forskellige tidspunkter ud fra kendskab til geologien imellem forureningens bund og grundvandet. Denne beregning forudsætter, at transporten foregår igennem en homogen og isotrop umættet zone. Beregningen medtager opløst transport i infiltrerende vand, adsorption, diffusion og dispersion, samt vertikal diffusion i gasfasen og det antages, at der ikke sker en nedbrydning under transporten.

<u>Fase 2:</u> Hvis det sandsynliggøres, at en række specifikke forudsætninger for, at der kan foregå en nedbrydning, er til stede, og hvis der er indikationer på, at en sådan nedbrydning rent faktisk foregår, kan der gennemføres en beregning, der medtager nedbrydning under transporten igennem den umættede zone. Beregningen foretages under forudsætning af, at der foregår en 1. ordens nedbrydning, og der vælges en konservativ nedbrydningsrate (dvs. en forholdsvist lav rate), baseret på raterne fra et omfattende litteraturstudium udført i forbindelse med opdateringen af JAGG. Der gennemføres en monitering til kontrol af at nedbrydningen, og betingelserne herfor, opretholdes over tid.

Fase 3: Der tilvejebringes lokalitetsspecifikke feltdata for beregning af den aktuelle 1. ordens nedbrydningsrate, som kan benyttes i beregningen af transporten igennem den umættede zone. Det sandsynliggøres, at denne rate kan forventes opretholdt over den tidshorisont, der gælder for kildens levetid, og der gennemføres en monitering til kontrol af, at forudsætningerne holder, og af at der ikke sker en overskridelse af grundvandskvalitetskriteriet i grundvandet under kilden.

Transporttid og nedbrydning

I ovenstående forslag til JAGG 2.0 åbnes der således op for at gennemføre risikovurderinger for grundvandet, hvor tidsperspektivet for transport igennem den umættede zone inddrages og hvor de processer der foregår under transporten (adsorption, diffusion, dispersion og nedbrydning) inddrages i vurderingen. Med tilføjelse af nedbrydningen i risikovurderingskonceptet vil den umættede zone – under givne betingelser – kunne fungere som en afskærende eller risikoreducerende faktor, som det ikke er/-var muligt at inddrage i JAGG 1.5.

Nødvendig dokumentation ifht. fase 2 og 3

I forhold til anvendelse af både fase 2 og 3, er det essentielt, at der foretages en grundig monitering, og at resultaterne af denne dokumenterer nedbrydningen på tre planer:

i) Antagelsen om at der foregår en nedbrydning i den umættede zone under kilden underbygges (smoking guns).
ii) Det dokumenteres, at forureningen ikke spreder sig uhensigtsmæssigt; altså at der er ”balance” imellem kildestyrken og nedbrydningen i den afskærende zone imellem forureningens bund og grundvandet. Sagt med andre ord skal det dokumenteres, at nedbrydningen er tilstrækkelig til at holde forureningsspredningen i ave (uden at det dog er nødvendigt at bestemme en decideret nedbrydningsrate).
iii) Slutteligt dokumenteres/sandsynliggøres det, at der – over tid – kan opretholdes en tilstrækkelig nedbrydning til at sikre den fornødne risikoreduktion indenfor kildens forventede levetid; altså, at der ikke blot er en tilstrækkelig nedbrydningskapacitet de næste 5 år, mens kildens levetid forventes at være eks. 50 år.

Yderligere dokumentation ifht. fase 3

Ved anvendelse af fase 3 – dvs. i det tilfælde, hvor risikovurderingen ikke baseres på en konservativ nedbrydningsrate fra litteraturen – skal der endvidere tilvejebringes data, der tillader estimering af en lokalitetsspecifik nedbrydningsrate.

Manglende strategier ifht. dokumentation af nedbrydning

Ifht. anvendelse af konceptet opstillet i /260/ er det dog væsentligt, at der ikke pt. foreligger direkte anvendelige strategier til dokumentation af nedbrydningen på en given lokalitet (fase 2 og 3), eller metoder der kan bringes i anvendelse ifht. en kvantificering af aktuelle nedbrydningsrater på en given lokalitet (fase 3).

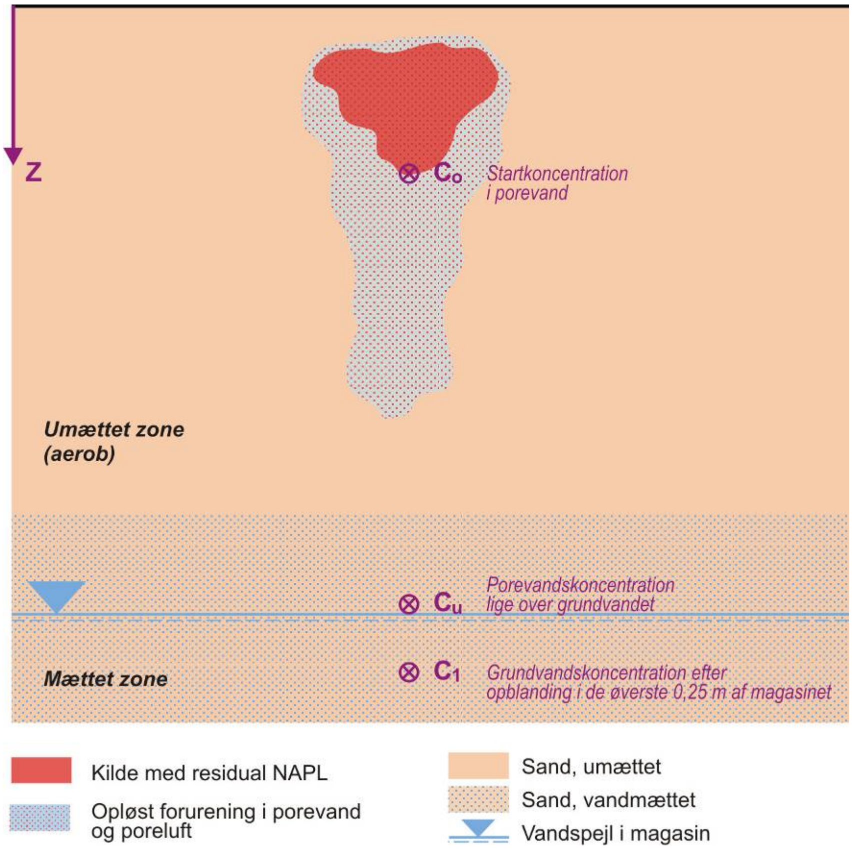
4 konceptuelle hydrogeologiske modeller

I forhold til resten af dette projekt, er det endvidere væsentligt, at der i /260/ er opstillet fire forskellige konceptuelle hydrogeologiske ”modeller” for vertikal transport mod det førstkommende grundvandsmagasin.

Herunder er de to første (Model A og B) rettet imod anvendelse under mættede forhold, hhv. uden og med sprækker, mens Model C og D inkluderer elementer af umættet zone transport; hhv. vertikalt igennem en homogen umættet zone, og horisontalt i en homogen umættet zone, der overlejres af en mættet/impermeabel zone (et låg). Det matematiske udtryk der er lagt op til at benytte til analyse af Model D, giver dog ikke mulighed for at inkludere effekten af nedbrydning.

Projektafgrænsning

Nærværende projekt er således rettet imod anvendelse ifht. Model C med vertikal transport igennem en homogen umættet zone med nedbrydning, jf. figur 2.1. Ydermere er projektet afgrænset til at fokusere på nedbrydning af benzin- og oliestoffer, samt primært på den opløste og gasformige forureningsfraktion; dvs. udenfor selve hot-spot. Med andre ord er det primære fokus for dette projekt at undersøge strategier/metoder, der kan anvendes til dokumentation af nedbrydning og/eller bestemmelse af nedbrydningsrater i den umættede zone i området imellem jordforureningen/kilden og receptoren (her det førstkommende grundvandsmagasin), og ikke ifht. en oprensning eller kildereduktion.



Figur 2.1 Principskitse over Model C for den umættede zone inddraget i JAGG 2.0 /260/.

2.2 Procesforståelse og -beskrivelse

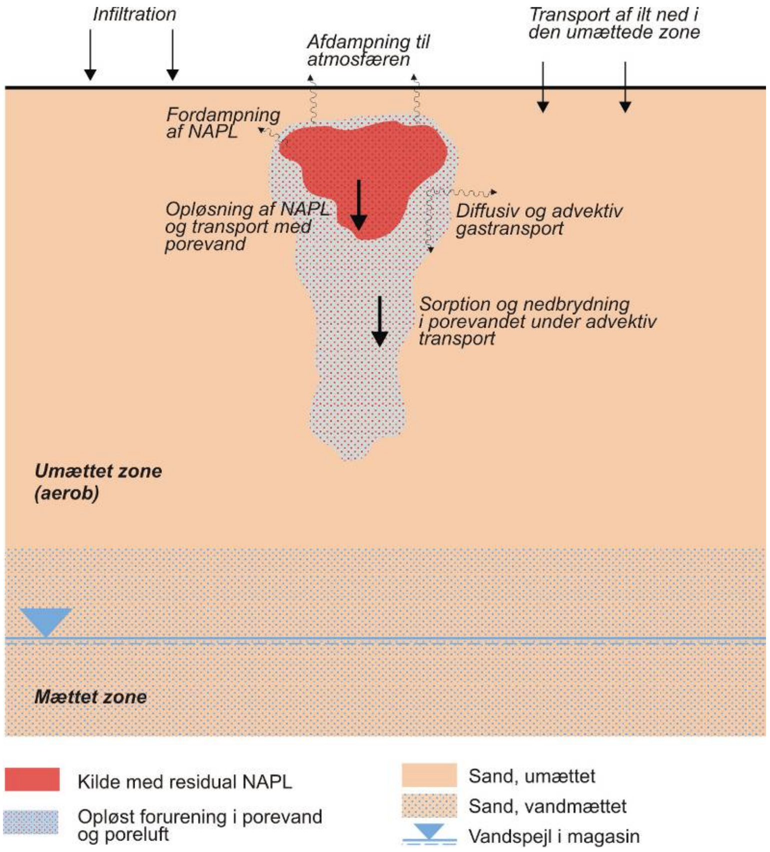
Den umættede zone er en del af hydrologiske vand- og stofkredsløb

Den umættede zone indgår i det hydrologiske kredsløb som et bindeled mellem jordoverfladen og dybereliggende grundvandsmagasiner. Under danske forhold varierer mægtigheden af den umættede zone fra under 1 m i visse områder (typisk lavtliggende kystnære områder) og til over 50 m i andre områder med mægtige sekvenser af istidsafleringer. I den umættede zone sker en transport af vand og gas samt en omsætning og transport af organisk kulstof ved mikrobiologiske processer.

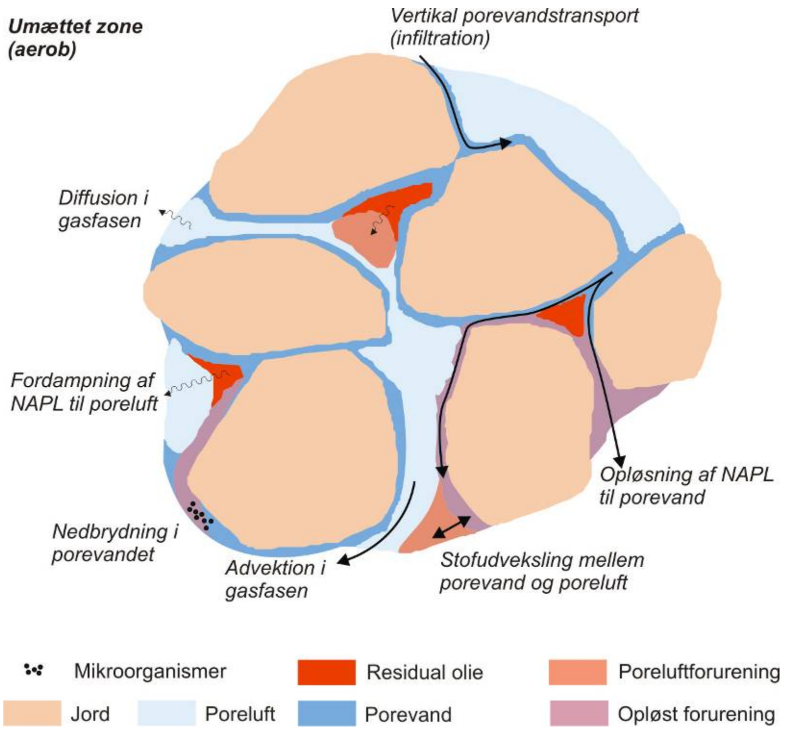
Processer i den umættede zone

I de følgende afsnit beskrives de overordnede processer, der er afgørende for forståelse af vand- og stoftransport i den umættede zone, idet der henvises til bl.a /249/ for en mere detaljeret gennemgang. På figur 2.2 og 2.3 er der vist en sammenfatning af de væsentligste processer både på makroskala (m) , der typisk er den skala der i praksis udføres målinger på, og på poreskala (µm til mm), hvor processerne i virkeligheden finder sted.

Karakteristisk for den umættede zone er, at jordens porer ikke er fuldt vandmættede, og at den ikke-vandfyldte porøsitet udgøres af en gasfase (poreluft). Transport af forureningsstoffer kan således foregå i såvel vandfasen, med infiltrerende vand, som i gasfasen.



Figur 2.2 Processer på makroskalaniveau.



Figur 2.3 Processer på poreskalaniveau.

På figur 2.2 er vist et legeme af residual NAPL der er beliggende i den umættede zone, og som derfor ikke længere er mobilt som fri fase. Den videre transport fra denne zone vil derfor ske via opløsning i det infiltrerende regnvand og via advektion og diffusion i gasfasen.

2.2.1 NAPL-fordeling og -udvaskning

Fordelingen af residual NAPL i den umættede zone - på både makro og poreskala er meget kompleks, og er styret af både de jordfysiske parametre omtalt tidligere, samt af NAPL egenskaberne, jf. tabel 2.1.

NAPL-fordeling og –udvaskning
Opløselighed
Damptryk
Henry's konstant
Densitet
Diffusionskoefficient
Viskositet
Kildegeometri
Alder af NAPL

Tabel 2.1 NAPL-fordeling og -udvaskning.

Egenskaberne for forskellige NAPL varierer markant, og således indeholder benzin stort set kun enkeltstoffer, der enten er flygtige og/eller vandopløselige. I modsætning hertil indeholder en tung fyringsolie stort set kun ikke-flygtige og svagt vandopløselige enkeltstoffer. De væsentligste processer på poreskalaniveau er illustreret på figur 2.3. De to væsentligste reduktioner i selve NAPL-massen som funktion af tiden skyldes fordampning fra den fri fase direkte til poreluften samt opløsning til den vandfilm, der findes mellem den fri fase og kornskelettet. Den flygtige del af NAPL-massen vil på gasform transporteres ved diffusion i de sammenhængende åbne porehulrum og derved spredes over mange meters afstand og udenfor selve området med residual NAPL. Her vil der kunne ske en faseovergang fra poregassen til selve porevandet, hvilket medfører en forurening af porevandet. Tilsvarende vil flygtige stoffer opløst i porevandet kunne transporteres med det infiltrerende porevand til større dybde og under denne transport delvis afgasse til poreluften. For jordarter med højt organisk indhold, vil en del af de opløste organiske enkeltstoffer blive bundet til jorden ved sorption.

2.2.2 Jordfysik

Transport af vand og organiske forureningsstoffer (på opløst og gasform) i den umættede zone er et kompliceret fænomen, der er styret af en række fundamentale parametre, hvoraf de væsentligste er sammenstillet i tabel 2.2.

Jordfysik
Nettonedsivning
Kornstørrelsesfordeling
Kapillartrykskurver/retentionskurver
Porøsitet
Vandmætning (variabel i tid og sted)
Luftfyldt porehulrum (variabel i tid og sted)
Hydraulisk ledningsevne
Indhold af organisk kulstof
Sprækker/aggregater og anden heterogenitet
Snoethed/tortuositet

Tabel 2.2 Jordfysiske parametre.

For såvel vand- som gasbåren transport af organiske forureningskomponenter igennem den umættede zone gælder, at transporten i høj grad er afhængig af jordens mætningsgrad. Mætningsgraden af jorden, og dermed fordelingen af vand og gas i jordens porehulrum, er igen stærkt afhængig af kornstørrelsesfordelingen og retentionskurven. For typisk moræneler med et højt indhold af ler og siltfraktioner vil vandindholdet henover året ofte være meget tæt på 100% af totalporøsiteten, mens det for velsorteret smeltevandsgrus kan være mindre end 5 % af totalporøsiteten. Parametre som hydraulisk ledningsevne og indhold af organisk kulstof, samt en eventuel tilstedeværelse af sprækker har betydning for hastigheden af vandtransporten og dermed for udbredelsen af den vandbårne forureningstransport. Jordens snoethed (tortuositet) har betydning for hastigheden af gastransporten i jordens poreluft, og er en parameter, der igen afhænger af jordens kornstørrelsesfordeling og vandmætningsgrad.

2.2.3 Jordgeokemi

De geokemiske forhold i den umættede zone er både styret af de naturgivne forhold, samt af en evt. tilstedeværelse af residual benzin/olie, der lokalt kan ændre forholdene markant. De jordgeokemiske forhold har især betydning for den (biologiske) omsætning, der kan foregå under transporten igennem jordens umættede zone, samt den påvirkning, som en given omsætning medfører – hvilket igen kan have betydning for omsætningen. I tabel 2.3 er de væsentligste parametre sammenstillet.

Jordgeokemi
Ilt
Kuldioxid
Methan
Kvælstof (N_2)
Nitrat og ammonium
Fosfor
Sulfat
Fe-/Mn-oxider
Redox-horisonter
pH
Karbonatindhold
Bufferkapacitet
Spormetaller

Tabel 2.3 Jordgeokemiske parametre.

For biologisk nedbrydning af organiske stoffer generelt i den umættede zone, er ilt den væsentligste elektronacceptor. Som det fremgår af figur 2.2 sker der løbende en geniltning af jorden ved, at ilt fra atmosfæren (20-21 vol.%.) ved diffusion kan trænge ned i jorden. Denne proces har stået på siden sidste istid, og der måles i dag stort set aerobe forhold selv i meget dybtliggende umættede, uforurenede sandlag (15-20 vol.%). Også i dybereliggende morænelersaflejringer (op mod 10 meter) er der påvist aerobe forhold (9-16 vol.% ilt), om end niveauet er lidt lavere end for tilsvarende sandaflejringer, grundet en lavere luftpermeabilitet. Tilgængelige litteraturværdier er gennemgået i bilag 3.

Respirationsprodukterne ved den aerobe nedbrydning af olie er kuldioxid og vand. Transporten af ilt og kuldioxid er domineret af gasdiffusion i de sammenhængende umættede porehulrum i jorden, jf. figur 2.2. Denne transport er 4-5 størrelsesordner hurtigere end diffusion i vandfasen. I de øverste meter af den umættede zone nær terræn, vil der ofte være et naturligt og svagt forhøjet indhold af kuldoxid på op til 1-2%, hvilket skyldes omsætning af enten naturligt forekommende organisk stof eller tilførsel i form af nedpløjning af organisk materiale. Da indholdet af kuldioxid i atmosfæren er ca. 0,035 vol. %, vil der kunne ske en vis afgasning af kuldioxid til atmosfæren.

Indholdet af nitrat, sulfat, jern-/mangan-oxider og jordens redoxhorisonter siger noget om potentialet for, at anden nedbrydning end aerob omsætning har mulighed for at foregå, mens tilgængeligheden af makronæringsstofferne kvælstof og fosfor (N og P), samt spormetaller, har betydning for mikroorganismernes mulighed for at opbygge ny biomasse, og dermed for at foretage en omsætning af organisk stof (jf. afsnit 2.2.4). pH, karbonatindhold og bufferkapacitet har indflydelse på jordens evne til at modstå den pH-sænkning, der typisk vil ske under aerob omsætning af organisk kulstof, ligesom et forhøjet karbonatindhold kan være en indikation på, at der foregår en mineralisering (udvikling af CO_2, der går i opløsning i porevandet).

2.2.4 Biologi

De biologiske (nedbrydnings)processer i den umættede zone er ofte meget betydningsfulde for problemstillingen omkring vertikal transport af benzin- og oliestoffer igennem den umættede zone imellem kilden og grundvandsspejlet. De vigtigste parametre for en forståelse af de biologiske processer fremgår af tabel 2.4.

Biologi
Organisk stofindhold
Ilt
Mikrobiologiske konsortier
Biomasse
Nedbrydningsrater (aerobt/anaerobt)
Kvælstof (N)
Fosfor (P)

Tabel 2.4 Biologiske parametre.

Indholdet af naturligt forekommende organisk kulstof aftager generelt med dybden, og derfor ses også den største tæthed af mikroorganismer (biomasse) nær terræn. En lang række meget forskellige mikroorganismer findes naturligt i jorden og har her specialiseret sig i bl.a. at omsætte kulstof (bl.a. plantemateriale i pløjelaget). Men også i større dybde findes der mikroorganismer, der er i stand til at nedbryde organiske stoffer, men deres antal er som udgangspunkt begrænset af det generelt lave indhold af kulstof (mad) og makronæringsstoffer (N og P). Den aerobe omsætning af naturligt organisk stof er meget effektiv (udbytterig) og det typisk forekommende konsortium af aerobe mikroorganismer kan også direkte aerobt nedbryde en lang række specifikke oliekomponenter, og selvom den naturlige baggrundspopulation af disse organismer måske ikke er særligt stor, tager det typisk ikke ret lang tid at få etableret en betydelig population af nedbrydende organismer ved en tilførsel af omsætteligt organisk kulstof /264/.

For at et oliestof skal kunne nedbrydes skal det dog være biotilgængeligt – dvs. det skal være opløst i porevandet omkring de enkelte jordkorn, hvor mikroorganismerne findes, jf. figur 2.3. Dernæst skal mikroorganismerne have adgang til et tilstrækkeligt indhold af opløst kvælstof og fosfor der indgår i opbygningen af nye celler (bestående primært af C, N og P). Oliestoffernes kemiske struktur er afgørende for, om de er let eller svært nedbrydelige – men typisk er de letteste, mindste og mest vandopløselige stoffer som BTEX og kortkædede alkaner let aerobt nedbrydelige, mens de tungeste og større PAH molekyler med lav vandopløselighed er vanskelige at nedbryde for mikroorganismerne. Både 0.- og 1.ordens nedrydningskinetik er observeret, og vil afhænge af den konkrete situation.

For at de biologiske processer kan forløbe effektivt anses en vandmætning på ca. 15-20 % af porøsiteten at være nødvendig. Iltindholdet i den umættede zone bør være større end 2-5 vol. %, svarende til omkring 1-2 mg ilt pr. liter porevand /342/, da undersøgelser viser, at nedbrydningshastigheden falder markant når iltindholdet falder til under 2 vol. % /14/.

For indhold af næringsstoffer anvendes ofte et C:N:P-forhold på 100:10:1 (baseret på masser) som en konservativ forudsætning for det indhold af næringsstoffer, der er tilstrækkeligt til, at der kan forventes en ubegrænset mineralisering af en given mængde oliestoffer /204, 264/. Nyere viden på dette felt indikerer, at der – for den problemstilling, der er relevant ifht. JAGG 2.0, hvor der er tale om en afskærende zone imellem kilden og grundvandet – kan anvendes totalkoncentrationer af N og P fremfor mere biotilgængelige faktioner /342/, hvilket skyldes, at der arbejdes med lange tidshorisonter (mere end 10 år) . Ifht. en decideret nedbrydning i kildeområder kan det derimod være relevant at forholde sig til mere umiddelbart tilgængelige puljer af næringssalte (f.eks. de vandopløselige fraktioner), idet nedbrydningen her forceres betydeligt og forventes at foregå over en kortere tidshorisont (3-5 år) /342/.

I bilag 3 er der endvidere redegjort for, at det nødvendige C:N:P-forhold muligvis kan være lavere end 100:10:1, som angivet ovenfor. I litteraturen er der således ligeledes indikationer på at C:N:P-forhold på 100:1,7:0,125 kan være tilstrækkelige til at sikre biologisk nedbrydning. Generelt er der dog tale om et meget dårligt belyst område, hvorfor det – indtil bedre dokumentation foreligger – anbefales, at anvende et (konservativt) ”nødvendigt” C:N:P-forhold på 100:10:1. Det anbefales ligeledes, at dette forhold anvendes på massebasis og baseres på totalkoncentrationer (ikke vandopløselige/biotilgængelige) fraktioner.

I bilag 3 er der anført tilgængelige litteraturværdier for indhold af N og P i dybere umættede zoner; herunder under danske forhold. Der er generelt tale om et yderst sparsomt datamateriale, som dog indikerer indhold af N_{tot} på 10-45 mg/kg TS og P_{tot} på ca. 270-370 mg/kg TS. Disse værdier indikerer, at N formentlig vil være den begrænsende faktor i forbindelse med biologisk nedbrydning af oliestoffer i dybe umættede zoner. En konklusion der dog skal tages med forbehold, da der i et amerikanst studie refereret i bilag 3 er fundet den omvendte sammenhæng, og som derfor bør underbygges i forbindelse med fremtidige studier.

3 Strategigennemgang

3.1 Indledning og strategioversigt

Litteraturindsamling og - gennemgang

Der er foretaget en omfattende indsamling af åben litteratur omkring strategier til vurdering/estimering af nedbrydning i den umættede zone. Litteraturdatabasen oprettet i forbindelse med projektet er vedlagt i bilag 4. Referencernes titel, forfatter, årstal og evt. abstract er sorteret og udskrevet efter først hvilken strategi de omhandler (se næste afsnit) og dernæst alfabetisk efter forfatter. Dette skulle gøre det muligt for interesserede læsere at orientere sig i de ca. 350 referencer.

Strategier og metoder

Der er fokuseret på strategier og metoder der *har* været bragt i anvendelse (f.eks. i udlandet) og metoder, hvor en anvendelse vurderes at være nært forestående, eller metoder der vurderes at kunne bringes i anvendelse med et (begrænset) teknologiløft. De detaljerede resultater af litteraturstudiet er sammenfattet i afsnit 3.2, mens der er foretaget en oversigtsmæssig sammenstilling af strategierne i indledningen til kapitel 6, som danner grundlag for projektgruppens anbefalinger til afprøvning under danske forhold.

Inddragede strategier/metoder

De identificerede overordnede strategier/metoder til dokumentation af nedbrydning i den umættede zone, eller som kan benyttes til en decideret estimering af nedbrydningsrater, er:

- Indirekte kvantitative metoder
- Fanemodellering i umættet zone (1D, 2D og 3D)
- Isotopteknikker
- Gas fase push-pull test
- Diffusiv emitter test
- Dual Point Degradation test (DPD-test)
- Kildestyrkekarakterisering og -dokumentation

Push-pull i den mættede zone

Endvidere er der, i henhold til kommissoriet for projektet, parallelt med litteratursøgningen på strategier/metoder for den umættede zone, indsamlet tilgængelig litteratur for push-pull test i den mættede zone. Resultaterne af dette arbejde fremgår af bilag 2, hvor der er givet en status for metodens anvendelse og en vurdering af teknologien i det omfang metoden relaterer sig til dokumentation af nedbrydning eller estimering af nedbrydningsrater for forureningsstoffer i grundvandsmagasiner.

3.2 Strategier til dokumentation af nedbrydning af oliestoffer i den umættede zone

Indhold i metodebeskrivelserne

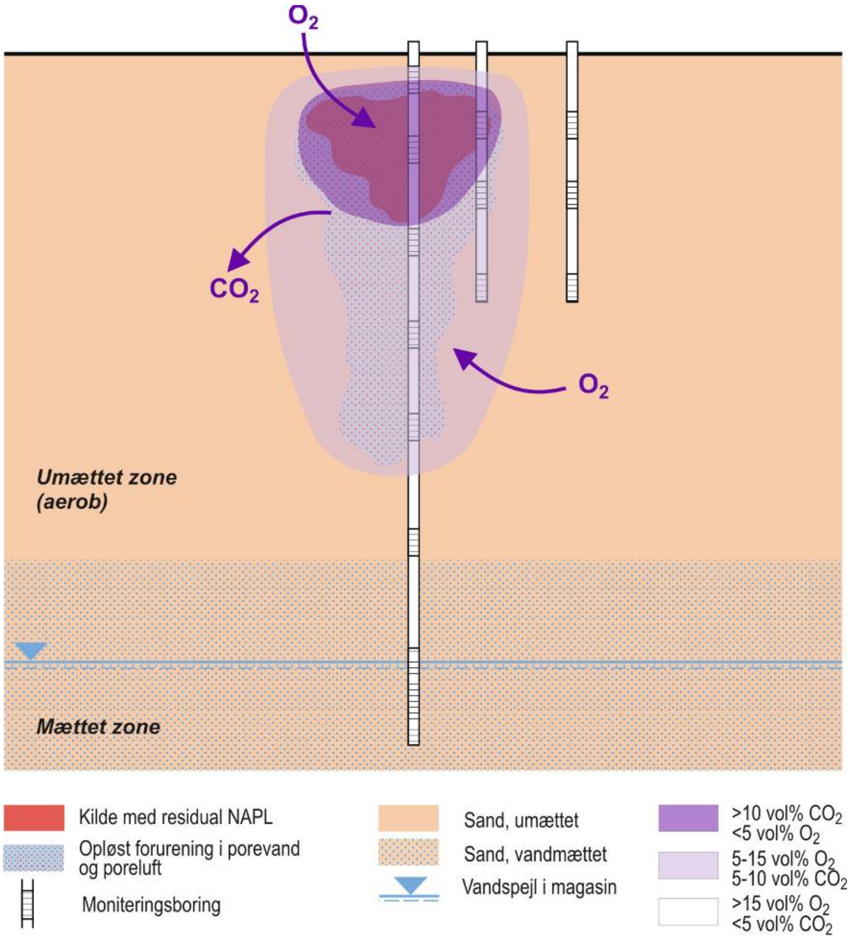
I de følgende afsnit beskrives en række strategier/metoder, der kan benyttes til dokumentation af nedbrydning af oliestoffer i jordens umættede zone. Herunder beskrives strategiens hovedelementer, fordele og ulemper (i den danske risikovurderingskontekst), usikkerheder og fejlkilder samt den relative økonomiske byrde, der er ved anvendelse af strategien. For visse af strategierne er der henvist til bilag 1, hvor illustrative danske feltsager er gennemgået oversigtsmæssigt.

De enkelte strategier/metoder er beskrevet på et niveau, hvor teknologien anvendes til at danne et øjebliksbillede af nedbrydningsforholdene, mens betragtninger omkring den forventede ”langtidsholdbarhed” af nedbrydningen ifht. den forventede kildestyrke – begge i et længere tidsperspektiv – diskuteres i kapitel 4.

3.2.1 Indirekte kvantitative metoder

Hovedelementer og forudsætninger

Ved aerob nedbrydning af oliestoffer forbruges ilt og der dannes kuldioxid (CO_2). Monitering af ilt- og CO_2-indholdet i den umættede zone i området omkring en olieforurening vil derfor kunne give en indikation af, hvorvidt der sker nedbrydning. Tydelige indikationer på naturlig nedbrydning vil være et fald i iltindholdet i områder med indhold af oliekomponenter i poreluften. Samtidig vil der ses en stigning i indholdet af CO_2, jf. figur 3.1.



Figur 3.1 Typisk konturering af ilt- og CO_2-indhold omkring en olieforurening i den umættede zone.

Eksempler på iltprofiler

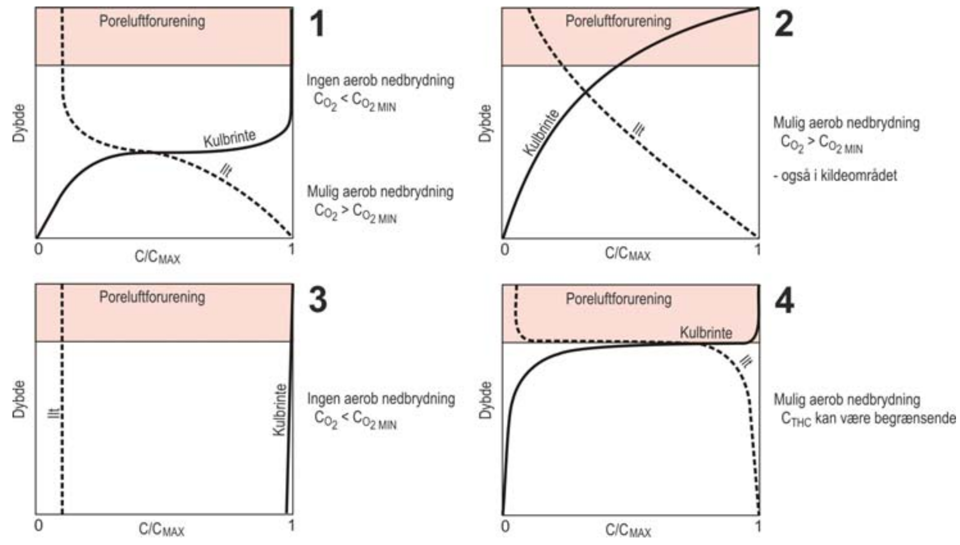
I figur 3.2 er der opstillet 4 konceptuelle modeller for målinger af ilt og forureningskomponenter som kulbrinter over dybden. Modellerne er baseret på observationer fra en lang række sager fra USA /6, 14/.

Model 1 viser en situation, hvor koncentrationen af f.eks. kulbrinter er høj omkring kildeområdet. Grundet det høje indhold af kulbrinter er ilten forbrugt og der er opstået anaerobe forhold, da der ikke kan tilføres tilstrækkeligt ilt til området. I dette område sker der derfor ingen signifikant nedbrydning. Faldet i indholdet af kulbrinter i den anaerobe zone skyldes primært diffusion. Under kildeområdet aftager poreluftforurening og iltindholdet stiger. I dette område vil der være mulighed for aerob nedbrydning.

I model 2 er iltindholdet omkring den kraftigste poreluftforurening tilstrækkeligt højt til, at der kan ske nedbrydning over hele dybden.

Model 3 illustrerer en situation, hvor der er anaerobe forhold over hele dybden, hvorfor der ikke kan forventes at ske nedbrydning. Faldet i indholdet af kulbrinter i den anaerobe zone skyldes primært diffusion. De anaerobe forhold kan være opstået, da raten hvormed ilten forbruges er større end raten hvormed den tilføres. Dette kan f.eks. forekomme i situationer, hvor ilttilførslen fra overfladen er begrænset af f.eks. en næsten vandmættet overfladejord, belægning eller bygninger. Denne situation kan desuden forekomme i dybere liggende lag, hvis der f.eks. findes et overliggende vandmættet lag.

Model 4 ses i situationer hvor ilt let kan diffundere fra terræn og ned i den umættede zone (evt. udenom forureningen). Her falder indholdet af kulbrinter i poreluften signifikant i den øverste del af den umættede zone, da iltindholdet er højt.



Figur 3.2 Konceptuelle modeller for sammenhænge mellem indhold af oliekomponenter og ilt i poreluften /6, 14/.

De 4 konceptuelle modeller viser, at iltindholdet i den umættede zone ikke som udgangspunkt kan forventes at være tilstrækkeligt til at der kan ske nedbrydning alene ved aerobe processer. Nogle zoner kan være anaerobe, mens andre kan være aerobe. Desuden kan faktorer som geologi og vandmætning samt belægning og bygninger have stor betydning for ilttransporten til den umættede zone /8/.

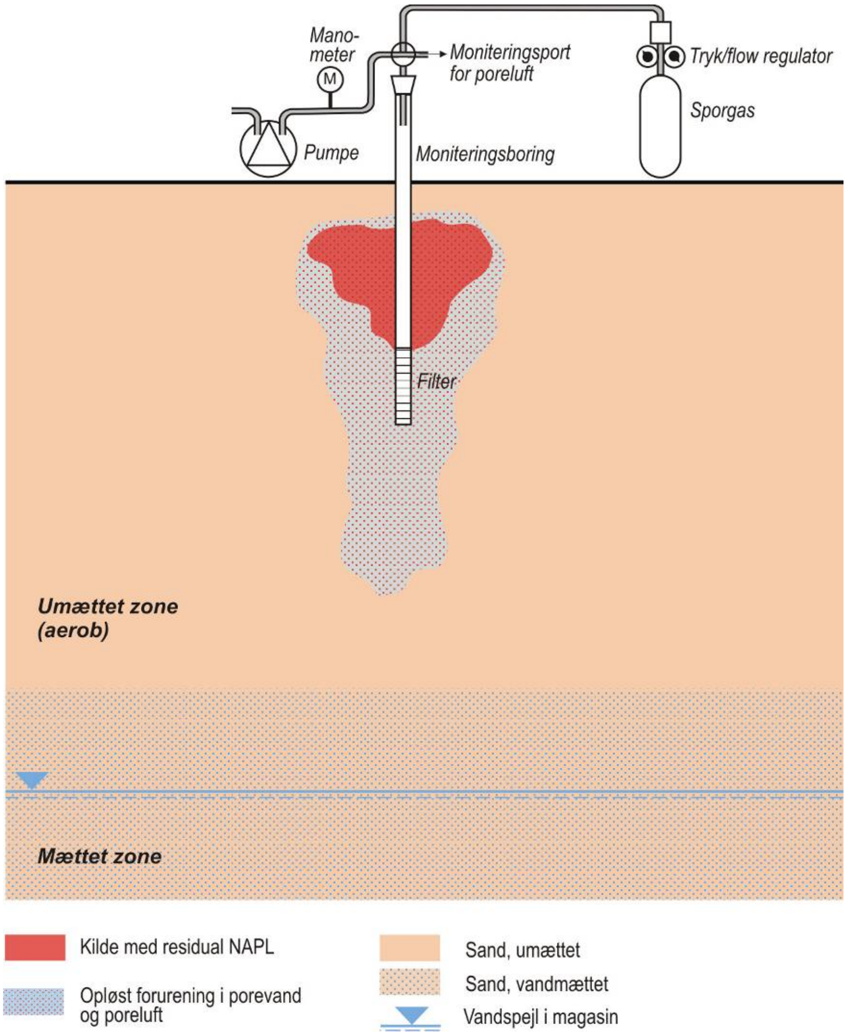
I forhold til tolkning af ilt og kuldioxiddata fra konkrete sager, ved sammenligning med de konceptuelle modeller i figur 3.2 er det væsentligt, at modellerne bygger på koncentrationsprofiler målt under en kilde med uendelig/stor udstrækning ifht. profilets centerlinje. Hvis der er tale om et forholdsvist lille kildeomfang ifht. den dybde som profilet er målt over – eller der af andre årsager sker en betydelig påvirkning ”fra siden” (f.eks. hvis profiler er målt i kanten af kildeområdet), vil der kunne ske fejltolkninger af processerne, således at fortyndingsfænomener evt. tolkes som nedbrydning.

Tilsvarende kan lagdelinger i den geologiske formation under kildeområdet give anledning til fejltolkning nedbrydningsforholdene da selv forholdsvist tynde finkornede/vandmættede lag kan føre til en væsentlig begrænsning af den diffusive tilførsel af såvel kulbrinter som ilt ovenfra, og ventilation af kuldioxid ovenud. Disse problemstillinger er yderliger diskuteret i bilag 2 og 3.

I bilag 1 og bilag 3 findes der eksempler fra danske sager på monitering af ilt- og CO_2-indhold i den umættede zone.

Respirationsforsøg

Ved udførelse af et respirationsforsøg kan en nedbrydningsrate for totalkulbrinter bestemmes på baggrund af måling af den tidslige udvikling af iltindholdet i poreluften. Testen giver ikke umiddelbart mulighed for bestemmelse af nedbrydningsrater for specifikke enkeltstoffer. Testen udføres ved injektion af en sporgas samt atmosfærisk luft til den umættede zone, jf. figur 3.3.



Figur 3.3 Principskitse for opstilling af respirationsforsøg.

Udførelse

Injektionen udføres i et område med en høj oliekoncentration. Efter injektionen følges ilt, CO_2 og sporgaskoncentrationen over tid. Koncentrationen af sporgassen benyttes til at vurdere, om der under testen sker signifikant diffusion af ilt fra jordoverfladen, om der sker fortynding eller diffusion fra/til den omkringliggende jord samt til at tjekke, om der kan have været utætheder i systemet under testen. Raten for iltforbrug bestemmes ud fra de målte data som en 0. ordens sammenhæng mellem iltkoncentrationen og tiden. Der vil typisk findes en lineær sammenhæng indtil iltkoncentrationen er faldet til under 5 vol. %. På baggrund af raten for iltforbruget under testen kan en nedbrydningsrate for totalkulbrinter estimeres som mg hexan-ækvivalent pr. kg bulk-jord pr. dag. Eksempler på udførelse af respirationstests findes i /205, 275/.

En meget udbredt måde at måle O_2/CO_2/CH_4 i poreluftprøver er ved brug af IR-baserede feltinstrumenter. Dette måleprincip vil ved et vist indhold af oliekulbrinter kunne vise falsk positive værdier for methan og for høje indhold af kuldioxid pga. interferensproblemer. Betydningen af dette problem bør vurderes nærmere inden der gives anbefalinger vedrørende måleteknikken. Indtil dette er undersøgt må måleteknik baseret på GC med termodetektor eller lignende anbefales.

Fordele

Måling af ilt og CO_2 i jordens umættede zone som indikator for potentialet for naturlig nedbrydning, har den helt overordnede fordel, at metoden belyser systemets overordnede redoxforhold – anaerobt/aerobt. Strategien bygger desuden på simpel/billig installation og er desuden veldokumenteret. Det vurderes at være relativt simpelt, at tolke og vurdere resultaterne. Det er ydermere ved denne metode muligt at gentage målinger i samme punkt, hvilket f.eks. kan give et indblik i ændringer over tid, eller forskellige steder i jordmatricen, hvilket kan give en indikation af den rumlige variation i nedbrydningsforholdene.

Ulemper

Ulempen ved metoden er, at den ikke er stofspecifik. Metoden giver et billede af, om der generelt er potentiale for naturlig nedbrydning, men ikke om enkeltstoffer som f.eks. benzen nedbrydes.

Usikkerheder og fejlkilder

Usikkerheden ved brug af iltindholdet som indikator for nedbrydning er, at andre organiske stoffer som f.eks. et naturligt organisk indhold i jorden kan forbruge ilt og producere CO_2. Herved kan et højt indhold af organisk materiale i jorden give indtryk af, at der sker nedbrydning af en olieforurening uden at dette er tilfældet. Denne usikkerhed kan dog reduceres betydeligt ved sammenligning med data fra en uforurenet del af samme jordmatrice, jf. ”baggrundsboringen” på figur 3.1.

Da metoden er baseret på poreluftmåling, vil der være tilsvarende fejlkilder og usikkerheder som for poreluftmålinger; f.eks. barometereffekt, nedbør, vandindhold og tidslige variationer.

Økonomi

En indledende undersøgelse af potentialet for naturlig nedbrydning, der omfatter en enkelt målerunde i 5-10 poreluftpunkter fordelt i det forurenede område i forskellige dybder vurderes at koste 25-75.000,- afhængigt af den nødvendige dybde for målingerne. Det antages her, at forureningsudbredelsen er undersøgt, og at punkterne derfor kan placeres i forhold til viden om denne.

Ønskes metoden benyttet som dokumentation for naturlig nedbrydning i den umættede zone, vil det være nødvendigt at udføre flere moniteringsrunder. Under antagelse af, at der moniteres kvartalsvis gennem 2 år, vil en sådan undersøgelse koste 75.000-300.000,- afhængigt af forureningsudbredelsen både vertikalt og horisontalt.

En respirationstest vurderes at kunne udføres for 20-50.000,-.

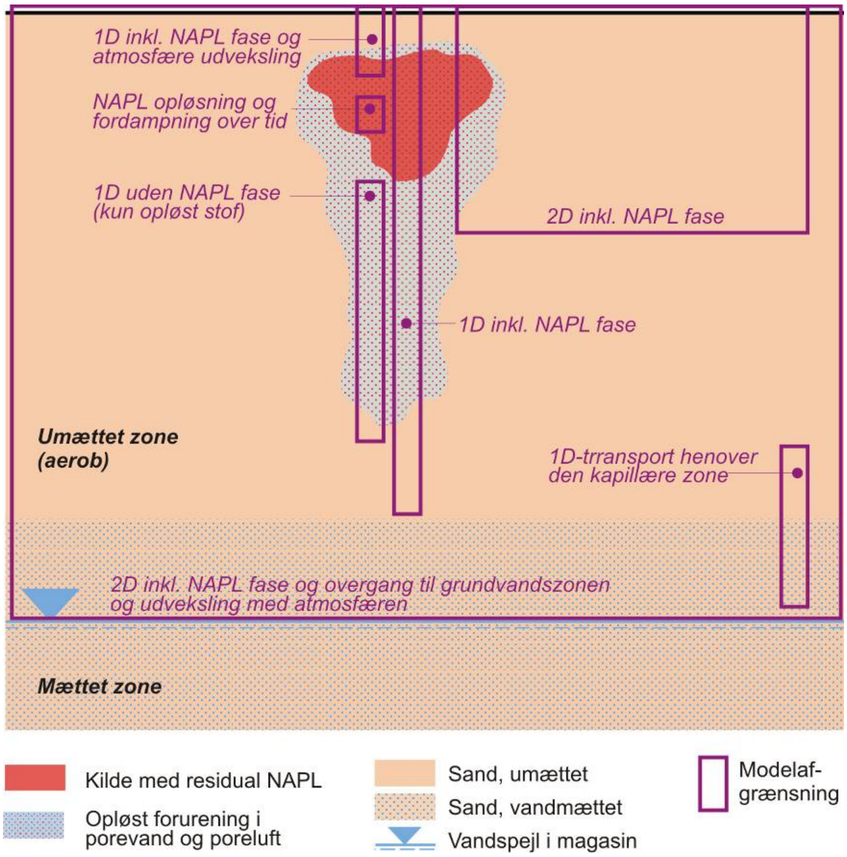
3.2.2 Fanemodellering i umættet zone (1D, 2D og 3D)

Hovedelementer

Ved passende simplificerede antagelser om kildegeometri samt vand- og stoftransport i den umættede zone, kan den forventede tidslige og rumlige udbredelse af oliekomponenter i både gas- og vandfasen beregnes. Herved kan modellen bruges som et værktøj til forståelse af et målt datasæt, og afhængig af kompleksiteten af datasættet kan en matchende model anvendes.

Generelt om modellering

Modellering af vand- og stoftransport i den umættede zone kræver ideelt set en holdbar teoretisk beskrivelse af samtlige af de delprocesser, der er beskrevet på figur 2.3 i det indledende afsnit om procesforståelse. I litteraturen er der således fundet eksempler på modellering af stort set alle tænkelige delprocesser på samme tid. Der findes dog i praksis ingen modeller der inkluderer alle processer, og samtidigt vil det være stort set umuligt at indsamle data og kalibrere en sådan model pga. dens kompleksitet.



Figur 3.4 Typisk anvendte modelafgrænsninger i litteraturen.

Modelafgrænsning og procesparametre

I litteraturen er der fundet mange forskellige afgrænsninger af modeldomænet, på figur 3.4 er vist en række af de mest hyppigt anvendte. På poreskala niveauet er opløsning og fordampning modelleret i bl.a /68/, hvilket i princippet svarer til fugacitetsberegningen i det eksisterende JAGG 1.5 /259/. Generelt er de gennemgående procesparametre i alle modeller indholdet af oliestoffer i gas- og vandfasen samt ilt, kuldioxid og methan – samt nedbrydningsrater for oliestofferne. Håndtering af en separat NAPL fase kun findes i et begrænset antal modeller /24, 235, 276, 82/. Også specifik håndtering af den aktive biomasse i jorden, samt opløsning af bl.a mineraler og deres interaktion med de biologiske processer er kun helt eller delvist indbygget i nogle få modeller /76, 151/.

1-Dimensionelle modeller

Den mest hyppige modeltype er den 1-dimensionelle model med transport kun i vertikal retning, jf. figur 3.4. Modellerne kan omfatte simpel konservativ stoftransport /81, 235, 277/ samt reaktiv transport i porevand og gasfase /276, 92, 94, 87, 98, 81, 88, 28/. Eksempler på beregning af opadrettet reaktiv stoftransport i forbindelse med vurdering af afdampning til terræn og evt. bygninger er detaljeret beskrevet i /14, 92, 278, 241/. Specielt situationen med nedadrettet transport fra en terrænnær NAPL zone og nedad mod grundvandet har været genstand for en lang række numeriske- og feltundersøgelser. Således er transporten af de typiske oliekomponenter indgående undersøgt i bl.a. /24, 280, 235/, mens transporten til grundvandet af forskellige tilsætningsstoffer som MTBE, TBA og ethanol er undersøgt i bl.a. /90, 87, 94, 89/.

2- og 3-Dimensionelle modeller

Antallet af projekter med kalibrerede 2-dimensionelle modeller er relativt få – og ofte knyttet til større forskningsprojekter der er resumeret i en række oversigtsartikler /249, 247, 33/. Enkelte numeriske modeller har en mulighed for at koble det støkiometriske forbrug af ilt og dannelse af CO_2 ved aerob nedbrydning af oliestoffer. Dette muliggør opstilling af massebalancer for både ilt, kuldioxid og oliestoffer /21, 90, 24, 278/. Der er kun fundet meget få eksempler på brugen af 3-dimensionelle modeller, og som for 2D modellerne er de primært udviklet og anvendt på forskningsprojekter /82, 27, 307/.

Nedbrydningsrater bestemt ved modellering

Ønskes specifikt et estimat for størrelsen af den aktuelle nedbrydning for udvalgte stoffer som BTEX, kan dette kan gøres såfremt samtlige øvrige parametre er kendt/estimeret. Dette kaldes ofte ”invers” modellering, hvor således kun nedbrydningsraten er ukendt. Denne metode er anvendt til bestemmelse af nedbrydningsraten for totalkulbrinter i gasfasen /278, 307/, BTEX /19/ samt en række andre flygtige oliestoffer /257, 35, 280/.

Fordele 1D-modeller

Den mest simple tilgang til 1D-modellering af vand- og stoftransport i den umættede zone er inkluderet i f.eks. det nye JAGG program /260/. For langt de fleste parametre er der her angivet standardparametre for jordegenskaber, netto infiltration, fysiske og kemiske egenskaber for udvalgte oliestoffer samt konservative estimater af deres nedbrydningsrater. Standardparametrene afspejler den generelle faglige erfaring, og herved reduceres muligheden for fejlagtige parametervalg og deraf afledt usikkerhed på resultatet. Det vil således være muligt for de fleste brugere af JAGG 2.0 at gennemføre en beregning med 1D-modellen og fortolke resultatet. Eksempler på 1D-modellering af nedbrydning i umættet zone ved brug af JAGG 2.0 findes i bilag 1.

Fordele 2- og 3D modeller

Anvendelse af numeriske modeller til fortolkning af måleresultater giver mulighed for en samlet forståelse af det komplicerede samspil mellem både fysiske, kemiske og biologiske processer. En detaljeret procesforståelse er således vigtig, hvis det ønskes af beskrive nedbrydningsprocesser og udregne tilsyneladende nedbrydningsrater. Endvidere vil det være muligt at vurdere den potentielle fremtidige risiko for udvaskning til grundvandet af enkeltstoffer som f.eks. nye additiver.

Ulemper

De relativt få eksempler på 3D tilgang til modellering indikerer tydeligt, at den nødvendige dataindsamling er en både teknisk og økonomisk hindring ved løsning af praktiske forureningssager. Samtidigt kræver denne type modellering en meget indgående teoretisk og praktisk erfaring med modellerne, hvilket kun meget få personer og firmaer besidder. Endelig medfører de meget komplekse og sammenhængende delprocesser, at beregningstiden for en stor 3D-model kan være dage til uger, hvilket begrænser anvendeligheden i praksis.

Usikkerheder og fejlkilder

Usikkerheden ved modellering af den type komplekse problemer er styret af dels selve formelapparatets evne til at beskrive de komplekse processer korrekt, samt usikkerheden på bestemmelse af modellens parametre. De eksisterende modeller vurderes i dag at kunne beskrive processerne tilstrækkeligt. De fysiske parametre (vandtransport mv.) og kemiske parametre (NAPL opløsning mv.) er de bedst undersøgte – og den største usikkerhed er knyttet til de biologiske parametre (nedbrydning, biomasse osv.). Det vil dog ofte være tilstrækkeligt at anvende 1D-modeller til beskrivelse af de fleste praktiske situationer, og kun i mere specielle situationer er der brug for 2D- og 3D-modeller /260/.

Økonomi

Den mest simple 1D-modellering baseret på JAGG 2.0 og indsamling af de nødvendig feltdata vurderes at ligge i intervallet 25-100.000 kr. ekskl. moms. Opsætning af en 2D-model og indsamling af nødvendige data vurderes at ligge i intervallet 75-250.000 afhængig af de specifikke spørgsmål der ønskes undersøgt, mens en 3D model vurderes at koste væsentligt mere, hvis det fulde potentiale i en sådan model skal udnyttes.

3.2.3 Isotopteknikker

Hovedelementer

Brugen af forskellige isotopteknikker har allerede en bred anvendelse inden for hydrologien, men er først i de seneste 20 år taget i anvendelse indenfor jordforureningsområdet. Brugen af isotopteknikker til direkte påvisning af nedbrydning af oliestoffer og chlorerede opløsningsmidler i grundvandszonen er i dag meget avanceret og veludviklet /60, 284/ og metoderne er kommercielt tilgængelige. Indenfor jordforureningsområdet åbner brugen af isotoper op for en række nye muligheder for bl.a vurdering af indeklimaproblemer og biotransformation af bl.a chlorerede opløsningsmidler /64, 107/. Det er dog først indenfor de sidste 10 år der for alvor er kommet gang i udviklingen af metoderne specifikt rettet mod den umættede zone.

Isotoper af kulstof og brint

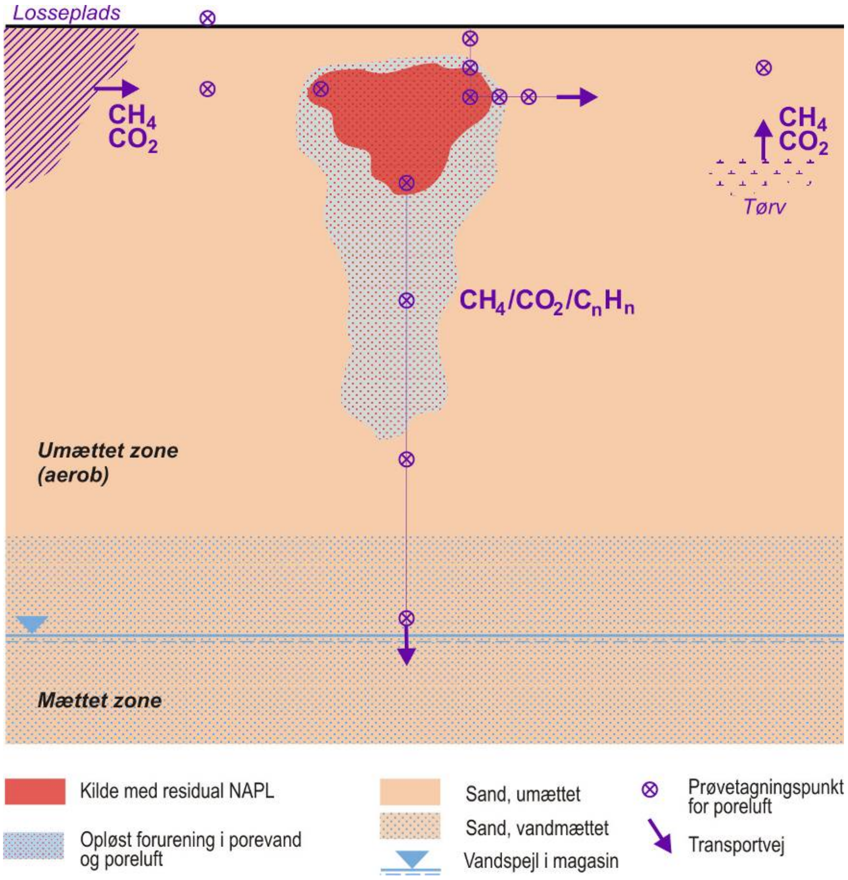
Da oliestoffer generelt består af organisk kulstof og brint (C_xH_n) er det isotoperne af C og H der principielt kan anvendes til vurdering af evt. nedbrydning /282/. Det er dog foreløbig primært de tre isotoper af kulstof (^{12}C, ^{13}C og ^{14}C) der anvendes. Isotoperne ^{12}C og ^{13}C har en meget lille masseforskel, og for de enkelte stoffer i en olieblanding vil dette forhold som udgangspunkt have en konstant værdi. De to isotoper ^{12}C og ^{13}C udgør hovedparten af kulstof i naturen, mens kulstof som ^{14}C kun findes i meget små mængder /252/. For brint udnyttes 2 isotoper (^{2}H- ^{1}H og ^{1}H-^{1}H) men til forskel fra kulstofisotoperne er den relative masseforskel større /318/.

Isotopfraktionering ved biologisk nedbrydning

Laboratorieforsøg har vist at den tungere ^{13}C isotop nedbrydes lidt langsommere en ^{12}C , hvorved forholdet mellem de to isotoper ændrer sig målbart. Dette resulterer i en relativ opkoncentrering af ^{13}C, og graden af opkoncentrering er specifik for det enkelte oliestof og benævnes på engelsk ”Isotope Fractionation Ratio” /252/. For en række olie- og benzinstoffer er dette forhold således bestemt eksperimentelt /252/. Også kulstoffet i de dannede reaktanter ved nedbrydning (CO_2/CH_4) vil have et forhold mellem ^{12}C og ^{13}C der er styret af isotopsammensætningen i det nedbrudte oliestof.

Udtagning af prøver til bestemmelse af isotopfraktionering

Isotopfraktionering som metode anvendes, i den umættede zone, primært ved opsamling af poreluftprøver og efterfølgende laboratorieanalyse. Det er dog også muligt direkte at måle isotopsammensætningen af evt. fri fase olie eller fra evt. vandprøver der udtages fra zoner med tilstrækkelig høj vandmætning.



Figur 3.5 Brug af isotopteknikker under feltforhold.

Brug af isotopfraktionering under feltforhold

Isotopfraktionering som metode anvendes under feltfold i en række forskellige sammenhænge. På figur 3.5 er dette illustreret. Udtagning af poreluftprøver kan således ske fra enkeltpunkter for at indsamle yderligere viden om de processer der foregår generelt – herunder om der er tegn på biologisk nedbrydning og om kildens sammensætning i forhold til den kendte viden om isotopsignaturen af forskellige typer organisk stof. Endvidere kan der udtages prøver i de retninger fra kildeområdet som stofferne må forventes at spredes – enten ved diffusion i gasfasen og/eller advektion i porevandfasen. Herved kan ændringen i isotopfraktioneringen langs transportvejen fastlægges og nedrydningsraten kan teoretisk set estimeres direkte hvis transporthastigheden kendes.

Isotopfraktionering anvendt i praksis på feltlokaliteter

Brug af isotopfraktionering til generel beskrivelse af transport og nedbrydning af oliestoffer i den umættede zone under feltforhold er ikke særligt udbredt, og er stort set kun anvendt i forbindelse med forskningsprojekter. For en oversigt se /64/. Anvendelse af isotopfraktionering til generel procesforståelse af aerob nedbrydning er rapporteret i /252, 107/ og for anaerob nedbrydning i /283, 284/. Egentlig bestemmelse af 1.ordens nedbrydningsrater af enkeltstoffer (bl.a. BTEX m.fl) er rapporteret i /63, 252/ mens rater for totalkulbrinter er rapporteret i /65, 278/. Brugen af brintisotper til påvisning af aerob nedbrydning af MTBE er dokumenteret i /319/. Laboratorieforsøg med umættet jord og aerob nedbrydning af benzen, viser en "Isotope Fractionation Ratio" for H på (εH=-11 o/oo) mens der kun ses en væsentlig mindre tilsvarende værdi for C (εC=-2 o/oo) /320/. Idet betydningen af diffusionsprocessen for isotopfraktioneringen af C og H er af samme størrelse, vil betydningen af diffusion teoretisk set have en relativt mindre indflydelse på fortolkningen af H isotopdata. Der er dog samtigt større usikkerhed forbundet med analyse af H-isotoper relativt til C-isotoper, men den større fraktioneringsfaktor opvejer dog denne usikkerhed /318/. For at kunne detektere isotoperne af H kræves en minimum koncentration i af kulbrinter poreluften på ca. 100 µg/m^3 – svarende til en opløst koncentration i porevandet på ca. 0,75 µg/l /321/.

Påvisning af andre typer kilder til CH_4 og CO_2

Isotopsammensætningen af kulstof i naturligt forekommende organisk stof som f.eks. tørv eller organisk affald i moderne lossepladser, afviger i mange tilfælde væsentligt fra isotopsammensætningen i fossilt materiale som benzin og olie. Dette kan i visse tilfælde udnyttes til påvisning af andre kilder til CH_4 og CO_2 i poreluften end olieforureninger /14, 16/.

Påvisning af CH_4 nedbrydning ved methanoxidation

Brugen af isotopfraktionering af kulstof til påvisning af methanoxidation til kuldioxid er en meget velafprøvet metode, og anvendes ofte i forbindelse med vurdering af drivhusgasbelastningen fra nedlagte deponier /9, 10, 11, 15/.

Fordele

Sorption, fordampning fra opløst fase og advektiv transport i porevandet ændrer ikke isotopsammensætningen af både C og H i et givent oliestof i særlig høj grad /252/, og dette er processer der ved traditionelle metoder er svære og omkostningskrævende at beskrive detaljeret i felten. Samtidig er prøvetagning af poreluftprøver en standardydelse for de fleste firmaer, og kræver således ikke noget specielt udstyr eller lignende. Metoden kan også give indblik i den rumlige variation af nedbrydningsforholdene forskellige steder i den umættede zone – og dermed give et godt supplerende datagrundlag til inddragelse i risikovurderinger i henhold til JAGG 2.0 (fase 3, jf. afsnit 2.1).

Ulemper

Under feltforhold, vil isotopfraktioneringen af kulstof som følge af biologisk nedbrydning kun i visse tilfælde dominere ifht. effekten af fraktionering ved diffusion, og kun i disse tilfælde vil det således være muligt at estimere nedrydningsraten direkte /252/. Metoden, baseret på analyse af poreluft, er kun brugbar op til C10-kulbrinter – dvs. typisk de mest flygtige aromatiske og alifatiske kulbrinter /252/. For tungere kulbrinter vil isotopanalyse af kulstof kunne udføres på porevandsprøver i det omfang det er teknisk muligt at udtage porevand fra den umættede zone. Analyse af isotopfraktionering af kulstof i både vand- og poreluftprøver udføres kun kommercielt på få laboratorier i udlandet.

Usikkerheder og fejlkilder

Da betydningen af diffusionen i forhold til nedbrydning under visse forhold (frisk spild og ved aftagende kilde) kan være vanskelig at afgøre, er metoden baseret på isotoperne af kulstof i praksis behæftet med en vis usikkerhed, hvis der ønskes bestemt præcise nedbrydningsrater. Selve analysen af brintisotoperne er behæftet med en større usikkerhed /318/ og der foreligger få felterfaringer med metoden brugt under umættede forhold.

Teknologistadium

Metoden baseret på isotoperne af kulstof er relativt veludviklet for oliekomponenter og testet i felten. For at øge anvendeligheden af denne metoden arbejdes der i øjeblikket med parallelt at anvende isotoperne af C og H.Det vurderes at brugen af H-isotoper er klar til at blive testet i felten, men analyserne udføres pt. kun af få forskningslaboratorier i Europa og USA.

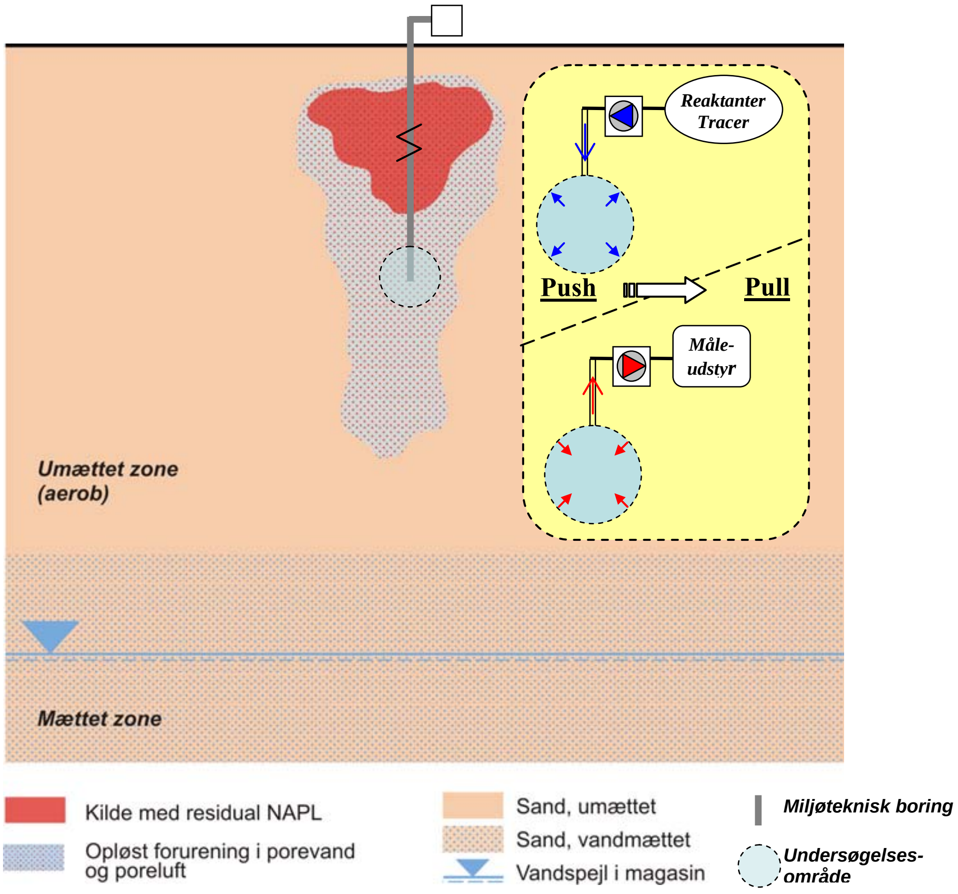
Økonomi

Analyser af en poreluftprøve for isotoperne ^{12}C og ^{13}C af kulstof koster i størrelsesordenen 1-2.000 kr. pr prøve, mens ^{14}C-analyser koster ca. 2.000 kr pr. prøve. Analyser af poreluftprøver for isotoperne af H (^{2}H- ^{1}H og ^{1}H- ^{1}H) udføres pt. primært af forskningslaboratorier og prisen er i størrelsesordenen 2-3.000 kr pr. prøve /321/.

3.2.4 Gas fase push-pull tests

Hovedelementer

Denne metode er baseret på en strategi, der er udviklet til brug i den mættede zone, bl.a. til bestemmelse af in-situ nedbrydningsrater (jf. bilag 2), og kaldes i litteraturen Gas Phase Push-Pull Test (GPPT). Der installeres et poreluftspyd i en relevant dybde og zone i forhold til jordforureningen hvorefter der nedpumpes (Push) en blanding af de forureningsstoffer, man ønsker nedbrydningsraten bestemt for, samt én eller flere tracere, der har stofmæssige egenskaber der ligner forureningsstofferne, men som ikke nedbrydes. Slutteligt foretages en oppumpning (Pull) af gasserne, alt imens der løbende måles på koncentrationen af forureningsstofferne og tracerne. Princippet er illustreret i figur 3.6.



Figur 3.6 Principskitse over push-pull test i umættet zone.

Kvalitativ dokumentation af nedbrydning

Afhængigt af nedbrydningshastigheden vil der være forsvundet en større eller mindre andel af forureningsstofferne mens de var i jorden, mens massetabet af traceren vil modsvare det abiotiske tab (diffusion, adsorption mv.). Forskellen i massetabet for forureningsstof og tracer kan benyttes til en kvalitativ dokumentation af nedbrydning. Dette forudsætter, at tracere og nedbrydningsstoffer ligner hinanden tilstrækkeligt, eller at tracerne er valgt konservativt med fysisk-kemiske egenskaber der – ud fra en teoretisk betragtning – vil give et mindre mass recovery end for forureningsstofferne (såfremt disse ikke blev nedbrudt)

Kvantitativ dokumentation af nedbrydning via matematisk analyse

Metoden har dog helt klart sin primære berettigelse ifht. en kvantitativ bestemmelse af nedbrydningsraterne for de undersøgte forureningsstoffer under de forhold som hersker naturligt på lokaliteten, idet det, via en matematisk analyse af koncentrationsforløbet for forureningsstoffer og tracere, er muligt at beregne nedbrydningsraten. Såfremt tracer og forureningsstof ligner hinanden tilstrækkeligt kan denne analyse udføres udelukkende på de målte data – uden nærmere kendskab til den jordmatrice som er omfattet af testen, men hvis det ikke er muligt at finde en tilstrækkelig god tracer vil der blive behov for at inddrage en numerisk analyse af strømningen i jordmatricen. I den forbindelse skal der indsamles prøver til karakterisering af jordmatricen for at kunne opnå en tilfredsstillende modeltolkning af data. Først kalibreres modellen til de opnåede tracerdata mht. indflydelsen af jordens egenskaber på stofudbredelsen (uden nedbrydning), hvorefter modellen køres igen med nye stofparametre der repræsenterer forureningsstoffet, og hvor nedbrydningen er den eneste ubekendte parameter. Når modeltolkning inddrages bliver metoden således betydeligt mere arbejdskrævende og omkostningstung, men, når modellen først er sat op, kan der for en forholdsvis beskeden merudgift, gennemføres en følsomhedsanalyse på den opnåede nedbrydningsrate og/eller gennemføres prediktive modelkørsler ("what if" simuleringer).

Teknologistadium

Teknologien har endnu ikke været afprøvet på benzin- eller oliekomponenter, men har været anvendt i felten, til kvantificering af methanoxidation i den umættede zone over en kulbrinteforurenet anaerob akvifer /253, 255/ og i dæklaget på to lossepladser /286/. Desuden er der lavet nogle forholdsvist grundige studier af anvendelsen af tre forskellige tracere ifht. methan (Helium, Neon og Argon), herunder ved meget forskellige vandindhold i forsøgsmatricen /285, 287/. Endvidere har stabile isotoper været inddraget i estimering af nedbrydningsrater for methan /253, 255/.

Forskellen på at anvende metoden ifht. methan eller benzin- og oliestoffer er, at methan, som et meget flygtigt organisk molekyle, næsten udelukkende befinder sig i poreluften, mens benzin- og oliekomponenter vil befinde sig i såvel poreluften, som jordvandet og adsorberet på jordpartiklerne. Den største opgave ved at løfte teknologien fra at kunne håndtere methan til at kunne håndtere benzin- og oliestoffer bliver således at finde én eller flere tracere, der kan repræsentere de forureningsstoffer som nedbrydningen undersøges for – og at håndtere de usikkerheder der vil opstå som følge af forskelle i fysisk-kemiske egenskaber for tracere og forureningskomponenter, samt de geologiske inhomogeniteter der måtte være på en typisk forureningssag.

Der er således ikke tale om en færdig og gennemtestet teknologi, som umiddelbart kan bringes i anvendelse på en given lokalitet, men en teknologi, som via gennemførte felttest på et simplere organisk stof vurderes at være modnet tilstrækkeligt til, indenfor en kort årrække, at kunne finde anvendelse ifht. benzin- og oliekomponenter. Overførslen indeholder dog en række ikke-trivielle problemstillinger og vil formentlig kræve udvikling og afprøvning under kontrollerede forhold i laboratoriet, inden anvendelse på en forureningssag.

Fordele

En af de største fordele ved push-pull teknologien er, at der skal forholdsvist få installationer til for at gennemføre en test, og ifht. diffusiv emitter testen beskrevet i afsnit 3.2.5 er push-pull testen mindre følsom overfor udførelsen af selve installationen. Såfremt teknologien overføres til at kunne gennemføres på benzin- og oliestoffer, vil en stor fordel være, at testen kan gennemføres flere steder i jordsøjlen/-matricen, hvorved man kan få en fornemmelse for den rumlige variation i nedbrydningspotentialet forskellige steder – og dermed give et godt datagrundlag til inddragelse i risikovurderinger i henhold til JAGG 2.0 (fase 3, jf. afsnit 2.1).

Ulemper

En åbenlys ulempe ved teknologien er, at den endnu ikke er afprøvet på benzin- og oliestoffer. Det er således et åbent spørgsmål om der kan findes én eller flere egnede tracere, der er gode repræsentanter for de mest almindelige risikodrivere for benzin- og olieforureninger, og som kan muliggøre en datatolkning uden en numerisk modellering af strømningen i jordmatricen (dvs. kun med en matematisk analyse af de målte gennembrudskurver, jf. diskussionen ovenfor). Eftersom benzin- og olieforureninger udgøres af en lang række forskellige stoffer med meget varierende fysisk-kemiske egenskaber er det under alle omstændigheder givet, at metoden (uanset direkte datatolkning eller modellering) egner sig bedst til anvendelse ifht. et eller nogle få udvalgte forureningsstoffer (herunder ofte benzen) og ikke ifht. totalindhold af kulbrinter. Det er heller ikke åbenlyst hvordan eventuelle baggrundsniveauer af forureningsstoffet/-stofferne skal håndteres i resultattolkningen, f.eks. jf. situationen i figur 3.6, hvor testen udføres i ”forureningsfanen” under kilden; en situation der har givet usikre resultater for methan /286/.

Dertil vurderes det, at kontrol- og måleudstyr til injektion og ekstraktion af gasserne samt on-line målinger vurderes at ville stille forholdsvist store krav til opstillingen og må forventes at være forbundet med forholdsvist store opstartsinvesteringer.

Usikkerheder og fejlkilder

I forhold til praktisk anvendelse af push-pull testen overfor benzin- og oliekomponenter bliver det afgørende, hvilke tracere der kan bringes i anvendelse; herunder hvordan de måles og hvor nøjagtigt de kan kvantificeres ifht. den analysemetode der benyttes til at kvantificere forureningsstofferne. Herunder er det specielt vigtigt, at der ikke er væsentligt større usikkerhed på tracermålingerne end på målingerne af forureningsstofferne, da der ellers vil blive (for) store usikkerheder på de estimerede nedbrydningsrater.

Tolkningen af data fra inhomogene geologier kan blive besværliggjort betydeligt, hvis det ikke er muligt at finde tracere, der er meget lig de forureningsstoffer der undersøges. Dette skyldes, at selv mindre forskelle i de parametre der styrer stoffernes fasefordeling (K_{oc} og K_H) vil kræve en grundig karakterisering af de jordfysiske parametre for at man efterfølgende kan udtrække en nogenlunde nøjagtig nedbrydningsrate. En grundig karakterisering af inhomogene jordmatricer bliver specielt vigtigt under forhold hvor nedbrydningsraten er forholdsvist lav.

Økonomi

Eftersom strategien endnu ikke er udviklet og afprøvet til brug for benzin- og oliestoffer, og der stadig er væsentlige usikkerheder omkring centrale emner ved en praktisk gennemførelse af testen, er det naturligvis svært at gætte på de økonomiske omkostninger, der vil være ved gennemførelse af testen på en given lokalitet. Dertil kommer uafklarede spørgsmål omkring instrumentering ifht. analysearbejdet; f.eks. om der kan benyttes automatiserede målemetoder til både tracer og forureningskomponenter. For at metoden kan bringes i ”rutinemæssig” anvendelse på større forurenede lokaliteter kræves således et teknologiløft, der umiddelbart vurderes at svare minimum til et Ph.D.-studium.

Når udstyret er kørt ind og afprøvet, og der er opnået nogle felterfaringer med metoden, kunne et bud dog være i størrelsesordenen 75-350.000 kr. ekskl. moms hvis testen kan gennemføres med en form for automatiseret instrumentering. Herunder er der taget højde for, at der skal gennemføres en indsamling af jordfysiske parametre og opstilling/kalibrering af en model til repræsentation af transporten i jordmatricen.

3.2.5 Diffusiv emitter test

Hovedelementer

Denne strategi er nært beslægtet med push-pull testen hvorfor mange delelementer i nedenstående diskussion er fælles for de to metoder. Teknologien er udviklet på DTU, jf. /288/, og er baseret på, at der installeres en kunstig kilde med en tracer i den umættede zone. Traceren hældes, som fri fase, i en såkaldt Diffusiv Tracer Emitter (DTE), som består af en glasdel i bunden og en plasticdel (polyethylen) for oven. Traceren befinder sig i glasdelen og diffunderer efterfølgende ud igennem polymerdelen til den omgivende umættede jordmatrice.

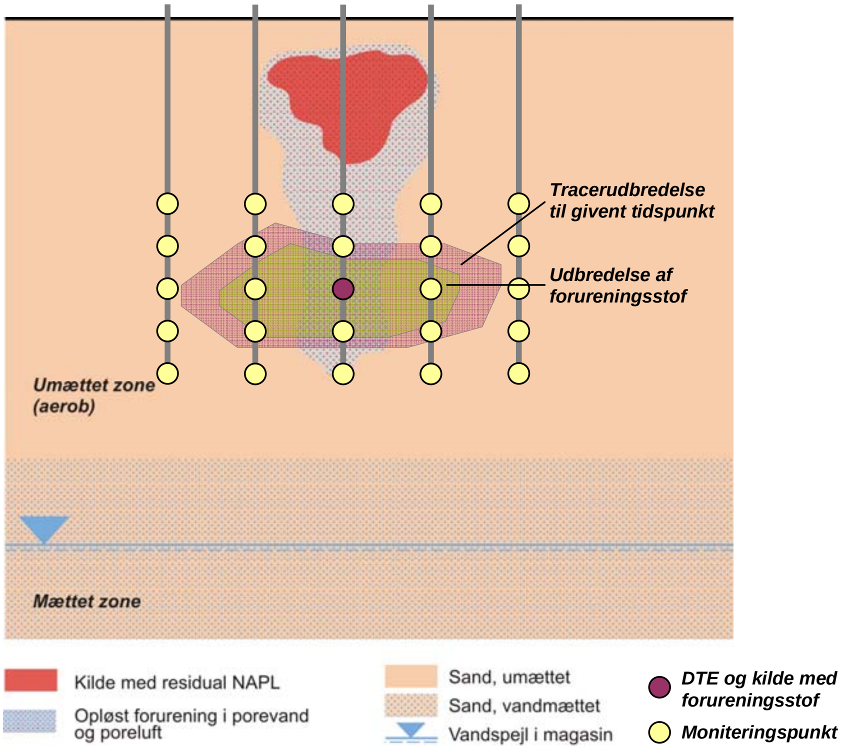
Installation af kilde(r)

For at strategien kan bruges til at dokumentere, at der foregår en nedbrydning, eller for at kunne bruges til at estimere en nedbrydningsrate for et givent benzin- eller oliestof, skal der – sammen med traceren – installeres en kilde af det stof der undersøges (f.eks. benzen). Den aktuelle tracer skal være unedbrydelig og vælges så stoffets egenskaber (damptryk/flygtighed, vandopløselighed og adsorptionsegenskaber) mest muligt ligner det stof som skal simuleres.

Kvalitativ dokumentation af nedbrydning

Efterfølgende moniteres udbredelsen af traceren og forureningsstoffet via et præinstalleret net af moniteringspunkter omkring kilden, og forskellen i den tidslige udbredelse af tracer og forureningsstof tilskrives nedbrydning, da stofegenskaberne er (næsten) ens og da det er den samme jordmatrice stofferne bevæger sig igennem. Dette niveau af testen kan benyttes til en kvalitativ dokumentation af nedbrydning.

Princippet i metoden fremgår af figur 3.7, hvor moniteringsprogrammet består af en monitering af udbredelse og koncentrationer af tracer og forureningsstof som funktion af tiden i moniteringspunkterne.



Figur 3.7 Principskitse over diffusiv emitter test.

Kvantitativ dokumentation af nedbrydning via modeltolkning

Hvis det er svært at finde en tracer, der ligner forureningsstoffet tilstrækkeligt (mht. stofegenskaber), kan der blive behov for at foretage en modeltolkning af resultaterne, f.eks. via en 1D diffusiv model. Først kalibreres modellen til de opnåede tracerdata mht. indflydelsen af jordens egenskaber på stofudbredelsen (uden nedbrydning), hvorefter modellen køres igen med nye stofparametre der repræsenterer forureningsstoffet, og hvor nedbrydningen er den eneste ubekendte parameter. Det er sandsynligt, at der skal indsamles prøver til karakterisering af jordmatricen for at kunne opnå en tilfredsstillende modeltolkning af data. Når modeltolkning inddrages bliver metoden således betydeligt mere arbejdskrævende og omkostningstung, men til gengæld opnås der et estimat på den aktuelle nedbrydningsrate samtidig med, at der fremkommer en kvalitativ dokumentation for, at der foregår en nedbrydning. Endvidere kan der, når modellen først er sat op, for en forholdsvis beskeden merudgift, gennemføres en følsomhedsanalyse på den opnåede nedbrydningsrate og/eller gennemføres prediktive modelkørsler.

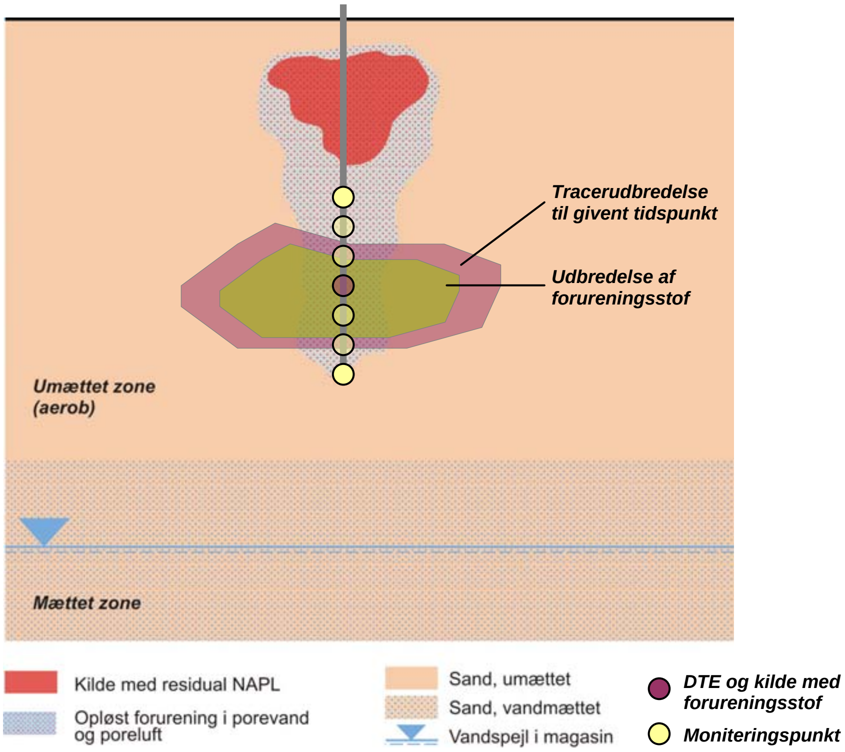
Teknologistadium

Teknologien er indtil videre på udviklingsstadiet og har pt. været afprøvet for så vidt angår udvikling og installation af DTE'en på en TCE-forurenet lokalitet /288/. I det udførte studium var det ikke hensigten at dokumentere nedbrydning eller estimere en nedbrydningsrate, men at foretage en tolkning af de meteorologiske og geologiske faktorers indflydelse på variationer i TCE-koncentrationen i poreluften på en given lokalitet.

I forstadiet til nærværende projekt blev der dog afholdt et møde med Peter Kjeldsen på DTU Miljø, hvor det blev diskuteret, at der var muligheder i, med nogle mindre modifikationer, at implementere metoden ifht.

vertikal transport og nedbrydning af benzin- og oliestoffer i jordens umættede zone. De diskuterede modifikationer til grundmetoden består i kun at udføre én boring, men med installation af moniteringspunkter i flere niveauer hhv. over og under DTE'en – og en efterfølgende (vertikal) 1D tolkning af den tidslige, diffusive udbredelse af hhv. tracer og forureningsstof, jf. figur 3.8.

Der er således ikke tale om en færdig og gennemtestet teknologi, som umiddelbart kan bringes i anvendelse på en given benzin- eller olieforurenet lokalitet. En teknologioverførsel til denne problemstilling indeholder en række ikke-trivielle problemstillinger som vil kræve udvikling og afprøvning under kontrollerede forhold i laboratoriet, inden anvendelse på en forureningssag. For at metoden kan bringes i "rutinemæssig" anvendelse på større forurenede lokaliteter kræves således et teknologiløft, der umiddelbart vurderes at svare minimum til et Ph.D.-studium.



Figur 3.8 Principskitse over modificeret diffusiv emitter test.

Fordele

En af de største fordele ved den diskuterede modificerede test er, at der skal forholdsvist få installationer til for at gennemføre en test, der er direkte målrettet problemstillingen i JAGG 2.0, jf. afsnit 2.1. Hvis der kan findes en tracer, der ligner forureningsstoffet tilstrækkeligt, er det således muligt, blot ud fra forskellene i koncentrationsudbredelsen af tracer og forureningsstof (jf. figur 3.8), direkte at dokumentere, at der foregår en nedbrydning. Ellers er det muligt at gennemføre en 1D modellering af diffusiv transport med henblik på at estimere en nedbrydningsrate til direkte anvendelse i JAGG 2.0 (fase 3, jf. afsnit 2.1). Det forholdsvist simple set-up muliggør, at der potentielt vil kunne gennemføres flere test forskellige steder i matricen, hvorved der kan opnås en fornemmelse for den rumlige variation i nedbrydningspotentialet.

Ulemper

En af de mest åbenlyse ulemper ved teknologien er, at den endnu ikke er afprøvet i praksis. Som diskuteret under push-pull testen er det også her et åbent spørgsmål om der kan findes en eller flere egnede tracere til de mest almindelige risikodrivere for benzin- og olieforureninger, der muliggør en direkte tolkning af resultaterne, uden modellering. Eftersom benzin- og olieforureninger udgøres af en lang række forskellige stoffer med meget varierende fysisk-kemiske egenskaber er det under alle omstændigheder givet, at metoden (uanset direkte datatolkning eller modellering) egner sig bedst til anvendelse ifht. et eller nogle få forureningsstoffer (herunder ofte benzen) og ikke ifht. totalindhold af kulbrinter. Det er heller ikke åbenlyst hvordan eventuelle baggrundsniveauer af forureningsstoffet/-stofferne skal håndteres i resultattolkningen, f.eks. jf. situationen i figur 3.8, hvor testen udføres i ”forureningsfanen” under kilden.

Det vurderes desuden at testen vil stille forholdsvist store krav til opstillingen og den må forventes at være forbundet med forholdsvist store opstartsinvesteringer.

Usikkerheder og fejlkilder

I forhold til praktisk anvendelse af den modificerede test bliver det afgørende hvordan selve installationen i et enkelt borehul udføres i praksis. Herunder er det afgørende, at der anvendes diffusionstætte materialer og at der foretages en tæt afpropning imellem DTE’en og de enkelte målepunkter, men med god kontakt imellem det enkelte målepunkt og matricen, således at de opnåede data repræsenterer transport og nedbrydning i matricen og ikke i installationsskakten/borehullet. Dertil er det afgørende, at der ved prøvetagning til udførelse af målinger over tid fra de forskellige prøvetagningsdybder (såfremt prøven opsamles/analyseres ved terræn) tænkes nøje over renpumpningsstrategien (flow, tryk og tid), således at renpumpningen ikke forstyrrer den naturlige diffusive transport i matricen, og så prøven rent faktisk repræsenterer poreluften i prøvetagningspunktet på det pågældende tidspunkt.

Tolkningen af data fra lagdelte geologier kan blive besværliggjort betydeligt, hvis det ikke er muligt at finde tracere, der er meget lig det forureningsstof der undersøges. Dette skyldes, at selv mindre forskelle i de parametre der styrer stoffernes fasefordeling (K_{oc} og K_H) vil kræve en grundig karakterisering af de jordfysiske parametre for at man efterfølgende kan udtrække en nogenlunde nøjagtig nedbrydningsrate. En grundig karakterisering af lagdelte jordmatricer bliver specielt vigtigt under forhold hvor nedbrydningsraten er forholdsvist lav.

Økonomi

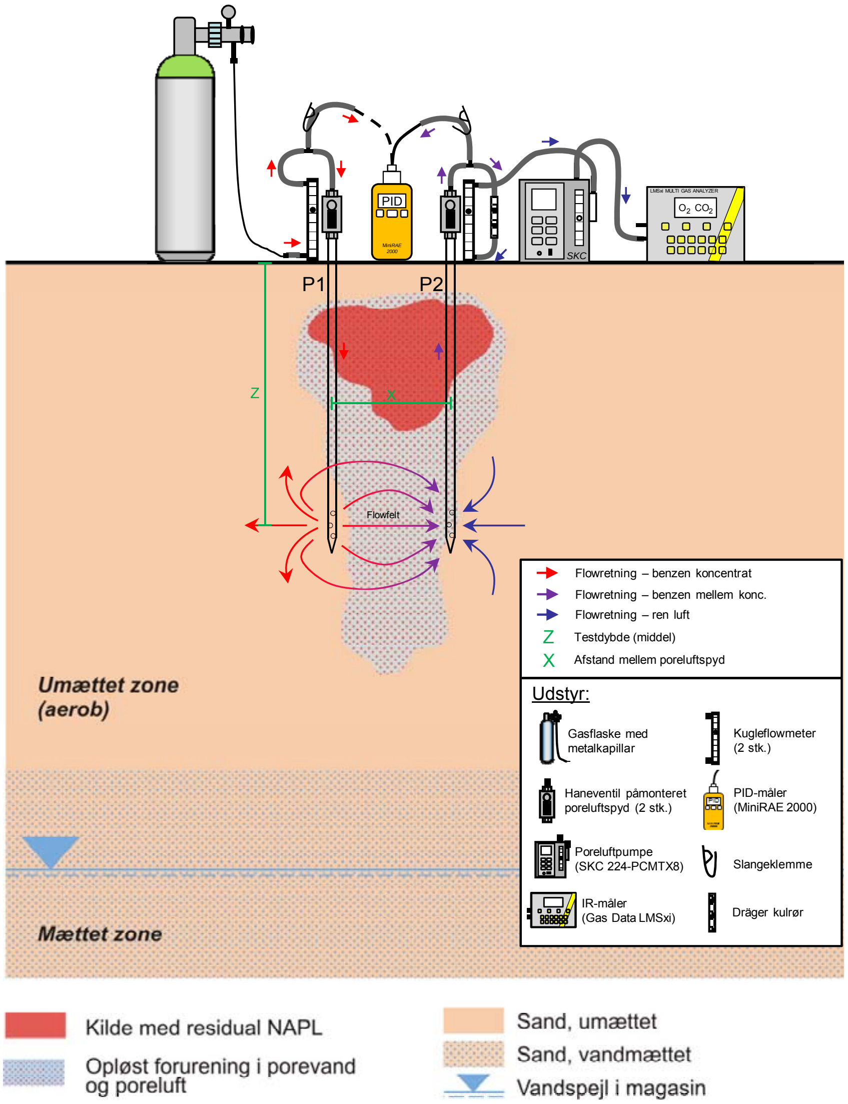
Eftersom strategien endnu ikke har været afprøvet, og der – som nævnt ovenfor – stadig er væsentlige usikkerheder omkring centrale emner ved en praktisk gennemførelse af testen, er det naturligvis svært at gætte på de økonomiske omkostninger, der vil være ved gennemførelse af testen på en given lokalitet. Dertil kommer uafklarede spørgsmål omkring instrumentering ifht. analysearbejdet; f.eks. om der kan benyttes automatiserede målemetoder til både tracer og forureningskomponenter.

Når der er opnået felterfaringer med metoden kunne et bud dog være i størrelsesordenen 75-350.000 kr. ekskl. moms, med et bud i den lave ende hvis testen kan gennemføres med en form for automatiseret instrumentering og uden modellering, og i den høje ende hvis der skal gennemføres supplerende indsamling af jordfysiske parametre og en modellering.

3.2.6 Dual Point Degradation test (DPD-test)

Hovedelementer

Denne metode er en helt ny dansk strategi, som primært er finansieret af Miljøstyrelsens Teknologiudviklingsprogram, og som er udviklet og afprøvet sideløbende med gennemførelsen af dette projekt /343, 344/. DPD-testen foretages ved, at forurening på gasform nedblæses i ét punkt og oppumpes i et nabopunkt, etableret i den umættede zone med poreluftspyd. På baggrund af et aerobt og et anaerobt testforløb, hvor forureningskomponenten benyttes som intern tracer, samt en simpel analyse af gennembrudskurven, dokumenteres in-situ nedbrydning og der kan estimeres en aerob nedbrydningsrate. Opstillingen er illustreret i figur 3.9.



Figur 3.9 Principskitse over DPD-testen i umættet zone.

Kvalitativ dokumentation af nedbrydning

Afhængigt af forsøgskonfiguration (dybde, afstand imellem de to spyd, påførte flow), jordtype, nedbrydningshastighed mv. vil der være forsvundet en større eller mindre andel af forureningsstofferne mens de var i jorden (under transport imellem de to spyd). Samtidig vil der være et større massetab til (aerob) nedbrydning under den aerobe testdel end under den anaerobe testdel, mens massetabet af stoffet under den anaerobe testdel primært vil være relateret til et abiotisk tab (diffusivt tab). Ved at fortsætte testforløbet indtil der er opnået ligevægt imellem den forureningsmængde der (pr. tid) nedblæses i punkt 1, det aktuelle jordsystem og den forureningsmængde der (pr. tid) trækkes op i punkt 2, kan der – ved sammenligning af det tidlige massetab under hhv. den aerobe og den anaerobe testdel – opnås en semi-kvantitativ dokumentation af at der forekommer nedbrydning iu den undersøgte umættede zone.

Kvantitativ dokumentation af nedbrydning

Via modellering af flowfeltet omkring og imellem de to spyd, eller en PID-afgrænsning af de aktiverede jordvolumen, kan der beregnes estimater på såvel 0. ordens som 1. ordens aerobe nedbrydningsrater i testvoluminet. Såfremt databehandlingen følger anbefalingerne i /344/ beregnes et konservativt estimat på den aerobe nedbrydningsrate.

Teknologistadium

Teknologien har indtil videre været afprøvet forholdsvist terrænnært (1,0 m u.t.) på en feltlokalitet, hvor der er efterladt en dielselolieforurening, med en ukendt blanding af lavtkogende TVOC og vurderes at være klar til afprøvning på enkeltkomponenter; f.eks. benzen. De umiddelbare perspektiver for metodens anvendelse sammen med JAGG 2.0 vurderes primært at være ifht. risikodrivende enkeltkomponenter, herunder specielt benzen. Der er opstillet en række perspektiver for det videre arbejde med metoden i /344/. Herunder er det anbefalet, at der arbejdes videre med:

1. Optimering af den fysiske konfiguration.
2. 3D-modellering af flowfelt og anvendelsesområde.
3. Instrumentering (felt-GC).
4. Gasblandinger der passer til aktuelle feltlokaliteter.
5. Installation i flere dybder og punkter i planen.
6. Brugen af stabile isotoper.

Fordele

En stor fordel ved DPD-konceptet er, at der i testens grundversion benyttes forholdsvist få og simple installationer for at gennemføre et testforløb, der kan dokumentere nedbrydning til anvendelse i JAGG 2.0 fase 2. Dertil er der tale om forholdsvist simple driftsbetingelser, hvor de største udfordringer består i at holde driftsbetingelserne (flow og koncentration) konstante over tid, og at dokumentere, at ser er opnået steady-state for hhv. det aerobe og det anaerobe testforløb. Når disse betingelser er opfyldt er databehandlingen simpel og til at overskue uden særlig ekspertise. Dertil kommer at testforløbet, i udgangspunktet, kan gennemføres indenfor en overskuelig tidshorisont på f.eks. 1-2 feltdage. Som med push-pull testen, vil testen dermed kunne gennemføres flere steder i jordmatricen, hvorved man kan få en fornemmelse for den rumlige variation i nedbrydningspotentialet forskellige steder – og dermed give et godt datagrundlag til inddragelse i risikovurderinger i henhold til JAGG 2.0.

I forhold til såvel push-pull testen og diffusiv emitter testen har DPD-testen den meget store fordel, at den benytter sig af forureningsstoffet som intern tracer, og at denne anvendelse af stoffet som intern tracer medfører at den estimerede nedbrydningsrate bliver konservativ.

Ulemper

For at der med testen kan uddrages 0. eller 1. ordensrater, der er sammenlignelige med litteraturværdier, skal der gennemføres en afgrænsning af det jordvolumen, som har været aktiveret under testen. I forholdsvist terrænnære aflejringer kan dette evt. gøres via en PID-afgrænsning efter selve testen, mens der i dybere aflejringer, må tages andre redskaber i brug. Til dette formål vil det være mest hensigtsmæssigt, at der opstilles en 3D gasmodel til modellering af flowfeltet imellem og omkring spyddene. En sådan model vil også kunne benyttes til at afsøge det mulige driftsområde for testen mht. spydafstand, flowbetingelser, effektive retardationsfaktorer (stoffer, vandindhold og f_{oc}), nedbrydningsrater og forventede testvarigheder.

Usikkerheder og fejlkilder

Pt. er der i /344/ identificeret en række usikkerheder, der bl.a. relaterer sig til den nøjagtighed, som forureningsgassen kan bestilles med, da testen i sit udgangspunkt fordrer samme stofkoncentration i den aerobe og anaerobe testgas. Er der således 10 % usikkerhed på den leverede gaskoncentration vil medføre, at der med testen muligvis ikke kan dokumenteres nedbrydning, selvom den foregår in-situ. Et tilsvarende forhold gælder omkring den analysesikkerhed der kan opnås i karakteriseringen af steady-state gaskoncentrationen i punkt 2 (hvor gassen trækkes op), under hhv. det aerobe og anaerobe testforløb, da estimatet på nedbrydningsraten er baseret på disse værdier. De største udikkerheder omkring testen kan således minimeres ved at sikre en høj sikkerhed og præcision i koncentrationen af de leverede gasser og en lav analyseusikkerhed i gasmålingerne.

Økonomi

Da testen endnu ikke har været forsøgt anvendt i en dyb umættet zone, og da der endnu kun har været gennemført én lovende pilottest, er nedenstående estimat behæftet med betydelige usikkerheder. Da udstyret, som udgangspunkt, er forholdsvist billigt vil en stor del af omkostningerne til gennemførelse af en felttest være forbundet med installation af spyd eller poreluftfiltre i flere ønskede dybder. Dertil lægges et par arbejdsdage til gennemførelse af selve testen (pr. dybde) og en dag til at lave dataanalysen og afrapporteringen.

Når udstyret er kørt ind og afprøvet, og der er opnået nogle felterfaringer med metoden, kunne et bud således være i størrelsesordenen 40-100.000 kr. ekskl. moms for gennemførelse af tests i 2-3 dybder under en forureningskilde. Beløbene i den lave ende dækker over dokumentation ifht. JAGG 2.0, fase 2, mens beløbene i den høje ende dækker over dokumentation ifht fase 3, hvor der gennemføres en indsamling af jordfysiske parametre og foretages opstilling/kalibrering af en 3D model til repræsentation af transporten i jordmatricen.

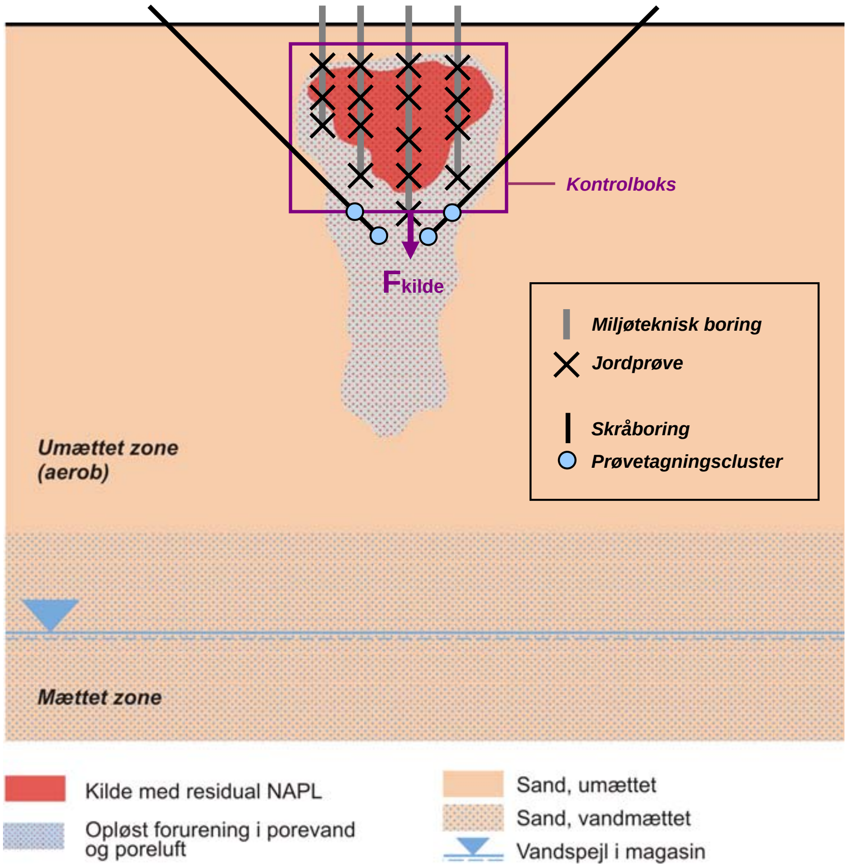
3.2.7 Kildestyrkekarakterisering og -dokumentation

Hovedelementer

I modsætning til de øvrige teknologier/metoder handler dette afsnit om en kontrolboks omkring kildeområdet (jf. figur 3.10). Der er tale om en sammenstilling af to delelementer; dels en karakterisering af kilden (mængde og sammensætning) vha. jordprøver, og dels en monitering i porevandet under kildeområdet (kildestyrkekoncentrationen). Teknologien benyttes dermed primært med henblik på at dokumentere kildestyrken.

Balance imellem kildestyrke og nedbrydning afgørende

Relevansen ifht. de øvrige teknologier er, at forureningsmængden og –sammensætningen i kilden, alt andet lige, er proportional med kildestyrken for den konkrete forurening (altså fluxen ud gennem kontrolboksens bund, F_{kilde}), og dermed for vurderingen af om den nedbrydning der dokumenteres i zonen mellem kilden og grundvandet (jf. afsnit 3.2.1 – 3.2.6) er tilstrækkelig. Sagt med andre ord kan der opnås den samme grad af risikoreduktion ved en forholdsvist stor nedbrydningsaktivitet og en given (stor) kildestyrke, som ved en mindre nedbrydningsaktivitet, når bare kildestyrken er tilsvarende mindre.



Figur 3.10 Principskitse over kontrolboks og prøvetagning til dokumentation af kildestyrke og -sammensætning.

Jordprøver udtaget i kilden

Denne strategi er meget basal og handler ganske simpelt om, at der over tid udtages og analyseres jordprøver i kildeområdet i den umættede zone med henblik på at estimere mængden, fordelt på forskellige stoffer eller stofgrupper, af benzin- eller olieforureningen i kildeområdet. Det handler altså dels om en fastlæggelse af mængder og dels den relative sammensætning på forskellige stoffer/stofgrupper.

Måling i porevand under kilden

Måling af porevandskoncentrationen i den umættede zone kan være en direkte måde at vurdere kildestyrken fra en overliggende forurening på, og samtidigt give mulighed for at karakterisere ikke kun de letteste og flygtige stoffer som BTEX (via poreluftmålinger) men også mindre flygtige og mere vandopløselige stoffer i olieprodukter herunder f.eks. MTBE. Metodisk indebærer udtagning af uforstyrrede porevandsprøver i større dybde en række udfordringer, hvilket afprøvning af forskellige koncepter i et tidligere teknologiprojekt tydeligt viser /191/. Siden dette projekt er der udviklet og afprøvet en række lovende færdige systemer, der kan installeres i den umættede zone ved hjælp af traditionelle boremetoder, og som muliggør en udtagning af porevandsprøver og poreluftprøver i diskrete niveauer. Specielt et system benævnt AMETIS /310/ udviklet i Israel til vurdering af bl.a. udvaskning af bl.a chlorid /324, 327/, nitrat/amonium /326, 327/, oliestoffer (BTEX og MTBE) /328/ samt tracere til studier af transport igennem umættet kalk /329, 330, 331/. Systemet er afprøvet i både laboratoriet og i felten over de seneste 5 år /311/. Da systemet har indbygget TDR-prober til kontinuert måling af den vertikale variation i vandindholdet, kan variationen henover året konstateres /322, 323, 325/. Systemet er færdigkommercialiseret og leveres som et standardsystem direkte til montering inklusiv prøvetagningssystem til porevand/poreluft samt dataloggersystem til registrering af vandindhold.

Teknologistadium

Der er tale om hhv. en velkendt teknologi, med udtagning af jordprøver med miljøteknisk bor og traditionel kemisk analyse på akkrediteret miljølaboratorium, gerne med en detaljeret opdeling af analyseresultatet i så mange fraktioner som muligt, og en teknologi som for ganske nyligt er udviklet til kommercielt brug og har været afprøvet overfor prøvetagning af benzin- og oliekomponenter /317/.

Mulig faldgruppe mht. jordprøver

Det er vigtigt, at holde sig for øje, at der ved udtagning af jordprøver er tale om en destruktiv prøvetagning (samme prøve kan kun udtages og analyseres én gang), hvorfor en tidsmæssigt tendens for koncentrationerne i et moniteringspunkt fastlægges på baggrund af prøver, der i bedste fald er udtaget meget tæt på tidligere prøver /313/. For f.eks. moræneaflejringer vil der være betydelige rumlige variationer i de geologiske lag og dermed i forureningskoncentrationerne (både fra start og igennem et givent forløb), hvorfor enkeltstående ”koncentrationsfald”, over tid i et givent punkt, ikke kan tolkes som et entydigt tegn på massefjernelse. Konsekvensen af denne logik ville være, at koncentrationsstigninger i et givent punkt skulle tolkes som en forureningsdannelse! Frem for at benytte enkeltstående koncentrationsforløb anbefales det således, i tråd med /289, 290/, primært at basere vurderingen af kildestørrelsen og -sammensætningen på middelværdibetragtninger ud fra et større antal prøver. Kildestyrken kan derefter fastlægges på baggrund af principperne i JAGG-modellen /309/.

Fordele

Den primære fordel ved at udføre en sideløbende monitering af jordkoncentrationerne i kilden over tid, eller en direkte monitering af porevandskoncentrationer under kildeområdet, er, at resultaterne vil kunne danne baggrund for en mere kvalificeret vurdering af de resultater der opnås via en monitering af nedbrydningen i zonen mellem kilden og grundvandet (jf. metoderne i afsnit 3.2.1 – 3.2.5). Specielt hvis der – som forventet –

påvises lavere nedbrydningsaktivitet som funktion af tiden via en monitering af nedbrydningsaktiviteten.

AMETIS-systemet

AMETIS-systemet giver et bud på løsning af en problemstilling, som har voldt væsentlige vanskeligheder siden udgivelse af /309/, og som det ikke hidtil har været muligt at finde en tilfredsstillende løsning på – trods et væsentligt ressourceinput /191/.

Ulemper

En ulempe ved udtagning af jordprøver kan være, at der for inhomogene kildeområder, mht. geologi og forureningsudbredelse, kan være behov for et forholdsvist stort antal boringer/prøver, for at få fastlagt middelkoncentrationen med en ønskelig grad af sikkerhed, således at det ved efterfølgende moniteringer er muligt at udtrække reelle tidslige tendenser /313/.

Hvad angår installation og tolkning af prøveresultater for prøver udtaget med AMETIS-systemet, vil der formentlig skulle foretages en form for verifikation af analyseresultaterne (som minimum på de første par sager), set i lyset af de tidligere dårlige erfaringer på området, jf. /191/. Dette er en ikke-triviel opgave, idet teknologien tilsyneladende løser et problem, som det ikke hidtil har været muligt at løse tilfredsstillende – da der ikke er noget at sammenligne resultaterne med bliver det derfor svært at foretage en decideret verifikation.

Usikkerheder og fejlkilder

De primære usikkerheder ved en kildekarakterisering ved jordprøver relaterer sig til at fastlægge et tilstrækkeligt sikkert estimat for forureningsniveauet (masse og koncentrationer) til et givet tidspunkt. Selv for forholdsvist små og overskuelige spild i en ensartet sandet geologi kan analysebehovet være betragteligt, jf. f.eks. /290/. Bemærk at der sjældent vil være udtaget et tilfredsstillende antal prøver i forbindelse med den almindelige forureningsundersøgelse, da denne er udført med et andet formål end at foretage en særligt nøjagtig fastlæggelse af middelforureningsniveauet, forureningsmassen eller -sammensætningen. Det anbefales, at der – specielt for den første analyserunde – tages rigeligt med prøver, da niveauet fra første runde skal danne udgangspunkt for alle senere sammenligninger og ikke efterfølgende kan suppleres.

For AMETIS-systemet er usikkerhederne relateret til installationen (dvs. kontakten imellem prøvetagningsceller og formationen) samt fasefordelingen imellem vand- og poreluftprøver når den umættede zone påføres et (mindre) undertryk i forbindelse med prøvetagningen. Endvidere vil det være vanskeligt at udtage vandprøver hvis vandindholdet i tørre perioder bliver meget lavt. Endelig er der en usikkerhed forbundet med at opnå en optimal placering af prøvetagningsportene i forhold til den vertikale forureningsfordeling der ønskes undersøgt.

Økonomi

Afhængigt af størrelsen, beliggenheden og (in)homogeniteten af kildeområdet, både geologisk og forureningsmæssigt, kan omkostningerne til en kildeundersøgelse variere ganske betydeligt. Til gengæld lader omkostningerne sig forholdsvist let estimere på en konkret lokalitet, da der er tale om en standardydelse, dog med et udvidet antal prøver til analyse.

Økonomien for AMETIS-systemet er relativt usikker men skønnes på indledende sager at ligge i størrelsesordenen 200-500.000 kr. ekskl. moms afhængig af installationsdybde, antallet af pøvetagningsdybder og graden af automatisering af prøvetagning mv.

4 Dokumentation af nedbrydningen over tid

Balancen imellem kildestyrke og nedbrydning *til et givent tidspunkt* kan i princippet dokumenteres og vurderes på baggrund af anvendelse af en kombination af metoderne i afsnit 3.2.7 og én eller flere af metoderne i afsnit 3.2.1 – 3.2.6. Resultaterne af sådanne undersøgelser kan dermed danne grundlag for udarbejdelse af en risikovurdering på undersøgelsestidspunktet, og der tilbagestår en opgave med at dokumentere/sandsynliggøre, at resultatet af risikovurderingen holder fremadrettet i tiden. Overvejelser som bør indgå i en sådan vurdering skal inkludere:

- Forståelsesramme og konceptuel model.
- Kildens henfaldsdynamik og forventede levetid.
- Tidslig udvikling i balancen mellem kildestyrke og nedbrydning.
- Overordnede massebalancer for ilt, N og P.
- Dokumentation/monitering.
- Diskussion af usikkerheder.

4.1 Forståelsesramme og konceptuel model

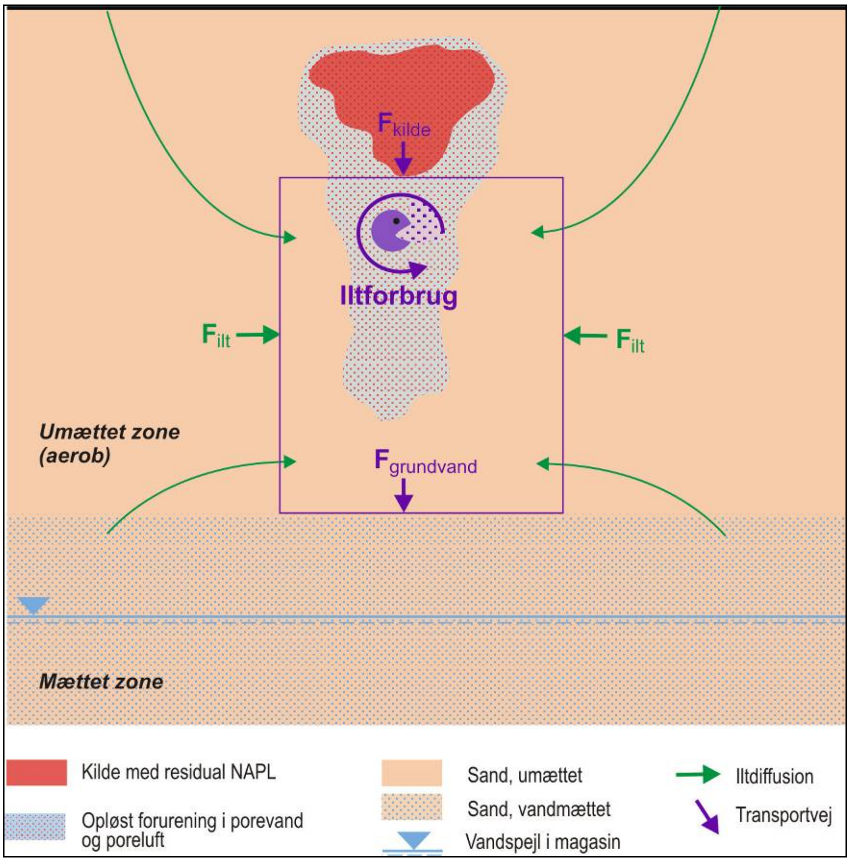
Forudsætninger

Som nævnt i afsnit 2.1, er den situation, som projektet er stilet imod, Model C fra /260/, hvor der foregår en vertikal transport fra en kilde, der ”hænger” i den umættede zone, og ned mod grundvandet igennem en homogen umættet zone. Kilden består af benzin- og/eller oliestoffer og transporten mod grundvandet foregår dels via nedsivning (i vandfasen) og dels via diffusion (i gasfasen). Under den vertikale transport igennem den umættede zone kan der foregå en aerob nedbrydning af forureningskomponenterne, dvs. der kræves et baggrundsiltindhold i tilsvarende uforurenede jordlag på min 2-5 vol.%.

Den situation, der kan håndteres via beregningsmodulet i JAGG 2.0, og de strategier og metoder, der er behandlet i dette projekt, er således afgrænset til den lilla kontrolboks i vist i figur 4.1. I den henseende er det vigtigt at pointere, at det samlede koncept skitseret i /260/og dette projekt – i udgangspunktet – ikke retter sig imod en egentlig kildefjernelse, selvom nogle af delelementerne i de to projekter formentlig kan finde anvendelse ifht. problemstillinger omkring kildefjernelse.

Usikkerheder

Såfremt ovenstående forudsætninger kun er delvist opfyldt på en given sag – hvilket formentlig vil være tilfældet i langt de fleste tilfælde – bør der foretages en grundig diskussion og håndtering af de usikkerheder der dermed introduceres i risikovurderingen. Dette emne er yderligere behandlet i afsnit 4.6.



Figur 4.1 Den kontrolboks, der er gældende ifht. det anbefalede koncept i JAGG 2.0.

Nødvendig dokumentation ifht. fase 2 og 3

Som nævnt i afsnit 2.1 bygger anvendelsen af fase 2 og 3 i JAGG 2.0 på tre niveauer af grundig dokumentation af:

i) at der foregår en nedbrydning i den umættede zone under kilden; kvalitativt eller kvantitativt, evt. via smoking guns.
ii) at forureningen ikke spreder sig uhensigtsmæssigt; altså at der er ”balance” imellem kildestyrke og nedbrydning.
iii) at der kan opretholdes en tilstrækkelig nedbrydning til at sikre den fornødne risikoreduktion indenfor kildens forventede levetid.

Mens konkrete metoder rettet mod (i) er behandlet i kapitel 3, behandles dokumentationen til (ii) og (iii) i de følgende afsnit, i henhold til de opstillede bullets i kapitlets indledning. Da der endnu ikke er etableret en praksis på området behandles emnerne på et overordnet niveau.

4.2 Kildens henfaldsdynamik og forventede levetid

Tidshorisont for påvirkning af den umættede zone

Som udgangspunkt for en fremadrettet risikovurdering er det essentielt, at man får et håndtag på hvor længe man kan forvente, at en given kilde påvirker den umættede zone under forureningen.

Et basalt bidrag til denne viden kan vi få dels ved at gennemføre modelberegninger, svarende til Model C i JAGG 2.0 /260/, der giver os en fornemmelse af dynamikken i den nedadrettede transporttid fra kilden til grundvandsspejlet; altså om der er f.eks. 1 eller 100 år til forureningen når grundvandet.

Estimat på kildens levetid

Dertil er det nødvendigt, at estimere kildestyrken, altså den årlige flux af forureningskomponenter der forlader kilden (F_{kilde} på figur 4.1), f.eks. jf. /309/. En balance imellem kildestyrken og den estimerede samlede forureningsmasse i kilden kan give os et indledende bud på kildens forventede levetid. I den forbindelse er det dog vigtigt, at afdampningen til atmosfæren, især af de mest flygtige stoffer og især det første år efter spildet, kan være ganske betydelig /156, 257, 269/ og principielt bør medregnes. Dette er dog ikke en triviel øvelse, og medregnes afdampningen til atmosfæren ikke, opnås under alle omstændigheder et konservativt bud på kildens forventede levetid.

Flux af kulstof (kildestyrke) og variation over tid

Den aktuelle kildestyrke vil være afhængig dels af kildens alder, olietypen, nedsivningens størrelse, kildens arealmæssige udbredelse og jordarterne. Denne anskuelse er især vigtig at holde sig for øje når vi taler om benzin- og olieforureninger, hvor der sker en relativt hurtig fjernelse af lettere, mere flygtige og opløselige komponenter fra kilden, mens fjernelsen af relativt tungere komponenter kan gå væsentligt langsommere /269, 278, 290, 306/. Dette fører til en præferentiel "tømning" af kilden for successivt tungere komponenter, som dels skyldes afdampning, herunder til atmosfæren, og dels opløsning i det nedsivende vand – og evt. igennem biologisk nedbrydning i selve kilden.

Efterhånden som de lettere komponenter forsvinder fra kilden, vil kildestyrken af totalkulbrinter; dvs. fluxen til zonen imellem kilden og grundvandet (F_{kilde} i figur 4.1), blive mindre. Samtidig med at den bliver mindre, vil sammensætningen gå mod tungere og tungere komponenter der, alt andet lige, nedbrydes langsommere – men som også bevæger sig langsommere, og dermed opholder sig i zonen/kontrolboksen i længere tid (hvormed nedbrydningen har længere tid til at virke).

Mulige dokumentationsstrategier

Et samlet overblik over kildens henfald, og ændring i sammensætning over tid, kan opnås ved udførelse af kildekarakterisering ved udtagning af jordprøver til forskellige tidspunkter, jf. afsnit 3.2.7, mens betydningen for kildestyrken evt. kan vurderes ved direkte udtagning af porevandsprøver fra den umættede zone under kilden, jf. afsnit 3.2.7, og/eller poreluftprøver til analyse for indhold af flygtige oliestoffer.

4.3 Tidslig udvikling i balance mellem kildestyrke og nedbrydning

Resultat af risikovurdering afhænger af balancen imellem kildestyrke og nedbrydning

Med betragtningerne fra afsnit 4.2 in mente, er det således ikke, i sig selv, afgørende for udfaldet af en risikovurdering i et fremadrettet perspektiv, om nedbrydningen i zonen imellem bunden af kilden og grundvandsmagasinet har en given størrelse. Dette skyldes, at der kan opnås samme grad af risikoreduktion ved en forholdsvist stor nedbrydningsaktivitet og en given (stor) kildestyrke, som ved en mindre nedbrydningsaktivitet og en tilsvarende mindre kildestyrke. Det er således den tidslige balance imellem kildestyrken (F_{kilde}) og nedbrydningen (illustreret ved den lille

Pacman i midten af forureningsfanen under kilden i figur 4.1), der er afgørende.

Moniteringsprogrammet bør derfor omfatte data, der kan illustrere den tidslige udvikling i balancen imellem kildestyrken og nedbrydningen i den umættede zone, jf. afsnit 4.5.

Monitering til dokumentation af stationære forhold

En indikator på status for denne balance kan opnås via monitering af udviklingen i VOC-koncentrationen samt ilt og CO_2 i og omkring nedsivningszonen under kilden; specielt når den første meget dynamiske periode efter spildet er overstået. I bilag 1 findes således eksempler på dataserier for ilt og CO_2, hvor moniteringsstrategien fra afsnit 3.2.1 er anvendt ved hhv. et nyt og et ældre oliespild. For oliespildet der er fulgt umiddelbart efter spildet og ca. 6 år frem, er der set stabile koncentrationer efter ca. 3 år. Endvidere viser data tidslige variationer i større eller mindre omfang. Data viser dog, at koncentrationerne generelt ikke vil variere med mere end nogle få vol. %, når først der ses stationære forhold.

Kvantitativ strategi

En anden – og noget mere omfattende/kvantitativ – mulighed er, at foretage en kortlægning af kildestyrken via f.eks. udtagning af porevandsprøver under kilden (AMETIS-systemet i afsnit 3.2.7), suppleret af VOC-analyser fra samme zone, og en tidslig dokumentation af nedbrydningsraten i samme zone (f.eks. via DPD-testen, jf. afsnit 3.2.6).

4.4 Overordnede massebalancer for ilt, N og P

Forudsætninger for biologisk omsætning

Det jordvolumen, der findes mellem undersiden af kilden og det underliggende grundvand, er et meget kompliceret system, omfattende dynamiske koblinger imellem fysiske, kemiske og biologiske processer. De biologiske processer er som tidligere beskrevet meget afhængige af tilgangen til bl.a. vand, næringsstoffer (N og P), ilt samt kulstofkilde (opløste forureningskomponenter).

Med hensyn til at dokumentere, at balancen imellem kildestyrke og nedbrydning kan opretholdes fremadrettet bør det overordnet dokumenteres, at forudsætningerne for biologisk nedbrydning, jf. afsnit 2.2.4, kan forventes at holde over en tidsperiode, der principielt svarer til kildens levetid; dog under hensyntagen til kildens henfaldsdynamik, jf. afsnit 4.2.

Simpel massebalancebetragtning for ilt

Antages en udvaskning af oliestoffer (kildestyrken, F_{kilde}) fra en kilde af dieselolie på ca. 10 g/år (svarende til nedsivning 100 mm/år, areal 10 m^2, opløst koncentration 10 mg/l) medfører det et årligt iltforbrug på ca. 30 gram ilt (aerob omsætning sker ved ca. forholdet 1:3 mellem ilt og kulbrinter). Betragtes en dybde eller reaktionslængde på blot f.eks. 1 meter under kilden, under arealet på 10 m^2, findes der initialt et iltindhold på ca. 1.000 g (svarende til et iltindhold i poreluften på 0,28 kg O_2/m^3 eller ca. 21 vol. %). Der er således mere en 30 gange den iltmængde tilstede, som vil blive forbrugt pr. år, og således principielt nok ilt til at opretholde nedbrydningen i mere end 30 år, dog kun med en samlet udvaskning på 300 g olie. I en tilsvarende situation, men med en nedsivning på 500 mm/år, vil kildestyrken være på 50 g/år og iltmængden i den øverste 1 meter under jordforureningen vil modsvare nedsivningen over en periode på 6 år. Dertil kommer et væsentligt bidrag af ilt via diffusion ind fra siden, som vist på figur 4.1.

Flux af ilt

Umiddelbart efter et spild vil det normalt fuldt aerobe miljø (jf. bilag 3) begynde at blive drænet for ilt i takt med at den biologiske omsætning kommer i gang. Dette vil give anledning til en stigende flux af ilt fra den omkringliggende jordmatrice og ind i det jordvolumen hvortil den opløste forurening spredes. For rimeligt permeable jorder vil nettofluxen af ilt ind i det forurenede volumen være tilstrækkelig til at der ikke opstår anaerobe forhold. Herved er en af de vigtigste forudsætninger for en langtidsholdbar og stabil nedbrydning opfyldt. Betydningen af denne geniltning er vurderet i /308/ ved en simpel massebalance for ilt og BTEX, og her er det fundet at fluxen af ilt ind i den umættede zone er flere størrelsesordner større end iltforbruget ved nedbrydning af BTEX. Denne konklusion illustreres ligeledes af eksemplerne præsenteret i bilag 1.

Simpel massebalance-betragtning for N og P

Som nævnt i afsnit 2.2.4 regnes, som en (måske konservativ) tommelfingerregel, med et nødvendigt massebaseret forhold imellem C, N og P på ca. 100:10:1 ved aerob heterotrof mikrobiel omsætning af benzin- og oliekomponenter. Altså for hver 100 gram olie, der skal nedbrydes (10 hhv. 2 års nedsivning i ovennævnte forureningsscenarium), skal der tilføres i størrelsesordenen 10 gram N og 1 gram P /264/. Som nævnt i afsnit 2.2.4 vurderes ovenstående masser i henhold til nærværende forståelsesramme (afsnit 4.1), at skulle kvantificeres som totalindhold opgivet pr. kg TS (ikke mere biotilgængelige indhold, f.eks. vandopløselige fraktioner), når vi ser på tidshorisonter over 10 år.

I sandede aflejringer i den dybe umættede zone er indholdet af næringssalte – jf. litteraturstudiet i bilag 3, måske i størrelsesordenen 10 mg N_{tot}/kg TS og 280 mg P_{tot}/kg TS /337/. Disse indhold svarer til, at det naturlige indhold af N og P i den øverste meter af den umættede zone under ovennævnte hypotetiske kilde (10 m^2 med en volumenvægt på 1,6 ton TS/m^3) vil indeholde omkring 160 g N_{tot} og 4.480 g P_{tot}. Med et masseforhold for C:N:P på 100:10:1, svarer disse indhold af N og P til nedbrydning af mellem ca. 1,6 og 450 kg nedsivende olie (for hhv. N og P), hvilket i dette tilfælde vil medføre en kraftig kvælstofbegrænsning.

Ovenstående estimater er dog meget usikre at udtale sig generelt på baggrund af, dels da der over lange tidshorisonter må forventes at ske en betydelig remineralisering af N og P fra hendøende biomasse, jf. diskussionen i /264/, og dels da der pt. kun foreligger meget sparsom viden om indholdet af hhv. N og P i dybereliggende umættede zoner, jf. bilag 3.

En aktuel vurdering må således bero på lokalitetsspecifikke data og det er vigtigt, at der sker en grundig karakterisering af N og P for samtlige lag imellem kilden og grundvandet. Herunder specielt frem til et tidspunkt, hvor der måske foreligger så mange data, at der kan indbygges konservative standardværdier i JAGG-modellens jordtypedatabase.

4.5 Dokumentation og monitering

Dokumentationens elementer

Som det fremgår af ovenstående bør dokumentationen i forbindelse med en risikovurdering for den umættede zone, hvori der inddrages nedbrydning i zonen under kilden, baseres på elementer, der indeholder betragtninger omkring:

- Kildestørrelse og –udbredelse.
- Kildens forventede levetid.
- Kildens sammensætning (over tid).
- Kildestyrken (over tid).
- Nedbrydningskapaciteten/-raten (over tid).
- Forudsætningerne for nedbrydning (ilt, N og P).

Det aktuelle moniteringsprogram og den nødvendige moniteringsfrekvens og -periode vil afhænge af en række lokalitetsspecifikke forhold, men vil som minimum skulle indeholde en dokumentation der, rent tidsmæssigt, går ud over den indledende forholdsvist hurtige udvaskning af letopløselige komponenter og afdampning af flygtige komponenter. Efter denne indledende periode (måske de første par år) er det projektgruppens opfattelse, at en kvalitativ eller kvantitativ dokumentation af nedbrydningen primært kan kombineres med en efterfølgende monitering af – og dokumentation for – at der er opnået stationære forhold. Her kan der med fordel oprettes og inddrages et moniteringsnet af gasfiltre, i den afskærende zone imellem kilden og grundvandet, til monitering af oliekomponenter (PID, felt-GC og/eller akkrediterede analyser) samt ilt og CO_2 både i og omkring nedsivningszonen.

Aftagende kildestyrke

Grundet en aftagende kildestyrke (bør dokumenteres i det enkelte tilfælde) er der således ringe risiko for at kildestyrken vil blive større med tiden, med mindre arealanvendelsen går fra impermeabel overflade til permeabel overflade eller lignende. Hvis det således dokumenteres, at der er indtrådt stationære forhold, og at der er basis for en fortsættelse af den biologiske nedbrydning (jf. afsnit 4.4) vil nedbrydningen med stor sandsynlighed kunne fortsætte og forureningen vil derfor ikke spredes uacceptabelt.

Moniteringsperiodens længde

En dokumentation af stationaritet kan opnås ved at monitere igennem en længere periode. Moniteringsresultaterne vil sandsynligvis variere gennem moniteringsperioden grundet naturlige tidslige variationer, men hvis resultaterne overordnet viser stabile forhold er der grundlag for at vurdere, om dette vil fortsætte fremadrettet. Moniteringsperiodens længde vil blandt andet afhænge af forureningens alder – og estimater over dynamikken i forureningsudvaskningen og en forventet kildelevetid.

Gode dokumentationssager mangler

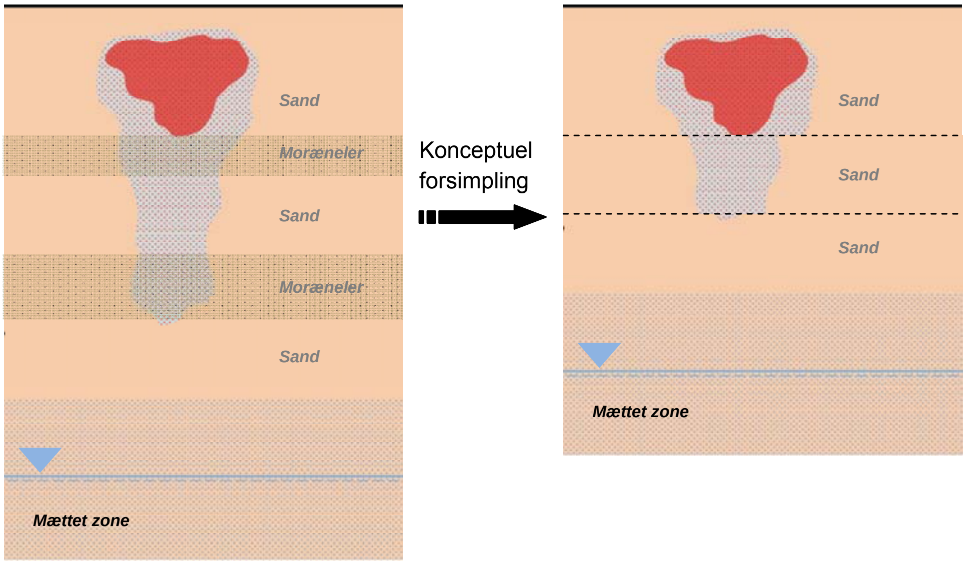
Både den nødvendige moniteringsfrekvens og –længde er pt. uafklarede spørgsmål da der er meget få sager at hente inspiration fra – der mangler helt enkelt nogle gode demonstrationsprojekter der kan danne præcedens for nogle generelle retningslinjer.

4.6 Diskussion af usikkerheder

Der er flere niveauer af potentielle usikkerheder . Helt overordnet kan der være usikkerheder forbundet med at den faktiske situation ikke passer til de geologiske eller forureningsmæssige forudsætninger, som er opsummeret i afsnit 4.1. Måske er der tale om lagdelte geologiske forhold i zonen mellem kilden og grundvandsspejlet; måske kan der være flere ”hængende kilder” i tilknytning til disse lagdelinger.

Komplicerede geologiske forhold

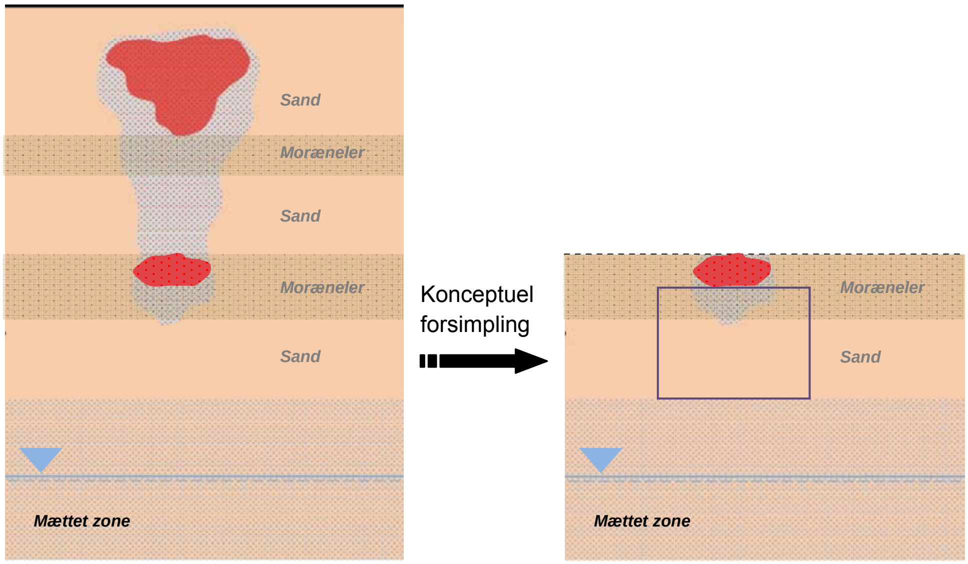
Under komplicerede geologiske forhold kan en mulig farbar vej være, at koncentrere den nedbrydningsmæssige dokumentationsindsats omkring ét eller flere lag, som forventes at være mest aktive mht. nedbrydning; oftest sandlag, hvor der er god mulighed for geniltning (fra siden), og se bort fra en eventuel nedbrydning, der måtte forekomme i de øvrige lag. Konceptuelt reduceres transportzonen imellem kildens underside og grundvandet til den samlede mægtighed af de(t) udvalgte lag, jf. figur 4.2. Jo flere lag, der ses bort fra i nedbrydningsmæssig henseende, jo mere konservativ bliver risikovurderingen. Det er dog vigtigt at pointere, at det kun er i nedbrydningsmæssig henseende at den konceptuelle forståelse simplificeres (ikke i fluxmæssig henseende); i transportmæssig og tidsmæssig henseende er det stadig vigtigt, at tage transporten igennem de ”frasorterede” lag i ed således, at den samlede risikovurdering bliver konservativ. Man kan f.eks. ikke se bort fra den del af samlede forureningsmasse, der måtte befinde sig i de ”bortsorterede” lag, eller en eventuel lang transporttid igennem mellemliggende lavpermeable lag, når der skal opstilles en fornuftig tidshorisont for moniteringsprogrammet i et dybereliggende sandlag.



Figur 4.2 Konceptuel forsimpling af de nedbrydningsmæssige forhold for en kompliceret geologisk situation.

Komplicerede forureningsmæssige forhold

I et tilfælde med flere hængende kilder, kan man forestille sig en konceptuel forsimpling, hvor der kun ses på nedbrydningen i den del af den umættede zone, der befinder sig under den nederste del af kilden, jf. figur 4.3. Igen er det essentielt, at der ikke ses bort fra den forureningsmasse der befinder sig i "bortsorterede" lag, eller den transporttid/dynamik ovenliggende lag repræsenterer ifht. den samlede problemstilling; f.eks. at der ikke ses bort fra en betydende forureningspuls, der er på vej ovenfra.



Figur 4.3 Konceptuel forsimpling af de nedbrydningsmæssige forhold for en kompliceret forureningsmæssig situation.

Ændrede randbetingelser

Da der i mange tilfælde formentlig vil skulle ses på en risikovurdering, der løber over en tidshorisont på dekader eller århundreder, vil der naturligvis være risiko for at randbetingelserne for problemstillingen ændrer sig. Det kan være, at der i en fremtidig situation er foretaget en fjernelse eller etablering af fast belægning, eller at der er sket ændringer i grundvandsspejlets beliggenhed grundet havstigninger eller ændrede nedbørsforhold. Det ligger udenfor projektets kommisorium, at tage endelig stilling til hvordan sådanne forhold skal håndteres, men i en eller forstand kan det måske være hensigtsmæssigt/nødvendigt, at udføre nogle simple følsomhedsanalyser til illustration af risikovurderingens robusthed.

Andre usikkerheder

Endelig kommer usikkerheder på diverse målinger, overslag og estimater på kildestyrken, kildens forventede levetid, estimerede nedbrydningsrater og massebalancer for indhold/tilførsel af ilt, samt indhold af næringssalte i den afskærende zone. Analyseusikkerheder og usikkerheder på diverse estimater og overslag bør håndteres og tolkes i henhold til almindelig praksis for udførelse af risikovurderinger, og adskiller sig i den henseende ikke fra alle andre risikovurderinger. Almindelig god praksis på området tilskriver, at der anvendes en konservativ tilgang når der er store usikkerheder eller rumlige variationer til stede, samt når datagrundlaget fra lokaliteten er dårligt/sparsomt eller når der anvendes litteraturværdier.

5 Nedbrydningsrater

Opdatering af rater fra Shell Global Solutions

Som opfølgning på /260/ er der rettet henvendelse til Shell Global Solutions, der stod bag en af nøglereferencerne i tidligere sammenstilling af rater /74/, for at undersøge om der er gennemført en opdatering af det tidligere udførte litteraturstudie af 1. ordens rater for BTEX og MTBE. Dette for at sikre, at datagrundlaget for valg af rater i JAGG 2.0 er rimeligt opdateret, når den endelige version af JAGG udsendes, og for at undersøge om nedbrydningsraterne for benzen kunne adskilles fra BTEX-raterne.

Shell har ikke opdateret selve databasen siden 2007, og det har ikke været muligt at få Shell til at foretage en udseparering af benzen-raterne fra gruppen af BTEX. Dette vurderes fortsat at kunne gøres ud fra rådata, men vil kræve en minutiøs gennemgang af Shells opstilling og evaluering af data, hvilket ligger ud over kommissoriet for dette projekt.

Shell oplyste dog, at de har gennemført en ny sammenstilling af 1. ordens nedbrydningsrater for benzen baseret på en database over vertikale poreluftprofiler der løbende opdateres af US-EPA /242, 243/.

EPA OUST VI Work Group Database

I forbindelse med udvikling af et paradigma for hvordan indeklimaproblemer på NAPL-grunde kan vurderes, er der af en arbejdsgruppe ledet af US-EPA sammenstillet vertikale poreluftprofiler, hvor både kulbrinter/-BTEX og ilt/kuldioxid er målt i en eller flere målerunder /244/.

Bestemmelse af rater for benzen ud fra database og model

På baggrund af den samlede database er der gennemført en udvælgelse af i alt 45 vertikale profiler fra 17 forskellige grunde. De vertikale profiler for benzen er tilpasset en 1. ordens nedbrydningsrate ved hjælp af en numerisk model, og der henvises til /239/ for yderligere detaljer.

1.ordens nedbrydningsrate for benzen

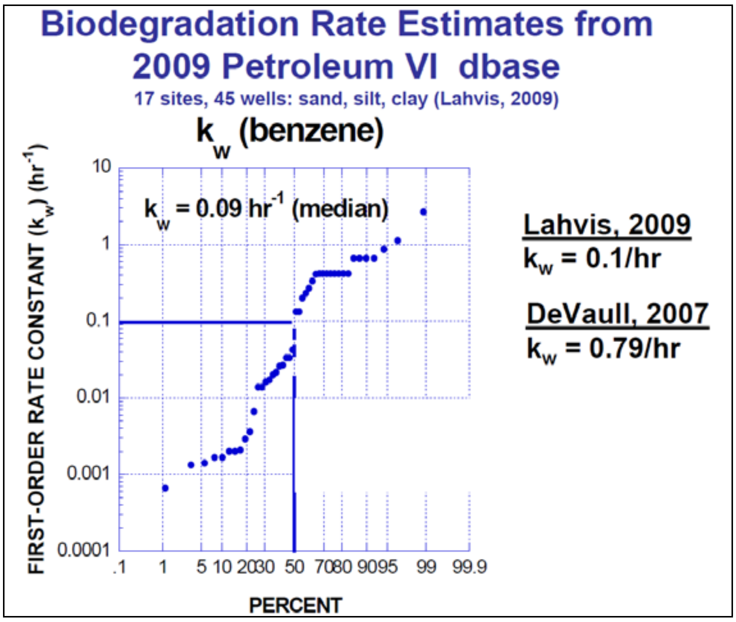
Sandsynlighedsfordelingen for de bestemte 1. ordens porevandsbaserede rater for benzen er vist på figur 5.1. Medianværdien for 1. ordens raten er 0,09 (time^{-1}) eller 2,4 (d^{-1}). Medianværdien for gruppen af BTEX i det tidligere Shell-studie refereret i /260/ var 6,8 (d^{-1}), og der er således konsistens mellem de to datasæt. De laveste rater udtrykt ved hhv. 1 og 5 % fraktilen er 0,019 (d^{-1}) hhv. 0,025 (d^{-1}).

Betydningen af permeabilitet og kildestyrke

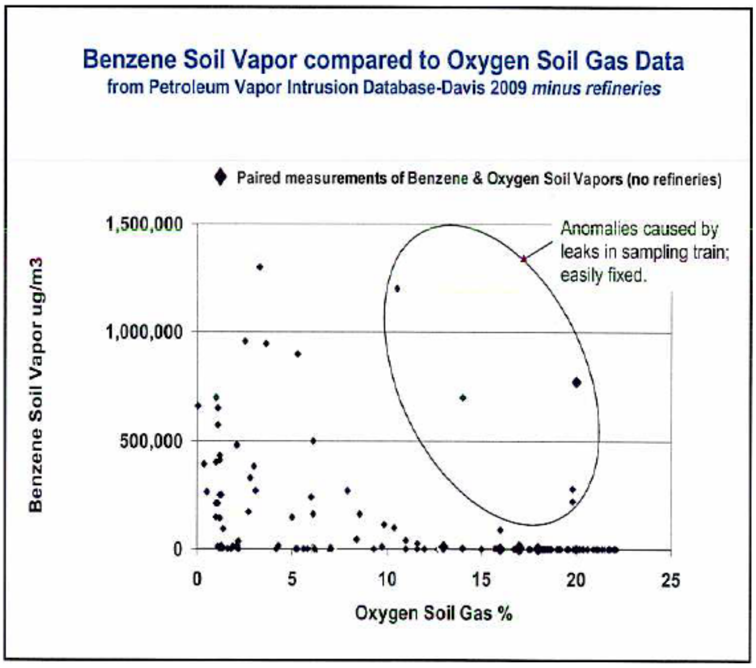
På baggrund af de anvendte jordtyper, er det konkluderet at raterne øges når jordens permeabilitet øges og når kildestyrken reduceres, dvs. når balancen imellem kildestyrke/stoftilførsel og ilttilførsel/elektronacceptor rykkes mod højere ilt:VOC-forhold. Disse forhold indikerer således, at den biologiske nedbrydning er styret af tilstedeværelse af ilt i jorden, og dette fremgår tydeligt af figur 5.2, der viser den målte sammenhæng mellem benzen og ilt i de poreluftprøver hvorpå raterne er bestemt.

Tidslig variation af nedbrydningsraten

På baggrund af 30 boringer fra 10 lokaliteter, hvor der er målt over en periode på et par år, er der generelt fundet en stabil nedbrydningsrate – og i enkelte tilfælde en stigende nedbrydningsrate.



Figur 5.1 Nedbrydningsrater for benzen i umættet zone fra /239/. k_w indikerer, at raterne er relateret til nedbrydning i vandfasen.



Figur 5.2 Sammenhæng mellem indholdet af benzen og ilt i poreluften for de punkter der er anvendt til beregning af nedbrydningsraten for benzen i vandfasen (k_w) /239/.

Erfaringer fra USA og Australien

Inkludering af nedbrydning af oliekomponenter i den umættede zone, er ikke almindelig i forbindelse med risikovurdering af olieforureninger. I Australien og USA er der udført en dataindsamling, der har haft til formål at undersøge, hvorvidt det er muligt at introducere nogle standard reduktionsfaktorer, der kan benyttes i forbindelse med risikovurdering af afdampning fra olieforureninger til indeklimaet. Sammenfatning af data fra en række amerikanske, canadiske og australske olieforureningssager har for det første vist, at ilt er den vigtigste begrænsende ressource i forbindelse med nedbrydning i den umættede zone. Sammenstilling af data har givet grundlag for at give følgende anbefalinger i forhold til at benytte reduktionsfaktorer for transport fra kilden til terræn grundet nedbrydning i den umættede zone /8/.

Reduktionsfaktorer

Krav til forholdene i den umættede zone:
- Der bør kunne påvises et iltindhold i poreluften større end 5 vol. % mere end 1 m u.t.
- Forureningskilden bør være beliggende mere end 2 m u.t.
- Den maksimale poreluftkoncentration bør være mindre end 100.000 mg/m^3 kulbrinter i kilden.

Er overstående krav opfyldt kan følgende reduktionsfaktorer til under gulv benyttes:
- En reduktionsfaktor på 10 kan benyttes hvor kilden er beliggende mere end 2 m u.t.
- Er kilden beliggende mere end 4 m u.t. kan en reduktionsfaktor på 100 benyttes.

I forhold til risikovurdering for grundvandet, vil det være relevant at udføre en lignende omfattende dataindsamling på danske sager og dermed undersøge, om det på sigt vil være muligt at opstille lignende anbefalinger i forhold til den nedadrettede transport.

6 Konklusion og anbefalinger

Sammenfatning af strategier

Med udgangspunkt i gennemgangen af de enkelte strategier i kapitel 3, er de vigtigste metodemæssige aspekter resumeret og sammenstillet i tabel 6.1. Tabellen giver et overblik over dels mulighederne i de enkelte metoder i forhold til bestemmelse af rater samt teknologistadie, økonomi og praktisk anvendelighed.

6.1 Strategier der anbefales afprøvet

Indirekte kvantitative metoder

Måling af poreluftens indhold af oliekomponenter, ilt, CO_2 og methan er en velkendt strategi i forbindelse med forureningsundersøgelser. Målingerne kan udføres relativt simpelt og kræver som udgangspunkt ikke brug af dyrt udstyr. De data der indsamles ved disse poreluftmålinger samt ligeledes i forbindelse med en respirationstest, vil være relativt simple at tolke. Strategien er på den baggrund velegnet i forbindelse med det videre arbejde med dokumentation af nedbrydning i den umættede zone. Dog vurderes det relevant at sammenholde målinger ved IR-baserede feltinstrumenter med måleteknik baseret på GC med termodetektor for at vurdere, hvilken måleteknik der fremadrettet bør benyttes.

Sammenfatning af empiriske data fra danske sager

En række udenlandske studier har, jf. /242/, vist en empirisk sammenhæng mellem indholdet af kulbrinter og iltindholdet i poreluften, hvor indholdet af kulbrinter generelt er aftagende med stigende indhold af ilt, jf. figur 5.2 i kapitel 5. For målinger på danske sager er der ikke udført en sådan sammenstilling af data, men dette kunne være meget nyttigt med henblik på at identificere den forventelige tilsvarende sammenhæng i danske datasæt. Dette kunne danne grundlag for at udarbejde et kriterium for et mindsteindhold af ilt, der skal være tilstede i en vis dybde under forureningen, for at den ikke vurderes at udgøre en risiko, jf. også afsnit 6.2.

Fanemodellering i umættet zone (1D, 2D og 3D)

Brugen af modellering vurderes at skulle koncentreres om, hvordan den eksisterende 1D-model i JAGG 2.0 kan videreudvikles, således at der som led i modellen kan laves en parallel beregning af transporten af ilt og kuldioxid. Forbruget af ilt kan direkte kobles til det målte indhold af kulbrinter, og det vil således være muligt at opstille en simpel massebalance der verificerer, at der ved diffusion transporteres tilstrækkelig ilt til at kunne sikre aerobe forhold over tid. Denne tilgang kan afprøves på en række danske cases – herunder på én eller begge sager i bilag 1.

Strategi	**Dokumentationsmetode**	**Forureningskomponent**	**Teknologistadium**	**Økonomi**	**Anvendelighed**
Indirekte kvantitative metoder	Kvantitative/kvalitative	Totalkulbrinter	Velkendt teknologi Målemetoder kan belyses nærmere	- Fase 2, 25-75.000,- - Fase 3, 75-300.000,-	Simpel metode Udbredte prøvetagningsmetoder
Fanemodellering i umættet zone	Bestemmelse af rate	Enkeltstoffer og stofgrupper	1D: afprøvet på mange lokaliteter 2D og 3D: primært brugt ifbm. forskningsprojekter	1D: 25-100.000,- 2D: 75-250.000,- 3D:250.000-???,-	1D: Relativ simpel 2D og 3D: Komplicerede
Isotopteknikker	Bestemmelse af rate	Enkeltstoffer – kun op til C10-kulbrinter	Ikke udbredt i umættet zone Fraktionering af H under udvikling	1.000-2.000,- pr. poreluftprøve	Simpel prøvetagningsmetode Teknologien udføres kun af få kommercielle laboratorier i udlandet
Gas fase push-pull tests	Bestemmelse af rate (kvalitativ afhænger af tracer)	Enkeltstoffer	Ikke afprøvet på olie- og benzinkomponenter Ikke færdig og gennemtestet teknologi Kræver udvikling og afprøvning	75-350.000,- (estimat)	Udførelse bør være relativ simpel Kræver dyrt og kompliceret udstyr
Diffusiv emitter test	Bestemmelse af rate (kvalitativ afhænger af tracer)	Enkeltstoffer	Ikke afprøvet på olie- og benzinkomponenter Ikke færdig og gennemtestet teknologi Kræver udvikling og afprøvning	75-350.000,- (estimat)	Udførelse bør være relativ simpel Kræver dyrt og kompliceret udstyr
Dual Point Degradation test	Bestemmelse af rate	Enkeltstoffer eller simple blandinger	Ny lovende teknologi med mange perspektiver 3D modellering krævet ifht. fase 3	40-100.000,- (estimat for 2-3 rater)	Udførelse og udstyr simpelt Simpel datatolkning ifht. fase 2
Kildestyrkekarakterisering og –dokumentation baseret på udtagning af porevand og poreluft	Direkte måling af vertikalt forureningsprofil (porevand, poreluft og vandindhold)	Enkeltstoffer og stofgrupper	Afprøvet i felten for olie- og benzinkomponenter samt andre organiske stoffer	200-500.000,- (estimat)	Installation ved standard boremetoder Prøvetagning fra installation relativ simpel
Kildestyrkekarakterisering og –dokumentation baseret på jordprøver	Kvantitative/kvalitative	Enkeltstoffer og stofgrupper	Velkendt teknologi	Pris afhænger af kildeområdets størrelse og homogenitet	Simpel metode Begrænset af forureningsheterogenitet Destruktiv prøvetagning

Tabel 6.1 Sammenstilling af strategier/metoder til dokumentation af nedbrydning i den umættede zone.

Isotopteknikker

Isotopteknikker baseret på en kombination af C og H er velafprøvet i laboratoriet og kun i mindre grad i felten hvad angår den umættede zone. Metoden vurderes at være en af de mest lovende af de metoder der er fundet i litteraturen – af flere årsager. Dels er den nem at anvende i praksis samt relativt billig, men det teknologiske stade gør også, at den næste fase er anvendelse i praksis på et antal sager for at dokumentere metoden under feltforhold. Praktisk og rutinemæssig anvendelse af metoden vurderes således kun at ligge 1-2 år ude i fremtiden.

Push-pull og diffusiv emitterPush-pull og diffusiv emitter

Bestemmelse af rater baseret på ”Push-Pull” og ”Diffusiv emittter” teknikker er principielt meget lovende teknikker – både ud fra en rent praktisk og økonomisk vinkel. Begge teknikker er dog uafprøvede for benzin- og oliekulbrinter, og det vurderes at der skal ske et teknologiløft førend disse metoder er klar til at blive testet i felten. Dette vil mest hensigtsmæssigt kunne gennemføres i form af et Ph.D.-studie i et nært samarbejde med rådgivningsfirmaer, der er de endelige slutbrugere og aftagere af teknologien. Hvis denne finansiering kan skaffes, vil der alligevel gå et par år førend metoderne er klar til feltafprøvning og herfra kan kommercialiseres. Dette vil sandsynligvis kræve betydelige investeringer i bl.a måleudstyr, hvilket betyder at der formentlig kun vil være meget få udbydere af en sådan metode.

DPD-testen

DPD-testen vurderes, på baggrund af et gennemført pilotstudium under danske forhold, at være en meget lovende tekonologi, der har et stort udviklings- og anvendelsesmæssigt potentiale. Teknologien benytter sig af forholdsvist simpelt/tilgængeligt udstyr, hvilket vil kunne medføre et konkurrencedygtigt prisleje ifht. de øvrige teknologier, og har endvidere vist lovende resultater, både ifht. kvalitativ (JAGG 2.0, fase 2) og kvantitativ dokumentation (JAGG 2.0, fase 3) af nedbrydning. Det vurderes, at metoden med et forholdsvist lille teknologiløft, indenfor 1-2 år, kan bringes til et teknologisk niveau, hvor rutinemæssig anvendelse kan komme på tale.

Kildestyrkekarakterisering og –dokumentation baseret på jordprøver

Udtagning af jordprøver i løbet af en periode på f.eks. 1-5 år er en metode der primært er relevant i forbindelse med oprensning af kildeområder, og derfor af stor interesse for entreprenører og rådgivere der udfører in-situ oprensninger. Ved metoden kan bulk nedbrydningsrater for totalkulbrinter estimeres, mens nedbrydningsrater for de mere flygtige/vandopløselige og dermed mobile stoffer er mere vanskelige at vurdere. Som omtalt i afsnit 3.2.7 vil det dog være muligt at konstatere en tidslig ændring i kildesammensætningen; herunder især en præferentiel tømning af kilden for vandopløselige, flygtige og risikopotente stoffer – og dermed også potentialet for opløsning og udvaskning til grundvandet, hvilket eventuelt yderligere kunne dokumenteres vha. AMETIS-systemet (se nedenfor).

Kildestyrkekarakterisering og -dokumentation

Direkte bestemmelse af porevandskoncentrationen både i selve kilden og i den umættede zone under kilden vil, sammen med bestemmelse poreluftkoncentrationen, give et mere direkte input til risikovurderingen i JAGG 2.0. De målte profiler i porevand/poreluft kan efterfølgende anvendes til at kalibrere 1D-modellen i JAGG 2.0 og herved kan rater estimeres. Samtidigt åbner det muligheder ved risikovurderingen af andre stoffer herunder chlorerede opløsningsmidler, pesticider og måske hormonstoffer der kunne være "emerging contaminants" også i Danmark. I praksis kunne en afprøvning af det israelske AMETIS-system /310/ gennemføres på et par af de velundersøgte danske cases (se bl.a. bilag 1) – herunder den eksisterende case, der ligger til grund for eksemplet i Appendix 5.2 i JAGG 2.0 /260/.

6.2 Koncept for dokumentation

JAGG 2.0

Det foreliggende koncept for JAGG 2.0 er, som nævnt i afsnit 2.1, inddelt i 3 faser/niveauer. Nedbrydning indgår ikke i fase 1, hvorfor dokumentationen af nedbrydningen ikke er relevant før fase 2 og 3.

Fase 2

I forbindelse med fase 2 skal det dokumenteres, at forudsætningerne for nedbrydning er til stede og der fremskaffes kvalitativ dokumentation for at nedbrydningen rent faktisk foregår på lokaliteten. Der udtages således jordprøver til dokumentation af indhold af kvælstof og fosfor samt jordens vandmætning. Desuden kan der udføree en poreluftundersøgelse omkring og under kilden, hvor indholdet af oliekomponenter, ilt og CO_2 belyses. Alternativt kan der gennemføres feltforsøg med henblik på at fremskaffe en kvalitativ dokumentation for at der foregår nedbrydning i den afskærende zone. Er forudsætningerne for nedbrydning til stede og er der indikationer på at nedbrydningen foregår, jf. kapitel 4, kan der i JAGG 2.0 opstilles en 1D-model, baseret på konservativt valgte rater fra litteraturen. Efterfølgende kan modellen tilpasses de målte data. Dette vil kunne danne grundlag for en vurdering af risikoen for grundvandet.

Fase 3

I fase 3 udføres yderligere dokumentation med henblik på at fastlægge en lokalitetsspecifik nedbrydningsrate, som kan anvendes i risikovurderingen i forhold til grundvandet. I fase 3 kan der inddrages teknologier som isotopfraktionering eller DPD-test og på længere sigt evt. push-pull tests samt diffisiv emitter test.

Monitering og dokumentation

På niveau 2 og 3 er det essentielt, at risikovurderingen følges op af en monitering til dokumentation/verificering af den inddragede nedbrydning. Herunder udføres en monitering af poreluftkoncentrationer (VOC, ilt og kuldioxid) over tid, således at det kan sikres at der er opnået stationære forhold. Endelig opstilles der massebalancer for kildestyrke, ilt, kvælstof og fosfor hvorved det sandsynliggøres, at der kan opretholdes balance imellem disse parametre over en tidshorisont, der svarer til kildens forventede levetid. Desuden kan der på baggrund af moniteringsdata opstilles 1D-modeller i JAGG 2.0, og det kan beregnes om iltfluxen på sigt vil være tilstrækkelig til at nedbrydningen vil fortsætte. Det vil ydermere – hvis prøvetagningsudstyret til porevand jf. afsnit 3.2.7 vurderes anvendeligt, være relevant at udtage niveauspecifikke porevandsprøver over dybden, hvilket vil give en tydelig indikation af en eventuel forureningsspredning mod grundvandet.

Dataindsamling til opstilling af kriterier ifht. nedadrettet transport

I forhold til risikovurdering for grundvandet, vil det være relevant at udføre omfattende dataindsamling på danske sager, med henblik på at undersøge om det er muligt, at opstille kriterier og anbefalinger til vurdering af den nedadrettede transport i den umættede zone af samme type som præsenteret i kapitel 5 for den opadrettede transport. Sådanne kriterier og evt. reduktionsfaktorer vil for nogle sager gøre dokumentationsprocessen mindre omfangsrig og langt mere operationel, og flere sager vil sandsynligvis kunne vurderes på baggrund af en risikovurdering efter fase 2. For andre sager vil det stadig være nødvendigt at udføre mere omfattede dokumentation af, at nedbrydningen er tilstrækkelig til at afskære forureningen fra grundvandet.

6.3 Anbefalinger

Temaer der kan arbejdes videre med

Som opfølgning på dette projekt anbefales det, at der arbejdes videre med en række konkrete tiltag hvoraf nogle har et relativt kort tidsperspektiv, mens andre har et væsentligt mere langsigtet perspektiv. De konkrete tiltag vurderes alle i væsentlig grad potentielt at kunne forbedre de værktøjer og den viden, der i praksis anvendes ved risikovurderinger vha. JAGG 2.0. Det anbefales således, at der arbejdes videre med følgende overordnede temaer:

- Indsamling af data til etablering af erfaringsværdier for indhold af ilt, kuldioxid og næringssalte (N og P) i dybe umættede zoner (afsnit 2.2.4 og bilag 3).
- Indsamling af sammenhængende danske datasæt for VOC og O_2-indhold i dybe umættede zoner.
- Metodeudvikling af nye måleteknikker (afsnit 3.2).
- Feltafprøvning af udvalgte metoder (afsnit 3.2).
- Feltafprøvning af dokumentationsstrategier under danske forhold, til etablering af best practise på området (kapitel 4).

Indsamling af feltdata (N og P)

Litteraturgennemgangen af tilgængelige data viste, at der kun er meget sparsomme datamængder tilgængelige ifht. at opstille erfaringsbaserede dataintervaller for almindeligt forekommende indhold af ilt og kuldioxid – men specielt af N og P – i dybe umættede zoner under danske forhold. Herunder foreligger der stort set ingen information om N- og P-variationen over dybden og i forskllige aflejringstyper. Derfor anbefales det, at der på en række sager indsamles erfaringstal for typiske værdier under danske forhold, således at disse evt. fremadrettet kan indbygges som velunderbyggede standardværdier i JAGG 2.0 modellens database.

Indsamling af feltdata (VOC og O_2)

Endvidere vil specifikke datasæt med VOC og O_2 kunne give indsigt i hvilken tærskelværdi for ilt der skal til og hvor højt et VOC-indhold der kan være i poreluften – mens der samtidigt kan findes en tilstrækkelig/-fuldstændig biologisk nedbrydning. Herunder bør der ske en verifikation af eksisterende feltmetoder til dokumentation af iltindhold ved feltmåling med primært IR-måleteknik.

Metodeudvikling – på langt sigt

Det anbefales at der arbejdes videre med både Push-Pull/Diffusiv Emitter metoderne, men at der her indledes en dialog med en eller flere relevante forskningsinstitutioner med henblik på at få igangsat f.eks. et eller flere Ph.D.-projekt(er).

Feltafprøvning - isotopmetoden

Med udgangspunkt i den eksisterende viden anbefales det at der igangsættes et eller flere feltprojekter hvor isotopmetoden (både C og H) testes på lokaliteter hvor der allerede er investeret et anseeligt beløb i installation af permanente moniteringsboringer og hvor der er gennemført monitering over en længere årrække. Feltlokaliteterne kunne evt. være de to gennemgået i bilag 2.

Feltafprøvning og videreudvikling af DPD-testen

Endvidere anbefales det at videreudvikle og dokumentere en ny in-situ test (DPD-testen) til kvalitativ og kvantitativ dokumentation, som sideløbende med dette projekt er blevet testet på et indledende stadium med støtte fra Miljøstyrelsens Teknologiudviklingsprogram. Herunder anbefales det specielt, at der arbejdes videre med følgende perspektiver /344/:

1. Den fysiske systemkonfiguration.
2. 3D-modellering af flowfelt og anvendelsesområde.
3. Brugen af stabile isotope (bade C og H).

Feltafprøvning – AMETIS-systemet

Endelig anbefales det, at AMETIS-systemet til måling af kildestyrken/porevandskoncentrationer under kilden testes på en enkelt lokalitet, således at denne direkte dokumentationsmetode af kildestyrkekoncentrationen og forureningsprofilet afprøves; gerne en af de veldokumenterede sager der er gennemgået i bilag 2.

Feltafprøvning af dokumentationsstrategier

I forlængelse af ovenstående anbefalinger anbefales det, at der gennemføres ét til to feltprojekter, hvor de opstillede anbefalinger til dokumentation og moniteringsstrategi samt grundlaget for dokumentationen på langt sigt kan afprøves og illustreres.

Viderudvikling af JAGG 2.0

Endelig bør det undersøges om der kan udarbejdes en simpel massebalancemodel til 1D-modellen i JAGG 2.0, der kobler kildestyrken og iltindholdet, for at kunne lave en vurdering af den langsigtede holdbarhed af nedbrydningspotentialet.

6.4 Perspektiver ifht. andre stoffer

Vurdering af risikoen for påvirkning af grundvandet med miljøfremmede organiske stoffer og næringstoffer er en hyppigt forekommende problemstilling i Danmark. Det er dog specielt for sager der også inkluderer transport igenem den umættede zone forbundet med store tekniske vanskeligheder at både måle og kvantificere de aktive transportprocesser.

Der vurderes derfor at være en række perspektiver i at udvikle og teste koncepterne beskrevet i afsnit 6.3, og for bl.a følgede problemstillinger med forskellige stoffer kan resultaterne sandsynligvis genbruges:

- MTBE og lignende kulbrinters transport og nedbrydning.
- Pesticid transport og nedbrydning.
- Næringsstoftransport (N og P) og evt. omsætning.
- Vurdering af risiko ved nedsivningsanlæg med tilledning direkte til den umættede zone.

7 Referencer

[1] Davis GB, Patterson BM, Trefry MG: Evidence for Instantaneous Oxygen-Limited Biodegradation of Petroleum Hydrocarbon Vapors in the Subsurface. Ground Water Monitoring and Remediation 2009;29:126-137.

[2] Deyo BG, Robbins GA, Binkhorst GK: Use of Portable Oxygen and Carbon-Dioxide Detectors to Screen Soil-Gas for Subsurface Gasoline Contamination. Ground Water 1993;31:598-604.

[3] Patterson BM, Davis GB: Quantification of Vapor Intrusion Pathways into a Slab-on-Ground Building under Varying Environmental Conditions. Environmental Science & Technology 2009;43:650-656.

[4] Davis GB, Rayner JL, Trefry MG, Fisher SJ, Patterson BM: Measurement and modeling of temporal variations in hydrocarbon vapor behavior in a layered soil profile. Vadose Zone Journal 2005;4:225-239.

[5] Lee CH, Lee JY, Cheon JY, Lee KK: Attenuation of petroleum hydrocarbons in smear zones: A case study. Journal of Environmental Engineering-Asce 2001;127:639-647.

[6] Davis GB, Patterson BM, Trefry MG. Typical Behaviour of Petroleum and Solvent Vapours: Updating our Understanding from Australian Field Investigations. Enviro 06 Conference and Exhibition: Managing Contaminated Land and Groundwater, 9-11 May 2006, Melbourne: Paper No.e6308. 2006. CSIRO Land and Water. 2006.
Conference Proceeding

[7] Davis GB, Trefry MG, Patterson BM. Petroleum and solvent vapours: Quantifying their behaviour, assessment and exposure. A report to the Western Australian Department of Environment. 2004. CSIRO.

[8] Davis GB, Patterson BM, Trefry MG. Biodegradation of Petroleum Hydrocarbon Vapours: Report for CRC CARE. 2009. CSIRO Land and Water.

[9] McNeel PJ, Dibley V. Case study comparisons of vapor inhalation risk estimates: ASTM RBCA model predictions vs site specific soil vapor data. HazWaste world superfund conference, Washington, DC (United States), 2-4 Dec 1997. 1997.
Conference Proceeding

[10] Lundegard PD. Soil Gas Behavior Beneath a Residential Building. 2005.
Slide

[11] Laubacher RC, Bartholomae P, Velasco P, Reisinger HJ. An Evaluation of the Vapor Profile in the Vadose Zone above a Gasoline Plume. GROUND WATER: PREVENTION, DETECTION AND REMEDIATION CONFERENCE, (NOVEMBER 12-14, 1997, HOUSTON, TEXAS). 1997.
Conference Proceeding

[12] Allen JP, Atekwana EA, Atekwana EA, Duris JW, Werkema DD, Rossbach S: The microbial community structure in petroleum-contaminated sediments corresponds to geophysical signatures. Applied and Environmental Microbiology 2007;73:2860-2870.

[13] Atekwana EA, Werkema DD, Duris JW, Rossbach S, Atekwana EA, Sauck WA, Cassidy DP, Means J, Legall FD: In-situ apparent conductivity measurements and microbial population distribution at a hydrocarbon-contaminated site. Geophysics 2004;69:56-63.

[14] Roggemans s, Bruce CL, Johnson PC, Johnson RL. Vadose Zone Natural Attenuation Of Hydrocarbon Vapors: An Empirical Assessment Of Soil Gas Vertical Profile Data. [december 2001 no. 15]. 2001. American Petroleum Institute.

[15] Davis GB, Trefry MG, Patterson BM. Petroleum vapour model comparison. 2009. CRCCare.

[16] Davis GB, Power TR, Briegel D, Patterson BM. BTEX vapour biodegradation rates in the vadose zone: initial estimates. Groundwater Quality: Remediation and Protection (Proceedings of the GQ'98 Conference held at Tubingen, Germany, September 1998). IAHS Publ. no. 250, 1998. 1998.
Conference Proceeding

[17] Fischer ML, Bentley AJ, Dunkin KA, Hodgson AT, Nazaroff WW, Sextro RG, Daisey JM: Factors affecting indoor air concentrations of volatile organic compounds at a site of subsurface gasoline contamination. Environmental Science & Technology 1996;30:2948-2957.

[18] Franzmann PD, Zappia LR, Power TR, Davis GB, Patterson BM: Microbial mineralisation of benzene and characterisation of microbial biomass in soil above hydrocarbon-contaminated groundwater. Fems Microbiology Ecology 1999;30:67-76.

[19] Hers I, Atwater J, Li L, Zapf-Gilje R: Evaluation of vadose zone biodegradation of BTX vapours. Journal of Contaminant Hydrology 2000;46:233-264.

[20] Ostendorf DW, Schoenberg TH, Hinlein ES, Long SC: Monod kinetics for aerobic biodegradation of petroleum hydrocarbons in unsaturated soil microcosms. Environmental Science & Technology 2007;41:2343-2349.

[21] Ostendorf DW, Kampbell DH: Biodegradation of Hydrocarbon Vapors in the Unsaturated Zone. Water Resources Research 1991;27:453-462.

[22] Ririe GT, Sweeney RE, Daugherty SJ: A comparison of hydrocarbon vapor attenuation in the field with predictions from vapor diffusion models. Soil & Sediment Contamination 2002;11:529-554.

[23] Sanders PF, Hers I: Vapor intrusion in homes over gasoline-contaminated ground water in Stafford, New Jersey. Ground Water Monitoring and Remediation 2006;26:63-72.

[24] Lahvis MA, Baehr AL: Estimation of rates of aerobic hydrocarbon biodegradation by simulation of gas transport in the unsaturated zone. Water Resources Research 1996;32:2231-2249.

[25] Trefry MG, Ohman J, Davis GB: A simple numerical approach for assessing coupled transport processes in partitioning systems. Applied Mathematical Modelling 2001;25:479-498.

[26] Trefry MG, Öhman J, Whyte DS, Davis GB. A time-synchronous domain decomposition code for multiphysics systems. The 9th Biennial Computational Techniques and Applications Conference and Workshops. ANU, Canberra. 2000.
Conference Proceeding

[27] Abreu LDV, Johnson PC: Simulating the effect of aerobic biodegradation on soil vapor intrusion into buildings: Influence of degradation rate, source concentration, and depth. Environmental Science & Technology 2006;40:2304-2315.

[28] Devaull GE: Indoor vapor intrusion with oxygen-limited biodegradation for a subsurface gasoline source. Environmental Science & Technology 2007;41:3241-3248.

[29] Lundegard PD, Johnson PC, Dahlen P: Oxygen transport from the atmosphere to soil gas beneath a slab-on-grade foundation overlying petroleum-impacted soil. Environmental Science & Technology 2008;42:5534-5540.

[30] Konopka A, Turco R: Biodegradation of Organic-Compounds in Vadose Zone and Aquifer Sediments. Applied and Environmental Microbiology 1991;57:2260-2268.

[31] Hinchee RE, Ong SK: A Rapid Insitu Respiration Test for Measuring Aerobic Biodegradation Rates of Hydrocarbons in Soil.

Journal of the Air & Waste Management Association 1992;42:1305-1312.

[32] Bezerra SMC, Zytner RG: Bioventing of Gasoline-Contaminated Soil: Some Aspects for Optimization.

[33] Baehr AL, Fischer ML: Overview of research on the transport, microbial degradation, and remediation of hydrocarbons at a subsurface gasoline-spill site in Galloway township, New Jersey.

[34] Newman WA, Barr KD. Assessment of natural rates of unsaturated zone hydrocarbon bioattenuation. In situ and on-site bioremediation. 1997.
Conference Proceeding

[35] Hohener P, Dakhel N, Christophersen M, Broholm M, Kjeldsen P: Biodegradation of hydrocarbons vapors: Comparison of laboratory studies and field investigations in the vadose zone at the emplaced fuel source experiment, Airbase Vaerlose, Denmark. Journal of Contaminant Hydrology 2006;88:337-358.

[36] Lahvis MA, Baehr AL, Baker RJ: Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions. Water Resources Research 1999;35:753-765.

[37] Baker RJ, Baehr AL, Lahvis MA: Estimation of hydrocarbon biodegradation rates in gasoline-contaminated sediment from measured respiration rates. Journal of Contaminant Hydrology 2000;41:175-192.

[38] Brauner JS, Killingstad M. In situ Bioremediation of Petroleum Aromatic Hydrocarbons. 1996.

[39] Kruse CW, Moldrup P, Iversen N: Modeling diffusion and reaction in soils .2. Atmospheric methane diffusion and consumption in a forest soil. Soil Science 1996;161:355-365.

[40] Grathwohl P: Dissolution kinetics; in Diffusion in natural porous media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics: 1998, pp 136-146.

[41] Grathwohl P: Risk assessment - remediation; in Diffusion in natural porous media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics: 1998, pp 147-160.

[42] Fischer JM, Baker RJ, Lahvis MA, Baehr AL: Determination of vapor-phase diffusion coefficients for unsaturated-zone sediments at a gasoline-spill site in Galloway township, New Jersey. unknown 9999.

[43] Myrand D, Gillham RW, Sudicky EA, Ohannesin SF, Johnson RL: Diffusion of Volatile Organic-Compounds in Natural Clay

Deposits - Laboratory Tests. Journal of Contaminant Hydrology 1992;10:159-177.

[44] Voudrias EA, Li CY: Benzene Vapor Transport in Unsaturated Soil - Adequacy of the Diffusion Equation. Journal of Hazardous Materials 1993;34:295-311.

[45] Thorstenson DC, Pollock DW: Gas-Transport in Unsaturated Zones - Multicomponent Systems and the Adequacy of Fick Laws. Water Resources Research 1989;25:477-507.

[46] Thorstenson DC, Pollock DW: Gas-Transport in Unsaturated Porous-Media - the Adequacy of Fick Law. Reviews of Geophysics 1989;27:61-78.

[47] Wang G, Reckhorn SBF, Grathwohl P: Volatile Organic Compounds Volatilization from Multicomponent Organic Liquids and Diffusion in Unsaturated Porous Media. Vadose Zone Journal 2003;2:692-701.

[48] Werner D, Hohener P: Diffusive partitioning tracer test for nonaqueous phase liquid (NAPL) detection in the vadose zone. Environmental Science & Technology 2002;36:1592-1599.

[49] Werner D, Hohener P. In Situ Method To Measure Effective and Sorption-Affected Gas-Phase Diffusion Coefficients in the unsaturated zone. 2nd International Workshop on Groundwater Risk Assessment at Contaminated sites and Integrated Soil and Water Protection, Tuebingen, March 20-21, 2003. 2003. Conference Proceeding

[50] Werner D, Hohener P: In Situ Method To Measure Effective and Sorption-Affected Gas-Phase Diffusion Coefficients in Soils. Environmental Science & Technology 2003;37:2502-2510.

[51] Werner D, Hohener P: Diffusive partitioning tracer test for nonaqueous phase liquid (NAPL) detection in the vadose zone. Environmental Science & Technology 2003.

[52] Laursen S: On Gaseous-Diffusion of Co2 in the Unsaturated Zone. Journal of Hydrology 1991;122:61-69.

[53] Hansen L, Waisner S, Ringelberg D, Fredrickson H, Wade R, Bajpai R, Talley J. Gasoline Alley, Fort Drum Bioremediation Evaluation, Area 1595, Phase I and Phase II. 2000.

[54] Weeks EP, Earp DE, Thompson GM: Use of Atmospheric Fluorocarbons F-11 and F-12 to Determine the Diffusion Parameters of the Unsaturated Zone in the Southern High-Plains of Texas. Water Resources Research 1982;18:1365-1378.

[55] Divine CE, McCray JE, Martib LMW, Blanford WJ, Blitzer DJ, Brusseau ML, Boving TB: Partitioning tracer tests as a remedia-

tion metric: Case study at naval amphibious base little creek, Virginia Beach, Virginia. Remediation Journal 2004;14:7-32.

[56] Cary JW, Mcbride JF, Simmons CS: Trichloroethylene Residuals in the Capillary-Fringe As Affected by Air-Entry Pressures. Journal of Environmental Quality 1989;18:72-77.

[57] Davis GB, Barber C: Methane volatilization from contaminated groundwater - The effects of recharge. Contaminated Transport in Groundwater 1989.

[58] Smith JA, Tisdale AK, Cho HJ: Quantification of natural vapor fluxes of trichloroethene in the unsaturated zone at Picatinny Arsenal, New Jersey. Environmental Science & Technology 1996;30:2243-2250.

[59] Klenk ID, Grathwohl P: Transverse vertical dispersion in groundwater and the capillary fringe. Journal of Contaminant Hydrology 2002;58:111-128.

[60] Hunkeler D, Jorger D, Haberli K, Hohener P, Zeyer J: Petroleum hydrocarbon mineralization in anaerobic laboratory aquifer columns. Journal of Contaminant Hydrology 1998;32:41-61.

[61] Holliger C, Gaspard S, Glod G, Heijman C, Schumacher W, Schwarzenbach RP, Vazquez F: Contaminated environments in the subsurface and bioremediation: organic contaminants. Fems Microbiology Reviews 1997;20:517-523.

[62] Bennett K. *In-Situ* Treatment of Soil Contaminated by Benzene (a BTEX compound).

[63] Bouchard D, Hunkeler D, Gaganis P, Aravena R, Hohener P, Broholm MM, Kjeldsen P: Carbon isotope fractionation during diffusion and biodegradation of petroleum hydrocarbons in the unsaturated zone: Field experiment at Vaerlose airbase, Denmark, and modeling. Environmental Science & Technology 2008;42:596-601.

[64] Aravena R. Use of Isotope Methods in Unsaturated Zones Studies.

[65] Conrad ME, DePaolo DJ: Carbon isotopic evidence for biodegradation of organic contaminants in the shallow vadose zone of the Radioactive Waste Management complex. Vadose Zone Journal 2004;3:143-153.

[66] Park HS: A method for assissing soil vapour intrusion from petroleum release sites: Multi-phase/multi-fraction partitioning.

[67] Gaganis P, Karapanagioti HK, Burganos VN: Modeling multicomponent NAPL transport in the unsaturated zone with the con-

stituent averaging technique. Advances in Water Resources 2002;25:723-732.

[68] Keller AA, Sirivithayapakorn S. Pore Scale Determination of the Rate of NAPL Dissolution or Volatilization. American Geophysical Union, Spring Meeting 2001. 9999.
Conference Proceeding

[69] Park HS, San Juan C: A method for assessing leaching potential for petroleum hydrocarbons release sites: Multiphase and multisubstance equilibrium partitioning. Soil & Sediment Contamination 2000;9:611-632.

[70] Lookman R, Van der Sterren G, Vanermen G, Van De Weghe H, Gemoets J, Alphenaar A. Oil characterisation: assessment of composition, risks, degradation and remediation potential of total petroleum hydrocarbons in soil. 9999.
Conference Proceeding

[71] Arey JS, Gschwend PM: Estimating partition coefficients for fuel-water systems: Developing linear solvation energy relationships using linear solvent strength theory to handle mixtures. Environmental Science & Technology 2005;39:2702-2710.

[72] Mccarthy KA, Johnson RL: Transport of Volatile Organic-Compounds Across the Capillary-Fringe. Water Resources Research 1993;29:1675-1683.

[73] Klenk ID. Transport of volatile organic compounds (VOC's) from soil-gas to groundwater. 2000.

[74] Devaull GE, Ettinger RA, Salanitro JP, Gustafson JB. Benzene, toluene, ethylbenzene, and xylenes (BTEX) degradation in vadose zone soils during vapor transport: First-order rate constants. NWWA/API Conference of petroleum hydrocarbons and organic chemicals in groundwater: prevention, detection and restoration. November 12-14 1997. 1997.
Conference Proceeding

[75] Baldwin CK, Hall BL, Dupont RR. In situ instrumentation for evaluating air injection remediation technologies.

[76] Walter T, Ederer HJ, Forst C, Stieglitz L: Sorption of selected polycyclic aromatic hydrocarbons on soils in oil-contaminated systems. Chemosphere 2000;41:387-397.

[77] Peterson MS, Lion LW, Shoemaker CA: Influence of Vapor-Phase Sorption and Diffusion on the Fate of Trichloroethylene in An Unsaturated Aquifer System. Environmental Science & Technology 1988;22:571-578.

[78] Culver TB, Shoemaker CA, Lion LW: Impact of Vapor Sorption on the Subsurface Transport of Volatile Organic-Compounds - A

Numerical-Model and Analysis. Water Resources Research 1991;27:2259-2270.

[79] Zytner RG: Sorption of Benzene, Toluene, Ethylbenzene and Xylenes to Various Media. Journal of Hazardous Materials 1994;38:13-126.

[80] Grathwohl P, Reinhard M: Desorption of Trichloroethylene in Aquifer Material - Rate Limitation at the Grain Scale. Environmental Science & Technology 1993;27:2360-2366.

[81] Troldborg M, Binning PJ, Nielsen S, Kjeldsen P, Christensen AG: Unsaturated zone leaching models for assessing risk to groundwater of contaminated sites. Journal of Contaminant Hydrology 2009;105:28-37.

[82] Battistelli A. MODELING THE BIODEGRADATION OF ORGANIC CONTAMINANTS WITH TMVOCBIO. PROCEEDINGS, TOUGH Symposium 2003 Lawrence Berkeley National Laboratory, Berkeley, California, May 12-14, 2003. 2003.
Conference Proceeding

[83] Vogele TJ, Kulresthra A, Nitao JJ, Lee K. Simulation of Soil Vapor Extraction at Building 518 Lawrence Livermore National Laboratory Livermore Site. 1996.

[84] Seely GE, Falta RW, Hunt JR: Buoyant Advection of Gases in Unsaturated Soil. Journal of Environmental Engineering-Asce 1994;120:1230-1247.

[85] Falta RW, Javandel I, Pruess K, Witherspoon PA: Density-Driven Flow of Gas in the Unsaturated Zone Due to the Evaporation of Volatile Organic-Compounds. Water Resources Research 1989;25:2159-2169.

[86] Battistelli A: Modeling multiphase organic spills in coastal sites with TMVOC V.2.0. Vadose Zone Journal 2008;7:316-324.

[87] Lahvis MA, Baehr AL. Transport of methyl tert-butyl ether (MTBE) and hydrocarbons to ground water from gasoline spills in the unsaturated zone. Technical meeting Charleston South Carolina March 8-12, 1999. 1999.
Conference Proceeding

[88] Walter GR, Geddis AM, Murray R, Bentley HW. Vapor Phase Transport as a Groundwater Contamination Process at Arid Landfill Sites.

[89] Lahvis MA. Evaluation of Small-Volume Releases of Ethanol-Blended Gasoline at UST Sites. 2003. American Petroleum Institute.

[90] Dakhel N, Pasteris G, Werner D, Hohener P: Small-volume releases of gasoline in the Vadose Zone: Impact of the additives MTBE and ethanol on groundwater quality. Environmental Science & Technology 2003;37:2127-2133.

[91] Johnson PC. Identification of critical parameters for the johnson and ettinger (1991) vapor intrusion model. 2003. American Petroleum Institute.

[92] Lahvis MA. Evaluation of potential vapor transport to indoor air associated with small-volume releases of oxygenated gasoline in the zadose zone. 2005. American Petroleum Institute.

[93] Srinivasan V, Clement TP, Lee KK: Domenico solution - Is it valid? Ground Water 2007;45:136-146.

[94] Lahvis MA. Maximum potential impacts of tertiary butyl alcohol (TBA) on groundwater from small-volume releases of ethanol-blended gasoline in the vadose zone. 2005. American Petroleum Institute.

[95] Friedel MJ: Coupled inverse modeling of vadose zone water, heat, and solute transport: calibration constraints, parameter non-uniqueness, and predictive uncertainty. Journal of Hydrology 2005;312:148-175.

[96] Silka LR: Simulation of vapor transport through the unsaturated zone - interpretation of soil-gas surveys.

[97] Rivett MO: Soil-Gas Signatures from Volatile Chlorinated Solvents - Borden Field Experiments. Ground Water 1995;33:84-98.

[98] Schneider W, Stöfen H: Relevanz des Quellterms bei der Sickerwasserprognose. Bodenschutz.

[99] Kechavarzi C, Soga K, Illangasekare T, Nikolopoulos P: Laboratory study of immiscible contaminant flow in unsaturated layered sands. Vadose Zone Journal 2008;7:1-9.

[100] Flaming Je, Knox RC, Sabatini DA, Kibbey TC: Surfactant Effects on Residual Water and Oil Saturations in Porous Media. Vadose Zone Journal 2003;2:168-176.

[101] Oostrom M, Dane JH, Wietsma TW: A review of multidimensional, multifluid intermediate-scale experiments: Nonaqueous phase liquid dissolution and enhanced remediation. Vadose Zone Journal 2006;5:570-598.

[102] Molins S, Mayer KU, Amos RT, Bekins BA: Vadose zone attenuation of organic compounds at a crude oil spill site — Interactions between biogeochemical reactions and multicomponent gas transport. Journal of Contaminant Hydrology 2009.

[103] Tindall JA, Friedel MJ, Szmajter RJ, Cuffin SM: Part 1: Vadose-zone column studies of toluene (enhanced bioremediation) in a shallow unconfined aquifer. Water Air and Soil Pollution 2005;168:325-357.

[104] Ronen D, Graber ER, Laor Y: Volatile organic compounds in the saturated-unsaturated interface region of a contaminated phreatic aquifer. Vadose Zone Journal 2005;4:337-344.

[105] Mills WB, Liu S, Rigby MC, Brenner D: Time-variable simulation of soil vapor intrusion into a building with a combined crawl space and basement. Environmental Science & Technology 2007;41:4993-5001.

[106] Cannavo P, Lafolie F, Nicolardot B, Renault P: Modeling seasonal variations in carbon dioxide and nitrous oxide in the vadose zone. Vadose Zone Journal 2006;5:990-1004.

[107] Kirtland BC, Aelion CM, Stone PA: Assessing in situ mineralization of recalcitrant organic compounds in vadose zone sediments using delta C-13 and C-14 measurements. Journal of Contaminant Hydrology 2005;76:1-18.

[108] Tillman FD, Weaver JW: Temporal moisture content variability beneath and external to a building and the potential effects on vapor intrusion risk assessment. Science of the Total Environment 2007;379:1-15.

[109] DeVaull G, Ettinger R, Gustafson J: Chemical vapor intrusion from soil or groundwater to indoor air: Significance of unsaturated zone biodegradation of aromatic hydrocarbons. Soil & Sediment Contamination 2002;11:625-641.

[110] Johnston CD, Desvignes A: Evidence for biodegradation and volatilisation of dissolved petroleum hydrocarbons during in situ air sparging in large laboratory columns. Water, Air and Soil Pollution 2003;25-33.

[111] Mchugh TE, Connor JA, Ahmad F: An empirical analysis of the groundwater-to-indoor-air exposure pathway: The role of background concentrations in indoor air. Environmental Forensics 2004;5:33-44.

[112] Patterson BM, Davis GB: An in situ device to measure oxygen in the vadose zone and in ground water: Laboratory testing and field evaluation. Ground Water Monitoring and Remediation 2008;28:68-74.

[113] Fitzpatrick NA, Fitzgerald JJ: An evaluation of vapor intrusion into buildings through a study of field data. Soil & Sediment Contamination 2002;11:603-623.

[114] Garbesi K, Sextro RG: Modeling and Field Evidence of Pressure-Driven Entry of Soil Gas Into A House Through Permeable Below-Grade Walls. Environmental Science & Technology 1989;23:1481-1487.

[115] Jin Y, Streck T, Jury WA: Transport and Biodegradation of Toluene in Unsaturated Soil. Journal of Contaminant Hydrology 1994;17:111-127.

[116] Little JC, Daisey JM, Nazaroff WW: Transport of Subsurface Contaminants Into Buildings. Environmental Science & Technology 1992;26:2058-2066.

[117] Ostendorf DW, Kampbell DH: Bioremediated Soil Venting of Light-Hydrocarbons. Hazardous Waste & Hazardous Materials 1990;7:319-334.

[118] Thorbjorn A, Moldrup P, Blendstrup H, Komatsu T, Rolston DE: A Gas Diffusivity Model Based on Air-, Solid-, and Water-Phase Resistance in Variably Saturated Soil. Vadose Zone Journal 2008;7:1230-1240.

[119] Werner D, Grathwohl P, Hohener P: Review of field methods for the determination of the tortuosity and effective gas-phase diffusivity in the vadose zone. Vadose Zone Journal 2004;3:1240-1248.

[120] Kawamoto K, Moldrup P, Schjonning P, Iversen BV, Rolston DE, Komatsu T: Gas transport parameters in the vadose zone: Gas diffusivity in field and lysimeter soil profiles. Vadose Zone Journal 2006;5:1194-1204.

[121] Bohy M, Dridi L, Schafer G, Razakarisoa O: Transport of a mixture of chlorinated solvent vapors in the vadose zone of a sandy aquifer: Experimental study and numerical modeling. Vadose Zone Journal 2006;5:539-553.

[122] Turcu VE, Jones SB, Or D: Continuous soil carbon dioxide and oxygen measurements and estimation of gradient-based gaseous flux. Vadose Zone Journal 2005;4:1161-1169.

[123] Evans D, Hers I, Wolters RM, Boddington RTB, Hall DH. Vapour transfer of soil contaminants. 2002.

[124] Batterman S, Kulshrestha A, Cheng HY: Hydrocarbon Vapor Transport in Low Moisture Soils. Environmental Science & Technology 1995;29:171-180.

[125] Hohener P, Duwig C, Pasteris G, Kaufmann K, Dakhel N, Harms H: Biodegradation of petroleum hydrocarbon vapors: laboratory studies on rates and kinetics in unsaturated alluvial sand. Journal of Contaminant Hydrology 2003;66:93-115.

[126] Pasteris G, Werner D, Kaufmann K, Hohener P: Vapor phase transport and biodegradation of volatile fuel compounds in the unsaturated zone: A large scale lysimeter experiment. Environmental Science & Technology 2002;36:30-39.

[127] Neale CN, Hughes JB, Ward CH: Impacts of unsaturated zone properties on oxygen transport and aquifer reaeration. Ground Water 2000;38:784-794.

[128] Hendry MJ, Mendoza CA, Kirkland R, Lawrence JR: An assessment of a mesocosm approach to the study of microbial respiration in a sandy unsaturated zone. Ground Water 2001;39:391-400.

[129] Bruell CJ, Hoag GE. The diffusion of gasoline-range hydrocarbon vapors in porous media, experimental methodologies. NWWA/API Conference of petroleum hydrocarbons and organic chemicals in groundwater: prevention, detection and restoration. November 12-14 1989, Houston, USA. 1986.
Conference Proceeding

[130] Influence of bioattenuation on vapor intrusion into buildings - model simulations using semi-analytical one-dimensional model. 2006. Golder Associates.

[131] Ririe T, Sweeney R. Fate and transport of volatile hydrocarbons in the vadose zone. Petroleum hydrocarbon and organic chemicals in groundwater. Houston, Texas 1995. 1995.
Conference Proceeding

[132] English CW, Loehr RC: Degradation of Organic Vapors in Unsaturated Soils. Journal of Hazardous Materials 1991;28:55-63.

[133] Freijer JI, deJonge H, Bouten W, Verstraten JM: Assessing mineralization rates of petroleum hydrocarbons in soils in relation to environmental factors and experimental scale. Biodegradation 1997;7:487-500.

[134] Hess A, Hohener P, Hunkeler D, Zeyer J: Bioremediation of a diesel fuel contaminated aquifer: Simulation studies in laboratory aquifer columns. Journal of Contaminant Hydrology 1996;23:329-345.

[135] Kelly WR, Hornberger GM, Herman JS, Mills AL: Kinetics of BTX biodegradation and mineralization in batch and column systems. Journal of Contaminant Hydrology 1996;23:113-132.

[136] Moyer EE, Ostendorf DW, Richards RJ, Goodwin S: Petroleum hydrocarbon bioventing kinetics determined in soil core, microcosm and tubing cluster studies. Ground Water Monitoring and Remediation 1996;16:141-153.

[137] Reilly TJ, Fishman NS, Baehr AL: Effect of Grain-Coating Mineralogy on Nitrate and Sulfate Storage in the Unsaturated Zone. Vadose Zone Journal 2009;8:75-85.

[138] O'Leary KE, Barker JF, Gillham RW: Remediation of dissolved BTEX through surface application: A prototype field investigation. Groundwater Mon Rev 1995;15:99-109.

[139] Pabich WJ, Valiela I, Hemond HF: Relationship between DOC concentration and vadose zone thickness and depth below water table in groundwater of Cape Cod, USA. Biogeochemistry 2001;55:247-268.

[140] Pinkart HC, Ringelberg DB, Stair JO, Sutton SD, Pfiffner SM, White DC: Phospholipid analysis of extant microbiota for monitoring in situ bioremediation effectiveness; in Hinchee RE, Douglas GS, Ong SK (eds): Monitoring and verification. Bioremedaition. 1995.

[141] Salminen JM, Tuomi PM, Suortti AM, Jorgensen KS: Potential for aerobic and anaerobic biodegradation of petroleum hydrocarbons in boreal subsurface. Biodegradation 2004;15:29-39.

[142] Schoefs O, Perrier M, Dochain D, Samson R: On-line estimation of biodegradation in an unsaturated soil. Bioprocess and Biosystems Engineering 2003;26:37-48.

[143] Song HG, Bartha R: Effects of Jet Fuel Spills on the Microbial Community of Soil. Applied and Environmental Microbiology 1990;56:646-651.

[144] Stout SA, Lundegard PD: Intrinsic biodegradation of diesel fuel in an interval of separate phase hydrocarbons. Applied Geochemistry 1998;13:851-859.

[145] Sublette KL, Kolhatkar RV, Borole A, Raterman KT, Trent GL, Javanmardian M, Fischer JB: Intrinsic bioremediation of gas condensate hydrocarbons: Results of over two years of ground water and soil core analysis and monitoring. Applied Biochemical and Biotechnology 1997;63-65:823-834.

[146] Totsche KU, Kogel-Knabner I, Haas B, Geisen S, Scheibke R: Preferential flow and aging of NAPL in the unsaturated soil zone of a hazardous waste site: implications for contaminant transport. Journal of Plant Nutrition and Soil Science-Zeitschrift fur Pflanzenernahrung und Bodenkunde 2003;166:102-110.

[147] Venkatraman SN, Kosson DS, Schuring JR: Transport and biological fate of toluene in low-permeability soils. Ground Water Monitoring and Remediation 1998;18:105-113.

[148] Wibbe M, Blanke MM: Aliphatic hydrocarbons in an oil-contaminated soil - Carbon economy during microbiological de-

contamination. Environmental Science and Pollution Research 1999;6:2-6.

[149] Wrenn BA, Haines JR, Venosa AD, Kadkhodayan M, Suidan MT: Effects of Nitrogen-Source on Crude-Oil Biodegradation. Journal of Industrial Microbiology 1994;13:279-286.

[150] Amos RT, Blowes DW: Versatile direct push profiler for the investigation of volatile compounds near the water table. Water Resources Research 2008;44.

[151] Molins S, Mayer KU: Coupling between geochemical reactions and multicomponent gas and solute transport in unsaturated media: A reactive transport modeling study. Water Resources Research 2007;43.

[152] Delin GN, Herkelrath WN: Use of soil moisture probes to estimate ground water recharge at an oil spill site. Journal of the American Water Resources Association 2005;41:1259-1277.

[153] Essaid HI, Cozzarelli IM, Eganhouse RP, Herkelrath WN, Bekins BA, Delin GN: Inverse modeling of BTEX dissolution and biodegradation at the Bemidji, MN crude-oil spill site. Journal of Contaminant Hydrology 2003;67:269-299.

[154] Bekins BA, Cozzarelli IM, Godsy EM, Warren E, Essaid HI, Tuccillo ME: Progression of natural attenuation processes at a crude oil spill site: II. Controls on spatial distribution of microbial populations. Journal of Contaminant Hydrology 2001;53:387-406.

[155] Choi JW, Smith JA: Geoenvironmental factors affecting organic vapor advection and diffusion fluxes from the unsaturated zone to the atmosphere under natural conditions. Environmental Engineering Science 2005;22:95-108.

[156] Christophersen M, Broholm MM, Mosbaek H, Karapanagioti HK, Burganos VN, Kjeldsen P: Transport of hydrocarbons from an emplaced fuel source experiment in the vadose zone at Airbase V ae rlose, Denmark. Journal of Contaminant Hydrology 2005;81:1-33.

[157] Shan C, Stephens DB: An Analytical Solution for Vertical Transport of Volatile Chemicals in the Vadose Zone. Journal of Contaminant Hydrology 1995;18:259-277.

[158] Ashley RP, Lerner DN, Lloyd JW: Distribution and Degradation of Diesel Oil in the Unsaturated Zone Following An Oil-Spill on A Chalk Aquifer. Journal of Hydrology 1994;159:43-59.

[159] Azadpour-Keeley A, Keeley JW, Russell HH, Sewell GW: Monitored natural attenuation of contaminants in the subsurface: Ap-

plications. Ground Water Monitoring and Remediation 2001;21:136-143.

[160] Berry KAT, Burton DL: Natural attenuation of diesel fuel in heavy clay soil. Canadian Journal of Soil Science 1997;77:469-477.

[161] Bhupathiraju VK, Krauter P, Holman HYN, Conrad ME, Daley PF, Templeton AS, Hunt JR, Hernandez M, varez-Cohen L: Assessment of in-situ bioremediation at a refinery waste-contaminated site and an aviation gasoline contaminated site. Biodegradation 2002;13:79-90.

[162] Boopathy R: Anaerobic biodegradation of no. 2 diesel fuel in soil: a soil column study. Bioresource Technology 2004;94:143-151.

[163] Capuano RM, Johnson MA: Geochemical reactions during biodegradation vapor-extraction remediation of petroleum contamination in the vadose zone. Ground Water 1996;34:31-40.

[164] Cohen BA, Krumholz LR, Kim HK, Hemond HF: In-Situ Biodegradation of Toluene in A Contaminated Stream .2. Laboratory Studies. Environmental Science & Technology 1995;29:117-125.

[165] Davis JW, Madsen S: Factors affecting the biodegradation of toluene in soil. Chemosphere 1996;33:107-130.

[166] Davis GB, Johnston CD, Patterson BM, Barber C, Bennett M: Estimation of Biodegradation Rates Using Respiration Tests During In Situ Bioremediation of Weathered Diesel NAPL. Ground Water Monitoring and Remediation 1998;18:123-132.

[167] Dror I, Gerstl Z, Prost R, Yaron B: Abiotic behavior of entrapped petroleum products in the subsurface during leaching. Chemosphere 2002;49:1375-1388.

[168] Fine P, Yaron B: Outdoor Experiments on Enhanced Volatilization by Venting of Kerosene Component from Soil. Journal of Contaminant Hydrology 1993;12:355-374.

[169] Franzmann PD, Robertson WJ, Zappia LR, Davis GB: The role of microbial populations in the containment of aromatic hydrocarbons in the subsurface. Biodegradation 2002;13:65-78.

[170] Gerhardt RA: Landfill Leachate Migration and Attenuation in the Unsaturated Zone in Layered and Nonlayered Coarse-Grained Soils. Ground Water Monitoring and Remediation 1984;4:56-65.

[171] Gidda T, Stiver WH, Zytner RG: Passive volatilization behaviour of gasoline in unsaturated soils. Journal of Contaminant Hydrology 1999;39:137-159.

[172] Grifoll J, Cohen Y: Contaminant migration in the unsaturated soil zone: The effect of rainfall and evapotranspiration. Journal of Contaminant Hydrology 1996;23:185-211.

[173] Hollender J, Althoff K, Mundt M, Dott WG: Assessing the microbial activity of soil samples, its nutrient limitation and toxic effects of contaminants using a simple respiration test. Chemosphere 2003;53:269-275.

[174] Huesemann MH: Predictive Model for Estimating the Extent of Petroleum Hydrocarbon Biodegradation in Contaminated Soils. Environmental Science & Technology 1995;29:7-18.

[175] Hupe K, Heerenklage J, Woyczechowski H, Bollow S, Stegmann R: Influence of oxygen on the degradation of diesel fuel in soil bioreactors. Acta Biotechnologica 1998;18:109-122.

[176] Hinchee RE, Alleman BC, Hoeppel RE, Miller RN: Hydrocarbon bioremediation. 1994.

[177] Jarsjo J, Destouni G, Yaron B: Retention and Volatilization of Kerosene - Laboratory Experiments on Glacial and Postglacial Soils. Journal of Contaminant Hydrology 1994;17:167-185.

[178] Kao CM, Wang YS: Field investigation of the natural attenuation and intrinsic biodegradation rates at an underground storage tank site. Environmental Geology 2001;40:622-631.

[179] Lee MD, Swindoll CM: Bioventing for In-Situ Remediation. Hydrological Sciences Journal-Journal des Sciences Hydrologiques 1993;38:273-282.

[180] Malina G, Grotenhuis JTC: The role of biodegradation during bioventing of soil contaminated with jet fuel. Applied Biochemistry and Biotechnology 2000;88:59-76.

[181] Margesin R, Zimmerbauer A, Schinner F: Monitoring of bioremediation by soil biological activities. Chemosphere 2000;40:339-346.

[182] Mclinn EL, Rehm BW: Biodegradation of petroleum hydrocarbons in fractured, unsaturated dolomite at a field site. Ground Water Monitoring and Remediation 1997;17:73-80.

[183] Rubin H, Narkis N, Carberry J: Soil and aquifer pollution: non-aqueous phase liquids; contamination and reclamation. 1998.

[184] Meier-Löhr M, Batterman G. Dissolution and degradation kinetics of BTEX compounds during large scale *in situ* bioremediation applying nitrate as an electron acceptor. *Groundwater Quality: Remediation and Protection* (Proceedings of the GQ'98 Conference held at Tubingen, Germany, September 1998). IAHS Publl.

no. 250, 1998. 1998.
Conference Proceeding

[185] De Visscher A, Thomas D, Boeckx P, Van Cleemput O: Methane oxidation in simulated landfill cover soil environments. Environmental Science & Technology 1999;33:1854-1859.

[186] Assessing the signifiance of subsurface contaminant vapor migration to enclosed spaces, site-specific alternatives to generic estimates. 1998. American Petroleum Institute.

[187] Collecting and Interpreting Soil Gas Samples from the Vadose Zone: A Practical Strategy for Assessing the Subsurface Vapor-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites. 2005. American Petroleum Institute.

[188] Lowell PS, Eklund B: VOC emission fluxes as a function of lateral distance from the source. Environmental Progress 2004;23:52-58.

[189] Poulsen M, Damborg A. Fordeling og transport i umættet og mættet zone. ATV møde 4.oktober 1990. 1990.
Conference Proceeding

[190] Barber C, Davis GB, Briegel D, Ward JK: Factors controlling the concentration of methane and other volatiles in groundwater and soil-gas around a waste site. Journal of Contaminant Hydrology 1990;5:155-169.

[191] Kjærgaard M. Bestemmelse af forureningskoncentrationen i mobilt porevand i den umættede zone. 1224. 2008. Miljøstyrelsen.

[192] Kjærgaard M. Prøvetagning af porevand i umættet zone. Et litteraturstudie. 540. 2000. Miljøstyrelsen.

[193] Davis GB, Patterson BM, Wright J. Field assessment of vapours. 2009. CRC Care.

[194] Guidance for Evaluating Soil Vapor Intrusion in the State of New York. 2006. New York State Department of Health.

[195] Fagerlund F, Niemi A. Multi-constituent modelling of a gasoline spill using T2VOC numerical simulator. TOUGH Symposiom 2003, Lawrence Berkeley National Laboratory, Berkley, California, May 12-13 2003. 2003.
Conference Proceeding

[196] O'Reilly KT, Magaw RI, Rixey WG. Predicting the effect of hydrocarbon and hydrocarbon-impacted soil on groundwater. 2001. American Petroleum Institute.

[197] Hettwer K, Warrelmann J, Heyser W, Martus P, Gabb S, Püttmann W, Drewes U, Walter U, Vehlhaber D. Langzeituntersu-

chungen zu den Möglichkeiten und Grenzen der Nutzung natürlicher Selbstreinigungsprozesse für ausgewählte Schadstoffe am Beispiel kontaminierter militärischer Liegenschaften. 2004. Umweltbundesamt.

[198] Juhler RK, Jacobsen OS, Larsen CL, Nilson B, van der Keur P. AFKLARINGSPROJEKT OM NEDSIVNING AF HUSSPILDEVAND. 2004. DANVA.

[199] Kreamer DK, James DE, Varner KE. Determination of Pollutant Distribution and Movement by Controlled Laboratory Experiments. 1997. US EPA.

[200] Minnich M. Behavior and Determination of Volatile Organic Compounds in Soil - A Literature Review. 1993. US EPA.

[201] Newell CJ, Fifai HS, Wilson JT, Connor JA, Aziz JA, Suarez MP. Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies.US EPA.

[202] Kjærgaard M, Ringsted JP. Naturlig nedbrydning af miljøfremmede stoffer i jord og grundvand - Et litteraturstudium af 1.-ordens nedbrydningshastigheder af miljøfremmede stoffer for hvilke der er fastsat et kvalitetskriterium i jord eller grundvand. Miljøprojekt nr. 408. 1998. Miljøstyrelsen.

[203] Broholm M, Christophersen M, Westergaard C, Hansen HCL, Baun DL, Andersen L, Hansen N, Hunkeler D, Klint KE, Skou H. Vurdering af naturlig nedbrydning af tjærestoffer i grundvand. Ringe Tjære- og Asfaltfabrik, Ringe, Fyn. 2009. Miljøstyrelsen.

[204] Kristensen AH. Naturlig nedbrydning i lag delt umættet zone. ATV møde 10.-11. marts 2009. 2009.
Conference Proceeding

[205] Bioventing Principles andPractice. Volume II: Bioventing Design. 1995. US EPA.

[206] Cameron RJ, Evans JC, Johnson MD, Liikala TL. Summary of Hanford Subsurface Air Flow and Extraction (SAFE) Activities for Fiscal Year 2002. 2002. Pacific Northwest National Laboratory.

[207] Jones K. Using atmospheric nobel gases and SF6 as indicators for transport and reaction processes in hydrocarbon contaminated sediments. 2009.
Thesis/Dissertation

[208] Lundstedt S. Analysis of PAHs and their transformation products in contaminated soil and remedial processes. 2003.

[209] Zytner RG. Organic compounds in unsaturated soil. 2002.
Thesis/Dissertation

[210] Peargin T. The significance of hydrocarbon biodegradation: Interpreting observations of hydrocarbon and oxygen behavior above shallow LNAPL source. 9999.

[211] Ririe GT. Top 10 issuses and workplan. Review-lessons learned. 2009.
Slide

[212] DeVaull G. Microcosm analyses in applied monitored natural attenuation of MTBE and TBA. 2006.
Slide

[213] Ririe GT. Case studies to evaluate hydrocarbon vapor attenuation in the vadose zone.
Slide

[214] Hartman B. Vapor intrusion risk pathway: Practical assessment methods. 2009.
Slide

[215] Evaluating the soil vapor intrusion pathway at petroleum release sites in NYS.
Slide

[216] Abreu L, Johnson P. Modeling the effect of aerobic biodegradation on vapor intrusion. 2005.
Slide

[217] Gallagher D. Status and application of DTSC's vapor intrusion guidance. 2005.
Slide

[218] Hopkins H. Data collection to support sound screening for vapor intrusion to indoor air at petroleum release sites. 2005.
Slide

[219] Mchugh T. Vapor intrusion investigation methods. 2005.
Slide

[220] Schuver H, Cooper D, Dawson H. Update on the OSWER vapor intrusion guidance. 2005.
Slide

[221] Vescio J. Update on EPA's petroleum vapor intrusion work group activities. 2005.
Slide

[222] Lahvis MA. Type curve approach for assessing potential effects on ground water from small releases of gasoline at UST sites. 2006.
Slide

[223] Nielsen SG. Gasdifussionskoefficienter i jord. Måleopstilling, prædiktionsmodeller og risikovurdering. 2004.
Thesis/Dissertation

[224] Werner D. Diffusive Partitioning Tracer Test for Nonaqueous Phase Liquid (NAPL) Detection in the Vadose Zone. 2002.
Thesis/Dissertation

[225] Quantifying effective vapor-phase diffusion coefficients. Underground Tank Technology Update . 2000.

[226] Hartman B. The downward migration of vapors. Investigation and remediation .

[227] Hartman B. Some enlightment on density. Investigation and remediation .

[228] Hartman B. The great escape (from the UST). Investigation and remediation .

[229] Hartman B. The upward migration of vapors. Investigation and remediation .

[230] Werner D, Hohener P. Diffusiver gastracertest zur quatifizierung von Schadstoffphasen (öle, lösungsmittel) im ungesättigten untergrund.

[231] Roelofson FJ, Hofstee C, van Meurs GAM, Streng JMA, Bowker AA. Modelcode Bronfunctie Olieverontriniging. 2003. Delft Cluster.

[232] Rixey WG, Joshi S. Dissolution of MTBE from a residually trapped gasoline source - a summary of research results. 2000.

[233] Grathwohl P. Formulierung einer verfahrensempfehlung zur bestimmung der emission leichflüchtiger organisher schadstoffe (LCKW, BTEX etc.) aus kontaminierten böden. 1996.

[234] Hartman B. Field techniques and strategies for documenting bioattenuation. 2005.
Slide

[235] 1-dimensional modeling of volatilization and dissolution of kerosene in the unsaturated zone at flughafen Niedergörsdorf. 9999.
Ref Type: Thesis/Dissertation

[236] DeVaull G. Basics of vapor intrusion modeling. 2002.
Slide

[238] Overview of BioVapor. 2009.
Slide

[239] Lahvis MA. Evaluation of 1st-order biodegradation rates of benzene for VI risk assessment at petroleum-hydrocarcon sites.
Pamphlet

[240] Bioaktivitetstest - aerob nedbrydning af olie. 2002.
Slide

[241] DeVaull G. Exclusion distance screening criteria. 2009.
Slide

[242] Davis RV. Bio-attenuation of petroleum hydrocarbon vapors in the subsurface - update on studies and proposed screening criteria for the vapor intrusion pathway. 2009.
Slide

[243] Davis R. An analysis of subsurface vapor attenuation data ffrom petroleum hydrocarbon sites. 2005.
Slide

[244] Davis R. OUST - soil gas DB analysis.
Slide

[245] Tindall JA, Kunkel JR, Anderson DE: Transport of heat and gas in the soil and the subsurface; in Unsaturated zone hydrology for scientists and engineers: pp 200-272.

[246] Tindall JA, Kunkel JR, Anderson DE: Soil remediation techniques; in Unsaturated zone hydrology for scientists and engineers: pp 494-523.

[247] Mayer KU, Amos RT, Molins S. Integrated investigation of natural attenuation processes at the Bemidji crude oil spill site. 9999.
Slide

[248] Kästner M. Parameter und methoden zur beurteilung der biologischen sanierbarkeit von böden.

[249] Grathwohl P, Halm D, Bonilla A, Broholm M, Burganos V, Christophersen M, Comas R, Gaganis P, Gorostiza I, Hohener P, Kjeldsen P, van der Sloot H. Guideline for groundwater risk assessment at contaminated sites (GRACOS). 2003.

[250] Downey DC, Hall FL. Using soil gas surveys to determine bioventing feasibility and natural attenuation potential.

[251] Ririe GT. Case study - Santa Maria.
Slide

[252] Bouchard D. Use of stable isotope analysis to assess biodegradation of volatile organic compounds in the unsaturated subsurface.
Thesis/Dissertation

[253] Urmann K, Gonzalez-Gil G, Schroth MH, Hofer M, Zeyer J: New field method: Gas push-pull test for the in-situ quantification of microbial activities in the vadose zone. Environmental Science & Technology 2005;39:304-310.

[254] Rehabilitation of the former camide landfill, Horsley Park. 2006. Centre for Water & Waste Technology (CWWT).

[255] Gonzalez-Gil G, Schroth MH, Gomez K, Papritz A, Zeyer J: Diffusional and microbial isotope fractionation of methane during gas push-pull tests. Geochimica et Cosmochimica Acta 2008;72:2115-2124.

[256] Williams GM, Ward RS, Noy DJ: Dynamics of landfill gas migration in unconsolidated sands. Waste Management & Research 1999;17:327-342.

[257] Gaganis P, Kjeldsen P, Burganos VN: Modeling natural attenuation of multicomponent fuel mixtures in the vadose zone: Use of field data and evaluation of biodegradation effects. Vadose Zone Journal 2004;3:1262-1275.

[258] Opgradering af JAGG indeklimamodul til version 2.0. 2007. Miljøstyrelsen.

[259] Andersen L, Obenrender A. Opgradering af JAGG - Revision af fugacitetsberegninger, håndtering af fri fase og blandingsforureninger. 2007. Miljøstyrelsen.

[260] Christensen AG, Binning PJ, Troldborg M, Kjeldsen P, Broholm M. Opgradering af JAGG til version 2.0 Vertikal transport ned til førstkommende betydende magasin. 2007. Miljøstyrelsen.

[261] Holden PA, Hersman LE, Firestone MK: Water content mediated microaerophilic toluene biodegradation in arid vadose zone materials. Microbial Ecology 2001;42:256-266.

[262] Kaufmann K, Christophersen M, Buttler A, Harms H, Hohener P: Microbial community response to petroleum hydrocarbon contamination in the unsaturated zone at the experimental field site Vaerlose, Denmark. Fems Microbiology Ecology 2004;48:387-399.

[263] Kristensen AH, Henriksen K, Mortensen L, Scow KM, Moldrup P: Soil Physical Constraints on Intrinsic Biodegradation of Petroleum Vapors in a Layered Subsurface. Vadose Zone Journal 2010;9:137-147.

[264] Loll P. Oprensning af olie- og benzinforureninger - status for naturlig nedbrydning og biologiske afværketeknikker med fokus på olie og benzinforureninger. 2008.
Conference Proceeding

[265] Loll P, Nørgaard D, Henriksen K, Larsen C. MTBE biodegradation in the vadose zone. In Situ and On-Site Bioremediation 2007 Proceedings of the Ninth International In Situ and On-Site Bioremediation Symposium
Baltimore, Maryland; May 7-10, 2007. 2007.
Conference Proceeding

[266] Margesin R, Walder G, Schinner F: Bioremediation assessment of a BTEX-contaminated soil. Acta Biotechnologica 2003;23:29-36.

[267] Scherr K, Aichberger H, Braun R, Loibner AP: Influence of soil fractions on microbial degradation behavior of mineral hydrocarbons. European Journal of Soil Biology 2007;43:341-350.

[268] Skopp J, Jawson MD, Doran JW: Steady-State Aerobic Microbial Activity As A Function of Soil-Water Content. Soil Science Society of America Journal 1990;54:1619-1625.

[269] Broholm MM, Christophersen M, Maier U, Stenby EH, Hohener P, Kjeldsen P: Compositional evolution of the emplaced fuel source in the vadose zone field experiment at airbase Vaerlose, Denmark. Environmental Science & Technology 2005;39:8251-8263.

[270] Holden PA, Fierer N: Microbial processes in the vadose zone. Vadose Zone Journal 2005;4:1-21.

[271] Kasai Y, Takahata Y, Hoaki T, Watanabe K: Physiological and molecular characterization of a microbial community established in unsaturated, petroleum-contaminated soil. Environmental Microbiology 2005;7:806-818.

[272] Labud V, Garcia C, Hernandez T: Effect of hydrocarbon pollution on the microbial properties of a sandy and a clay soil. Chemosphere 2007;66:1863-1871.

[273] Aichberger H, Hasinger M, Braun R, Loibner AP: Potential of preliminary test methods to predict biodegradation performance of petroleum hydrocarbons in soil. Biodegradation 2005;16:115-125.

[274] Pearce K, Pretorius WA: A bioventing feasibility test to aid remediation strategy. Water Sa 1998;24:5-9.

[275] Videncenter for jordforurening - Projekteringsparametre. Nedbrydningsrate, umættet zone. 2009.
Ref Type: Internet Communication

[276] Baehr AL: Selective Transport of Hydrocarbons in the Unsaturated Zone Due to Aqueous and Vapor-Phase Partitioning. Water Resources Research 1987;23:1926-1938.

[277] Bonroy J, van de Steene J, van de Velde R, van Eatvelde G, Verplancke H, Verfailie F, Boucneau G. Monitored Natural Attenuation of Domestic Fuel Oil in the Unsaturated Zone. In Situ and On-Site Bioremediation 2007
Proceedings of the Ninth International In Situ and On-Site Bioremediation Symposium
Baltimore, Maryland; May 7-10, 2007. 2007.
Conference Proceeding

[278] Chaplin BP, Delin GN, Baker RJ, Lahvis MA: Long-Term Evolution of Biodegradation and Volatilization Rates in a Crude Oil-Contaminated Aquifer. Bioremediation Journal 2002;6:237-255.

[279] Christensen AG, Kjeldsen P, Lassen E. Undersøgelse af fyringsolies transport og nedbrydning i den umættede zone. ATV meeting 6.- 7. march 2007. 2007.
Conference Proceeding

[280] Karapanagioti HK, Gaganis P, Burganos VN, Hohener P: Reactive transport of volatile organic compound mixtures in the unsaturated zone: modeling and tuning with lysimeter data. Environmental Modelling & Software 2004;19:435-450.

[281] Bouchard D, Hunkeler D, Hohener P, Aravena R, Kjeldsen P, Broholm M. Assessment of Biodegradation of Organic Contaminants in the Unsaturated Zone Using Isotopes. In Situ and On-Site Bioremediation 2007
Proceedings of the Ninth International In Situ and On-Site Bioremediation Symposium
Baltimore, Maryland; May 7–10, 2007. 2007.
Conference Proceeding

[282] Bouchard D, Hohener P, Hunkeler D: Carbon Isotope Fractionation During Volatilization of Petroleum Hydrocarbons and Diffusion Across a Porous Medium: A Column Experiment. Environmental Science & Technology 2008;42:7801-7806.

[283] Coffin RB, Pohlman JW, Grabowski KS, Knies DL, Plummer RE, Magee RW, Boyd TJ: Radiocarbon and stable carbon isotope analysis to confirm petroleum natural attenuation in the vadose zone. Environmental Forensics 2008;9:75-84.

[284] Conrad ME, Tempeton AS, Daley PF, varez-Cohen L: Isotopic evidence for biological controls on migration of petroleum hydrocarbons. Organic Geochemistry 1999;30:843-859.

[285] Gomez K, Gonzalez-Gil G, Schroth MH, Zeyer J: Transport of methane and noble gases during gas push-pull tests in variably saturated porous media. Environmental Science & Technology 2008;42:2515-2521.

[286] Gomez KE, Gonzalez-Gil G, Lazzaro A, Schroth MH: Quantifying methane oxidation in a landfill-cover soil by gas push-pull tests. Waste Management 2009;29:2518-2526.

[287] Gonzalez-Gil G, Schroth MH, Zeyer J: Transport of methane and noble gases during gas push-pull tests in dry porous media. Environmental Science & Technology 2007;41:3262-3268.

[288] Rose MB, Thomsen M, Kjeldsen P, Tuxen N. Spredning af TCE i den umættede zone under en industrigrund. ATV meeting 6.-7. march 2007. 2007.
Conference Proceeding

[289] Loll P, Larsen C, Henriksen K. Stimuleret biologisk nedbrydning af fyringsolie - feltresultater der viser muligheder og brgrænsninger. ATV meeting 6.7-7- march 2007. 2007.
Conference Proceeding

[290] Loll P, Larsen C, Henriksen K, Brask P. Bio-nedbrydning af fyringsolieforurening. Vand og jord . 2007.

[291] Addy K, Kellogg DQ, Gold AJ, Groffman PM, Ferendo G, Sawyer C: In situ push-pull method to determine ground water denitrification in riparian zones. Journal of Environmental Quality 2002;31:1017-1024.

[292] Cunningham JA, Rahme H, Hopkins GD, Lebron C, Reinhard M: Enhanced in situ bioremediation of BTEX contaminated groundwater by combined injection of nitrate and sulfate. Environmental Science & Technology 2001;35:1663-1670.

[293] Hageman KJ, Field JA, Istok JD, Schroth MH: "Forced mass balance" technique for estimating in situ transformation rates of sorbing solutes in groundwater. Environmental Science & Technology 2003;37:3920-3925.

[294] Haggerty R, Schroth MH, Istok JD: Simplified method of "push-pull" test data analysis for determining in situ reaction rate coefficients. Ground Water 1998;36:314-324.

[295] Istok JD, Field JA, Schroth MH: In situ determination of subsurface microbial enzyme kinetics. Ground Water 2001;39:348-355.

[296] Reinhard M, Shang S, Kitanidis PK, Orwin E, Hopkins GD, Lebron CA: In situ BTEX biotransformation under enhanced nitrate- and sulfate-reducing conditions. Environmental Science & Technology 1997;31:28-36.

[297] Schroth MH, Istok JD: Approximate solution for solute transport during spherical-flow push-pull tests. Ground Water 2005;43:280-284.

[298] Schroth MH, Istok JD, Conner GT, Hyman MR, Haggerty R, O'Reilly KT: Spatial variability in in situ aerobic respiration and denitrification rates in a petroleum-contaminated aquifer. Ground Water 1998;36:924-937.

[299] Schroth MH, Istok JD, Haggerty R: In situ evaluation of solute retardation using single-well push-pull tests. Advances in Water Resources 2001;24:105-117.

[300] Schroth MH, Istok JD: Models to determine first-order rate coefficients from single-well push-pull tests. Ground Water 2006;44:275-283.

[301] Snodgrass MF, Kitanidis PK: A method to infer in situ reaction rates from push-pull experiments. Ground Water 1998;36:645-650.

[302] Wiedemeier TH, Swanson MA, Wilson JT, Kampbell DH, Miller RN, Hansen JE: Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in ground water. Ground Water Monitoring and Remediation 1996;16:186-194.

[303] DeVaull G. MTBE / TBA Biodegradation Rates. 2007.
Slide

[304] Pejter HM. Transport and degradation of heating oil in soil - a soil column study. 2006.
Thesis/Dissertation

[305] Pedersen SR, Sø HU. Nedbrydning af kulbrintet i den umættede zone. 2004.
Thesis/Dissertation

[306] Christensen AG. Projekt om umættet zone - undersøgelse af fyringsolies transport og nedbrudning i den umættede zone. 2006.

[307] Maier U. Modeling of Natural Attenuation in Soil and Groundwater. 2004. Der Geowissenschaftlichen Fakultät der Eberhard - Karls- Universität Tübingen.
Thesis/Dissertation

[308] Aktor H. GEOPROC - edb program til vurdering af geokemiske processer. Miljøprojekt nr. 883 2004. 2004. Miljøstyrelsen.

[309] Oprydning på forurenede lokaliteter. 6 + 7 (1998). 1998. Miljøstyrelsen.

[310] Dahan O, Bones S. Vadose-zone monitoring system – key to groundwater protection and optimization of remediation conditions.
Pamphlet

[311] Dahan O, Talby R, Yechieli Y, Adar E, Lazarovitch N, Enzel Y: In Situ Monitoring of Water Percolation and Solute Transport Using a Vadose Zone Monitoring System. Vadose Zone Journal 2009;8:916-925.

[312] Muchitsch N. Laenvej, Glesborg. Monitering af naturlig nedbrydning af benzin i den umættede zone. Afsluttende afrapportering. OM-SAG 8585-47-9165. 2009. NIRAS Allerød.

[313] Loll P, Larsen C. Anbefalinger til sagsforløb ved in-situ oprensning af jordforurening. Miljøprojekt nr. 1255. 2008. Miljøstyrelsen.

[314] Istok JD, Humphrey MD, Schroth MH, Hyman MR, OReilly KT: Single-well, "push-pull" test for in situ determination of microbial activities. Ground Water 1997;35:619-631.

[315] Hageman KJ, Istok JD, Field JA, Buscheck TE, Semprini L: In situ anaerobic transformation of trichlorofluoroethene in trichloroethene contaminated groundwater (vol 35, pg 1729, 2001). Environmental Science & Technology 2001;35:2860.

[316] Kim Y, Azizian J, Istok JD, Semprini L. Field push-pull test protocol for aerobic cometabolism of chlorinated aliphatic hydrocarbons. ESTCP report 4/21/2005. 2005. Oregon State University Civil, Construction, and Environmental Engineering Department Corvallis, OR 97331.

[317] Dahan O, Bones S. Vadose-zone monitoring as a key to groundwater protection and optimization of remediation strategies. 2010.
Slide

[318] Meckenstock, R.U., Morasch, B., Griebler, C., Richnow, H.H. Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated aquifers. Journal of contaminant hydrology 75, 215-255, 2004.

[319] Gray, J.R., Coulome, G.L., Gandhi, D., Wilson, R.D., Mackay, D.M., Lollar, B.S.. Carbon and Hydro-gen isotope fractionation during biodegradation of methyl tert-Butyl ether. Environ. Sci. Technology 36(9), 1931-1938, 2002.

[320] Hunkeler, D.N., Andersen,N.,Aravena, R., Bernasconi, S.M., and Butler, J. Hydrogen and carbon iso-tope fractionation during aerobic biodegradation of benzene. Environmental science and technology. 35. 3462-3467, 2001.

[321] Hunkeler, D.N. Personlig kommunikation. 2011.

[322] Dahan, O., B. Tatarsky, Y. Enzel, C. Kulls, M. Seely, and G. Benito. Dynamics of flood water infiltra-tion and ground water recharge in hyperarid desert. Ground Water 46:450–461, 2008.

[323] Rimon, Y., O. Dahan, R. Nativ, and S. Geyer. Water percolation through the deep vadose zone and groundwater recharge: Preliminary results based on a new vadose zone monitoring system. Water Resour. Res. 43:W05402, 2007.

[324] Rimon, Y., Nativ. R., and Dahan, O., Physical and Chemical Evidence for Pore-Scale Dual-Domain Flow in the Vadose Zone. Vadose Zone J. Vol. 10, 2011.

[325] Dahan, O., Y. Shani, Y. Enzel, Y. Yechieli, and A. Yakirevich. Direct measurements of floodwater infiltration into shallow alluvial aquifers. J. Hydrology 344:157–170, 2007.

[326] Avshalom, B., Lazarovitch, N., Kurtzman, D. and Dahan, O. Influence of intensive agriculture in greenhouse on groundwater quality. Abstract. 2011. Manuscript under preparation.

[327] Baram, S. and Dahan, O. Pollutant transport through clayey vadose zone underlying dairy farm waste lagoons. Abstract. 2011. Manuscript under preparation.

[328] Dahan, O., Mandelbaum, R., and Ronen, Z. Optimization of remediation conditions using vadose zone monitoring technology . Abstract. 2011. Manuscript under preparation.

[329] Dahan, O., Nativ, R., Adar, E. M., Berkowitz, B. and WeisbrodB, N. On Fracture Structure and Prefer-ential Flow in Unsaturated Chalk. Ground Water, 38: 444–451. doi: 10.1111/j.1745-6584.2000.tb00231.x, 2000.

[330] Dahan, O., Nativ, R., Adar, E. and Berkowitz, B. A Measurement System to Determine Water Flux and Solute Transport Through Fractures in the Unsaturated Zone. Ground Water, 36: 444–449, 1998.

[331] Dahan, O., R. Nativ, E. M. Adar, B. Berkowitz, and Z. Ronen Field observation of flow in a fracture intersecting unsaturated chalk, Water Resour. Res., 35(11), 3315–3326, doi:10.1029/1999WR900198. 1999.

[332] Atlas. R.M. Microbial degradation of petroleum hydrocarbons : an environmental perspective. Micro-biological reviews. 45(1):180-209, 1981.

[333] Kristensen, A. H. Controlling factors for natural attenuation of petroleum vapors in a layered subsurface. Ph.D. defence, June 23, 2010, Aalborg University.

[334] Kristensen, A.H., Loll, P., Henriksen, K., Mortensen, L., og Møldrup, P. 2011. Nedbrydning af oliestoffer i den umættede zone. Vand & Jord, nr. 1, 12-16, 2011.

[335] Rambøll. Upublicerede data. 2011.

[336] DMR. Upublicerede data. 2011.

[337] Kristensen, A.H., Poulsen, T.G., Mortensen, L., Moldrup, P. Variability of soil potential for biodegra-dation of petroleum hydrocarbons in a heterogeneous subsurface. Journal of Hazardous Materials 179: 573-580. 2010.

[338] Ernstsen, V. Fosforindhold og fosforbindingskapacitet i sandede jorde og sedimenter. Danmarks og Grønlands Geologiske Undersøgelse Rapport 2008/43, 37 pp. 2008.

[339] Ernsten, V., Jacobsen, P.R., og von Platen, F. Et første landsdækkende redoxkort. Vand & Jord, nr. 4, 159-160. 2010.

[340] Downey, D.C., Hinchee, R.E., og Miller, R.N. Cost-Effective Remediation and Closure of Petroleum-Contaminated Sites. Battelle Press, Columbus, Ohio. ISBN 1-57477-071-3. 1999.

[341] Dibble, J.T. and Bartha, R., 1979. Leaching aspects of oil sludge biodegradation in soil. Soil Science 127, 365-370.

[342] Kristensen, A.H., Loll, P., Møller, M.G., Mortensen, L., Henriksen, K., og Møldrup, P. Forudsætninger for naturlig nedbrydning af oliestoffer i den umættede zone under typiske danske forhold. ATV vintermøde, 185-193. 2011.

[343] Loll, P., Kristensen, A.H., Larsen, P., Henriksen, K., og Larsen, C. In situ test til dokumentation af nedbrydning i umættet zone. ATV vintermøde, 285-295. 2011.

[344] Loll, P., Kristensen, A.H., Larsen, P., Nielsen, J.L., og Henriksen, K. Nye metoder til dokumentation af naturlig nedbrydning af oliestoffer i den umættede zone. Udkast til miljøprojekt – under udarbejdelse. 2011.

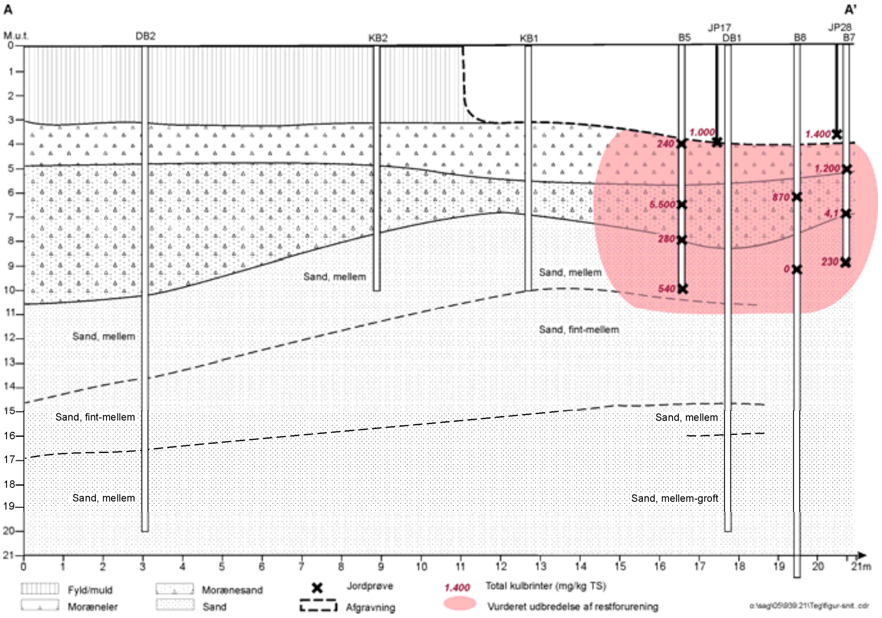
Bilag 1: Eksempler fra umættet zone

B.1: Ældre oliespil på lokalitet på Djursland

På en lokalitet på Djursland er der konstateret forurening med gasolie og benzin, herunder indhold af tilsætningsstoffet MTBE. Forureningen er relateret til det tidligere detailsalg af motorbrændstoffer, der fandt sted på lokaliteten i perioden 1964 til 2004. Data præsenteret i det følgende stammer fra /312/.

I forbindelse med forureningsundersøgelsen er der konstateret forurening med benzin og gasolie i et interval på 110-5.500 mg total kulbrinter/kg TS. Forureningen er konstateret i intervallet 2 til ~10 m u.t. Ved opgravning af tanke og forurenet jord på lokaliteten er de øverste ~4 m jord bortgravet.

Den vurderede udbredelse af restforureningen i et nord-sydgående profil er illustreret i figur 1.



Figur 1 Vurderet udbredelse af efterladt restforurening.

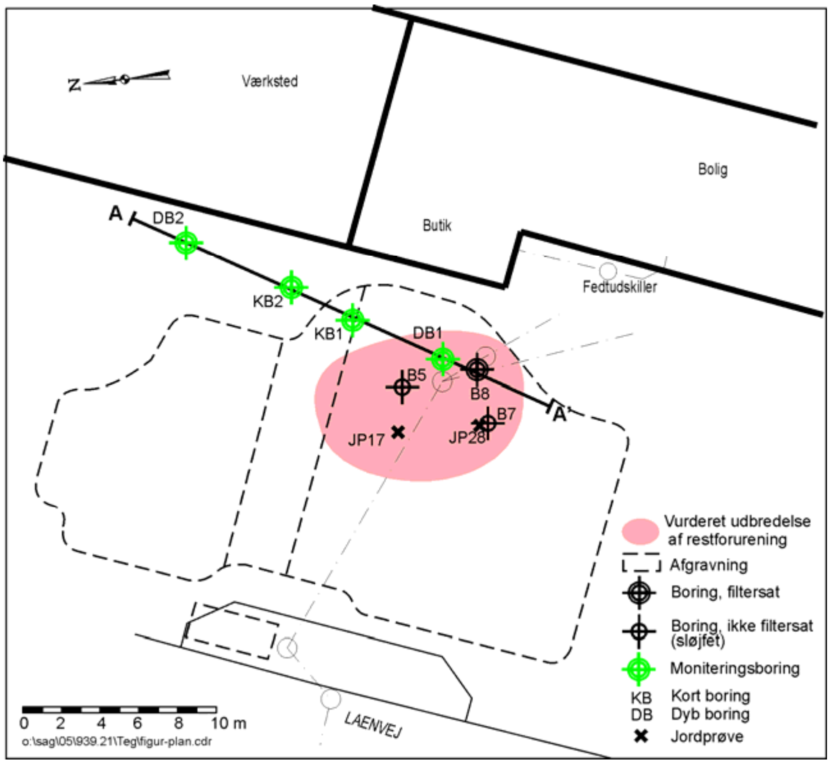
Forureningsniveauet vurderes at være kraftigst 5-6 m u.t. I B8 er der ikke påvist forurening i 9 m u.t. I boringerne B5 og B7 er forureningen ikke afgrænset nedadtil, men niveauet er under ~500 mg THC/kg TS i 9-10 m u.t. og forventes at aftage signifikant over få meter i sandlaget herunder.

Ud fra det påviste indhold af kulbrinter i jorden og en estimeret forureningsudbredelse er det skønnet, at der er efterladt omtrent 250-350 kg oliekomponenter i den umættede zone fra 4-10 m u.t.

Formålet med undersøgelsen er at dokumentere den naturlige nedbrydning af benzinforureningen i den umættede zone samt på baggrund af målte data at udføre en overslagsmæssig beregning af nedbrydningsrater.

Der er udført monitering af forureningskomponenter, ilt og CO_2 gennem flere moniteringsrunder over en moniteringsperiode på 1½ år for at belyse, hvorvidt koncentrationsniveauerne er stabile og fortsat kan forventes at ligge på de dokumenterede niveauer. Dokumentationen af, at ilt ikke vil være en begrænsende faktor, er især relevant for dokumentationen af den fortsatte naturlige nedbrydning i den umættede zone.

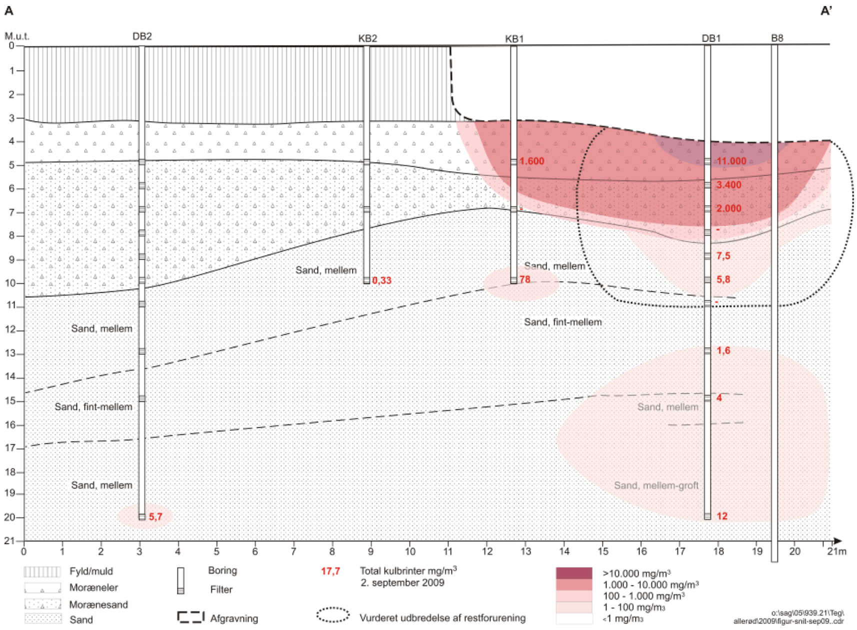
Der er etableret 4 moniteringsboringer på lokaliteten DB1 og DB2 samt KB1 og KB2. Boringerne er placeret således at DB1 er placeret ved den kraftigste jordforurening, mens forureningen i poreluften forventes at aftage fra DB1 til DB2. Ved DB2 forventes der ikke at være forurenet.



Figur 2 Placering af moniteringsboringer.

Poreluftmonitering

Det ses af figur 3, at indholdet af total kulbrinter i poreluften er afgrænset til området omkring DB1 og KB1. Desuden ses, at koncentrationen er højst umiddelbart under afgravningen ved DB1, hvorfra koncentrationen aftager over dybden samt mod KB1.

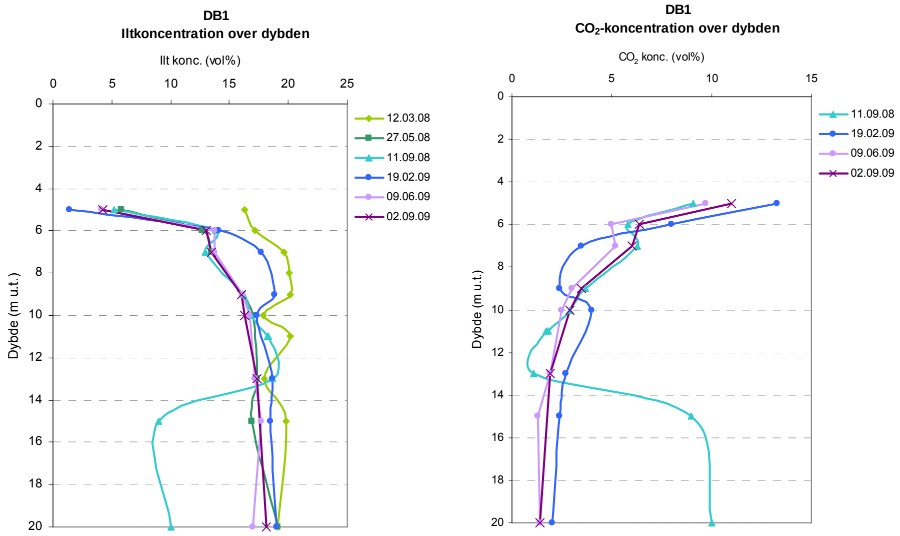


Figur 3 Koncentration af totalkulbrinter d. 2. september 2009 i tværsnittet fra DB2 til DB1

I figur 4 er resultaterne for O_2 og CO_2 over moniteringsperioden optegnet over dybden for moniteringsboring DB1.

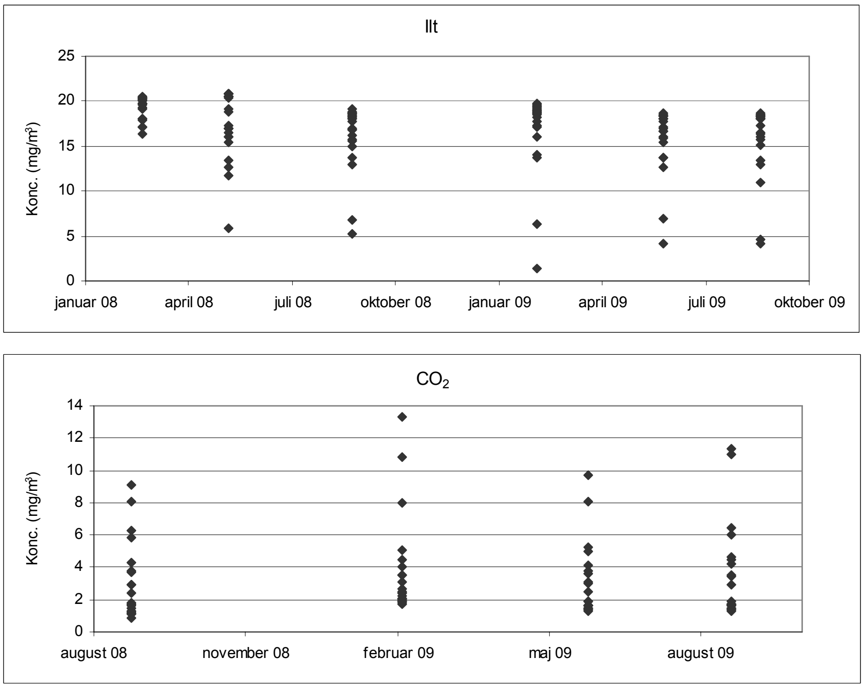
Af figur 4 ses, at de laveste iltkoncentrationer forekommer umiddelbart under afgravningen. Dette stemmer overens med, at jordforureningen primært findes i dette område, og at en del af ilten hermed bliver forbrugt til nedbrydning. Resultaterne viser desuden, at iltkoncentrationen generelt er stigende over dybden, dog falder de to nederste målinger fra d. 11. september 2008 uden for denne tendens. Yderligere ses en tendens til, at iltindholdet er faldet svagt gennem moniteringsperioden.

For CO_2 forekommer de højeste koncentrationer under afgravningen og falder med dybden, hvilket ligeledes stemmer overens med, at der ved nedbrydning af forureningen vil ske en produktion af CO_2 i det forurenede område.



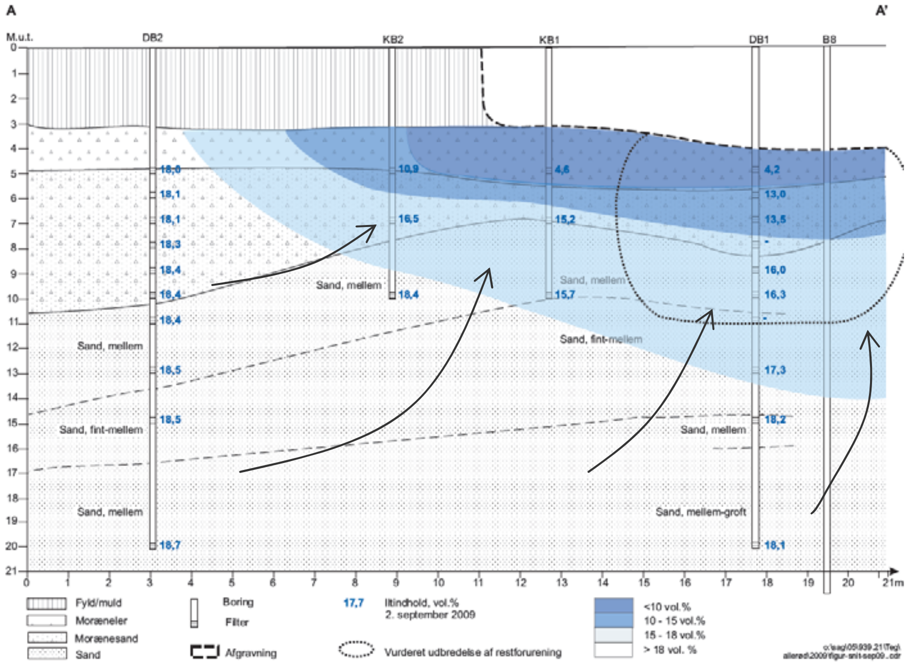
Figur 4 Ilt og CO_2 over dybden for moniteringsboring DB1.

Af ilt- og CO_2-profilerne i figur 4 fremgår det, at ilt- og CO_2-indholdet i jorden har ligget på et stabilt niveau gennem de seneste 3 moniteringsrunder. Dette fremgår desuden af figur 5, hvor samtlige målinger for ilt og CO_2 er plottet ind.



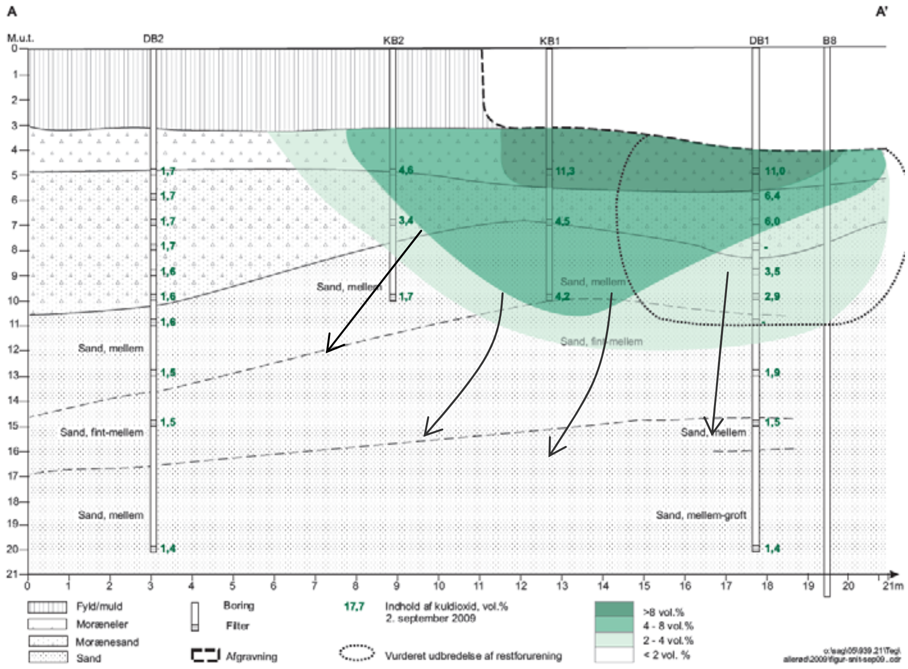
Figur 5 Samtlige målinger (2008-2009) af ilt- og CO_2-indhold i poreluften.

Konturplot for ilt- og CO_2-koncentrationerne i tværsnittet fra DB2 til DB1 ses i figur 6 og 7. Optegningen af iltindholdet i poreluften viser, at indholdet er lavest umiddelbart under afgravningen (< 10 vol. % O_2), hvor forureningen er kraftigst (5-6 m u.t.), og stigende mod KB2 og DB2, samt med dybden.



Figur 6 Iltkoncentration i tværsnittet fra DB2 til DB1. Pilene illustrerer ilttransporten i den umættede zone.

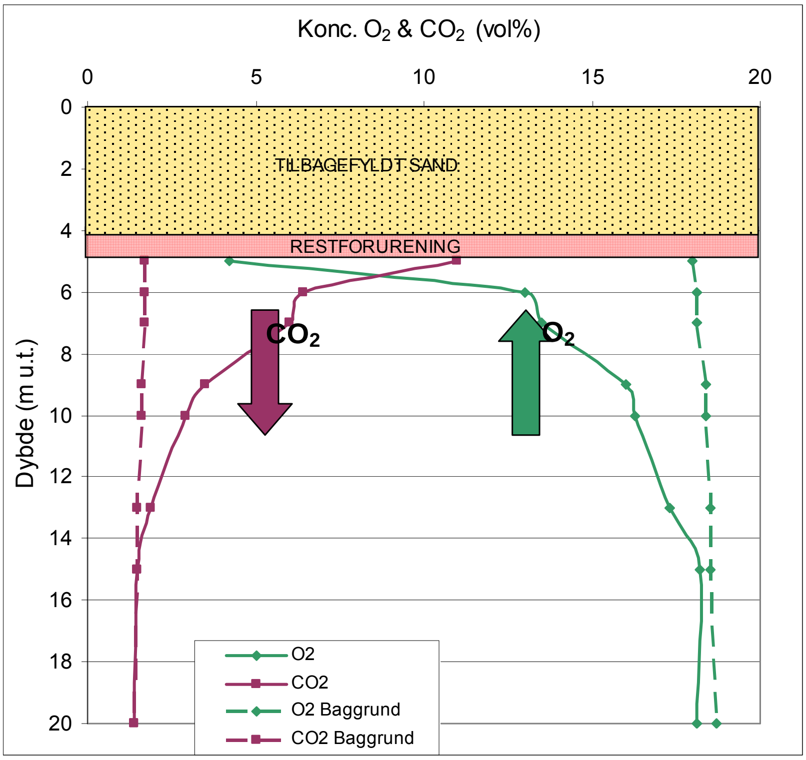
Der er ikke på noget tidspunkt indikationer på fuldstændigt iltfrie forhold i noget målepunkt. Desuden ses, at iltindholdet under restforureningen er højt (>10-14 vol. %), hvilket indikerer, at iltindholdet ikke vil være en begrænsende faktor for den igangværende nedbrydning af forureningen i den umættede zone.



Figur 7 CO_2-koncentration i tværsnittet fra DB2 til DB1. Pilene illustrerer CO_2-transporten i den umættede zone.

Koncentrationen af CO_2 er modsat iltkoncentrationen størst, hvor forureningen er kraftigst, og aftager herfra over dybden mod DB2. Dette stemmer overens med, at der produceres CO_2 ved nedbrydningen af forureningen.

Poreluftmoniteringen har vist et naturligt baggrundsniveau af ilt i den umættede zone på ca. 18-19 vol. %. Indholdet af ilt i poreluften vurderes derfor ikke at være en begrænsende faktor for nedbrydningen i den umættede zone.



Figur 8 Ilt- og CO_2-profil over dybden for DB1.

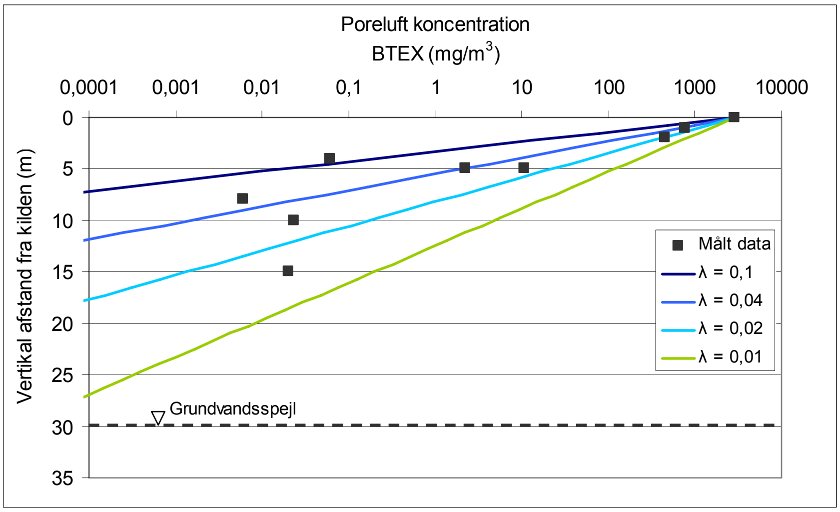
Estimering af nedbrydningsrater ved 1D-modellering

Ved brug af JAGG modellen 2.0 kan 1. ordens nedbrydningsrater i den umættede zone estimeres på baggrund af målte data. Som udgangspunkt benyttes data fra DB1, da forureningen her er kraftigst. Er der målt højere koncentrationer i en anden boring i samme dybde, benyttes også denne koncentration.

1D-modellen tilpasses de målte data plottet på en logaritmisk skala ved at variere nedbrydningsraten λ.

Nedbrydningsraterne estimeres på baggrund af de målte koncentrationsændringer over dybden (dybden regnes fra kilden). Kilden vurderes placeret ca. 5 m u.t. og det forudsættes, at der ikke herunder findes lokale kildeområder.

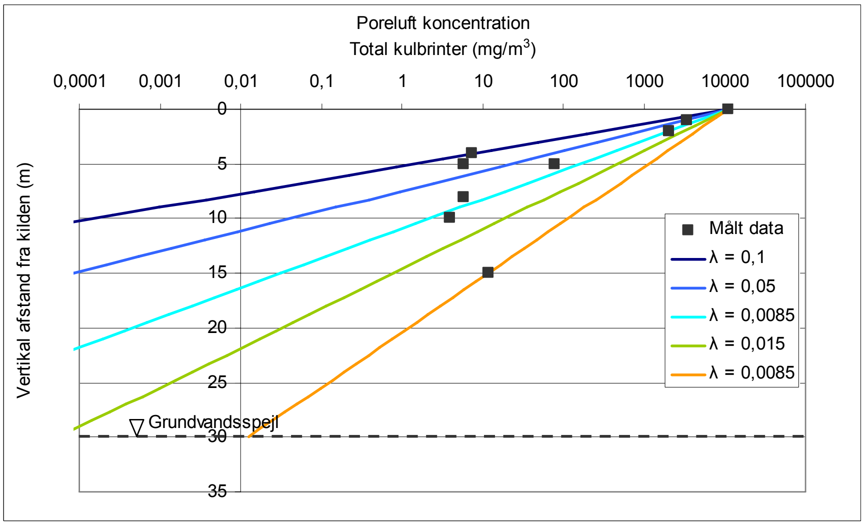
I figur 9 er de målte poreluftkoncentrationer for BTEX'er plottet i forhold til den vertikale afstand til kilden, der vurderes placeret ca. 5 m u.t. Den teoretiske koncentrationsudvikling over dybden ved 4 forskellige nedbrydningsrater er desuden illustreret i figuren.



Figur 9 Estimerede nedbrydningsrater for BTEX. Raterne er angivet i [dag^{-1}].

Figuren viser, at en nedbrydningsrate omkring 0,02 dag^{-1} for BTEX'er stemmer nogenlunde overens med koncentrationsprofilet i den umættede zone på lokaliteten.

For total kulbrinter følger de målte data tilnærmelsesvist 1-D modellen, svarende til en nedbrydningsrate på 0,05 dag^{-1}, hvis der ses bort fra målepunktet 15 m under kilden, der afviger i forhold til de resterende data.



Figur 10 Estimerede nedbrydningsrater for kulbrinter. Raterne er angivet i [dag^{-1}].

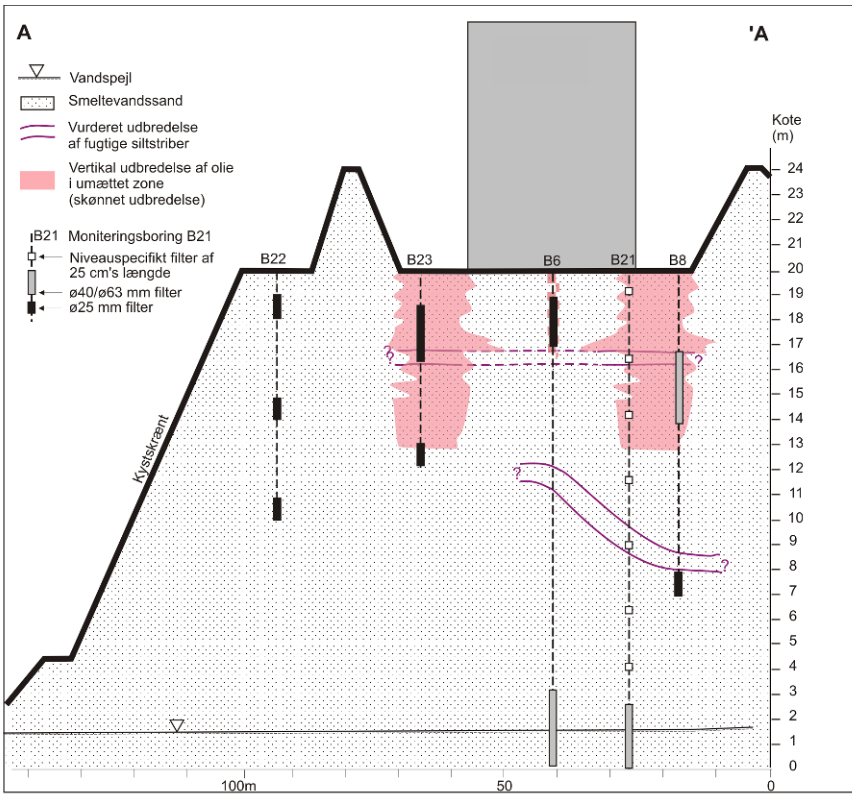
Diskussion af usikkerheder

I det konkrete eksempel er der en række usikkerheder i både den konceptuelle forståelse samt på de fysisk indsamlede data. Generelt er den konceptuelle forståelse baseret på en relativt detaljeret undersøgelse af de geologiske, hydrogeologiske og geokemiske forhold. Grundet jordens naturlige heterogenitet mht. hydrauliske egenskaber mv. vil det ofte være påkrævet med en relativt omfattende undersøgelse førend en robust generel konceptuel 3D-model kan opstilles. Som det ses af de optegnede figurer, sker transporten i poreluftfasen (BTEX, ilt og kuldioxid) således i både horisontal og vertikal retning – og der kræves derfor en del målepunkter med en passende rumlig fordeling. Moniteringen af poreluftkoncentrationerne viser, at de største gradienter i både O_2/CO_2 og VOC/THC optræder i grænsen mellem jord med egentlig NAPL i jordmatricen og den omkringliggende jord hvor forureningskomponenterne primært er opløst i porevandet og poreluften. Da det vurderes, at det netop er i denne zone, at den væsentligste nedbrydning sker, er det afgørende, at have en speciel høj vertikal opløsning af koncentrationsfordelingen i denne zone. Den tidsmæssige variation i poreluftkoncentrationerne er i det aktuelle tilfælde relativ lille og resultaterne er generelt reproducerbare ved de halvårlige målinger udført over ca. 2 år. Dette bekræfter således, at der er tale om et ældre spild, hvor der nu er indtrådt tilnærmelsesvist stationære forhold og at der ikke er tegn på at der over tid vil opstå anaerobe forhold. De anvendte egenskaber for nedsivning og jordegenskaber er valgt som standardparametrene i JAGG 2.0 modellen (infiltration 200 mm, totalporøsitet 0,45 (-), vandfyldt porøsitet 0,15 (-) og foc=0,2 %). I det konkrete eksempel afviger de målte jordegenskaber ikke væsentligt fra de anvendte standardparametre, og resultaterne ved brug af målte parametre medfører ingen signifikant forskel i resultatet. På baggrund af det samlede datasæt, vurderes det rimeligt at konservativt tilnærme situationen med den viste 1D model, og på baggrund heraf bestemme den tilsyneladende 1. ordens aerobe nedbrydningsrate for summen af BTEX-forbindelserne samt totalkulbrinter.

B.2: Nyere oliespild på lokalitet i Nordsjælland

På en lokalitet i Nordsjælland skete der i sommeren 2003 et stort oliespild. Det blev vurderet at 10-35 m^3 olie var trængt ned i de underliggende jordlag. Udførte undersøgelser på lokaliteten påviste, at olien helt overvejende fandtes i de øverste 0-3,5 m u.t. – dog lokalt ned til 8 m u.t. Derudover blev det vurderet, at de nødvendige forudsætninger for en stabil og naturlig nedbrydning af oliekomponenterne i den umættede zone var til stede. For at følge den løbende udvikling af forureningens spredning og nedbrydning, er der moniteret på lokaliteten siden 2004.

Formålet med moniteringen har været at dokumentere forureningsspredningen og den naturlige nedbrydning af olieforureningen i den umættede zone.

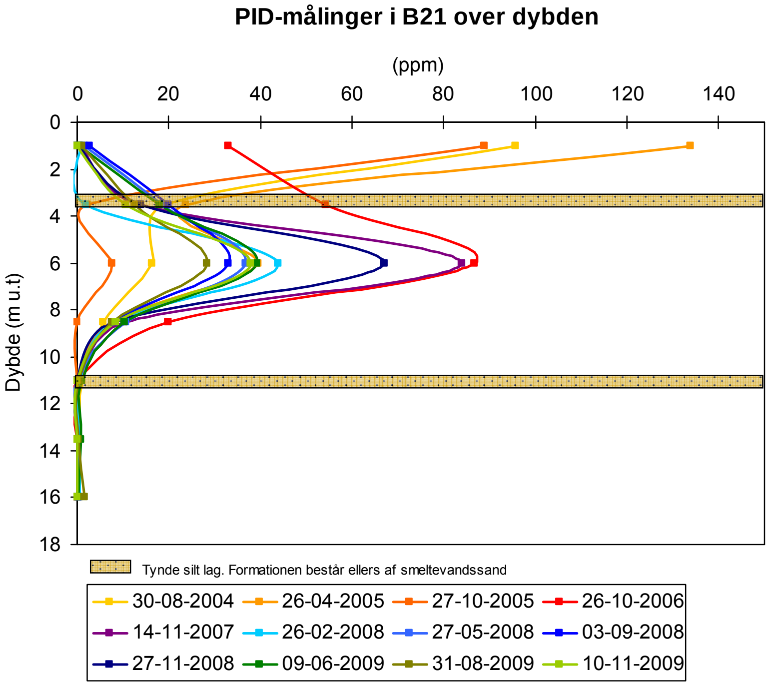


Figur 11 Vertikal udbredelse af olieforurenet jord.

Poreluftmonitering

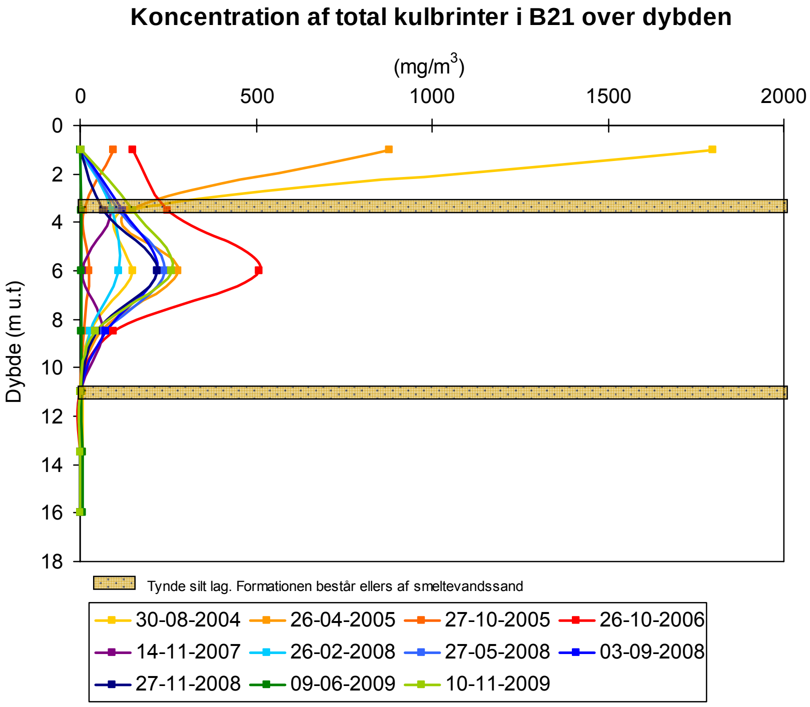
Forureningens fordeling og udvikling over tid kan vurderes ud fra de gennemførte målinger i de 7 filtre i boring B21. Den oprindelige forureningsfordeling i boring B21 vurderes at være typisk for området og kan derfor bruges som en rettesnor for, hvad der sandsynligvis sker under resten af området.

Generelt viser PID-målingerne foretaget fra 2004 til 2009, at koncentrationsniveauet er faldet. Især er der sket markante fald i den øverste meter. Ca. 6 m u.t. er PID-niveauet steget frem til 2006 (~80 ppm) hvorefter niveauet er aftaget til ~30 – 40 ppm. Herunder aftager koncentrationen skarpt ned til 10 m u.t. jf. figur 12.



Figur 12 Vertikal variation i B21 for PID-niveauet ved de enkelte moniteringsrunder.

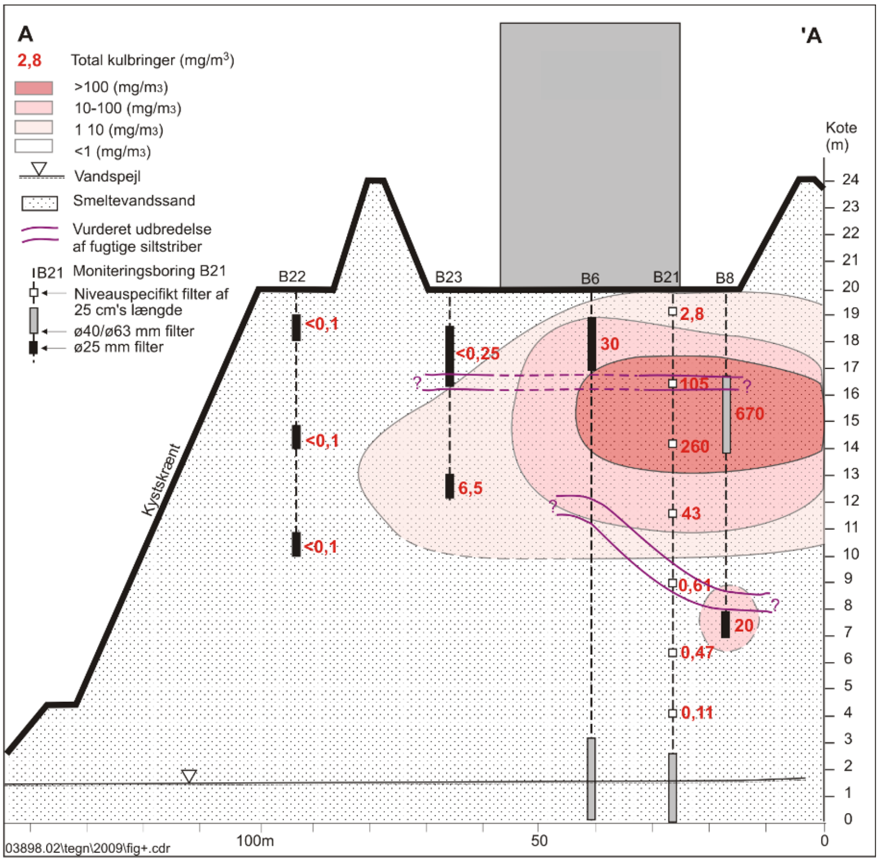
På figur 13 er målingerne af totalkulbrinter i boring B21 optegnet som funktion af dybden. Som for PID-målingerne ses et fald i den øverste meter siden 2004. Koncentrationen af totalkulbrinter omkring 6 m u.t. er steget tilsvarende i perioden 2004-2006 til et maksimum på 500 mg/m^3, hvorefter der er sket et fald til ca. halvdelen. Faldet i særligt de øverste meter viser, at der her er sket nedbrydning af oliestoffer, da tilgængeligheden af ilt fra den atmosfæriske luft er stort set ubegrænset.



Figur 13 Vertikal variation i B21 for indholdet af total kulbrinter ved de enkelte moniteringsrunder.

Det maksimale koncentrationsniveau på ca. 250 mg/m^3 findes i dag ca. 6 m u.t. Fra 6 til 10 m u.t. ses en skarp gradient i koncentrationen og fra 10 m u.t. til grundvandet, der findes ca. 18 m u.t., er der stort set ikke påvist indhold af totalkulbrinter i poreluften. Desuden fremgår det af figur 13, at koncentrationen af kulbrinter i poreluften har været relativ stabil siden 2007.

Til illustration af den rummelige udbredelse af poreluftforureningen, er der i figur 14 optegnet et konturplot for indholdet af total kulbrinter i poreluften.

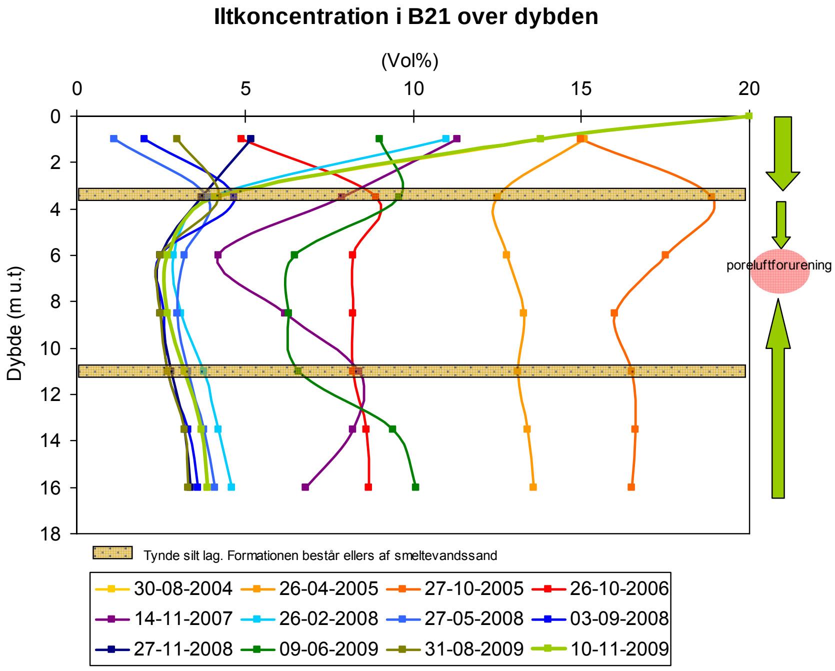


Figur 14 Koncentration af totalkulbrinter i tværsnit.

På figur 15 er målingerne af iltindholdet i boring B21 optegnet som funktion af dybden. De optegnede iltprofiler for de forskellige målerunder indikerer i hvilken dybde ilt forbruges og transporteres ved diffusion.

Iltkoncentrationen i poreluften er faldet markant siden starten af moniteringen i 2004, hvor der er målt iltindhold på over 15 vol. %. Det aftagende indhold af ilt, skyldes den igangværende aerobe nedbrydning.

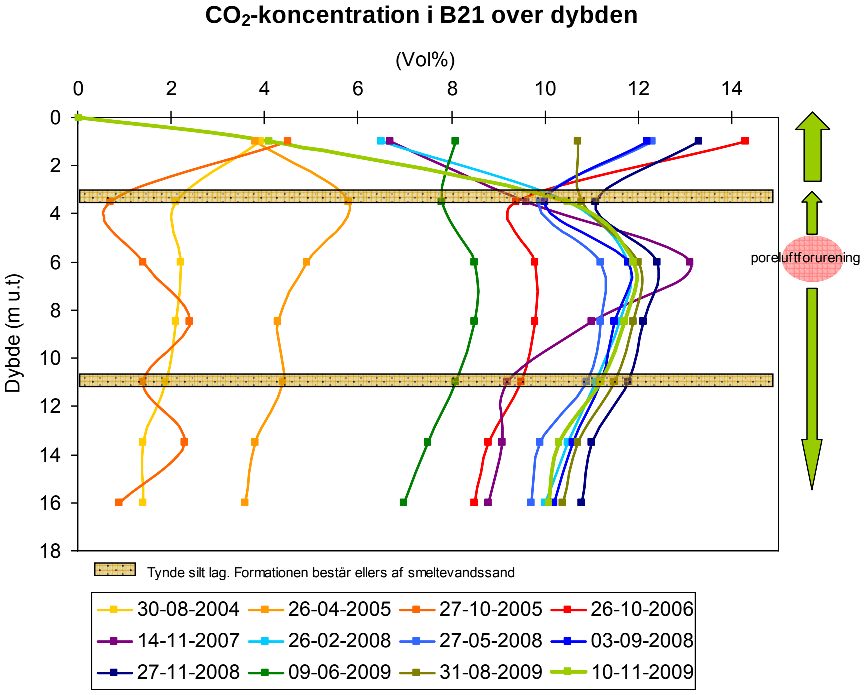
For de seneste 8 moniteringsrunder ses, at iltindholdet i poreluften falder omkring 6 m u.t., hvor poreluftforureningen er kraftigst. Den vertikale koncentrationsforskel indikerer, at der sker en kontinuert transport af ilt fra terræn ned i den umættede zone, hvor ilten forbruges ved nedbrydning.



Figur 15 Vertikal variation i B21 for iltindholdet ved de enkelte moniteringsrunder.

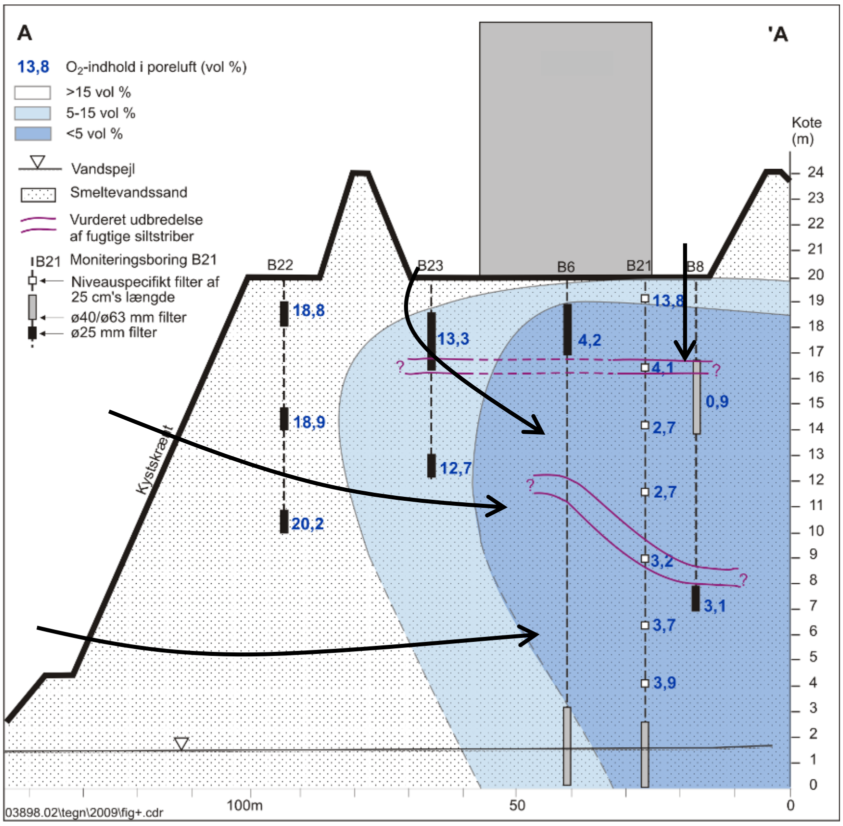
I figur 16 er målingerne af kuldioxidindholdet i boring B21 optegnet som funktion af dybden. De optegnede kuldioxidprofiler for de forskellige målerunder indikerer i hvilke dybder kuldioxid dannes og transporteres ved diffusion. Dette er desuden som ved iltprofilerne illustreret for den seneste moniteringsrunde med grønne pile, der viser den op- og nedadrettede transport af CO_2.

Koncentrationen af CO_2 i poreluften er steget markant siden starten af moniteringen i 2004, hvor det målte indhold var forholdsvist lavt – mindre end 5 vol. %, mens der siden 2008 er målt CO_2-koncentrationer på ca. 12 vol. %. Det stigende indhold af CO_2, skyldes den igangværende aerobe nedbrydning.

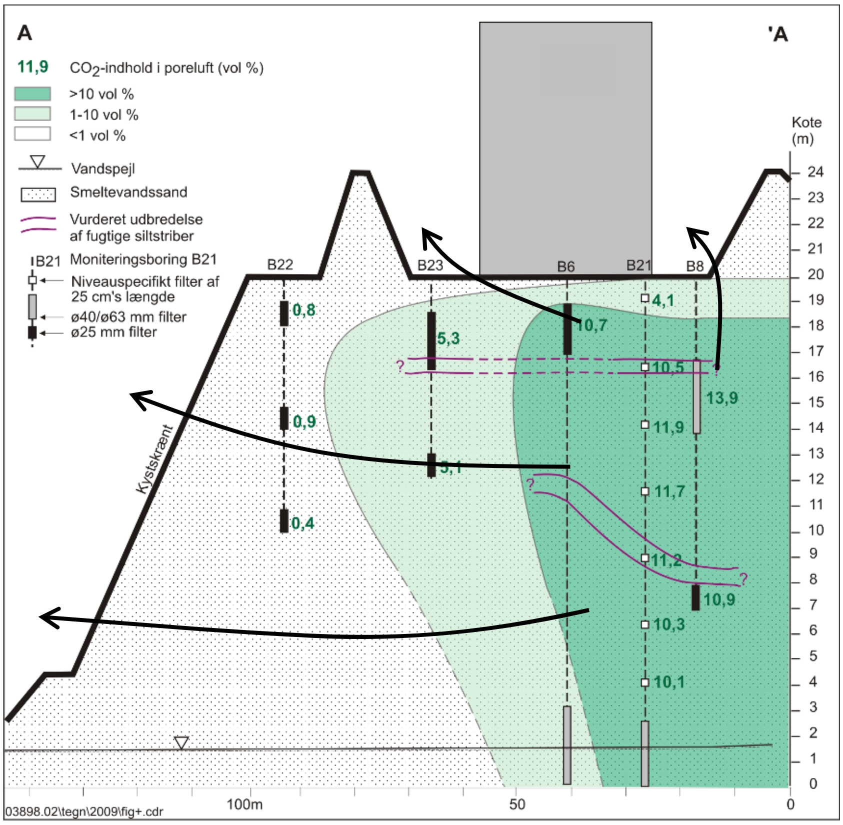


Figur 16 Vertikal variation i B21 for CO_2-indholdet ved de enkelte moniteringsrunder.

Sammenholdes dybdeprofilerne for kulbrinter med CO_2- og iltprofilerne ses overensstemmelse mellem målingerne. Iltkoncentrationen falder mest, hvor koncentrationen af total kulbrinter er højest, og samtidig ses en stigning i indholdet af CO_2. Denne sammenhæng er en tydelig indikation på, at der foregår aerob nedbrydning af total kulbrinter i den umættede zone.



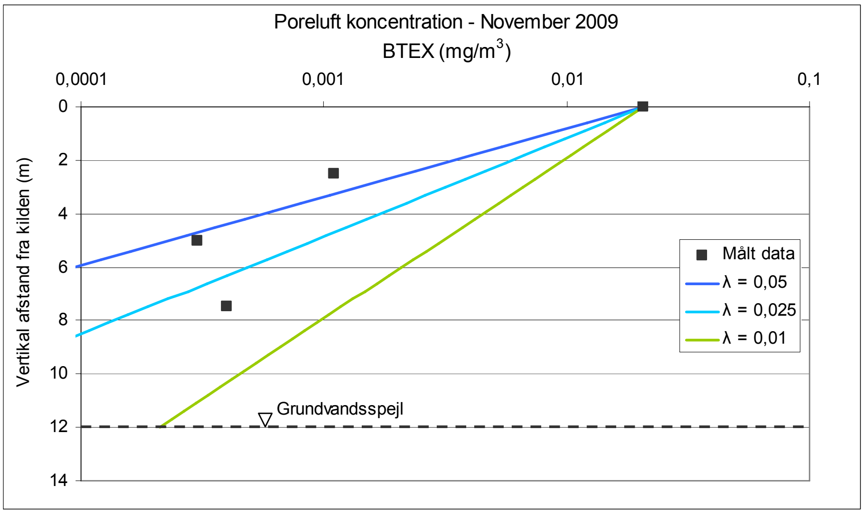
Figur 17 Iltkoncentration.



Figur 18 CO$_2$-koncentration.

Estimering af nedbrydningsrater ved 1D-modellering

Ved brug af JAGG modellen 2.0 kan 1.ordens nedbrydningsrater for summen af BTEX i den umættede zone estimeres på baggrund af målte data. Som udgangspunkt benyttes data fra B21, da forureningsprofilet over dybden her er bedst dokumenteret. Desuden vurderes forholdene ved B21 at være repræsentative for hele det forurenede område.



Figur 19 Estimerede nedbrydningsrater for BTEX. Raterne er angivet i [dag^{-1}].

Figuren viser, at en nedbrydningsrate mellem 0,01 og 0,05 dag^{-1} stemmer overens med koncentrationsprofilet i den umættede zone.

Diskussion af usikkerheder

I det konkrete eksempel B.2 er der, som i eksempel B.1, en række usikkerheder i både den konceptuelle forståelse samt på de fysisk indsamlede data. Da kilden til jordforureningen her har været en nedsivning igennem tankgården der løber hele vejen rundt om tanken, er geometrien af selve kildeområdet væsentlig anderledes end ved en traditionel lækage på en tank eller et rør i jorden. Også her er den konceptuelle forståelse baseret på en relativt detaljeret undersøgelse af de geologiske, hydrogeologiske og geokemiske forhold samt en række boringer placeret væk fra tankområdet for at kunne vurdere de naturlige uforstyrrede forhold mht. iltindhold samt N og P.

Som det ses af de optegnede figurer, sker transporten i poreluftfasen også i dette eksempel (THC, ilt og kuldioxid) i både horisontal og vertikal retning – og der kræves derfor en del målepunkter med en passende rumlig fordeling. Moniteringen af poreluftkoncentrationerne over en 5-årig periode viser, at de flygtige stoffer målt med en PID-måler i løbet af 1-2 år næsten fuldstændigt forsvinder fra terræn og ned til 2 m u.t. Det maksimale koncentrationsniveau ses i ca. 6 m u.t. svarende til den dybde hvortil der er påvist olie i jordprøver, og her ses også et aftagende niveau over tid, men stabile forhold opnås først efter 4-5 år. At der først er stabile forhold efter 4-5 år ses mest tydeligt på ilt- og kuldioxid profilerne for B21, og dette er et forhold der vanskeliggør denne type målinger på nyere spild. Efter at stabile forhold er opnået, vurderes det rimeligt at konservativt tilnærme situationen med den viste 1D model hvor ilt ved diffusion fra de dybere lag transporteres vertikalt op til dybdeintervallet omkring 6 m u.t. hvor det forbruges og kuldioxid dannes og transporteres i modsat retning ved diffusion. Da der ikke er tegn på, at der skulle opstå anaerobe forhold over tid, vurderes forudsætningerne for at antage, at der sker en stabil aerobe nedbrydning at være til stede, og der kan derfor bestemmes en tilsyneladende 1. ordens aerob nedbrydningsrate for totalkulbrinter. I det konkrete eksempel afviger de målte jordegenskaber heller ikke væsentligt fra de anvendte standardparametre, og resultaterne ved brug af målte parametre medfører ingen signifikant forskel i resultatet.

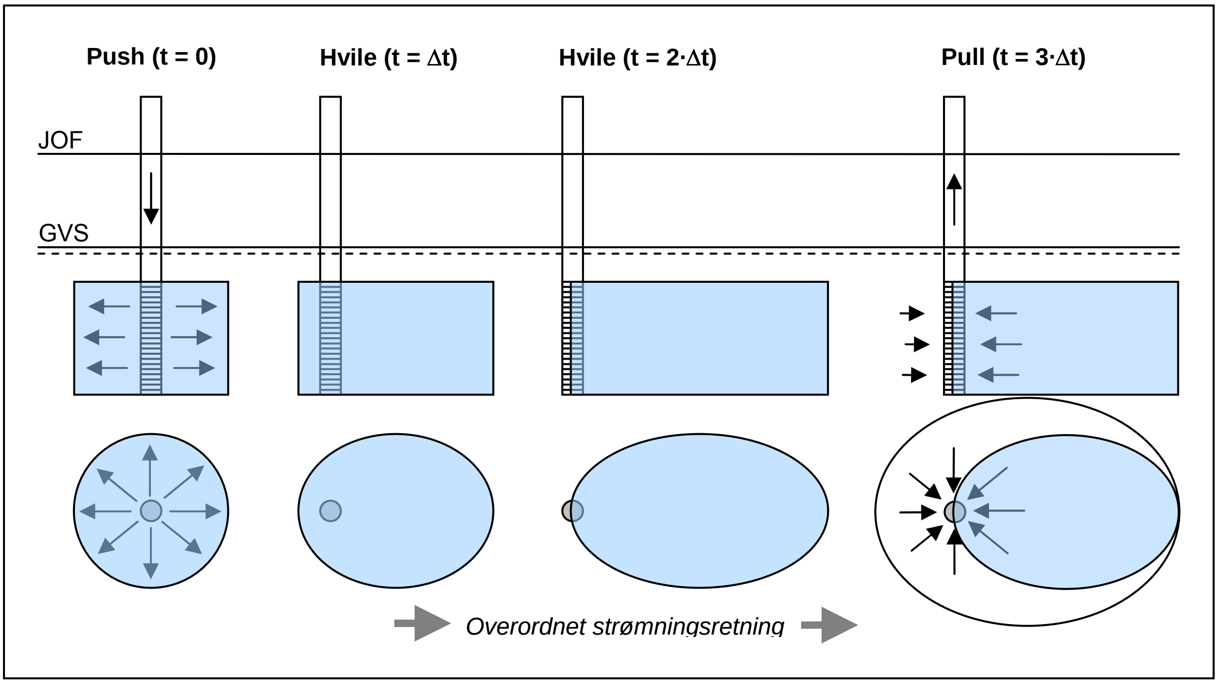
Bilag 2: Push-pull i mættet zone

Hovedelementer

Som nævnt i afsnit 3.2.4 er gas fase push-pull testen udviklet på baggrund af push-pull testen for den mættede zone, som præsenteres oversigtsmæssigt i dette afsnit. De grundlæggende principper for Push-Pull strategien er præsenteret i en række internationale artikler /314, 293, 294, 301/, samt i en manual for dokumentation af cometabolisk aerob nedbrydning af chlorerede alifater /316/ fra Environmental Security Technology Certification Program (ESTCP) i USA.

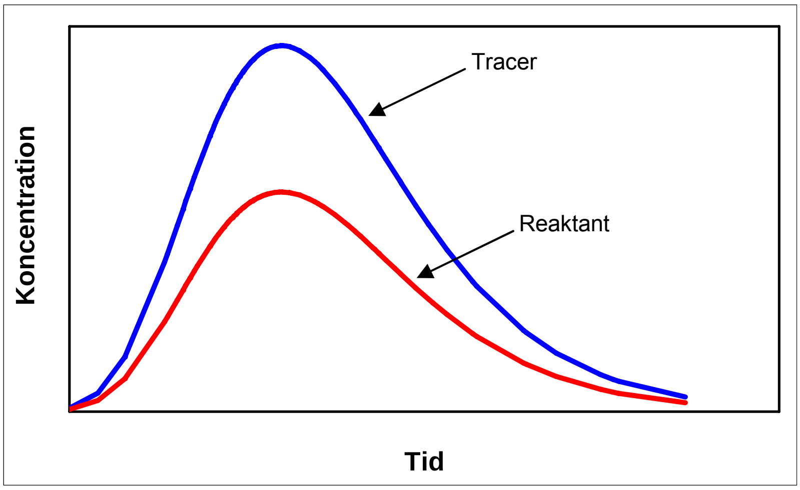
- push og pull af tracer og reaktanter

Metoden består i en nænsom injektion (Push) af en kendt mængde reaktanter og tracer i en filtersat boring. Injektionen efterfølges af et ”hviletidsrum” uden pumpeaktivitet, hvor de undersøgte nedbrydningsprocesser kan forløbe. Herefter oppumpes der vand fra injektionsboringen (Pull), mens der løbende måles på tracer, reaktanter og eventuelle nedbrydningsprodukter i det oppumpede vand. Et skematisk forløb for Push-Pull testen fremgår af figur 20.



Figur 20 Skematisk forløb af en push-pull test i mættet zone.

Figur 21 viser et hypotetisk koncentrationsforløb af hhv. tracer og reaktant under pull-fasen af en push-pull test.



Figur 21 Hypotetisk koncentrationsforløb under pull-fasen af en push-pull test.

- matematisk analyse af data

Ud fra en matematisk analyse af koncentrationsforløbet for reaktanterne (jf. figur 21) og traceren kan in-situ nedbrydningsraterne for de anvendte reaktanter estimeres. På baggrund af en total massebalance for tracer og reaktanter opnås et estimat på 0.ordens nedbrydningsraten, mens der kan estimeres en 1.ordens nedbrydningsrate ud fra en analyse af det relative forløb af tracerens og reaktantens gennembrudskurver. Traceren benyttes i begge tilfælde til at korrigere for et eventuelt ”tab” af reaktanterne via fortynding og spredning, således at de opnåede estimater på nedbrydningsraterne udelukkende er et udtryk for massefjernelse.

Metoden kan således benyttes til at opnå estimater på nedbrydningsraten for de undersøgte reaktanter (f.eks. en blanding af BTEX’er), der er repræsentative for sedimentet omkring den benyttede boring, under de grundvandskemiske forhold der rent faktisk råder omkring boringen.

Hovedelementer

Metoden kan benyttes både på eksisterende filtersatte boringer og nyudførte boringer. Hvis der udføres nye boringer i forbindelse med push-pull testen, kan der med fordel udtages sedimentprøver fra den filtersatte strækning af magasinet, som kan benyttes til:

- Fastlæggelse af nedbrydningsforholdene (redox-kemi m.m.) omkring boringen.
- Bestemmelse af indholdet af organisk stof, så der kan opnås et stedspecifikt bud på retardationsfaktoren for de indgående forureningsstoffer.

Udover at kunne benyttes til at opnå en langt bedre risikovurdering, med udstrakt brug af stedspecifikke parametre frem for litteraturværdier, kan begge dele helt naturligt benyttes til, at designe Push-Pull testen på den konkrete lokalitet hensigtsmæssigt.

Teknologistadium

Indtil videre har Push-Pull metoden primært været anvendt til måling af respirationsrater, dvs. med elektronacceptorer som reaktanter (O_2, NO_3^-, osv.), mens det i nærværende sammenhæng naturligvis vil være langt mere interessant, at undersøge nedbrydningsraterne for benzin- og oliekomponenter, herunder eventuelle additiver. En variant af metoden har da også, i et enkelt studie, været anvendt til at estimere in-situ nedbrydningsrater (såvel 0.ordens som 1.ordens rater) for BTEX'er /296/, mens en række referencer præsenterer forskellige modeltilgange til tolkning af push-pull data der nærmer sig praktisk anvendelse ifht. benzin- og oliekomponenter; 1.ordens rater uden adsorption af tracer og reaktant /294/; 0. og 1.ordensrater ved lave baggrundskoncentrationer og uden adsorption /301/; en såkaldt Forced Mass Balance (FMB) metode til bestemmelse af 1.ordens nedbrydningsrater under adsorption (afprøvet for trichlorfluoroethen) /293/; og nedbrydningsrater for reduktiv dechlorering af TCE og trichlorfluoroethen i TCE-forurenet grundvand /315/. Endelig er to forskellige modeller til bestemmelse af 1.ordens nedbrydningsrater undersøgt og sammenlignet i /300/.

Ulemper

Nogle af de barrierer der indtil nu vurderes at have været i forhold til en udstrakt udbredelse af strategien til bestemmelse af in-situ nedbrydningsrater for forureningskomponenter er:

1. Mangel på omkostningseffektive måleteknikker til hyppig måling af forureningskomponenter, mens elektronacceptorer kan måles stort set kontinuert med billige og nøjagtige prober.
2. Lange reaktionstider for typiske forureningskomponenter i forhold til elektronacceptorer, især under anaerobe redoxforhold/i kildeområder. Kravet til forholdsvist lange reaktionstider udgør specielt et problem i forhold til at den kunstigt skabte "fane" under push-fasen vil kunne nå at brede sig længere væk fra injektionsboringen. Derved skal der, alt andet lige, oppumpes en større mængde grundvand under pull-fasen for at indfange mest muligt af den injicerede tracer og reaktant. Dette vil føre til en relativt lang pull-fase, med behov for mange dyre kemiske analyser, hvilket er det egentlige problem ved at se på reaktanter med lange reaktionstider.
3. Metoden fordrer, at der injiceres reaktanter/forureningskomponenter i koncentrationer, der ligger målbart over baggrundsniveauet, hvilket kan være svært at retfærdiggøre overfor de relevante miljømyndigheder og grundejere.

Ovenstående problemer/ulemper mener vi dog vil kunne afhjælpes via følgende:

<u>ad 1)</u> Anvendelse af f.eks. MIMS (Membrane Inlet Mass Spectrometry) til on-line måling af forureningskomponenter, frem for at udtage og afsende traditionelle vandprøver til ekstern kemisk analyse. Ved anvendelse af MIMS åbnes der mulighed for hyppig måling af en lang række forureningskomponenter. Da der ydermere kan analyseres parallelt på flere boringer falder analysernes stykpris væsentligt. Måling vha. MIMS kan endvidere forholdsvist let kombineres med on-line måling af andre ting af interesse: ilt, pH, redoxpotentiale, m.v.

<u>ad 2)</u> Problemet afhjælpes som ovenfor.

<u>ad 3)</u> Såfremt det ikke er muligt, at komme igennem med en modelmæssig dimensionering af push-pull testen, er der mulighed for at

gennemføre en push-pull test, udelukkende med tilsætning af tracer (f.eks. Cl^-), for at kvantificere det massetab som det aktuelle push-pull design vil medføre via spredning. Derved kan det dokumenteres, at massetabet af reaktanter ved det aktuelle push-pull design er ubetydeligt i forhold til de mængder der i forvejen ligger i magasinet.

Fordele

Udover, at der via push-pull metoden vurderes at kunne opnås nogle forholdsvis omkostningseffektive estimater på nedbrydningsraterne for de indgående forureningsparametre, sammenlignet med andre metoder /202/, herunder analyse af stofkoncentration som funktion af transporttid fra kilden og invers modellering af vand- og stoftransport, så giver push-pull metoden, uden væsentlige meromkostninger (frem for kun at udføre testen på en enkelt boring), mulighed for at vurdere nedbrydningsraternes variation indenfor forureningsfanen, f.eks. under forskellige redoxforhold og koncentrationsniveauer. Dette vurderes, at være en væsentlig fordel, da:

1. Information om nedbrydningsraternes rumlige variation, som minimum, vil kunne benyttes i en følsomhedsanalyse i forbindelse med risikovurderingen.
2. Det bliver muligt, at foretage risikovurderingen baseret på, at redoxforhold, koncentrationer og nedbrydningsrater varierer i forureningsfanen.

Ydermere er det en naturlig del af designproceduren for push-pull testen, at der foretages en vurdering af de hydrauliske forhold omkring boringen, f.eks. via udførsel af slug-tests og/eller pumpetest.

Hvis lokalitetsspecifikke informationer omkring rumlige variationer i nedbrydningsrater, hydrauliske forhold og retardationsfaktoren helt naturligt sammenkobles i en integreret metode, vurderes det, at der kan opnås væsentligt mere kvalificerede risikovurderinger i forhold til grundvandsressourcen end det ofte er tilfældet i dag.

Økonomi

Den aktuelle økonomi på en konkret sag vil i meget høj grad afhænge af balancen imellem transporthastigheder og aktuelle nedbrydningsrater idet høje porevandshastigheder og/eller lave nedbrydningsrater, alt andet lige, vil medføre længere pull-faser og større analyseomkostninger. Da metoden – til projektgruppens kendskab – endnu ikke har fundet anvendelse på benzin- eller olieforurenede lokaliteter, eller anvendelse i Danmark i det hele taget, er der heller ikke meget erfaringsmateriale at trække på. Et slag på tasken er dog i størrelsesordenen 100-300.000 kr. ekskl moms.

Denne pris skal dog sammenlignes med andre tilgængelige metoder der kan være forbundet med et betydeligt (iterativt) arbejde til planlægning og udførelse af boringer med de rette filtersætninger, karakterisering af hydrogeologiske parametre, vandprøvetagning, kemiske analyser, opstillinger af modeller og tolkning af data. Konklusionen må blive, at hverken push-pull eller andre metoder til bestemmelse af in-situ nedbrydningsrater i mættet zone forventes at finde anvendelse på små sager, men på sager af betydelig størrelse, og hvor en manglende fastlæggelse af nedbrydningsrater kan have endnu større økonomiske omkostninger.

Bilag 3: Baggrundsniveauer af ilt, kuldioxid og næringssalte

Som beskrevet i afsnit 2.2.4 er tilgængeligheden af ilt (O_2), kvælstof (N) og fosfor (P) afgørende for i hvilket omfang der kan foregå biologisk nedbrydning af oliestoffer i den umættede zone. Derudover er poreluftens indhold af kuldioxid (CO_2) en indikator for den biologiske aktivitet i jorden.

I det følgende foretages en gennemgang af data, der beskriver typiske niveauer af hhv. ilt/kuldioxid og N/P i umættede aflejringer på både ikke-forurenede og kulbrinteforurenede lokaliteter. Data er udvalgt så de primært beskriver den dybe umættede zone (dybere end 1-2 meter under terræn) under danske forhold. De anvendte studier inkluderer både publicerede og upublicerede måledata.

Ved indsamling af data er der rettet henvendelse til DTU, AAU, RAMBØLL og GEUS ligesom der er inddraget data fra NIRAS og DMR.

Poreluftindhold af ilt og kuldioxid

Ilt er den absolut vigtigste forudsætning for naturlig nedbrydning af oliestoffer i umættet jord. Aerobe nedbrydningsprocesser forudsætter generelt omkring 1-2 mg O_2/liter porevand, svarende til omkring 2-5 % O_2 i poreluften /332, 334/.

Ikke-forurenede aflejringer

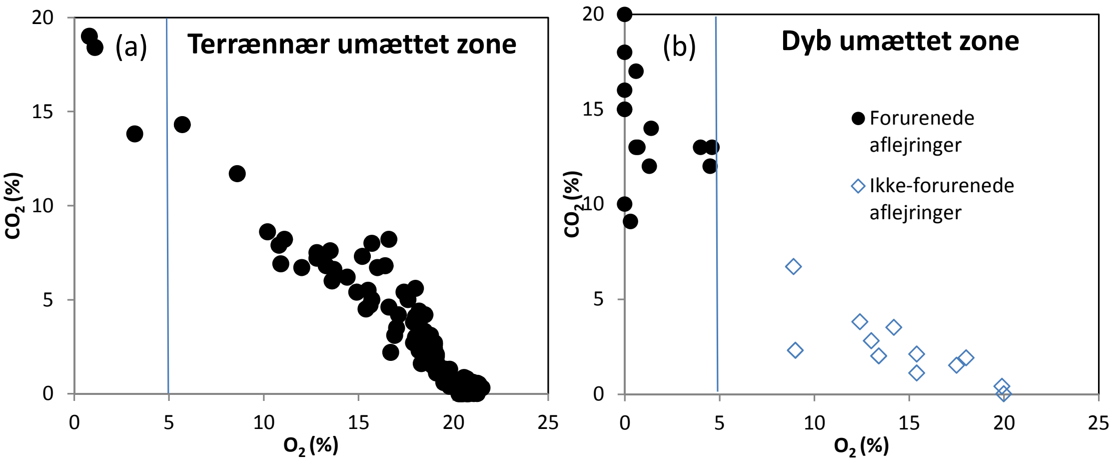
Poreluften i sandede og ikke-forurenede aflejringer har typisk høje naturlige iltindhold. Dette er bl.a. vist i et feltstudie udført af DTU på Flyvestation Værløse, hvor der blev målt atmosfæriske ilt- og kuldioxidkoncentrationer i en ca. 3,3 meter dyb og ikke-forurenet umættet zone bestående af smeltevandssand (20-21 % O_2 og < 0,5 % CO_2) /204/.

Også i dybe og ikke-forurenede sandaflejringer træffes erfaringsmæssigt høje iltindhold, hvilket er illustreret ved to eksempler i bilag 1. Her var jordens iltindhold større end 15 % O_2 ned til ca. 17 meters dybde /306/. I aflejringer af moræneler er der ligeledes påvist aerobe forhold omkring 10 meter under terræn. Dog bevirker den lavere luftpermeabilitet i moræneler et lettere reduceret iltindhold og forøget kuldioxidindhold (9-16 % O_2 og 2-4 % CO_2) /263/.

Olie og benzinforurenede aflejringer

I forurenet jord vil naturlig omdannelse af oliestoffer, under aerob respiration, bevirke en omtrentlig omvendt lineær sammenhæng imellem poreluftens indhold af O_2 og CO_2. Figur 22a viser resultatet af poreluftmålinger foretaget i terrænnære aflejringer på 4 olieforurenede lokaliteter /335, 336/, samt én lokalitet med en kunstigt tilført kulbrinteforurening /204/. Kun en meget lille andel af målingerne (3 ud af 152) viser iltkoncentrationer lavere end 5 % O_2, hvilket er et resultat af den korte afstand til atmosfæren. I olieforurenet jord umiddelbart under bygninger træffes erfaringsmæssigt ligeledes aerobe forhold såfremt jorden er sandet eller gruset /335/.

I dybtliggende olieforurenet jord er muligheden for atmosfærisk geniltning dårligere end den er nær terrænoverfladen. Figur 22b viser poreluftmålinger foretaget mellem 5 og 15 meter under terræn i benzinforurenede aflejringer. I dette datasæt er omkring halvdelen af de målte iltindhold (13 ud af 25) lavere end 5 % O_2, hvilket antyder, at nedbrydningsprocesserne er iltbegrænsede flere steder på lokaliteten. Forskellen mellem figur 22a og 22b er et eksempel på dybdens betydning for poreluftens iltindhold.



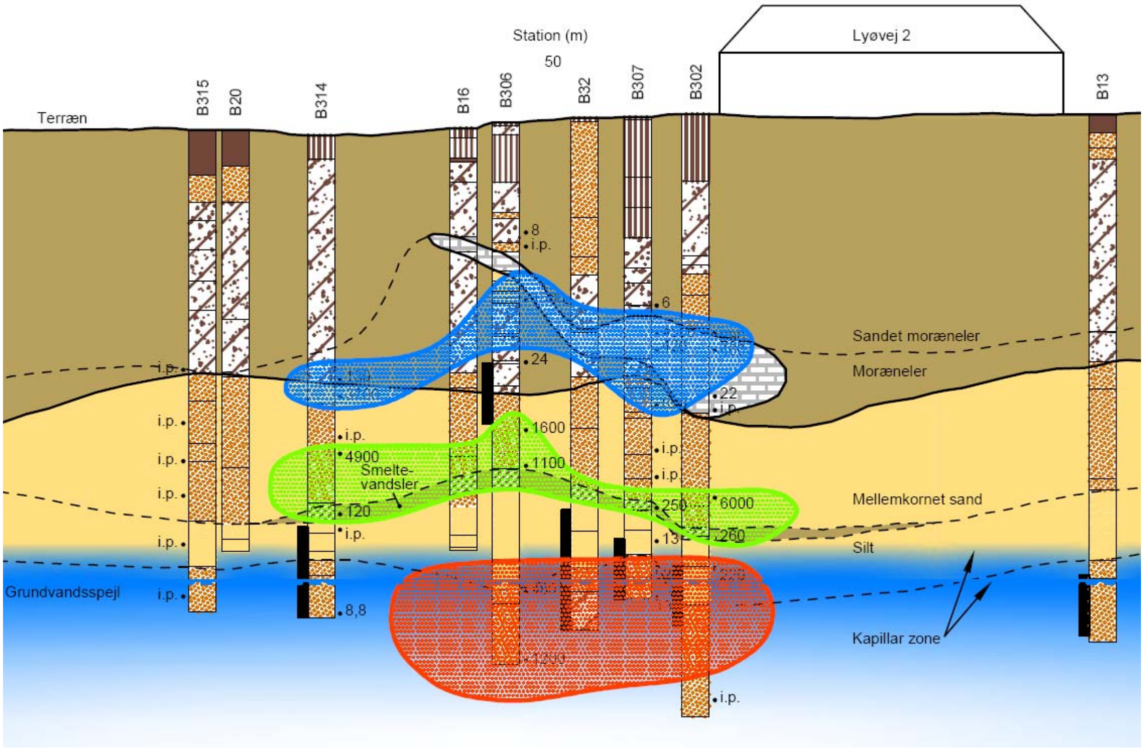
Figur 22 Målinger af ilt og kuldioxid foretaget i poreluftprøver fra (a) terrænnær umættet zone (0,45-3,3 meter under terræn) på fire olieforurenede lokaliteter /335, 336/ samt på én forsøgslokalitet med kunstig tilsætning af en kulbrinteblanding /262/ og (b) dyb umættet zone (5-15 meter under terræn) på en større benzin- og dieselforurenet lokalitet /263/.

Lagdelt geologi

På lokaliteten beskrevet i figur 22b var den umættede zone stærkt lagdelt med dominerende aflejringer af grusholdigt moræneler, vandholdigt kalk og fint smeltevandssand (se figur 23), der hver især havde signifikant forskellige jordfysiske egenskaber (se tabel 1) /204, 334/. Lagdelingen betød, at variationen af fysiske og kemiske faktorer i jorden var 2-5 gange større i vertikal retning end i horisontal retning /337/.

Poreluftens iltindhold var under 2 % i moræneler (blåt område i figur 23) og 4-5 % i finsand (grønt område i figur 23). Til sammenligning var iltkoncentrationen i uforurenet moræneler i udkanten af kildeområdet 9-16 %. Poreluftens indhold af kuldioxid var op mod 19 % i de mest forurenede områder på lokaliteten, mens det var 1-5 % i ikke-forurenede aflejringer.

Ved tracerforsøg blev det vist, at høje vandindhold i kalkaflejringer reducerede den vertikale tilførsel af atmosfærisk ilt til dybliggende forurening til et minimum /263/. Alligevel kunne der måles 4-5 % O_2 i forurenet sand i 10-13 meters dybde, hvilket vurderes, at være et resultat af horisontal gastransport af ilt gennem permeable sandlag fra ikke-forurenede og iltrige zoner udenfor det forurenede kildeområde. Denne transport muliggjorde en naturlig nedbrydning af oliestoffer i dybtliggende sandaflejringer /204, 263/.



Figur 23 De farvede områder repræsenterer forurening i hhv. moræneler/kalk (blå), fint sand (grøn) og mellemkornet sand under grundvandsspejlet (rød) /333/.

Dybde	**Lagfølge**	**Kulbrinter**	**ρ_b**	**V_L**	**D_p/D_0**	**O_2**	**CO_2**
m.u.t.		mg/kg TS	kg TS/L	L luft/L jord	-	%	%
<2	FYLD/MULD						
2-10	MORÆNELER: gruset, kalkholdigt, brunt	0-8	1,7-2,0	0,093 (0,046)	0,021 (0,025)	0-1,5	9-12
6-8	KALK: slammet, hvidt, vådt	0-450	1,6-1,7	0,04	0,007 (0,017)	i.m.	i.m.
10-13	SAND: fint, gråt, tørt	0-6.400	1,5-1,6	0,21	0,031 (0,071)	4-5	12-13
13-16	MORÆNELER/ SILT/KALK: slammet, vådt	0-14	1,5-1,7	0,06 (0,07)	0,009 (0,035)	i.m.	i.m.
i.m.: ikke målt, m.u.t.: meter under terræn.							

Tabel 1 Jordfysiske parametre, samt ilt og CO_2, målt i forureningens hot-spot (ved B307 i figur 23) i dybden 2-15 meter under terræn /334/. Tal i parentes angiver standardafvigelsen. ρ_b er jordens volumenvægt, V_L er jordens luftfyldte porøsitet, og D_p/D_0 er jordens gasdiffusivitet, dvs. forholdet mellem gasdiffusionskoefficienten i jord og i fri luft.

Naturlige jordkoncentrationer af kvælstof of fosfor

Næringsfattige forhold i undergrunden kan begrænse væksten af bakterier og hæmme nedbrydningsprocesserne. Nedbrydning vil ganske vist finde sted uden mikrobiologisk vækst, men på lang sigt kan næringsfattige forhold udsulte jordens biomasse og forhindre effektiv nedbrydning /332/. Desuden viser erfaringer fra laboratoriet, at tilførsel af kvælstof (N) og fosfor (P) til jordprøver næsten altid stimulerer den observerede nedbrydning.

Jordens indhold af næringssalte afhænger primært af nedenstående forhold /338, 339/:

- Jordtype – herunder geologisk oprindelse, organisk stofindhold og kalkindhold.
- Redoxforhold og pH – begge er afgørende for i hvilken form næringssaltene vil findes på.
- Områdets arealanvendelse – herunder eventuel tilførsel af kunstgødning eller animalsk gødning, der kan medføre forhøjede koncentrationer af kvælstof og fosfor. I byområder vil koncentrationen af næringssalte derfor typisk være lavere end i landbrugsjord.
- Dybde - dybtliggende aflejringer er typisk lavorganiske, hvorfor man ser en drastisk reduktion af næringssaltindhold i jordprøver udtaget dybere end 1 meter under terræn (dvs. under rodzonen/pløjelaget).

Indhold af kvælstof og fosfor kan måles som hhv. total-koncentrationer og opløste/tilgængelige koncentrationer. Totalindhold bestemmes normalt efter oxidering af det organiske materiale ved kogning med syre/oxidationsmiddel. Opløst eller tilgængeligt kvælstof og fosfor kvantificeres spektrofotometrisk efter ekstraktion i hhv. KCl og $NaHCO_3$.

N- og P-fraktioner relevante ifht. kildereduktion og biologisk afskæring

Ofte benyttes en C:N:P på 100:10:1 (målt i masser) som en tommelfingerregel for det indhold af makronæringsstoffer, der vil tillade en langtidsholdbar naturlig nedbrydning i olieforurenet jord uden mangel på kvælstof eller fosfor. Forholdet regnes traditionelt ud fra totalindhold af kulbrinter (C), kvælstof (N) og fosfor (P) og anvendes ved vurdering af mulig nedbrydning i forurenede kildeområder /264/.

Ovenstående tommelfingerregel har imidlertid vist sig i visse situationer at give et konservativt bud på det optimale indhold af næringssalte. For eksempel viser erfaringer med bioventilering fra 135 olieforurenede lokaliteter i det amerikanske flyvevåben, at nedbrydning kan finde sted på trods af teoretisk N- og P-begrænsning /340/. Derudover er der i undersøgelser med tilsætning af NPK-gødning til olieforurenet jord ved ”land farming” foreslået en optimal C:N:P på 100:1,7:0,125 (målt i masser) /341/. Dette svarer til et forhold imellem N og P på 13-14.

Man skal være opmærksom på, at totalindhold af kvælstof og fosfor ikke nødvendigvis repræsenterer den mængde, der er umiddelbart tilgængelig for bakterierne. Derimod svarer totalkoncentrationer snarere til den pulje, der kan frigives til porevandet (og jordbakterierne) over en længere tidshorisont (mere end 10 år). Under naturlige og ikke-stimulerede forhold er det netop den tidshorisont, der vil være relevant ved vurdering af naturlig kildereduktion eller biologisk afskæring af forureningens spredning i den umættede zone. Derfor vurderes totalindhold af N og P formentlig de mest relevante i forbindelse med nedsivningsberegninger i JAGG 2.0.

Ved vurdering af naturlig nedbrydning under stimulerede eller forcerede forhold (f.eks. bioventilering eller forceret udvaskning) kan det være hensigtsmæssigt i stedet, at anvende opløste næringssaltkoncentrationer som et mål for den "tilgængelige" pulje, da man her arbejder med en væsentligt kortere tidshorisont (typisk 3-5 år) /264/. Der findes ingen generelt anvendelig tommelfingerregel for forholdet mellem opløste og totalkoncentrationer af næringssalte /338/. De fleste studier i litteraturen anvender totalindhold frem for "tilgængelige" indhold, da sidstnævnte kan være vanskelige at definere.

Baggrundsniveauer fra litteraturen
I tabel 2 findes et sammendrag af totalindhold af kvælstof (N) og fosfor (P) målt i den dybe umættede zone (> 2 meter). Tabellen indeholder datasæt, hvor totalindhold af begge næringssalte (N_{tot} og P_{tot}) er målt på de samme jordprøver. Det begrænsede udvalg af data omfatter to danske studier /263, 262/ og ét amerikansk studie /30/, hvoraf sidstnævnte er baseret på landbrugsjord.

Generelt var N- og P-koncentrationerne 30-240 % højere i moræneler end i sand, hvilket er i overensstemmelse med et højere indhold af organisk stof i moræneler. Studie C (landbrugsjord) viste som ventet N-indhold, der var betydeligt højere end for de øvrige studier (op til 305 mg N/kg TS). Øvrige totalindhold af kvælstof varierer mellem 10 og 44 mg N/kg TS.

I de tre studier i tabel 2 varierer det totale fosforindhold mellem 162 og 363 mg P/kg TS. Dette er i overensstemmelse med resultatet af en undersøgelse foretaget af GEUS /338/. Undersøgelsen indbefattede 25 danske sandlokaliteter anvendt til landbrug og viste totalindhold af fosfor (målt efter ekstraktion i H_2SO_4) mellem 9 og 340 P mg/kg TS i dybder ned til 10 meter /338/.

I tabel 2 er N_{tot}:P_{tot} betydeligt under 10, og generelt er totalindholdet af fosfor højere end totalindholdet af kvælstof. Det indikerer, at kvælstof sandsynligvis er det begrænsende næringsstof for biologisk nedbrydning i den dybe umættede zone.

Ét kg kvælstof antages traditionelt, at muliggøre nedbrydning af 10 kg kulbrinter (jf. C:N = 100:10 /264/). På denne baggrund er der i tabel 2 beregnet potentielle (teoretiske) nedbrydningsmængder på ca. 100-3.000 mg kulbrinter/kg TS. Da olie- og benzinforurening ofte findes i jordkoncentrationer op mod 5.000-30.000 mg/kg TS er det tydeligt, at risikoen for kvælstofbegrænsning vil være reel i hot-spots på mange olieforurenede lokaliteter /262/.

Ved nedsivning igennem en afskærende umættet zone skal volumenet af den afskærende zone (på baggrund af ovenstående) således være op mod 10-300 gange større end volumenet af den forurenede zone, som den vertikale spredning sker ud fra. Denne beregning er selvsagt meget afhængig af hvilken kritisk C:N der er gældende.

	Antal	**f_{oc} (-)**		**N_{tot} (mg N/kg TS)**		**P_{tot} (mg P/kg TS)**		**N_{tot}: P_{tot} $**	**Potentiel nedbrydning# (mg C/kg TS)**
SAND		Middel	Std.afv.	Middel	Std.afv.	Middel	Std.afv.	Middel	
Kristensen et al. (2010)^A /337/	17	0,00067	0,1	10	4,7	279	37	0,036	100
Kaufmann et al. (2004)^B /262/	6	0,00048	0,03	44	3,5	270	99	0,16	440
Konopka og Turcu (1991)^C /30/	2	0,00031	0,01	90	20	267	197	0,34	900
MORÆNELER									
Kristensen et al. (2010)^A /337/	45	0,0011	0,21	20	10	363	88	0,055	200
Konopka og Turcu (1991)^C /30/	3	0,00078	0,04	305	59	162	13	1,88	3100

A: Befæstet byområde i Nyborg. Prøverne var kalkholdige (10-30 % $CaCO_3$). Prøveudtagning fra 2-15 m.u.t.
B: Ubefæstet område med homogent sand på Flyvestation Værløse. Prøver udtaget fra 2-3,3 m.u.t.
C: Landbrugsjord i det centrale USA. Prøver udtaget fra en enkelt boring imellem 2 og 25,5 m.u.t.
$: N_{tot}:P_{tot}<10 indikerer, at kvælstof vil være det begrænsende næringsstof.
#: Potentiel N-begrænset nedbrydning af oliestoffer ved antagelse af et behov for kvælstof svarende til C:N = 10. Dvs. potentiel nedbrydning = 10 × N_{tot}

Tabel 2 Totalindhold af kvælstof of fosfor i dybereliggende umættede zoner (>2 m.u.t.).

Opsummering

På baggrund af ovenstående erfaringsopsamling kan følgende konstateres:

1. Der er generelt sparsomme oplysninger i litteraturen om "almindeligt" forekommende koncentrationer af ilt og kuldioxid samt kvælstof og fosfor i den dybe umættede zone.
2. På de fleste lokaliteter forventes mangel på ilt eller næringssalte ikke at ville forhindre målbar naturlig nedbrydning i at finde sted – både som kildereduktion og biologisk afskæring.
3. Lavpermeable aflejringer kan reducere tilførslen af atmosfærisk ilt til forurenede aflejringer. Derudover kan nedbrydningsprocesser i dybe aflejringer skabe delvist anaerobe forhold og dermed hæmme den fremtidige nedbrydning.
4. Det foreliggende datagrundlag for N og P indikerer, at risikoen for N-begrænsning, i dybe afskærende zoner på forurenede lokaliteter, er større end risikoen for P-begrænsning.
5. Med hensyn til naturlig biologisk afskæring, vurderes totalindhold af N og P at være repræsentative for den pulje af næringssalte, der over en længere tidshorisont kan anvendes til biologisk nedbrydning. Der er dog mangel på viden om

den kritiske C:N – dvs. hvornår jordbakteriernes aktivitet på forurenede lokaliteter i praksis vil blive hæmmet af kvælstofmangel, samt hvor hurtigt kvælstofpuljen i forurenet jord reduceres og remineraliseres.

6. Datagrundlaget fra en forurenet lokalitet skal vurderes i forhold til den tredimensionelle geologi. Eksempelvis kan permeable linser af sand eller grus være styrende for fordelingen af ilt og gasformig forurening. Desuden er puljen af tilgængeligt kvælstof også styret af de geologiske forhold. Ved risikovurderinger bør man derfor altid tage jordens lagdeling og heterogenitet i betragtning.

Bilag 4: Litteraturdatabase

B 3.1: Konceptuelt framework

COWI. Opgradering af JAGG indeklimamodul til version 2.0. 2007. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 258
Keywords: JAGG/models/transport/unsaturated zone/vapour intrusion
Notes: Conceptual framework

Andersen, L. and A. Obenrender. Opgradering af JAGG - Revision af fugacitetsberegninger, håndtering af fri fase og blandingsforureninger. 2007. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 259
Keywords: free phase/fugacitet/JAGG/models
Notes: Conceptual framework

Christensen, A. G., P. J. Binning, M. Troldborg, P. Kjeldsen, and M. Broholm. Opgradering af JAGG til version 2.0 Vertikal transport ned til førstkommende betydende magasin. 2007. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 260
Keywords: advection/AQUIFER/colloid/conceptual models/ConSin/degradation/dispersion/free phase/JAGG/models/numerical code/partitioning/R-UNSAT/RISC Workbench 4.0/risk assessment/sorption/transport/transport processes/unsaturated zone/volatility
Notes: Conceptual framework

B 3.2: Procesforståelse

Aktor, H. GEOPROC - edb program til vurdering af geokemiske processer. Miljøprojekt nr. 883 2004. 2004. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 308
Keywords: degradation/geochemistry/GEOPROC/Groundwater geochemistry/modeling/PLUME/soil contamination/unsaturated zone
Notes: Process understanding

Bennett, K. *In-Situ* Treatment of Soil Contaminated by Benzene (a BTEX compound). 9999. (GENERIC)
Ref Type: Report
Ref ID: 62
Keywords: BACTERIA/benzene/BIODEGRADATION/biosparging/BTEX/hydrocarbon/hydrogen peroxide/In-situ method/iron chelates/oxygen/SVE/transport processes
Notes: Process understanding

Broholm, M. M., M. Christophersen, U. Maier, E. H. Stenby, P. Hohener, and P. Kjeldsen 2005. Compositional evolution of the emplaced fuel source in the vadose zone field experiment at airbase Vaerlose, Denmark. Environmental Science & Technology 39:8251-8263.
Reference ID: 269

Keywords: BIODEGRADATION/concentration/fate/hydrocarbon/modeling/NAPL/partitioning/pore water/prediction/raoult's law/SPILL/tracer/vapor/volatility/ZONE
Notes: Process understanding - NAPL
Abstract: A field experiment was performed in a sandy vadose zone, studying the fate of an emplaced fuel-NAPL source, composed of 13 hydrocarbons and a tracer. The UNIFAC model was used to test the nonideal behavior of the source, and the numerical model MIN3P was used for assessing the effect of biodegradation on source evolution. The diffusive loss to the surrounding vadose zone and the atmosphere created temporary gradients in mole fractions of the individual compounds within the source NAPL. The evolution of the source composition corresponded in general with expectations based on Raoult's Law, with the exception that the mole fractions of aromatic compounds in the source NAPL decreased faster than fractions of aliphatic compounds of similar volatility. Calculation of activity coefficients (gamma) using the UNIFAC model implied nonideal conditions, with composition-dependent gamma's different from 1. Positive deviations were calculated for the aromatic compounds. The effect of biodegradation on source depletion, evaluated by numerical modeling, was greater for the aromatic as compared to the aliphatic compounds. Hence, the faster depletion of the aromatic relative to aliphatic compounds of similar volatility is both a result of the nonideality of the mixture and a result of partitioning and biodegradation in the pore-water. Vapor concentrations of the compounds in the source were in reasonable agreement with predictions based on the modified Raoult's Law with the UNIFAC predicted gamma's and the NAPL composition for the most volatile compounds. For the less volatile compounds, the measured vapor concentrations were lower than predicted with the largest deviations for the least volatile compounds. This field experiment illustrated that nonideal behavior and bioenhanced source depletion need to be considered at multicomponent NAPL spill sites

Davis, J. W. and S. Madsen 1996. Factors affecting the biodegradation of toluene in soil. Chemosphere 33:107-130.
Reference ID: 165
Keywords: BIODEGRADATION/concentration/degradation/degradation rates/fate/hydrocarbon/microorganisms/nitrogen/substrate/toluene
Notes: Process understanding - soil physic and chemistry
Abstract: The biodegradation of toluene in soil microcosms was examined in order to identify the physical, chemical, and biological factors which determine the fate and lifetime of organic chemicals in soils, Toluene degradation rates were proportional to the initial substrate concentration and these rates reached a maximum at a concentration of 200 mu g/g. No degradation occurred above this concentration presumably due to the toxicity of the hydrocarbon to the soil microorganisms. Small differences were observed in the degradation rates in soils at different moisture content. However, the availability of water in soil appeared to limit toluene degradation only at a very low water content. The lifetime of toluene in soil was also related to the initial level and activity of the soil microorganisms. Toluene was metabolized rapidly in those soils which initially contained high levels of degrading microorganisms, Furthermore, exposure of the soil to toluene resulted in an increase in the number of degrading organisms. The lack of inorganic nutrients such as nitrogen prevented complete degradation of toluene in a clay soil which contained high levels of degrading microorganisms. The biodegradation

of organic chemicals in soil is not an intrinsic property of the molecule and cannot be predicted without first delineating the environment in which it is found. The biodegradation of a compound is defined by the biological, physical, and chemical characteristics of the soil environment. The lifetime of a chemical in soil results from a combination of all three of these parameters. Copyright (C) 1996 Elsevier Science Ltd

Ernstsen, V. Fosforindhold og fosforbindingskapacitet i sandede jorde og sedimenter. Danmarks og Grønlands Geologiske Undersøgelse Rapport 2008/43, 37 pp. 2008.
Reference ID: 338

Ernsten, V., Jacobsen, P.R., og von Platen, F. Et første landsdækkende redoxkort. Vand & Jord, nr. 4, 159-160. 2010.
Reference ID: 339

Hettwer, K., J. Warrelmann, W. Heyser, P. Martus, S. Gabb, W. Püttmann, U. Drewes, U. Walter, and D. Vehlhaber. Langzeituntersuchungen zu den Möglichkeiten und Grenzen der Nutzung natürlicher Selbstreinigungsprozesse für ausgewählte Schadstoffe am Beispiel kontaminierter militärischer Liegenschaften. 2004. Umweltbundesamt. (GENERIC)
Ref Type: Report
Ref ID: 197
Keywords: attenuation/BTEX/degradation/electron acceptor/hydrocarbon/monitoring/NATURAL ATTENUATION/natural degradation/petroleum/sorption/unsaturated zone/ZONE
Abstract: The potentials and limitations of natural degradation and sorption processes of the contaminants petroleum hydrocarbons and BTEX in the vadose zone are investigated during the research and development project on the example of former military sites.
The publication comprises the extensive screening of literature to identify criterias and parameters for the detection of 'Natural Attenuation'- processes in the unsaturated zone.
About 40 parameters (contaminants, hydrogeological parameters, soil parameters, physicalchemical and biological parameters, electron acceptors, nutrients, etc.) were evaluated for their basic functions and effects on 'Natural Attenuation'.
Notes: Process understanding

Holden, P. A., L. E. Hersman, and M. K. Firestone 2001. Water content mediated microaerophilic toluene biodegradation in arid vadose zone materials. Microbial Ecology 42:256-266.
Reference ID: 261
Keywords: BIODEGRADATION/concentration/oxygen/toluene/ZONE
Notes: Process understanding - soil physic and chemistry
Abstract: We investigated the conditions promoting toluene biodegradation for gasoline-contaminated nearsurface (0.6 m depth) and subsurface (4.7 to 5.0 m depth) vadose zone soils sampled from an and environment. At both depths, water addition was required for toluene biodegradation to occur. In near-surface samples, no inorganic nutrient addition was necessary and (i) biodegradation was fastest at 0.0 MPa, (ii)

biodegradation rates decreased with decreasing water potential down to -1.0 MPa, and (iii) biodegradation was undetectable at -1.5 MPa. For subsurface material, toluene depletion was stimulated either by slurrying with a nutrient solution or by adjusting the moisture content to 20% (0.0 MPa) with nutrient solution and lowering the oxygen concentration (to effectively 1 mg L-1 in the aqueous phase). Thus, in the subsurface material, toluene depletion was microaerobic and nutrient-limited, occurring only under low oxygen and with inorganic nutrient addition. Our studies implicate microaerophily as an important characteristic of the toluene-degrading communities in these dry soils, with soil water as a primary controller of oxygen availability

Holden, P. A. and N. Fierer 2005. Microbial processes in the vadose zone. Vadose Zone Journal 4:1-21.
Reference ID: 270
Keywords: DIVERSITY/fate/groundwater/microbial communities/microbial processes/remediation/ZONE
Notes: Process understanding - biology
Abstract: Surface soils and their microbiology have been studied for decades. However, subsurface soil, more broadly referred to as the vadose zone, is of increasing interest to microbiologists. The vadose zone, extending from the terrestrial surface to the groundwater table, is in microbes of many types. This review summarizes what is known the abundance and diversity of microbes in the vadose zone and the environmental factors that influence vadose zone microbes and microbial processes. We discuss the roles of vadose zone microbes in nutrient cycling as well as their importance in pollutant remediation. We address a number of fundamental questions in vadose zone microbial ecology, including: What do we need to learn about vadose zone microbes to improve our ability to predict the fates of pollutants? How different are microbial communities and microbial activities in the terrestrial subsurface compared with surface soil? Numerous questions and arguments justify "deepening" soil microbiology's spatial context to include the whole unsaturated subsurface

Holliger, C., S. Gaspard, G. Glod, C. Heijman, W. Schumacher, R. P. Schwarzenbach, and F. Vazquez 1997. Contaminated environments in the subsurface and bioremediation: organic contaminants. Fems Microbiology Reviews 20:517-523.
Reference ID: 61
Keywords: aerobic/AQUIFER/AQUIFERS/BACTERIA/BIOREMEDIATION/carbon dioxide/electron acceptor/hydrocarbon/nitrate/nitrogen/organic compounds/SPILL/transport
Notes: Process understanding
Abstract: Due to leakages, spills, improper disposal and accidents during transport, organic compounds have become subsurface contaminants that threaten important drinking water resources. One strategy to remediate such polluted subsurface environments is to make use of the degradative capacity of bacteria. It is often sufficient to supply the subsurface with nutrients such as nitrogen and phosphorus, and aerobic treatments are still dominating. However, anaerobic processes have advantages such as low biomass production and good electron acceptor availability, and they are sometimes the only possible solution. This review will focus on three important groups of environmental organic contaminants: hydrocarbons, chlorinated and nitroaromatic compounds. Whereas hydrocarbons are oxidized and completely mineralized under

anaerobic conditions in the presence of electron accepters such as nitrate, iron, sulfate and carbon dioxide, chlorinated and nitroaromatic compounds are reductively transformed. For the aerobic often persistent polychlorinated compounds, reductive dechlorination leads to harmless products or to compounds that are aerobically degradable. The nitroaromatic compounds are first reductively transformed to the corresponding amines and can subsequently be bound to the humic fraction in an aerobic process. Such new findings and developments give hope that in the near future contaminated aquifers can efficiently be remediated, a prerequisite for a sustainable use of the precious subsurface drinking water resources

Hunkeler, D., D. Jorger, K. Haberli, P. Hohener, and J. Zeyer 1998. Petroleum hydrocarbon mineralization in anaerobic laboratory aquifer columns. Journal of Contaminant Hydrology 32:41-61.
Reference ID: 60
Keywords: AQUIFER/BIODEGRADATION/columns/concentration/degradation/ground water/hydrocarbon/petroleum/remediation/toluene
Notes: Process understanding
Abstract: The anaerobic biodegradation of hydrocarbons at mineral oil contaminated sites has gathered increasing interest as a naturally occurring remediation process, The aim of this study was to investigate biodegradation of hydrocarbons in laboratory aquifer columns in the absence of O-2 and NO3- and to calculate a mass balance of the anaerobic biodegradation processes. The laboratory columns contained aquifer material from a diesel fuel contaminated aquifer. They were operated at 25 degrees C for 65 days with artificial groundwater that contained only SO42- and CO2 as externally supplied oxidants. After 31 days of column operation, stable concentration profiles were found for most of the measured dissolved species. Within 14 h residence time, about 0.24 mM SO42- were consumed and dissolved Fe(II) (up to 0.012 mM), Mn(II) (up to 0.06 mM), and CH4 (up to 0.38 mM) were produced. The alkalinity and the dissolved inorganic carbon (DIC) concentration increased and the DIC became enriched in C-13. In the column, n-alkanes were selectively removed while branched alkanes persisted, suggesting a biological degradation. Furthermore, based on changes of concentrations of aromatic compounds with similar physical-chemical properties in the effluent, it was concluded that toluene, p-xylene and naphthalene were degraded. A carbon mass balance revealed that 65% of the hydrocarbons removed from the column were recovered as DIG, 20% were recovered as CH4, and 15% were eluted from the column. The calculations indicated that hydrocarbon mineralization coupled to SO42- reduction and methanogenesis contributed in equal proportions to the hydrocarbon removal. Hydrocarbon mineralization coupled to Fe(III) and Mn(IV) reduction was of minor importance. DIG, alkalinity, and stable carbon isotope balances were shown to be a useful tool to verify hydrocarbon mineralization. (C) 1998 Elsevier Science B.V. All rights reserved

Juhler, R. K., O. S. Jacobsen, C. L. Larsen, B. Nilson, and P. van der Keur. AFKLARINGSPROJEKT OM NEDSIVNING AF HUSSPILDEVAND. 2004. DANVA. (GENERIC)
Ref Type: Report
Ref ID: 198
Keywords: concentration/domestic sewage/OM/recharge
Abstract: Rapporten identificerer potentielle risici, der kan være for-

bundet med nedsivning af husspildevand i det åbne land (nedsivningsanlæg < 30 PE). Som baggrund for vurderingen er der foretaget en litteraturgennemgang af eksisterende danske og internationale undersøgelser. Der lægges særlig vægt på de miljøfremmede stoffers koncentrationsniveau og mobilitet, men der udføres ikke egentlige modelleringer eller PEC beregninger (PEC = Predicted Environmental Concentration), idet sådanne beregninger ligger udenfor projektets rammer. I rapporten kan der således identificeres potentielle problemstoffer uden at disse nødvendigvis forekommer i koncentrationsniveauer der ligger over grænseværdier eller frembyder sundhedsfarer for mennesker eller miljø ved en evt. efterfølgende gennemregning. Rapportens konklusioner og anbefalinger skal således levere baggrunden for en diskussion af evt. behov for yderligere undersøgelser, og leverer ikke forudsigelser af koncentrationsniveauer, absolutte belastningsniveauer eller risici. Formålet er således at identificere eventuelle uklarheder med relevans for nedsivning af husspildevand fra mindre anlæg i det åbne land under hensyntagen til:
a) stofspecifikke forhold
b) geologisk specifikke forhold
c) anlægsspecifikke forhold
Notes: Process understanding

Kasai, Y., Y. Takahata, T. Hoaki, and K. Watanabe 2005. Physiological and molecular characterization of a microbial community established in unsaturated, petroleum-contaminated soil. Environmental Microbiology 7:806-818.
Reference ID: 271
Keywords: aerobic/benzene/contamination/degradation/degradation rates/electron acceptor/hydrocarbon/microbial communities/nitrate/petroleum/toluene/unsaturated zone/ZONE
Notes: Process understanding - biology
Abstract: The microbial communities established in soil samples from an unsaturated, petroleum-contaminated zone and from an adjacent uncontaminated site were characterized by physiological and molecular approaches. Possible electron acceptors such as sulfate and nitrate had been completely depleted in these soil samples. Slurries of these soil samples were incubated in bottles in the presence of hydrocarbon indicators (benzene, toluene, xylene and decane), and the degradation of these compounds was examined. Supplementation with electron acceptors stimulated hydrocarbon degradation, although the stimulatory effect was small in the contaminated soil. The initial degradation rates in the contaminated soil under fermentative/methanogenic conditions were comparable to those under aerobic conditions. The microbial populations in the original soil samples were analysed by cloning and sequencing of polymerase chain reaction (PCR)-amplified bacterial and archaeal 16S rRNA gene fragments, showing that the sequences retrieved from these soils were substantially different. For instance, Epsilonproteobacteria, Gammaproteobacteria, Crenarchaeota and Methanosarcinales could only be detected at significant levels in the contaminated soil. Denaturing gradient gel electrophoresis (DGGE) analyses of 16S rRNA gene fragments amplified by PCR from the incubated soil-slurry samples showed that supplementation of the electron acceptors resulted in a shift in the major populations, while the DGGE profiles after incubating the contaminated soil under the fermentative/methanogenic conditions were not substantially changed. These results suggest that petroleum contamination of the unsaturated zone resulted in the establishment of a

fermentative/methanogenic community with substantial hydrocarbon-degrading potential

Kaufmann, K., M. Christophersen, A. Buttler, H. Harms, and P. Hohener 2004. Microbial community response to petroleum hydrocarbon contamination in the unsaturated zone at the experimental field site Vaerlose, Denmark. Fems Microbiology Ecology 48:387-399.
Reference ID: 262
Keywords: concentration/contamination/hydrocarbon/microbial communities/monitoring/nitrogen/petroleum/PLUME/soil gas/unsaturated zone/vapor/ZONE
Notes: Process understanding - soil physic and chemistry
Abstract: This study investigates the influence of petroleum hydrocarbons on a microbial community in the vadose zone under field conditions. An artificial hydrocarbon mixture consisting of volatile and semi-volatile compounds similar to jet-fuel was emplaced in a previously uncontaminated vadose zone in nutrient-poor glacial melt water sand. The experiment included monitoring of microbial parameters and CO2 concentrations in soil gas over 3 months in and outside the hydrocarbon vapor plume that formed around the buried petroleum. Microbial and chemical analyses of soil and vadose zone samples were performed on samples from cores drilled to 3.3 m depth on three dates and three lateral distances from the buried petroleum mass. Significantly elevated CO2 concentrations were observed after contamination. Total cell numbers as determined by fluorescence microscopy were strongly correlated with soil organic carbon and nitrogen content but varied little with contamination. Redundancy analysis (RDA) allowed direct analysis of effects of selected environmental variables or the artificial contamination on microbiological parameters. Variation in biomass and CO2 production was explained by soil parameters, to 46%, and by the duration of contamination, to 39.8%. The microbial community structure was assessed by community level physiological profiles (CLPP) analysis using Biolog(TM) Eco-Plates. In the CLPP data only 35.9% of the variation could be linked to soil parameters and contamination, however, the samples with greatest exposure to hydrocarbons grouped together on RDA plots. It is concluded that, at this nutrient-poor site, the microbial community was dominated by natural heterogeneity and that the influence of petroleum hydrocarbon vapors was weak. (C) 2004 Federation of European Microbiological Societies. Published by Elsevier B.V. All rights reserved

Kästner, M. Parameter und methoden zur beurteilung der biologischen sanierbarkeit von böden. 9999. (GENERIC)
Ref Type: Report
Ref ID: 248
Keywords: aggregation/BIOREMEDIATION/grain size/methods/permeability/porosity/remediation/soil contamination/soil properties
Notes: Process understanding

Kreamer, D. K., D. E. James, and K. E. Varner. Determination of Pollutant Distribution and Movement by Controlled Laboratory Experiments. 1997. US EPA. (GENERIC)
Ref Type: Report
Ref ID: 199
Keywords: batch test/diffusion/diffusion coefficient/distribution/laboratory experiments/partitioning/petroleum/vapour

transport/VOCs
Notes: Process understanding

Kristensen, A. H., K. Henriksen, L. Mortensen, K. M. Scow, and P. Moldrup 2010. Soil Physical Constraints on Intrinsic Biodegradation of Petroleum Vapors in a Layered Subsurface. Vadose Zone Journal 9:137-147.
Reference ID: 263
Keywords: aerobic/aerobic biodegradation/benzene/BIODEGRADATION/hydrocarbon/in situ/metabolism/petroleum/porosity/respiration/saturation/vapor/ZONE
Notes: Process understanding
Abstract: Naturally occurring biodegradation of petroleum hydrocarbons in the vadose zone depends on the physical soil environment influencing field-scale gas exchange and pore-scale microbial metabolism. In this study, we evaluated the effect of soil physical heterogeneity on biodegradation of petroleum vapors in a 16-m-deep, layered vadose zone. Soil slurry experiments (soil/water ratio 10:30 w/w, 25 degrees C) on benzene biodegradation under aerobic and well-mixed conditions indicated that the biodegradation potential in different textured soil samples was related to soil type rather than depth, in the order: sandy loam > fine sand > limestone. Similarly, O-2 consumption rates during in situ respiration tests performed at the site were higher in the sandy loam than in the fine sand, although the difference was less significant than in the slurries. Laboratory and field data generally agreed well and suggested a significant potential for aerobic biodegradation, even with nutrient-poor and deep subsurface conditions. In slurries of the sandy loam, the biodegradation potential declined with increasing in situ water saturation (i.e., decreasing air-filled porosity in the field). This showed a relation between antecedent undisturbed field conditions and the slurry biodegradation potential, and suggested air-filled porosity to be a key factor for the intrinsic biodegradation potential in the field

Kristensen, A. H. Controlling factors for natural attenuation of petroleum vapors in a layered subsur-face. Ph.D. defence, June 23 2010, Aalborg University.
Reference ID: 333

Kristensen, A.H., Poulsen, T.G., Mortensen, L., Moldrup, P. Variability of soil potential for biodegra-dation of petroleum hydrocarbons in a heterogeneous subsurface. Journal of Hazardous Materials 179: 573-580. 2010.
Reference ID: 337

Kristensen, A.H., Loll, P., Henriksen, K., Mortensen, L., og Møldrup, P. 2011. Nedbrydning af oli-estoffer i den umættede zone. Vand & Jord, nr. 1, 12-16, 2011.
Reference ID: 334

Labud, V., C. Garcia, and T. Hernandez 2007. Effect of hydrocarbon pollution on the microbial properties of a sandy and a clay soil. Chemosphere 66:1863-1871.
Reference ID: 272
Keywords: concentration/contamination/hydrocarbon/p/petroleum/respiration/toxicity
Notes: Process understanding - biology
Abstract: The aim of this work was to ascertain the effects of different

types of hydrocarbon pollution on soil microbial properties and the influence of a soil's characteristics on these effects. For this, toxicity bioassays and microbiological and biochemical parameters were studied in two soils (one sandy and one clayey) contaminated at a loading rate of 5% and 10% with three types of hydrocarbon (diesel oil, gasoline and crude petroleum) differing in their volatilisation potential and toxic substance content. Soils were maintained under controlled conditions (50-70% water holding capacity, and room temperature) for six months and several microbiological and toxicity parameters were monitored 1, 60, 120 and 180 days after contamination. The toxic effects of hydrocarbon contamination were greater in the sandy soil. Hydrocarbons inhibited microbial biomass, the greatest negative effect being observed in the gasoline-polluted sandy soil. In both soils crude petroleum and diesel oil contamination increased microbial respiration, while gasoline had little effect on this parameter, especially in the sandy soil. In general, gasoline had the highest inhibitory effect on the hydrolase activities involved in N, P or C cycles in both soils. All contaminants inhibited hydrolase activities in the sandy soil, while in the clayey soil diesel oil stimulated enzyme activity, particularly at the higher concentration. In both soils, a phytotoxic effect on barley and ryegrass seed germination was observed in the contaminated soils, particularly in those contaminated with diesel or petroleum. (c) 2006 Elsevier Ltd. All rights reserved

Loll, P., D. Nørgaard, K. Henriksen, and C. Larsen 2007. MTBE biodegradation in the vadose zone. (Anonymous,).
Reference ID: 265
Keywords: aerobic/BIODEGRADATION/BIOREMEDIATION/degradation/degradation rates/in situ/MTBE/SPILL/toluene/VOCs/ZONE
Notes: Process understanding - soil physic and chemistry
Abstract: This study presents an effort to improve the knowledge of biodegradation of MTBE, a recalcitrant VOC, in the vadose zone, by providing a basis for discussing the extent to which MTBE biodegradation can be expected to occur in the vadose zone at LUST sites and potential degradation rates. Soil samples were collected from the vadose zone at five gas stations with gasoline spills containing MTBE, both at the hot-spots and at non-polluted reference locations at each site. The samples were included in a batch screening study, in which we investigated the aerobic MTBE degradation potential (primary and pseudo-cometabolic with addition of 5% propane). Primary MTBE degradation was found in hot-spot samples from four out of five sites, and in non-polluted reference samples from one out of five sites. Pseudo-cometabolic degradation (both primary and cometabolic with 5% propane added) was found in four out of five samples for both hot-spot and unpolluted reference samples. Primary degradation rates were found in the range of (1.order) 0.046–1.1 d-1 and (0.order) 0.16–1.4 ìg MTBE/g TS/d. Degradation rates with 5% propane were generally found to be 1.1–3.9 times higher than primary rates. However, samples from one site showed a 55% decrease in the degradation rates with propane added. Addition of toluene (10 mg/L) to hot-spot samples from one site was observed to have a stimulating effect on the primary MTBE degradation with a 10 fold rate increase. Toluene addition had no effect on the pseudo-cometabolic degradation of MTBE.

Loll, P. 2008. Oprensning af olie- og benzinforureninger - status for naturlig nedbrydning og biologiske afværketeknikker med fokus på olie og ben-

zinforureninger. (Anonymous,).
Reference ID: 264
Keywords: BIOREMEDIATION/degradation/in situ/methods/natural degardation/petroleum/remediation/unsaturated zone/ZONE
Notes: Process understanding - soil physic and chemistry
Abstract: I denne artikel gives et overblik over naturlig nedbrydning og biologisk afværge anvendt som in-situ metode i forhold til benzin- og olieforureninger. I artiklen berøres metodens basale principper og anvendelsesområder, herunder fordele og ulemper, effektivitet og oprensningstider m.v. I artiklen tages primært udgangspunkt i mine egne erfaringer med metoden (i umættet zone), men jeg vil dog også forsøge at krydre (lidt) med nogle andre danske og udenlandske erfaringer.

Margesin, R., G. Walder, and F. Schinner 2003. Bioremediation assessment of a BTEX-contaminated soil. Acta Biotechnologica 23:29-36.
Reference ID: 266
Keywords: assessment/benzene/BIODEGRADATION/BIOREMEDIATION/BTEX/contamination/sorption/toluene
Notes: Process understanding - soil physic and chemistry
Abstract: The elimination of BTEX (benzene, toluene, ethylbenzene, o-xylene) compounds from soil was studied. After 18 days at 20degreesC, 21% of the initial total BTEX contamination (400 mg/kg soil) was lost due to sorption onto soil. Biodegradation decreased in the order ethylbenzene > toluene > benzene > o-xylene. NPK fertilisation stimulated biodegradation, particularly that of benzene and toluene, significantly, and oleophilic fertilisation inhibited biodegradation. After 18 days, the residual contamination in the NPK-fertilised, unfertilised and with oleophilic nutrients amended soil was 96, 166 and 196 mg total BTEX/kg soil, respectively. The presence of BTEX initially inhibited the biological activity of the soil (fluorescein diacetate hydrolysis) considerably. This short-term, reversible inhibition was significantly higher in the unfertilised soil than in the fertilised soil

Mayer, K. U., R. T. Amos, and S. Molins. Integrated investigation of natural attenuation processes at the Bemidji crude oil spill site. 9999. (GENERIC)
Ref Type: Slide
Ref ID: 247
Keywords: attenuation/CRUDE-OIL/NATURAL ATTENUATION/redox conditions/SPILL
Notes: Process understanding

Minnich, M. Behavior and Determination of Volatile Organic Compounds in Soil - A Literature Review. 1993. US EPA. (GENERIC)
Ref Type: Report
Ref ID: 200
Keywords: concentration/contamination/fate/GROUNDWATER/methods/organic compounds/remediation/transport/VOCs
Abstract: Accurate measurement of soil volatile organic compound (VOC) concentrations is crucial to site investigation, evaluation, and remediation efforts at Superfund sites contaminated by VOCs Soils that are contaminated with VOCs are potential reservoirs of long-term ground water contamination. This report summarizes literature pertaining to (1) the fate and transport of soil VOCs and, (2) the sampling and analysis of soil VOCs by SW-846 Methods 8240/8260 using purge-and-

trap/gas chromatography/mass spectrometry (PT/GC/MS).
Notes: Process understanding

Scherr, K., H. Aichberger, R. Braun, and A. P. Loibner 2007. Influence of soil fractions on microbial degradation behavior of mineral hydrocarbons. European Journal of Soil Biology 43:341-350.
Reference ID: 267
Keywords: BIODEGRADATION/BIOREMEDIATION/concentration/contamination/CRUDE-OIL/degradation/density/DESIGN/distribution/fate/hydrocarbon/microbial communities/sorption
Notes: Process understanding - soil physic and chemistry
Abstract: Various interactions occurring between organic chemicals and soil constituents participate in the determination of the fate of these pollutants, including their biodegradability. These relations need to be characterized in order to design and successfully implement a bioremediation application. In the present study, biodegradation of spiked and aged crude oil contamination in two dissimilar soils was related to their composition. GC-FID analysis of bulk soil samples as well as sand- and <63 mu m fractions showed considerable differences in contaminant distribution and degradation behavior within these fractions. Whereas a freshly spiked silty soil showed reasonable degradation (51% degradation was not significant after ageing. By contrast, a sandy soil was degraded by 25% (recently contaminated) and 19% (aged). Biodegradation occurred in the fine fraction only, with a comparably high content of organic carbon whereas hydrocarbon concentration remained constant in the sand fraction. This was correlated with sorption to the fine fraction where hydrocarbon concentrations were higher by over an order of magnitude compared to the sand fraction. Soil composition, biology and chemistry exert a pronounced influence on microbial degradation in respect to (i) contaminant availability and (ii) the structure and density of the microbial community. (c) 2007 Elsevier Masson SAS. All rights reserved

Skopp, J., M. D. Jawson, and J. W. Doran 1990. Steady-State Aerobic Microbial Activity As A Function of Soil-Water Content. Soil Science Society of America Journal 54:1619-1625.
Reference ID: 268
Keywords: aerobic/diffusion/diffusion coefficient/management/porosity/prediction/soil physical properties/substrate
Notes: Process understanding - soil physic and chemistry
Abstract: Soil physical properties often regulate aeration-dependent microbial activities important to nutrient cycling, soil fertility and environmental quality. Microbial activity depends on soil water content and is maximum at a water content where the limiting effects of substrate diffusion and O2 supply are equal. The mechanism whereby this occurs and predictions of the soil water content where aerobic microbial activity is a maximum were the objectives of this study. In particular, this study predicted the shape of the microbial activity vs. water content function from soil physical concepts. Soil physical processes are assumed to influence microbial activity by limiting the steady flux of a required substrate or O2 to sites of microbial activity. Steady-state flux relations are used to define the activity function. The dependence of diffusion coefficient on water content or air-filled porosity is assumed. With these assumptions, it is possible to show that a maximum in the activity function exists. The predicted shape of the activity curve is consistent with experimental observations. The relationship between aera-

tion-dependent microbial activity and soil water content facilitates evaluating the indirect effects of soil management practices, such as tillage, on microbial activity

Tindall, J. A., J. R. Kunkel, and D. E. Anderson 9999. Transport of heat and gas in the soil and the subsurface. Pp. 200-272 in Unsaturated zone hydrology for scientists and engineers (Anonymous,).
Reference ID: 245
Keywords: heat/soil gas/transport/unsaturated zone/ZONE
Notes: Process understanding

Tindall, J. A., J. R. Kunkel, and D. E. Anderson 9999. Soil remediation techniques. Pp. 494-523 in Unsaturated zone hydrology for scientists and engineers (Anonymous,).
Reference ID: 246
Keywords: remediation/unsaturated zone/ZONE
Notes: Process understanding

B 3.2.1 Generelt om den umættede zone

American Petroleum Institute. Collecting and Interpreting Soil Gas Samples from the Vadose Zone: A Practical Strategy for Assessing the Subsurface Vapor-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites. 2005. American Petroleum Institute. (GENERIC)
Ref Type: Report
Ref ID: 187
Keywords: hydrocarbon/migration/petroleum/soil gas/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone

Batterman, S., A. Kulshrestha, and H. Y. Cheng 1995. Hydrocarbon Vapor Transport in Low Moisture Soils. Environmental Science & Technology 29:171-180.
Reference ID: 124
Keywords: diffusion/diffusion coefficient/dispersion/hydrocarbon/methane/methods/models/remediation/retardation factor/saturation/soil gas/sorption/toluene/transport/unsaturated zone/vapor/ZONE
Notes: Generally on the unsaturated zone
Abstract: Gas-phase transport of hydrocarbons in unsaturated soils is important in the assessment and remediation of. volatile subsurface contaminants and other environmental applications. This paper presents models and measurements of diffusion, dispersion, and retardation parameters developed for several hydrocarbon vapors in unsaturated soils using laboratory column systems. Diffusion coefficients are determined in dry soils using steady-state methods. Retardation and dispersion parameters are found using transient methods and a range of soil moisture contents below the saturation soil moisture content. Media tested included sand, fill, loam, and glass beads as controls; contaminants included toluene, trichlorethylene, and methane, The experiments clearly demonstrate the role of humidity in absorption and transport of vapors in soils. Soil gas humidities below 30% result in considerable retardation of hydrocarbon vapors in all media. Retardation factors range up to 80 for toluene and to 46 for trichloroethylene, Retardation coefficients decrease but remain large with increasing humidity in organic-rich soils.

No significant retardation is seen for methane. Based on soil-water isotherms, these results suggest competitive sorption between hydrocarbon and water vapors on soil surfaces, especially the mineral fraction

Bohy, M., L. Dridi, G. Schafer, and O. Razakarisoa 2006. Transport of a mixture of chlorinated solvent vapors in the vadose zone of a sandy aquifer: Experimental study and numerical modeling. Vadose Zone Journal 5:539-553.
Reference ID: 121
Keywords: AQUIFER/capillary fringe/concentration/modeling/prediction/raoult's law/saturation/TCE/transport/unsaturated zone/vapor/volatilization/ZONE
Notes: Generally on the unsaturated zone
Abstract: Experimental and modeling studies were performed to investigate the simultaneous transport of trichloroethylene (TCE) and perchloroethylene (PCE) in the vadose zone of a large (25 by 12 by 3 m) well-instrumented artificial aquifer called SCERES. The experimental facility, made up of a 1-m-thick saturated zone and a 2-m-thick unsaturated zone, allowed direct measurements of the contaminants in both the liquid and gas phases. Main objectives of the study were to obtain a better understanding of the fate and transport of chlorinated solvents in the subsurface and, more specifically, to compare simultaneously measured TCE and PCE volatilization rates from the soil surface with predictions obtained with both a comprehensive multiphase multicomponent numerical model (SIMUSCOPP) and a quasianalytical approach based on Fick's first law. The numerical and quasianalytical results generally agreed very well with the observed data. Transient PCE and TCE vapor phase concentrations calculated with the numerical model were found to be close to the observations, which indicated applicability of Raoult's Law. A comparison of observed and calculated TCE and PCE concentrations in the capillary fringe showed more impact of water infiltration on the simulations as compared with the observed data, which may reflect a lack of equilibrium between the gaseous and aqueous phase during leaching for the given experimental flow conditions. A sensitivity analysis showed that the adopted source boundary condition (a fixed nonaqueous phase liquid [NAPL] saturation distribution instead of an injected DNAPL source) did not have much influence on the concentration breakthrough curves, but that temperature can be an important factor influencing the results

Bruell, C. J. and G. E. Hoag 1986. The diffusion of gasoline-range hydrocarbon vapors in porous media, experimental methodologies. (Anonymous,).
Reference ID: 129
Keywords: diffusion/groundwater/hydrocarbon/petroleum/unsaturated zone/vapor/ZONE
Notes: Generally on the unsaturated zone

Cannavo, P., F. Lafolie, B. Nicolardot, and P. Renault 2006. Modeling seasonal variations in carbon dioxide and nitrous oxide in the vadose zone. Vadose Zone Journal 5:990-1004.
Reference ID: 106
Keywords: aerobic/carbon dioxide/concentration/gas transport/modeling/nitrous oxide/soil gas/transport/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone
Abstract: Soil CO2 and N2O concentrations were simulated with a model predicting C and N transport in the vadose zone during a 7-mo

field experiment, after maize (Zea mays L.) harvesting and incorporation of maize residues into the soil. The gas transport model was based on the dusty gas theory and combined with the PASTIS model. During the experiment, soil atmosphere (CO2 and N2O), soil solution (NO3- and dissolved organic carbon [DOC]), soil water content and temperature, and potential denitrifying and aerobic respiratory activities were measured in a 2.50-m-thick soil profile. Soil gas concentrations were correctly simulated even though the model did not simulate all the biological processes that produced N2O. Nitrous oxide concentration peaks after rain were slightly overestimated, as the WFPS (water-filled pore space) was not estimated accurately enough to predict local anoxic conditions. To model CO2 concentrations, account had to be taken of DOC adsorption onto soil mineral particles and of zymogenous biomass death during the period when the ground was frozen. The model satisfactorily simulated NO3- concentrations in the top soil profile, notably during major rainfall events, and maize residue dry matter loss during the experiment. The modeling of biological processes needs to be improved to provide a better simulation of C and N transport in the vadose zone. In particular, the use of WFPS was not sufficient to predict anoxic periods; simulations should improve if soil aggregate structure is also taken into account

DeVaull, G., R. Ettinger, and J. Gustafson 2002. Chemical vapor intrusion from soil or groundwater to indoor air: Significance of unsaturated zone biodegradation of aromatic hydrocarbons. Soil & Sediment Contamination 11:625-641.
Reference ID: 109
Keywords: aerobic/aerobic biodegradation/assessment/benzene/BIODEGRADATION/BTEX/groundwater/hydrocarbon/management/modeling/models/petroleum/TCE/toluene/transport/unsaturated zone/vapor/ZONE
Notes: Generally on the unsaturated zone
Abstract: The soil vapor to indoor air exposure pathway is considered in a wide number of risk-based site management programs. In screening-level assessments of this exposure pathway, models are typically used to estimate the transport of vapors from either subsurface soils or groundwater to indoor air. Published studies indicate that the simple models used to evaluate this exposure pathway often over estimate the impact for aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylene or BTEX), while showing reasonable agreement for estimates of chlorinated hydrocarbon impacts (e.g., PCE, TCE, DCE). Aerobic biodegradation of the petroleum hydrocarbons is most often attributed as the source of this disparity in the model/data comparisons. This paper looks at the significance of aerobic biodegradation of aromatic hydrocarbons as part of the assessment of chemical vapor intrusion from soil or groundwater to indoor air. A review of relevant literature summarizing the available field data as well as various modeling approaches that include biodegradation is presented. This is followed by a simple modeling analysis that demonstrates the potential importance of biodegradation in the assessment of the soil vapor to indoor air exposure pathway. The paper concludes with brief discussions of other model considerations that are often not included in simple models but may have a significant impact on the intrusion of vapors into indoor air

Devaull, G. E. 2007. Indoor vapor intrusion with oxygen-limited biodegradation for a subsurface gasoline source. Environmental Science & Technology

41:3241-3248.
Reference ID: 28
Keywords: aerobic/BIODEGRADATION/concentration/hydrocarbon/kinetics/organic matter/oxygen/petroleum/respiration/transport/unsaturated zone/vapor/ZONE
Notes: Generally on the unsaturated zone
Abstract: Development and results are presented for a subsurface soil to indoor air chemical vapor intrusion model that includes oxygen-limited biodegradation. The algebraic model incorporates a steady-state subsurface gasoline vapor source, diffusion-dominated soil vapor transport in a homogeneous subsurface soil layer, and mixing within a building enclosure. The soil is divided into a shallow aerobic layer including biodegradation and a deeper anaerobic layer in which biodegradation is neglected. Biodegradation of multiple chemicals is included, with aerobic first-order reaction kinetics estimated from measured data. Oxygen is supplied at the soil surface below the building foundation. Oxygen demand is attributed to a sum of multiple biodegrading chemicals and to baseline respiration of native soil organic matter. The model is solved by iteratively varying the aerobic depth to match oxygen demand to oxygen supply. Model results are calculated for ranges of source concentrations, unsaturated soil characteristics, and building parameters. Results indicate vapor intrusion of petroleum hydrocarbons can be significantly less than indicated by estimates that neglect biodegradation

Evans, D., I. Hers, R. M. Wolters, R. T. B. Boddington, and D. H. Hall. Vapour transfer of soil contaminants. 2002. (GENERIC)
Ref Type: Report
Ref ID: 123
Keywords: guidance/management/models/riskbased approach/transport/unsaturated zone/vapour/vapour intrusion/ZONE
Notes: Generally on the unsaturated zone

Fitzpatrick, N. A. and J. J. Fitzgerald 2002. An evaluation of vapor intrusion into buildings through a study of field data. Soil & Sediment Contamination 11:603-623.
Reference ID: 113
Keywords: concentration/contamination/groundwater/migration/models/soil gas/transport/unsaturated zone/vapor/VOCs/volatilization/ZONE
Notes: Generally on the unsaturated zone
Abstract: A systematic examination of cases on file with the Massachusetts Department of Environmental Protection was undertaken to identify a universe of sites with volatile organic compound (VOC) contamination in groundwater in close proximity to buildings. Such locations were grouped according to site variables, such as contaminants of concern and concentrations in various media; soil type; depth to groundwater; distance to building; and building construction. Indoor air, soil gas, and/or groundwater field data collected from these sites was then assembled and used to: (1) evaluate available transport models which describe the intrusion of vapors into buildings and predict indoor air contaminant concentrations resulting from the volatilization of VOCs in the subsurface; (2) examine the validity of established regulatory criteria; (3) identify specific trends and field conditions which appear to most influence vapor phase contaminant migration and intrusion processes; a and (4) evaluate the possibility of vapor migration being inhibited by a "freshwater lens"

Flaming, J. e., R. C. Knox, D. A. Sabatini, and T. C. Kibbey 2003. Surfactant Effects on Residual Water and Oil Saturations in Porous Media. Vadose Zone Journal 2:168-176.
Reference ID: 100
Keywords: saturation/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone

Garbesi, K. and R. G. Sextro 1989. Modeling and Field Evidence of Pressure-Driven Entry of Soil Gas Into A House Through Permeable Below-Grade Walls. Environmental Science & Technology 23:1481-1487.
Reference ID: 114
Keywords: modeling/soil gas/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone

Hendry, M. J., C. A. Mendoza, R. Kirkland, and J. R. Lawrence 2001. An assessment of a mesocosm approach to the study of microbial respiration in a sandy unsaturated zone. Ground Water 39:391-400.
Reference ID: 128
Keywords: assessment/capillary fringe/concentration/in situ/respiration/soil gas/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone
Abstract: Microbial respiration rates were determined through a 3.2 m thick, sandy unsaturated zone in a 2.4 m diameter x 4.6 m high mesocosm. The mesocosm was maintained under near constant temperature (18 degrees to 23 degreesC) and reached steady moisture content conditions after several hundred days. Soil-gas CO2 concentrations in the mesocosm ranged from 0.09 % to 3.31 % and increased with depth. Respiration rates within the mesocosm were quantified over a 342-day period using measured CO2 concentrations and a transient, one-dimensional finite-element model. Microbial respiration rates were 2 x 10(-1) mug C.g(-1).d(-1) throughout most of the system, but decreased to 10(-4) to 10(-3) mug C.g(-1).d(-1) within the capillary fringe. Microbial respiration rates were also determined in minicosms (500 g sample mass) over a range in temperatures (4 degrees to 30 degreesC) and volumetric moisture contents (0.044 to 0.37). The functional dependence of CO2 production on temperature and soil-moisture content was similar for the two scales of laboratory observation. Respiration rates in the minicosms, for temperatures and moisture contents in the mesocosm, were up to an order of magnitude greater than those determined for the mesocosm, The higher respiration rates in the minicosms, compared to the mesocosm, were attributed to greater disturbance of the samples and to shorter acclimation time in the minicosms. Extrapolating the laboratory respiration rates to field conditions yielded rates that were two to three orders of magnitude greater than rates previously determined in situ for C-horizon material. Results show that in situ microbial reaction rates determined using disturbed samples in minicosms and mesocosms yielded respiration rates that greatly exceeded field conditions. Mesocosms can, however, provide a useful environment for conducting process-related research in unsaturated environments

Hohener, P., C. Duwig, G. Pasteris, K. Kaufmann, N. Dakhel, and H. Harms 2003. Biodegradation of petroleum hydrocarbon vapors: laboratory studies on rates and kinetics in unsaturated alluvial sand. Journal of Contaminant Hydrology 66:93-115.
Reference ID: 125
Keywords: aerobic/aerobic biodegradation/assessment/attenuation/BIODEGRADATION/CFC/concentration/d

egradation/hydrocarbon/kinetics/models/MTBE/NATURAL ATTENUATION/organic compounds/petroleum/prediction/reactive transport/risk assessment/saturation/soil gas/sorption/substrate/toluene/transport/unsaturated zone/vapor/VOCs/ZONE
Notes: Generally on the unsaturated zone
Abstract: Predictions of natural attenuation of volatile organic compounds (VOCs) in the unsaturated zone rely critically on information about microbial biodegradation kinetics. This study aims at determining kinetic rate laws for the aerobic biodegradation of a mixture of 12 volatile petroleum hydrocarbons and methyl tert-butyl ether (MTBE) in unsaturated alluvial sand. Laboratory column and batch experiments were performed at room temperature under aerobic conditions, and a reactive transport model for VOC vapors in soil gas coupled to Monod-type degradation kinetics was used for data interpretation. In the column experiment, an acclimatization of 23 days took place before steady-state diffusive vapor transport through the horizontal column was achieved. Monod kinetic parameters K-s and nu(max) could be derived from the concentration profiles of toluene, m-xylene, n-octane, and n-hexane, because substrate saturation was approached with these compounds under the experimental conditions. The removal of cyclic alkanes, isooctane, and 1,2,4-trimethylbenzene followed first-order kinetics over the whole concentration range applied. MTBE, n-pentane, and chlorofluorocarbons (CFCs) were not visibly degraded. Batch experiments suggested first-order disappearance rate laws for all VOCs except n-octane, which decreased following zero-order kinetics in live batch experiments. For many compounds including MTBE, disappearance rates in abiotic batch experiments were as high as in live batches indicating sorption. It was concluded that the column approach is preferable for determining biodegradation rate parameters to be used in risk assessment models. (C) 2003 Elsevier Science B.V. All rights reserved

Jin, Y., T. Streck, and W. A. Jury 1994. Transport and Biodegradation of Toluene in Unsaturated Soil. Journal of Contaminant Hydrology 17:111-127.
Reference ID: 115
Keywords: BACTERIA/BIODEGRADATION/columns/concentration/degradation/diffusion/diffusion coefficient/saturation/soil gas/substrate/toluene/transport/transport processes/unsaturated zone/volatilization/ZONE
Notes: Generally on the unsaturated zone
Abstract: Degradation of volatile organic chemicals during transport has received little attention in the past. In this study we report the results of a series of experiments on toluene movement through soil columns of different length in sterilized, pre-exposed and unexposed soil. Toluene was added to 25-cm-diameter soil columns through an inlet chamber that maintained a constant concentration throughout the experiment. The toluene diffused through the soil to an outlet chamber at the top which was continuously swept with humidified air and samples were periodically analysed to determine toluene flux. The first experiment, conducted under sterilized conditions, was used to measure the soil gas diffusion coefficient, and subsequent experiments in which biodegradation occurred were used to estimate the degradation rate coefficient by fitting the outflow to a mathematical model. The degradation rate was very rapid under both pre-exposed and unexposed soil conditions, corresponding to a half-life of approximately 2 h when bacterial activity reached high levels. Prior to this stage, the volatilization flux was very

erratic, implying that growth rates of the bacteria were out of phase with the transport process. Overall, the degradation process was not well described by a first-order model until the population stabilized. Preexposure of the soil to the substrate prior to the transport experiment greatly increased the rate of removal of toluene during transport. Under such conditions, a 30-cm cover could virtually stop volatilization losses of the compound when the inlet concentration was well below saturation, and could decrease it by a factor of greater-than-or-equal-to 30 even when the inlet concentration was saturated

Johnston, C. D. and A. Desvignes 2003. Evidence for biodegradation and volatilisation of dissolved petroleum hydrocarbons during in situ air sparging in large laboratory columns. Water, Air and Soil Pollution25-33.
Reference ID: 110
Keywords: air sparging/BIODEGRADATION/columns/hydrocarbon/in situ/petroleum/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone

Kawamoto, K., P. Moldrup, P. Schjonning, B. V. Iversen, D. E. Rolston, and T. Komatsu 2006. Gas transport parameters in the vadose zone: Gas diffusivity in field and lysimeter soil profiles. Vadose Zone Journal 5:1194-1204.
Reference ID: 120
Keywords: distribution/gas diffusivities/gas transport/lysimeter/models/porosity/root zone/soil gas/transport/unsaturated zone/volatilization/ZONE
Notes: Generally on the unsaturated zone
Abstract: The main soil-gas transport parameters, gas diffusivity and air permeability, and their variations with soil type and air-filled porosity play a key role in soil-gas emission problems including volatilization of toxic chemicals at polluted sites and the production and emission of greenhouse gases. Only limited information on soil-gas transport parameters across the vadose zone is available, especially for soil layers below the root zone. In a series of studies, we developed new data for the soil-gas transport parameters in different soil profiles and tested existing and new predictive models. In this first study, we measured gas diffusivity at different soil-water matric potentials on undisturbed soil samples for three lysimeter soil profiles down to 1.4-m depth and for two field soil profiles down to 5.6-m depth, representing a total of 22 different soil layers with soil texture ranging from sand to sandy clay loam. Five commonly used predictive gas diffusivity models were tested. The three-porosity model (TPM) performed best for both shallow and deep soil layers. The tortuosity-connectivity parameter X in the TPM varied with soil texture and pore size distribution, and the TPM predicted well the depth distributions of measured soil-gas diffusivities. The TPM also requires less detailed information on the soil-water characteristic curve than other well-performing predictive models, and is therefore recommended for predicting variations in soil-gas diffusivity within the vadose zone

Kechavarzi, C., K. Soga, T. Illangasekare, and P. Nikolopoulos 2008. Laboratory study of immiscible contaminant flow in unsaturated layered sands. Vadose Zone Journal 7:1-9.
Reference ID: 99
Keywords: contamination/distribution/hydrophobic/modeling/permeability/prediction/saturati

on/SPILL/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone
Abstract: Little quantitative experimental data are available describing the behavior of immiscible contaminants in unsaturated heterogeneous porous media. Such data are, however, essential to the fundamental understanding of the processes governing nonaqueous phase liquid behavior and for the validation of modeling tools. The effect of macroheterogeneity on light nonaqueous phase liquid (LNAPL) flow and distribution in the unsaturated zone was investigated experimentally by simulating LNAPL spills in layered soil systems consisting of sands with various textures. Two multiphase flow experiments were conducted in a two-dimensional flume (180 x 120 x 8 cm). The vertical distribution of water and LNAPL pressure were measured using hydrophilic and hydrophobic tensiometers. An image analysis technique was used to estimate the saturation distribution of the fluids in a two-dimensional vertical plane. The experiments show that LNAPL entrapment, which contributes to long-term soil and water contamination, depends strongly on the initial water saturation and water pressure at the layer interfaces and on the texture contrasts between the soil layers, which lead to permeability and capillary barrier effects. Thus, the knowledge of the initial water pressure and saturation distribution in unsaturated layered soil formations is critical to the correct prediction of LNAPL infiltration and drainage

Kirtland, B. C., C. M. Aelion, and P. A. Stone 2005. Assessing in situ mineralization of recalcitrant organic compounds in vadose zone sediments using delta C-13 and C-14 measurements. Journal of Contaminant Hydrology 76:1-18.
Reference ID: 107
Keywords: attenuation/BIODEGRADATION/C14/concentration/hydrocarbon/in situ/methane/methods/monitored natural attenuation/monitoring/NATURAL ATTENUATION/organic compounds/organic matter/prediction/respiration/TCE/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone
Abstract: Few techniques exist to measure the biodegradation of recalcitrant organic compounds such as chlorinated hydrocarbons (CHC) in situ, yet predictions of biodegradation rates are needed for assessing monitored natural attenuation. Traditional techniques measuring O-2, CO2, or chemical concentrations (in situ respiration, metabolite and soil air monitoring) may not be sufficiently sensitive to estimate biodegradation rates for these compounds. This study combined isotopic measurements (C-14 and delta(13)C Of CO2 and delta(13)C of CHCs) in conjunction with traditional methods to assess in situ biodegradation of perchloroethylene (PCE) and its metabolites in PCE-contaminated vadose zone sediments. CHC, ethene, ethane, methane, O-2, and CO2 concentrations were measured over 56 days using gas chromatography (GC). 613C of PCE, trichloroethylene (TCE) and cis- 1,2-dichloroethylene (DCE), delta(13)C and C-14 of vadose zone CO2 and sediment organic matter, and delta(13)C, C-14, and deltaD of methane were measured using a GC-isotope ratio mass spectrometer or accelerator mass spectrometer. PCE metabolites accounted for 0.2% to 18% of CHC concentration suggesting limited reductive dechlorination. Metabolites TCE and DCE were significantly enriched in C-13 with respect to PCE indicating metabolite biodegradation. Average delta(13)C-CO2 in source area wells (-23.5parts per thousand) was significantly lower

compared to background wells (- 18.4%o) indicating CHC mineralization. Calculated CHC mineralization rates were 0.003 to 0.01 mg DCE/kg soil/day based on lower C-14 values Of CO2 in the contaminated wells (63% to 107% modem carbon (pMC) relative to the control well (117 pMC). Approximately 74% of the methane was calculated to be derived from in situ CHC biodegradation based on the C-14 measurement of methane (29 pMC). C-14-CO2 analyses was a sensitive measurement for quantifying in situ recalcitrant organic compound mineralization in vadose zone sediments for which limited methodological tools exist. (C) 2004 Elsevier B.V All rights reserved

Little, J. C., J. M. Daisey, and W. W. Nazaroff 1992. Transport of Subsurface Contaminants Into Buildings. Environmental Science & Technology 26:2058-2066.
Reference ID: 116
Keywords: transport/unsaturated zone/VOCs/ZONE
Notes: Generally on the unsaturated zone

Mchugh, T. E., J. A. Connor, and F. Ahmad 2004. An empirical analysis of the groundwater-to-indoor-air exposure pathway: The role of background concentrations in indoor air. Environmental Forensics 5:33-44.
Reference ID: 111
Keywords: attenuation/concentration/groundwater/guidance/hydrocarbon/models/organic compounds/petroleum/transport/unsaturated zone/vapor/VOCs/volatilization/ZONE
Notes: Generally on the unsaturated zone
Abstract: To further our understanding of the groundwater-to-indoor-air exposure pathway, a database of 270 paired groundwater and indoor air measurements of volatile organic compounds (VOCs) from 31 sites has been compiled and analyzed. Using regression analyses, these data have been analyzed to (1) detect evidence of indoor air impacts from dissolved petroleum hydrocarbons or chlorinated solvents in underlying groundwater, (2) estimate the true attenuation factor for volatilization from groundwater to indoor air, and (3) assess the utility of popular groundwater-to-indoor-air transport models for evaluating this exposure pathway. Key findings include the following: (1) >95% of the indoor air concentrations fall within or below the range of national background indoor air values; (2) there is no correlation between petroleum constituent concentrations measured in groundwater and the concentrations of these VOCs in indoor air of overlying structures; and (3) for chlorinated solvent cases, a correlation between groundwater and overlying indoor air is observed; however, the average true attenuation factor, after correcting for background, is approximately 6.9 x 10(-5), well below the default I x 10(-3) value used by USEPA Vapor Intrusion Guidance to determine groundwater screening levels

Mills, W. B., S. Liu, M. C. Rigby, and D. Brenner 2007. Time-variable simulation of soil vapor intrusion into a building with a combined crawl space and basement. Environmental Science & Technology 41:4993-5001.
Reference ID: 105
Keywords: advection/chorinated solvent/concentration/diffusion/groundwater/Laplace/models/PLUME/prediction/transport/unsaturated zone/vapor/vapour intrusion/ZONE
Notes: Generally on the unsaturated zone
Abstract: A time-variable one-dimensional model (called ViM for Vapor Intrusion Model)to predict indoor vapor concentrations in a dwell-

ing with a combined basement and crawl space has been developed. ViM predicts vapor concentrations in each of the three compartments. Volatile chemicals that intrude into the dwelling are assumed to originate from soil, groundwater (where an attenuating plume is simulated), or ambient air. Processes included in the model are advection, diffusion, biodecay, and adsorption in the soil column; transport by diffusion and advection into individual crawl space and basement compartments; advection from each compartment into an overlying dwelling space; and exchange of ambient air and indoor air. The time-variable concentration fields are solved by first transforming the partial and ordinary differential equations into Laplace space, solving the resulting ordinary differential equations or algebraic equations, and numerically inverting those equations. This approach was an expedient way of handling the coupling between the subsurface and the dwelling. ViM was applied to a building (Building 20) located at the former Moffett Field Naval Air Station, in Mountain View, CA. The building is a former bachelor officer's quarters. The shallow groundwater beneath the building is contaminated with a number of volatile chemicals, including trichloroethene, cis-1,2-dichloroethene, and trans-1,2-dichloroethene, all of which were simulated. Using indoor air data collected in 2003-2004, and other field data collected prior to that time, the accuracy of the model's predictions was demonstrated. ViM's results were also compared against a version of the steady-state Johnson and Ettinger model (1) that was modified to accommodate a dwelling with a combined crawl space and basement (called the JEM model in this paper). The predictions from the JEM model were consistently higher than the predictions from ViM, but still near the upper range of the observed data

Molins, S., K. U. Mayer, R. T. Amos, and B. A. Bekins 2009. Vadose zone attenuation of organic compounds at a crude oil spill site — Interactions between biogeochemical reactions and multicomponent gas transport. Journal of Contaminant Hydrology.
Reference ID: 102
Keywords: attenuation/CRUDE-OIL/gas transport/organic compounds/SPILL/transport/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone

Neale, C. N., J. B. Hughes, and C. H. Ward 2000. Impacts of unsaturated zone properties on oxygen transport and aquifer reaeration. Ground Water 38:784-794.
Reference ID: 127
Keywords: AQUIFER/bioattenuation/diffusive flux/GROUNDWATER/hydrocarbon/oxygen/oxygen transport/PLUME/transport/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone
Abstract: This study investigated the unsaturated zone properties that affect ground water reaeration (i.e., the diffusive flux of oxygen through the unsaturated zone and into an aquifer system), Laboratory column experiments were undertaken to quantify oxygen flux into anaerobic ground water as a function of soil type, soil water content, soil oxygen demand, and unsaturated zone thickness. Soils used in these studies included coarse sand, sand, loamy fine sand, fine sandy loam, silt, silty flay loam, bentonite, kaolin, and peat, The results showed that reaeration flux rates ranging from 11,000 to 12,000 mg/m(2)-day u ere possible under conditions;;;: typical of the natural environment. Soil water content provided the greatest resistance to oxygen transport in the unsaturated zone while the remaining factors of soil type, soil oxygen de-

mand, and unsaturated zone thickness did not significantly inhibit reaeration flux into ground water. An unsaturated zone transport model based on Fick's second law and gas-liquid interfacial mass transport was developed and showed good agreement with the experimental results derived from the column studies. The results of this study suggest that unsaturated zone reaeration of anaerobic ground water may be a contributing factor in controlling the steady-state size and shape of hydrocarbon plumes and incorporating reaeration into ground water models-based on unsaturated zone properties-may allow for a more accurate representation of bioattenuation reactions taking place in subsurface environments

Oostrom, M., J. H. Dane, and T. W. Wietsma 2006. A review of multidimensional, multifluid intermediate-scale experiments: Nonaqueous phase liquid dissolution and enhanced remediation. Vadose Zone Journal 5:570-598.
Reference ID: 101
Keywords: air sparging/BIOREMEDIATION/dissolution/LIQUIDS/models/NAPL/remediation/transport/transport processes/unsaturated zone/vapor/ZONE
Notes: Generally on the unsaturated zone
Abstract: A review is presented of original multidimensional, intermediate-scale experiments involving NAPLs (nonaqueous phase liquids). The experimental approach at this scale can be viewed as an important intermediary between column studies and field trials. The primary advantage of intermediate-scale flow cell experiments is that field-scale processes can be simulated under controlled conditions. The experiments are frequently conducted to provide data sets to test and verify numerical and analytical flow and transport models. The controlled setting and laboratory instrumentation reduces the uncertainty in parameter estimation, allowing comparisons between simulation and experimental results to focus on flow and transport processes. A total of about 125 original contributions were identified and reviewed. Depending on the main topic of NAPL experimental research, the papers were divided into the following sections: (i) aqueous dissolution, (ii) enhanced remediation, (iii) flow behavior, (iv) quantification, and (v) imaging. In this review, the first two categories are discussed and suggestions for future research are provided. In a companion review, experimental work related to the other three categories is investigated. The aqueous dissolution category includes experiments in which pooled and entrapped NAPL removal occurs due to water flushing. The enhanced remediation section contains experimental contributions investigating surfactant flushing, alcohol flushing, surfactant and alcohol flushing combinations, dense brine strategies, hydraulic NAPL recovery, soil vapor extraction, air sparging, heat-based remediation, bioremediation, and other techniques

Ostendorf, D. W. and D. H. Kampbell 1990. Bioremediated Soil Venting of Light-Hydrocarbons. Hazardous Waste & Hazardous Materials 7:319-334.
Reference ID: 117
Keywords: advection/analytical solution/BIODEGRADATION/bioreactor/capillary fringe/concentration/contamination/degradation/hydrocarbon/kinetics/sorption/SPILL/unsaturated zone/vapor/ZONE
Notes: Generally on the unsaturated zone
Abstract: The effectiveness and feasibility of bioremediated soil venting

of light hydrocarbons in the unsaturated zone was investigated. Degradation mechanics were considered as a one dimensional balance of storage, linear sorption, vertical advection, and Michaelis-Menton kinetics. The resulting analytical solution was tested successfully against field performance data of an unsaturated clay soil bioreactor for a propellant waste gas mixture of propane, n-butane, and isobutane. A series of venting simulations was run to assess the biodegradation of vapors above an aviation gasoline spill in sandy soil at Traverse City, Michigan, based on field and microcosm estimates of the kinetic parameters. Acclimated, nutrient rich soil effectively and feasibly reduced effluent vapor concentration from the strong influent concentration associated with dispersed residual gasoline in the contaminated capillary fringe. Aggregated residual contamination required a stronger airflow for a longer duration while natural kinetics were too slow for feasible and effective treatment by bioremediated soil venting at Traverse City

Pasteris, G., D. Werner, K. Kaufmann, and P. Hohener 2002. Vapor phase transport and biodegradation of volatile fuel compounds in the unsaturated zone: A large scale lysimeter experiment. Environmental Science & Technology 36:30-39.
Reference ID: 126
Keywords: aerobic/aerobic biodegradation/AQUIFER/BIODEGRADATION/diffusion/groundwater/hydrocarbon/lysimeter/microorganisms/MTBE/NAPL/NAPL saturation/petroleum/saturation/tracer/transport/unsaturated zone/vapor/volatilization/ZONE
Notes: Generally on the unsaturated zone
Abstract: The vapor phase transport and biodegradation of typical fuel compounds including volatile petroleum hydrocarbons and methyl tert-butyl ether (MTBE) was studied in a large scale field lysimeter representing a 2.3 m thick sandy unsaturated zone over a gravel aquifer. A mixture of 13 fuel compounds with MTBE (5%) was placed at a defined depth in the unsaturated zone to obtain a homogeneous source zone with a residual NAPL saturation. The upward and downward transport of fuel vapors and the biodegradation by indigenous microorganisms were monitored during 70 days. Using tracers in water and NAPL, it was shown that fuel compounds were transported by vapor phase diffusion only. All fuel compounds except MTBE disappeared from the lysimeter below the analytical detection limits within 70 days. MTBE accumulated in groundwater but volatilized from the unsaturated zone. First-order biodegradation rates were estimated in the unsaturated zone to range from <0.05 d(-1) for MTBE up to 8.7 d(-1) for octane. Aerobic biodegradation of degradable fuel compounds to CO2 started without any lag phase and removed about 3 times more fuel mass than volatilization. The study illustrates the recalcitrance of MTBE vapors compared to other fuel vapors, leading to a significant groundwater pollution with MTBE

Patterson, B. M. and G. B. Davis 2008. An in situ device to measure oxygen in the vadose zone and in ground water: Laboratory testing and field evaluation. Ground Water Monitoring and Remediation 28:68-74.
Reference ID: 112
Keywords: air sparging/assessment/BIODEGRADATION/BIOREMEDIATION/calibration/concentration/distribution/GROUND-WATER/hydrocarbon/in situ/laboratory experiments/microorganisms/monitoring/oxygen/unsaturated zone/ZONE

Notes: Generally on the unsaturated zone
Abstract: Oxygen probes developed to measure in situ oxygen concentrations in gaseous and aqueous environments were evaluated in laboratory tests and during long-term field evaluation trials at contaminated sites. The oxygen probes were shown to have a linear calibration and to be accurate compared to conventional dissolved oxygen electrodes and gas chromatography, both of which require labor-intensive sample collection and processing. The probes, once calibrated, required no maintenance or recalibration for up to a period of 7 years in low-oxygen environments, demonstrating long-term stability. Times to achieve 90% of the stabilized concentration (t(90)) after a step change in aqueous oxygen concentration were 100-120 min in laboratory experiments and up to 180 min in field experiments, which is adequate for monitoring subsurface changes. Field application data demonstrated that the oxygen probes could monitor oxygen concentrations in hydrocarbon-contaminated ground water to a depth of 20 m below the water table or in pyritic vadose zones over extended periods. During bioremediation field trials, oxygen monitoring enabled estimation of oxygen utilization rates by microorganisms and hydrocarbon biodegradation rates. Also, probes were able to monitor the development of ground water desaturation during air sparging trials, enabling the automated assessment of the distribution of injected air

Ronen, D., E. R. Graber, and Y. Laor 2005. Volatile organic compounds in the saturated-unsaturated interface region of a contaminated phreatic aquifer. Vadose Zone Journal 4:337-344.
Reference ID: 104
Keywords: AQUIFER/concentration/diffusion/groundwater/methods/monitoring/organic compounds/passive multilayer sampler/saturated-unsaturated interface region/TCE/temporal variation/unsaturated zone/vapor/ZONE
Notes: Generally on the unsaturated zone
Abstract: Three volatile organic compound (VOC) field profiles were obtained during a period of 13 mo with a passive multilayer sampler (MLS) from a monitoring well located in the VOC-contaminated phreatic Coastal Plain aquifer of Israel in the Tel Aviv area. The profiles presented here are unique in that they span both the and unsaturated zones, through the saturated - unsaturated interface region (SUIR), and represent VOC concentrations from a single borehole. In groundwater just below the water table, the major contaminant, trichloroethylene TCE), was present in concentrations up to 260 000 mu g/L water, and in the unsaturated zone just above the water table, in concentrations up to 124 000 mu g/L air. Other contaminants detected in high concentrations (as high as several thousands of mu g/L) included tetrachloroethylene PCE), cis-1,2-dichloroethylene (cis-1,2-DCE) and 1,1-dichloroethylene (1,1-DCE). In the three profiles, TCE and PCE concentrations were greatest at the water table and decreased with increasing distance from the water table both into the saturated and unsaturated zones. Temporal variations in maximal TCE vapor concentrations ranging from 44 000 to 124 000 mu g/L air were also observed between profiles. The passive diffusion sampling characteristic of the MLS makes it possible to obtain unmixed vertical samples such that, for example, differences as great as 24 000 mu g TCE/L air can be measured in consecutive samples located only 12 cm apart in the unsaturated zone. The vertical detail is unique compared with other field sampling methods. Vertical detail is of utmost importance in interface regions, such as the SUIR, where water

content in both the unsaturated and saturated zones varies significantly with depth, time, and space

Thorbjorn, A., P. Moldrup, H. Blendstrup, T. Komatsu, and D. E. Rolston 2008. A Gas Diffusivity Model Based on Air-, Solid-, and Water-Phase Resistance in Variably Saturated Soil. Vadose Zone Journal 7:1230-1240.
Reference ID: 118
Keywords: assessment/diffusion/diffusion coefficient/fate/gas diffusivities/gas transport/models/p/porosity/prediction/risk assessment/transport/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone
Abstract: Gas diffusion in soil is governed by the gas diffusion coefficient (D-p) and its variation with air-filled porosity (epsilon). Accurate or an upper-limit (risk assessment standpoint) prediction of D-p(epsilon) is essential when carrying out gas transport and fate calculations. We developed a D-p(epsilon) model for relatively unstructured soil separating the individual resistance of soil air, solids, and moisture to D-p. Assuming the total soil resistance to gas diffusion can be described by three power-law terms representing air-content reduction, solids-induced tortuosity,and water-induced disconnectivity yields the socalled Soil Air Phase Individual Resistances (SAPHIR) model. The SAPHIR model predicts D-p as a function of the actual epsilon, a particle shape factor (p), the volumetric soil water content (theta), and a water-blockage factor (w). The D-p(epsilon) was measured at different theta on repacked and undisturbed soil samples. The new D-p data combined with literature data implied values of p in the interval 0 to 1 and w in the interval 1 to 7, depending on particle diameter, fine-particle content, and compaction. Tested against 810 measurements of D-p on undisturbed soils, SAPHIR with average values of p = 0.6 and w = 3 performed equally well or better than traditional models; however, the test implied a need for different parameter values for more sandy soils (lower p and higher w), as well as for more compacted soils (lower p)

Tillman, F. D. and J. W. Weaver 2007. Temporal moisture content variability beneath and external to a building and the potential effects on vapor intrusion risk assessment. Science of the Total Environment 379:1-15.
Reference ID: 108
Keywords: assessment/concentration/migration/modeling/models/risk assessment/unsaturated zone/vapor/ZONE
Notes: Generally on the unsaturated zone
Abstract: Migration of vapors from organic chemicals residing in the subsurface into overlying buildings is known as vapor intrusion. Because of the difficulty in evaluating vapor intrusion by indoor air sampling, models are often employed to determine if a potential indoor inhalation exposure pathway exists and, if such a pathway is complete, whether long-term exposure increases the occupants' risk for cancer or other toxic effects to an unacceptable level. For site-specific vapor intrusion assessments, moisture content is, at times, determined from soil cores taken in open spaces between buildings. However, there is little published information on how moisture content measured outside a building structure compares with the moisture content directly beneath the building - where the values are most critical for vapor intrusion assessments. This research begins to address these issues by investigating the movement of soil moisture next to and beneath a building at a contaminated field site and determining the effect on vapor intrusion risk assessment. A two-dimensional, variably-saturated water flow model,

HYDRUS-2D, is used with 2 years of hourly, local rainfall data to simulate subsurface moisture content in the vicinity of a hypothetical 10 x 10-m building slab at a contaminated field site. These moisture content values are used in vapor intrusion risk assessment simulations using the Johnson and Ettinger model with instantaneous and averaged moisture contents. Results show that vapor intrusion risk assessments based on moisture content determined from soil cores taken external to a building structure may moderately-to-severely underestimate the vapor intrusion risk from beneath the structure. Soil under the edges of a slab may be influenced by rainfall events and may show reduced vapor intrusion risk as a consequence. Data from a building instrumented with subslab moisture probes showed results similar to the modeling, but with a smaller difference between the subslab and outside average moisture contents. These results indicate that, depending upon the point of vapor ingress into the structure and soil type, risk-based cleanup concentrations based on outside-of-slab or default moisture content values may not be predictive of exposure to organic vapors from below a building. (c) 2007 Elsevier B.V. All rights reserved

Tindall, J. A., M. J. Friedel, R. J. Szmajter, and S. M. Cuffin 2005. Part 1: Vadose-zone column studies of toluene (enhanced bioremediation) in a shallow unconfined aquifer. Water Air and Soil Pollution 168:325-357.
Reference ID: 103
Keywords: aerobic/air sparging/AQUIFER/BACTERIA/BIOREMEDIATION/columns/degradation/hydrocarbon/hydrogen peroxide/in situ/respiration/soil gas/SPILL/toluene/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone
Abstract: The objectives of the laboratory study described in this paper were (1) to determine the effectiveness of four nutrient solutions and a control in stimulating the microbial degradation of toluene in the unsaturated zone as an alternative to bioremediation methodologies such as air sparging, in situ vitrification, or others (Part I), and (2) to compare the effectiveness of the addition of the most effective nutrient solution from Part I (modified Hoagland type, nitrate-rich) and hydrogen peroxide (H2O2) on microbial degradation of toluene for repeated, simulated spills in the unsaturated zone (Part II). For Part 1, fifteen columns (30-cm diameter by 150-cm height), packed with air-dried, 0.25-mm, medium-fine sand, were prepared to simulate shallow unconfined aquifer conditions. Toluene (10 mL) was added to the surface of each column, and soil solution and soil gas samples were collected from the columns every third day for 21 days. On day 21, a second application of toluene (10 mL) was made, and the experiment was run for another 21 days. Solution 4 was the most effective for microbial degradation in Part I. For Part II, three columns were designated nutrient-rich 3-day toluene columns and received toluene injections every 3 days; three columns were designated as nutrient-rich 7-day columns and received toluene injections every 7 days; and two columns were used as controls to which no nutrient was added. As measured by CO2 respiration, the initial benefits for aerobic organisms from the O-2 enhancement were sustained by the bacteria for only a short period of time (about 8 days). Degradation benefits from the nutrient solution were sustained throughout the experiment. The O-2 and nutrient-enhanced columns degraded significantly more toluene than the control columns when simulating repeated spills onto the unsaturated zone, and demonstrated a potentially effective in situ bioremediation technology when used immediately or within days after a spill. The combined usage of H2O2 and nitrate-rich nutri-

ents served to effectively maximize natural aerobic and anaerobic metabolic processes that biodegrade hydrocarbons in petroleum-contaminated media. Applications of this technology in the field may offer economical advantages to other, more intrusive abatement technologies

Turcu, V. E., S. B. Jones, and D. Or 2005. Continuous soil carbon dioxide and oxygen measurements and estimation of gradient-based gaseous flux. Vadose Zone Journal 4:1161-1169.
Reference ID: 122
Keywords: carbon dioxide/concentration/diffusion/diffusion coefficient/distribution/methods/oxygen/respiration/unsaturated zone/ZONE
Notes: Generally on the unsaturated zone
Abstract: The magnitude and dynamics of soil gaseous fluxes play critical roles in the global gas balance; yet, these processes are not captured at sufficient temporal resolution by standard methods based on periodic sampling and surface chamber measurements. A novel method for continuous measurement of soil surface gas fluxes based on subsurface CO2 and O-2 concentration gradient measurements was developed. We tested the gradient-based method under steady- and transient-state soil water content and temperature conditions and compared results with a state-of-the-art surface chamber CO2 flux system. The new aspects of the method include fast-response sensors installed in the soil profile providing continuous record of concentration gradients coupled with concurrent estimates of water content-dependent gaseous diffusion coefficient enabling calculation of surface gaseous fluxes. Low-cost infrared sensors were used for CO2 concentration measurements, and galvanic cells for O-2 measurements. An imposed CO2 concentration gradient in a dry soil column resulted in a quasilinear CO2 concentration profile and surface CO2 flux in agreement with chamber-measured fluxes. A series of continuous concentration measurements under variable water content conditions and wetting events showed agreement with surface chamber measurements. Within several days of surface wetting, soil CO2 concentrations attained 10 mL L-1, one order of magnitude higher than the ambient concentrations, whereas O-2 concentrations decreased. The gradient-based approach minimizes soil surface perturbations and provides insights into subsurface soil CO2 and O-2 dynamics and the distribution and magnitude of soil respiration processes as related to soil environmental factors. The subsurface gradient-based measurement system represents an order-of-magnitude reduction in cost compared with research-grade surface chamber devices

Werner, D., P. Grathwohl, and P. Hohener 2004. Review of field methods for the determination of the tortuosity and effective gas-phase diffusivity in the vadose zone. Vadose Zone Journal 3:1240-1248.
Reference ID: 119
Keywords: assessment/diffusion/diffusion coefficient/in situ/methods/modeling/porosity/prediction/remediation/risk assessment/tortuosity/tracer/unsaturated zone/VOLUME/ZONE
Notes: Generally on the unsaturated zone
Abstract: Modeling the gas exchange flux between soil and the atmosphere, risk assessment, and the evaluation of remediation strategies at contaminated sites require the knowledge of gas-phase diffusivities in the We review methods to measure the tortuosity factor or the effective gas-phase diffusion coefficient in situ. The strong dependency of these parameters on the structure and volume of the air-filled pore space in the subsurface calls for an accurate and robust in situ measurement. A

variety of approaches have been proposed during the last decades, each based on the observation and interpretation of gaseous tracer diffusion in near-surface soils or the deeper vadose zone under various initial and boundary conditions. We briefly describe the conceptual basis and experimental setup of each method and give insight into error propagation. We then discuss 115 effective diffusion coefficients D-e compiled from the original method papers and applications. In situ methods and laboratory measurements on undisturbed soil cores yield comparable results. The Penman relationship, D-e/D-m = 0.66theta(a), sets an upper limit for the field-determined effective diffusion coefficient in the case of uniform porosity. The Moldrup relationship, D-e/D-m = theta(a)(2.5)/theta(t), originally proposed for sieved and repacked soils, gave the best predictions of several porosity-based relationships, but the relative deviation between observed and predicted D-e can be substantial. Therefore, the application of such a relationship for the site-specific modeling of gas-phase diffusion should be justified with in situ measurements, especially in heterogeneous environments

B 3.2.2 Opløsning og transport af LNAPL

Arey, J. S. and P. M. Gschwend 2005. Estimating partition coefficients for fuel-water systems: Developing linear solvation energy relationships using linear solvent strength theory to handle mixtures. Environmental Science & Technology 39:2702-2710.
Reference ID: 71
Keywords: dissolution/partitioning/raoult's law/transport
Notes: Dissolution and transport of LNAPL
Abstract: In many environmental transport problems, organic solutes partition between immiscible phases that consist of liquid mixtures. To estimate the corresponding partition coefficients, we evaluated the efficacy of combining linear solvation energy relationships (LSERs) developed for pure 1:1 systems via application of linear solvent strength theory. In this way, existing LSERs could be extended to treat solute partitioning from gasoline, diesel fuel, and similar mixtures into contacting aqueous mixtures. Unlike other approaches, this method allowed prediction of liquid-liquid partition coefficients in a variety of fuel-water systems for a broad range of dilute solutes. When applied to 37 polar and nonpolar solutes partitioning between an aqueous mixture and 12 different fuel-like mixtures (many including oxygenates), the root-mean-squared error was a factor of similar to 2.5 in the partition coefficient. This was considerably more accurate than application of Raoult's law for the same set of systems. Regulators and scientists could use this method to estimate fuel-water partition coefficients of novel additives in future fuel formulations and thereby provide key inputs for environmental transport assessments of these compounds

Fagerlund, F. and A. Niemi 2003. Multi-constituent modelling of a gasoline spill using T2VOC numerical simulator. (Anonymous,).
Reference ID: 195
Keywords: dissolution/modeling/SPILL/T2VOC/transport
Notes: Dissolution and transport of LNAPL

Gaganis, P., H. K. Karapanagioti, and V. N. Burganos 2002. Modeling multicomponent NAPL transport in the unsaturated zone with the constituent averaging technique. Advances in Water Resources 25:723-732.
Reference ID: 67
Keywords: dissolu-

tion/fate/hydrocarbon/kerosene/modeling/NAPL/partitioning/solubility/transport/unsaturated zone/ZONE
Notes: Dissolution and transport of LNAPL
Abstract: Using composite constituents to simulate the average behavior and fate of groups of individual hydrocarbons in the subsurface may provide the means for dealing with mixtures of tens or hundreds of individual hydrocarbons while reducing the computational cost. There are two additional sources of uncertainty associated with this technique, namely, the time dependence of the effective properties of a composite constituent due to temporal composition changes, and the approximation in determining their effective property values. In this work, an approach to limit these sources of uncertainty is described and certified with published experimental data, that involved an artificially mixed kerosene. An inverse analysis is used to estimate the effective property values of composite constituents, and a methodology is introduced for optimizing component grouping, based on the minimization of an objective function. Aqueous solubility is found to be the optimal grouping criterion for the multicomponent organic mixture considered here. Under the assumption of equilibrium partitioning among phases, the effective property values of the composite constituents are expressed in terms of the property values of the member components using a stepwise inverse analysis. Simple arithmetic averages are found to provide poor approximations to the effective group properties and alternative schemes are proposed, based on experimental data. (C) 2002 Elsevier Science Ltd. All rights reserved

Grathwohl, P. Formulierung einer verfahrensempfehlung zur bestimmung der emission leichflüchtiger organisher schadstoffe (LCKW, BTEX etc.) aus kontaminierten böden. 1996. (GENERIC)
Ref Type: Report
Ref ID: 233
Keywords: BTEX/dissolution/NAPL/transport
Notes: Dissolution and transport of LNAPL

Keller, A. A. and S. Sirivithayapakorn 9999. Pore Scale Determination of the Rate of NAPL Dissolution or Volatilization. (Anonymous,).
Reference ID: 68
Keywords: dissolution/flow rate/modeling/NAPL/NAPL saturation/saturation/transport/volatilization
Notes: Dissolution and transport of LNAPL
Abstract: The objective of this project was to experimentally observe the dissolution and volatilization processes at the pore scale as a function of saturation and pore space geometry for various NAPLs, and then to determine how the inter-phase mass transfer coefficient, kp, is functionally related to the observed contact area, ac and how this correlates with NAPL saturation, Sn. The hypothesis was that the relationship between ac and Sn varies with time, as the mass transfer process proceeds and the shape of the NAPL blob changes, producing a very different effective interfacial area. Using this information, a field-measurable value (Sn) can be used to estimate kp, for applications in numerical modeling. A micromodel setup was used to observe the mass transfer processes within a controlled pore scale geometry, with known fluid flow rates. The images were captured dynamically through a video camera, for numerical processing of the digitized images to determine both NAPL saturation, Sn, and interfacial contact area, ac as a function of time. This information allowed the experimental determination of the mass transfer coefficient, kp, as a function of ac or Sn. Our results indicate that this

relationship is non-linear, but can be expressed as a power function. In addition, the relationship between kp and Peclet number, Pe, is better understood through our theoretical and experimental work

Lookman, R., G. Van der Sterren, G. Vanermen, H. Van De Weghe, J. Gemoets, and A. Alphenaar 9999. Oil characterisation: assessment of composition, risks, degradation and remediation potential of total petroleum hydrocarbons in soil. (Anonymous,).
Reference ID: 70
Keywords: assessment/degradation/dissolution/hydrocarbon/petroleum/remediation/transport
Notes: Dissolution and transport of LNAPL

O'Reilly, K. T., R. I. Magaw, and W. G. Rixey. Predicting the effect of hydrocarbon and hydrocarbon-impacted soil on groundwater. 2001. American Petroleum Institute. (GENERIC)
Ref Type: Report
Ref ID: 196
Keywords: dissolution/groundwater/hydrocarbon/transport
Notes: Dissolution and transport of LNAPL

Park, H. S. 1999. A METHOD FOR ASSESSING SOIL VAPOR INTRUSION FROM PETROLEUM RELEASE SITES: MULTI-PHASE/MULTI-FRACTION PARTITIONING. unknown.
Reference ID: 66
Keywords: dissolution/partitioning/petroleum/raoult's law/release/transport/vapor
Notes: Dissolution and transport of LNAPL
Abstract: A model and spreadsheet-based numeric approximation for computing risk-based soil cleanup level to
be protective of petroleum-contaminated soil to an indoor air exposure pathway is presented. The algorithm
incorporates traditional equilibrium partitioning equations (3 or 4-phase) for the conservation of
mass and volume, as well as Raoult's law convention, and subsequent diffusive and convective transport
mechanisms.

Park, H. S. and C. San Juan 2000. A method for assessing leaching potential for petroleum hydrocarbons release sites: Multiphase and multisubstance equilibrium partitioning. Soil & Sediment Contamination 9:611-632.
Reference ID: 69
Keywords: attenuation/benzene/dissolution/fate/groundwater/henry's law/hydrocarbon/leaching/NAPL/partition coefficient/partitioning/petroleum/prediction/raoult's law/release/solubility/toluene/transport
Notes: Dissolution and transport of LNAPL
Abstract: This article presents the rationale for the mathematical fate and transport model, which has been provided in the accompanying spreadsheet (GWProt). This spreadsheet model may be used as a simple and scientifically defensible regulatory tool for determining the risk-based soil clean up level of petroleum release sites to protect groundwater quality. The model incorporates either a three- or four-phase partitioning equilibrium mechanism, depending on the detection of Non-Aqueous Phase Liquid phase presence mathematically, as well as Raoult's Law convention and default dilution and attenuation factors. A

database of contaminant-specific parameters, including solubility and organic-carbon partition-coefficient, molecular weight, and Henry's Law constant is assembled for benzene, toluene, ethylbenzene, xylenes, and 12 other TPH equivalent carbon fractions. In addition to distributing organic chemicals among aqueous, sorbed solid, air, and NAPL phases, according to traditional partitioning equations, the algorithm incorporates equations for the conservation of mass and volume. A unique solution is obtained by solving a series of mass balance equations simultaneously using the iterative spreadsheet routine built in MICROSOFT EXCEL(TM) Solver - with the restrictions that the volume is conserved and the sum of the mole fractions is equal to one. Sample calculations are presented fora range of parameter values to illustrate the use of the model and the relative leachability of a wide range of representative fuels. Sensitivity analysis was also performed to quantify the effects of uncertainty in the estimates of the key model parameters on model results. Model predictions were compared with the results from a wafer-fuel experiment The noncarcinogenic Hazard Index (HI) for groundwater through direct ingestion was calculated using predetermined oral reference dose (R-fd) values. Applications and limitations of the model are also discussed

Rixey, W. G. and S. Joshi. Dissolution of MTBE from a residually trapped gasoline source - a summary of research results. 2000. (GENERIC)
Ref Type: Report
Ref ID: 232
Keywords: dissolution/MTBE/transport
Notes: Dissolution and transport of LNAPL

Roelofson, F. J., C. Hofstee, G. A. M. van Meurs, J. M. A. Streng, and A. A. Bowker. Modelcode Bronfunctie Olieverontriniging. 2003. Delft Cluster. (GENERIC)
Ref Type: Report
Ref ID: 231
Keywords: dissolution/NAPL/transport
Notes: Dissolution and transport of LNAPL

B 3.2.3 Diffusionsprocesser

Anonymous. Quantifying effective vapor-phase diffusion coefficients. Underground Tank Technology Update . 2000. (GENERIC)
Ref Type: Magazine Article
Ref ID: 225
Keywords: diffusion/diffusion coefficient
Notes: Diffusion processes

Fischer, J. M., R. J. Baker, M. A. Lahvis, and A. L. Baehr 9999. Determination of vapor-phase diffusion coefficients for unsaturated-zone sediments at a gasoline-spill site in Galloway township, New Jersey. unknown.
Reference ID: 42
Keywords: BIODEGRADATION/degradation rates/depth profile/diffusion/diffusion coefficient/heterogeneous media/hydrocarbon/Millington-Quirk equation/models/Stefan-Maxwell equation/unsaturated zone/vapour flux/vapour transport
Notes: Diffusion processes

Grathwohl, P. 1998. Dissolution kinetics. Pp. 136-146 in Diffusion in natural porous media: Contaminant Transport, Sorption/Desorption and Disso-

lution Kinetics (Anonymous,).
Reference ID: 40
Keywords: diffusion/diffusion coefficient/dissolution/fick's law/film diffusion model/kinetics/NAPL/NAPL pool/solubility/transport/two-film diffusion
Notes: Diffusion processes

Grathwohl, P. 1998. Risk assessment - remediation. Pp. 147-160 in Diffusion in natural porous media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics (Anonymous,).
Reference ID: 41
Keywords: assessment/capillary fringe/desorption/diffusion/dissolution/fick's law/flow rate/groundwater flow/kinetics/NAPL pool/raoult's law/remediation/remediation/release rates/risk assessment/transport/VOCs
Notes: Diffusion processes

Hartman, B. The downward migration of vapors. Investigation and remediation . 9999. (GENERIC)
Ref Type: Magazine Article
Ref ID: 226
Keywords: diffusion/migration/vapor/vapour flux/vapour migration
Notes: Diffusion processes

Hartman, B. Some enlightment on density. Investigation and remediation . 9999. (GENERIC)
Ref Type: Magazine Article
Ref ID: 227
Keywords: density/diffusion/NAPL
Notes: Diffusion processes

Hartman, B. The great escape (from the UST). Investigation and remediation . 9999. (GENERIC)
Ref Type: Magazine Article
Ref ID: 228
Keywords: diffusion/henry's constant/henry's law/ideal gas law/MTBE/UST/vapor/vapour/vapour migration
Notes: Diffusion processes

Hartman, B. The upward migration of vapors. Investigation and remediation . 9999. (GENERIC)
Ref Type: Magazine Article
Ref ID: 229
Keywords: contamination/diffusion/migration/vapor/vapour flux/vapour migration
Notes: Diffusion processes

Kruse, C. W., P. Moldrup, and N. Iversen 1996. Modeling diffusion and reaction in soils .2. Atmospheric methane diffusion and consumption in a forest soil. Soil Science 161:355-365.
Reference ID: 39
Keywords: concentration/diffusion/diffusion coefficient/gas diffusivities/methane/modeling/ZONE
Notes: Diffusion processes
Abstract: A mixed hardwood forest with a maximum potential atmospheric methane consumption at 4 to 6 cm depth was investigated. Vertical variation of soil-water content, gas diffusivity and atmospheric

methane uptake was measured with high spatial resolution in intact soil cores (2-5 cm depth intervals), Gas diffusivity increased rapidly with decreasing soil-water potential and a linear relationship between gas diffusivity, and the logarithm to the volumetric soil-water content was found (R(2) greater than or equal to 0.98), Using this relationship in a simple, dynamic diffusion-reaction model, the vertical methane concentration profiles in intact soil cores were simulated, Only diffusion of methane in the soil air and variable methane consumption with depth was considered in the model. An excellent agreement between simulated and measured methane profiles indicated that a main control of methane consumption in non-waterlogged soils is methane diffusion in the soil air, Simulated methane uptake rates, calculated by summing up the methane oxidation at each 1-cm-depth interval, agreed well. with measured methane fluxes into the soil cores, Model sensitivity analyses showed an accurate estimation of the effective gas diffusion coefficient at and above the zone of maximum methane consumption td be the most critical parameter for a realistic simulation of methane concentration profiles and total uptake rates

Laursen, S. 1991. On Gaseous-Diffusion of Co2 in the Unsaturated Zone. Journal of Hydrology 122:61-69.
Reference ID: 52
Keywords: carbon dioxide/diffusion/models/root zone/transport/unsaturated zone/ZONE
Notes: Diffusion processes
Abstract: The extent to which simple diffusion may account for transport of CO2 in the unsaturated zone is investigated. The diffusion equation is solved with a periodic but otherwise arbitrary boundary condition below the root zone and a condition of reflection at the water table. The model is in good agreement with measurements by Reardon et al. and suggests that diffusion is an important process in such cases

Myrand, D., R. W. Gillham, E. A. Sudicky, S. F. Ohannesin, and R. L. Johnson 1992. Diffusion of Volatile Organic-Compounds in Natural Clay Deposits - Laboratory Tests. Journal of Contaminant Hydrology 10:159-177.
Reference ID: 43
Keywords: batch test/benzene/chlorobenzene/concentration/depth profile/diffusion/diffusion coefficient/diffusive processes/distribution/foc/hydrophobic/Kd/organic compounds/sorption/TCE/toluene/transport/VOCs
Notes: Diffusion processes
Abstract: Diffusion coefficients for four volatile organic compounds of environmental concern, benzene, trichloroethylene, toluene and chlorobenzene, were measured on cores of saturated, unweathered glacio-lacustrine clay obtained. from boreholes at a hazardous waste disposal site near Sarnia, Ontario. The core material was transferred to stainless-steel cylinders constructed such that a closed solution reservoir was in contact with the upper surface of the core. The decline in concentration of the organic compounds in the reservoir was monitored over time and diffusion coefficients were determined by fitting a solution of the diffusion equation to the resulting data. The measured diffusion coefficients ranged from 0.3 . 10(-7) to 1.1 . 10(-7) cm2 s-1 for the four compounds, and were in reasonable agreement with values determined from concentration profiles in the clay material beneath the disposal pits. Diffusion coefficients were also calculated on the basis of distribution coefficients (K(d)) determined from laboratory batch tests and from correlations

with the organic carbon content of the clay material (f(oc)). Values calculated on the basis of batch tests were substantially lower than the measured values, and those calculated on the basis of f(oc) exceeded the measured values by almost an order of magnitude. The results indicate that reasonable estimates of diffusion coefficients for hydrophobic organic contaminants, for the purpose of predicting diffusive transport in natural fine-grained geologic materials can be obtained using the diffusion-cell procedure described in this paper. The poor estimate of the diffusion coefficients provided by the f(oc) correlation procedure is consistent with significant sorption onto the mineral phase. Though not investigated, sample disturbance may have contributed to the low values calculated on the basis of batch K(d)'s

Nielsen, S. G. 2004. Gasdifussionskoefficienter i jord. Måleopstilling, prædiktionsmodeller og risikovurdering.
Reference ID: 223
Keywords: diffusion/diffusion coefficient/monitoring/prediction/risk assessment/stochastic modeling
Notes: Diffusion processes

Thorstenson, D. C. and D. W. Pollock 1989. Gas-Transport in Unsaturated Zones - Multicomponent Systems and the Adequacy of Fick Laws. Water Resources Research 25:477-507.
Reference ID: 45
Keywords: Ar/diffusion/diffusive processes/fick's law/gas transport/Klinkenberg effect/Knudsen diffusivity/Knudsen transport/N2/Stefan-Maxwell equation/unsaturated zone/vapour transport/viscous effects/ZONE
Notes: Diffusion processes

Thorstenson, D. C. and D. W. Pollock 1989. Gas-Transport in Unsaturated Porous-Media - the Adequacy of Fick Law. Reviews of Geophysics 27:61-78.
Reference ID: 46
Keywords: diffusion/diffusive flux/dusty gas model/fick's law/gas transport/Klinkenberg effect/Knudsen diffusivity/Knudsen transport/transport processes/unsaturated zone/viscous flux/VOCs
Notes: Diffusion processes

Voudrias, E. A. and C. Y. Li 1993. Benzene Vapor Transport in Unsaturated Soil - Adequacy of the Diffusion Equation. Journal of Hazardous Materials 34:295-311.
Reference ID: 44
Keywords: bezene/BIODEGRADATION/columns/concentration/depth profile/diffusion/Kd/partitioning/retardation factor/sorption/sorption capacity/sorption coefficient/transport/vapor/vapor sorption/vapour transport
Notes: Diffusion processes
Abstract: Experimental data for unsteady state benzene vapor transport in large (10.5 cm x 100 cm) columns packed with dry and wet soil were used to evaluate the adequacy of the diffusion equation. It was shown that the diffusion equation and local equilibrium, accounting for water phase partitioning and linear sorption, adequately described vapor transport in dry soil. In wet soil, however, possible benzene biodegradation resulted in deviation of the diffusion equation from the experimental data. At steady-state, the dimensionless vapor concentration versus distance profile for the dry soil was linear, as opposed to the same pro-

file in the wet soil column. The best fit retardation factor of benzene vapor for wet soil (R = 12) was lower than that for dry soil (R = 46), because of a reduction in vapor sorption capacity, due to competition with water molecules. A vapor phase sorption coefficient, K(d)' = 5.05 cm3/g, was computed for the dry soil and K(d)' = 0 for the wet soil

Wang, G., S. B. F. Reckhorn, and P. Grathwohl 2003. Volatile Organic Compounds Volatilization from Multicomponent Organic Liquids and Diffusion in Unsaturated Porous Media. Vadose Zone Journal 2:692-701.
Reference ID: 47
Keywords: diffusion/diffusion coefficient/evaporation/LIQUIDS/MTBE/organic compounds/partitioning/pressure gradients/raoult's law/toluene/transport/transport processes/unsaturated zone/vapor/VOCs/volatilization/ZONE
Notes: Diffusion processes
Abstract: Vapor phase diffusion is an important transport process in the unsaturated zone affecting evaporation of volatile organic compounds (VOCs) from pure and multicomponent organic liquids. To evaluate some widely used empirical relationships for the estimation of effective diffusion coefficients in the unsaturated zone and to assess the validity of Raoult's Law during aging of organic mixtures, two series of laboratory-scale column experiments were performed using pure toluene, pure methyl tert-butyl ether (MTBE), and two multicomponent "kerosene-type" liquids containing four to seven compounds. The analytical one-dimensional solution of Fick's Second Law described the diffusion process of pure compounds very well in two sands with different water contents. The effective diffusion coefficients obtained correspond well to a recently published empirical relationship (Moldrup et al., 2000); the capacity factors fitted indicate equilibrium partitioning of the solute between gas phase and water. A one-dimensional numerical model based on the combination of Fick's Second Law and Raoult's Law was used to predict the volatilization and the diffusion process from multicomponent organic liquids. Both the vapor phase diffusion process of the VOCs and the aging of the organic mixtures were predicted very well solely on the basis of effective diffusion coefficients estimated from the empirical relationship and assuming an ideal mixture (e.g., an activity coefficient of 1 in Raoult's Law).

Werner, D. Diffusive Partitioning Tracer Test for Nonaqueous Phase Liquid (NAPL) Detection in the Vadose Zone. Ph. D. Theises. 2002.
Reference ID: 224
Keywords: diffusion/diffusion coefficient
Notes: Diffusion processes

Werner, D. and P. Hohener 2002. Diffusive partitioning tracer test for nonaqueous phase liquid (NAPL) detection in the vadose zone. Environmental Science & Technology 36:1592-1599.
Reference ID: 48
Keywords: CFC/columns/concentration/diffusion/in situ/kerosene/lysimeter/NAPL/NAPL partitioning coefficient/NAPL saturation/partitioning/partitioning tracer test/porosity/remediation/saturation/soil gas/tracer/unsaturated zone/ZONE
Notes: Diffusion processes
Abstract: This paper proposes the theory and practical application of a new partitioning tracer test for nonaqueous phase liquid (NAPL) detec-

tion in the vadose zone, which is based on diffusion. A mixture of chlorofluorocarbons as gaseous tracers is injected into the vadose zone to form a point source at the injection point. While the tracers diffuse away, small volumes of gas are withdrawn from the, injection point. The quantitative determination of the NAPL saturation is based on a comparison of the concentration decline of tracers with different air-NAPL partitioning coefficients. The test has been evaluated in laboratory sand columns contaminated with dodecane. NAPL in saturations of 0.8-4% of the total porosity have been quantified in a wide range of different water contents. Actual and measured NAPL saturations calculated as an average from four different tracer pairs agreed within +/- 30%. The new method was successfully used for repeated NAPL quantification in a large-scale field lysimeter contaminated with artificial kerosene. This rapid and inexpensive test is potentially of value for site investigations especially in combination with soil gas measurements, because it requires similar equipment. Possible applications are source delineation and repeated NAPL quantification in situ during a remediation

Werner, D. and P. Hohener 2003. In Situ Method To Measure Effective and Sorption-Affected Gas-Phase Diffusion Coefficients in the unsaturated zone. (Anonymous,).
Reference ID: 49
Keywords: assessment/diffusion/diffusion coefficient/groundwater/in situ/In-situ method/risk assessment/tracer/unsaturated zone/VOCs/ZONE
Notes: Diffusion processes

Werner, D. and P. Hohener 2003. In Situ Method To Measure Effective and Sorption-Affected Gas-Phase Diffusion Coefficients in Soils. Environmental Science & Technology 37:2502-2510.
Reference ID: 50
Keywords: batch test/columns/concentration/diffusion/diffusion coefficient/gas diffusivities/in situ/In-situ method/kerosene/lysimeter/modeling/NAPL/NAPL saturation/partitioning/partitioning tracer test/porosity/reactive transport/remediation/risk assessment/saturation/soil gas/sorption/tortuosity/tracer/transport/unsaturated zone/VOCs/VOLUME/ZONE
Notes: Diffusion processes
Abstract: This paper proposes the theory and practical application of a new partitioning tracer test for nonaqueous phase liquid (NAPL) detection in the vadose zone, which is based on diffusion. A mixture of chlorofluorocarbons as gaseous tracers is injected into the vadose zone to form a point source at the injection point. While the tracers diffuse away, small volumes of gas are withdrawn from the, injection point. The quantitative determination of the NAPL saturation is based on a comparison of the concentration decline of tracers with different air-NAPL partitioning coefficients. The test has been evaluated in laboratory sand columns contaminated with dodecane. NAPL in saturations of 0.8-4% of the total porosity have been quantified in a wide range of different water contents. Actual and measured NAPL saturations calculated as an average from four different tracer pairs agreed within +/- 30%. The new method was successfully used for repeated NAPL quantification in a large-scale field lysimeter contaminated with artificial kerosene. This rapid and inexpensive test is potentially of value for site investigations especially in combination with soil gas measurements,

because it requires similar equipment. Possible applications are source delineation and repeated NAPL quantification in situ during a remediation

Werner, D. and P. Hohener 2003. Diffusive partitioning tracer test for nonaqueous phase liquid (NAPL) detection in the vadose zone. Environmental Science & Technology.
Reference ID: 51
Keywords: CFC/columns/concentration/diffusion/in situ/kerosene/lysimeter/NAPL/NAPL partitioning coefficient/NAPL saturation/partitioning/partitioning tracer test/porosity/remediation/saturation/soil gas/tracer/unsaturated zone/VOLUME/ZONE
Notes: Diffusion processes
Abstract: This paper proposes the theory and practical application of a new partitioning tracer test for nonaqueous phase liquid (NAPL) detection in the vadose zone, which is based on diffusion. A mixture of chlorofluorocarbons as gaseous tracers is injected into the vadose zone to form a point source at the injection point. While the tracers diffuse away, small volumes of gas are withdrawn from the, injection point. The quantitative determination of the NAPL saturation is based on a comparison of the concentration decline of tracers with different air-NAPL partitioning coefficients. The test has been evaluated in laboratory sand columns contaminated with dodecane. NAPL in saturations of 0.8-4% of the total porosity have been quantified in a wide range of different water contents. Actual and measured NAPL saturations calculated as an average from four different tracer pairs agreed within +/-30%. The new method was successfully used for repeated NAPL quantification in a large-scale field lysimeter contaminated with artificial kerosene. This rapid and inexpensive test is potentially of value for site investigations especially in combination with soil gas measurements, because it requires similar equipment. Possible applications are source delineation and repeated NAPL quantification in situ during a remediation

Werner, D. and P. Hohener. Diffusiver gastracertest zur quatifizierung von Schadstoffphasen (öle, lösungsmittel) im ungesättigten untergrund. 9999. (GENERIC)
Ref Type: Report
Ref ID: 230
Keywords: diffusion/gas tracer test/tracer test
Notes: Diffusion processes

B 3.2.4 Transport henover kapillarzonen

Cary, J. W., J. F. Mcbride, and C. S. Simmons 1989. Trichloroethylene Residuals in the Capillary-Fringe As Affected by Air-Entry Pressures. Journal of Environmental Quality 18:72-77.
Reference ID: 56
Keywords: AQUIFER/capillary fringe/columns/TCE/transport
Notes: Transport over capillary fringe
Abstract: Trichloroethylene (TCE) was allowed to drain through columns of soil with the capillary water fringe controlled at various depths. Outflow was measured as well as the TCE content when TCE drainage stopped. Two soils, a sand and a loamy sand, with air-entry values of 23 and 3 cm of water, respectively, were used. The sand with the large air-entry value retained more TCE below the capillary water fringe follow-

ing TCE drainage than the loamy sand with a smaller air-entry pressure. The TCE below the saturated water fringe in both soils varied from almost 7% on a volume basis to <2%. The majority of the TCE in both soils was shown to resist further drainage when water was passed through the soils, suggesting the TCE phase was mostly fragmented. After 10 pore volumes of water was passed, the residual TCE content was 5.5 and 2.1% for the sand and loamy sand, respectively. Even though TCE has a greater specific gravity than water, it was shown in agreement with capillary theory, that TCE will not necessarily sink through the saturated water fringe to the bottom of an aquifer. Its tendency to do so is inversely proportional to the air-entry pressure of the porous mineral phase. The results bring out several practical points for managing contaminated areas.

Davis, G. B. and C. Barber 1989. Methane volatilization from contaminated groundwater - The effects of recharge. Contaminated Transport in Groundwater.
Reference ID: 57
Keywords: capillary fringe/groundwater/methane/transport/volatilization
Notes: Transport over capillary fringe

Klenk, I. D. and P. Grathwohl 2002. Transverse vertical dispersion in groundwater and the capillary fringe. Journal of Contaminant Hydrology 58:111-128.
Reference ID: 59
Keywords: capillary fringe/dispersion/dispersivity/electron acceptor/groundwater/PLUME/TCE/tortuosity/transport
Notes: Transport over capillary fringe
Abstract: Transverse dispersion is the most relevant process in mass transfer of contaminants across the capillary fringe (both directions), dilution of contaminants, and mixing of electron acceptors and electron donors in biodegrading groundwater plumes. This paper gives an overview on literature values of transverse vertical dispersivities alpha(tv) measured at different flow velocities and compares them to results from well-controlled laboratory-tank experiments on mass transfer of trichloroethene (TCE) across the capillary fringe. The measured values of transverse vertical dispersion in the capillary fringe region were larger than in fully saturated media, which is credited to enhanced tortuosity of the flow paths due to entrapped air within the capillary fringe. In all cases, the values observed for alpha(tv) were << 1 mm. The new measurements and the literature values indicate that alpha(tv) apparently declines with increasing flow velocity. The latter is attributed to incomplete diffusive mixing at the pore scale (pore throats). A simple conceptual model, based on the mean square displacement and the pore size accounting for only partial diffusive mixing at increasing flow velocities, shows very good agreement with measured and published data. (C) 2002 Elsevier Science B.V. All rights reserved

Mccarthy, K. A. and R. L. Johnson 1993. Transport of Volatile Organic-Compounds Across the Capillary-Fringe. Water Resources Research 29:1675-1683.
Reference ID: 72
Keywords: capillary fringe/concentration/diffusion/dispersion/groundwater/models/molecular diffusion/numerical simulation/organic compounds/TCE/transport/unsaturated zone/ZONE

Notes: Transport over capillary fringe
Abstract: Physical experiments were conducted to investigate the transport of a dissolved volatile organic compound (trichloroethylene, TCE) from shallow groundwater to the unsaturated zone under a variety of conditions including changes in the soil moisture profile and water table position. Experimental data indicated that at moderate groundwater velocities (0.1 m/d), vertical mechanical dispersion was negligible and molecular diffusion was the dominant vertical transport mechanism. Under these conditions, TCE concentrations decreased nearly 3 orders of magnitude across the capillary fringe and soil ps concentrations remained low relative to those of underlying groundwater. Data collected during a water table drop showed a short-term increase in concentrations throughout most of the unsaturated zone, but these concentrations quickly declined and approached initial values after the water table was returned to its original level. In the deep part of the unsaturated zone, the water table drop resulted in a long-term decrease in concentrations, illustrating the effects of hysteresis in the soil moisture profile. A two-dimensional random walk advection-diffusion model was developed to simulate the experimental conditions, and numerical simulations agreed well with experimental data. A simpler, one-dimensional finite-difference diffusion-dispersion model was also developed. One-dimensional simulations based on molecular diffusion also agreed well with experimental data. Simulations which incorporated mechanical dispersion tended to overestimate flux across the capillary fringe. Good agreement between the one- and two-dimensional models suggested that a simple, one-dimensional approximation of vertical transport across the capillary fringe can be useful when conditions are appropriate

Smith, J. A., A. K. Tisdale, and H. J. Cho 1996. Quantification of natural vapor fluxes of trichloroethene in the unsaturated zone at Picatinny Arsenal, New Jersey. Environmental Science & Technology 30:2243-2250.
Reference ID: 58
Keywords: advection/AQUIFER/capillary fringe/concentration/diffusion/fick's law/soil gas/TCE/transport/unsaturated zone/vapor/ZONE
Notes: Transport over capillary fringe
Abstract: The upward flux of trichloroethene (TCE) vapor through the unsaturated zone above a contaminated, water-table aquifer at Picatinny Arsenal, New Jersey, has been studied under natural conditions over a 12-month period. Vertical gas-phase diffusion fluxes were estimated indirectly by measuring the TCE vapor concentration gradient in the unsaturated zone and using Fick's law to calculate the flux. The total gas-phase flux (e.g., the sum of diffusion and advection fluxes) was measured directly with a vertical flux chamber (VFC). In many cases, the upward TCE vapor flux was several orders of magnitude greater than the upward TCE diffusion flux, suggesting that mechanisms other than steady-state vapor diffusion are contributing to the vertical transport of TCE vapors through the unsaturated zone. The measured total flux of TCE vapor from the subsurface to the atmosphere is approximately 50 kg/yr and is comparable in magnitude to the removal rate of TCE from the aquifer by an existing pump-and-treat system and by discharge into a nearby stream. The net upward flux of TCE is reduced significantly during a storm event, presumably due to the mass transfer of TCE from the soil gas to the infiltrating rainwater and its subsequent downward advection. Several potential problems associated with the measurement of total gas-phase fluxes are discussed

B 3.2.5 Vapor sorption

Culver, T. B., C. A. Shoemaker, and L. W. Lion 1991. Impact of Vapor Sorption on the Subsurface Transport of Volatile Organic-Compounds - A Numerical-Model and Analysis. Water Resources Research 27:2259-2270.
Reference ID: 78
Keywords: advection/diffusion/dispersion/models/organic compounds/partition coefficient/sorption/transport/unsaturated zone/vapor/vapor sorption/VOCs/volatilization
Notes: Vapor sorption
Abstract: A flexible finite element transport model, which includes the impact of vapor sorption, is developed to simulate the movement of volatile organic compounds (VOCs) in variably saturated porous media. The two-dimensional numerical model predicts contaminant transport by aqueous advection, aqueous dispersion, aqueous and vapor diffusion, and surface volatilization. For a soil with increasing water contents with depth, one-dimensional simulations demonstrate that strong vapor sorption may reduce the total amount of VOC that volatilizes in 100 days from 84.6% of the initial mass volatilized without vapor sorption to 73.2%. Yet, for a soil with low water contents at depth, such as in an area with limited recharge, vapor sorption enhanced the rate of volatilization in 100 days from 72.4% without vapor sorption to a peak of 90.3%. When low soil moisture was combined with a soil type that has strong vapor sorption characteristics, VOC transport was significantly retarded

Grathwohl, P. and M. Reinhard 1993. Desorption of Trichloroethylene in Aquifer Material - Rate Limitation at the Grain Scale. Environmental Science & Technology 27:2360-2366.
Reference ID: 80
Keywords: AQUIFER/columns/desorption/diffusion/flow rate/pore water/soil gas/sorption/TCE/vapor/vapor sorption
Notes: Vapor sorption
Abstract: Soil-gas venting for the removal of sorbed trichloroethylene (TCE) was studied in columns packed with either wet or oven-dry Santa Clara aquifer material. After the wet columns were vented up to 1 h, the removal rate was independent of the flow rate and limited by slow intraparticle mass transfer. In contrast, removal of TCE from columns filled with oven-dry material was proportional to the flow rate after 20 days of venting. This suggests that intraparticle pore water limits mass transfer from the internal sorption sites. Desorption was modeled using an intraparticle diffusion model assuming homogeneous porous spheres. The model was calibrated in batch sorption studies using the apparent diffusion rate constant as a fitting parameter

Peterson, M. S., L. W. Lion, and C. A. Shoemaker 1988. Influence of Vapor-Phase Sorption and Diffusion on the Fate of Trichloroethylene in An Unsaturated Aquifer System. Environmental Science & Technology 22:571-578.
Reference ID: 77
Keywords: AQUIFER/diffusion/diffusion coefficient/fate/partition coefficient/prediction/sorption/TCE/transport/unsaturated zone/vapor/vapor sorption/ZONE
Notes: Vapor sorption
Abstract: This research evaluates the influence of vapor-phase sorption and diffusion on the fate and transport of a common volatile pollutant, trichloroethylene (TCE). Vapor-phase sorption of TCE by a porous

aluminum oxide surface coated with humic acids (to simulate an aquifer material) was observed to be highly dependent on moisture content. Linear partition coefficients for binding of TCE vapor under a range of unsaturated conditions were 1-4 orders of magnitude greater than the value measured for the saturated sorbent. In addition, laboratory measurement of the TCE diffusion coefficient through the simulated aquifer material indicated that an existing empirical formula used to estimate this parameter can be in error by as much as 400%. The significance of differences in sorptive partition coefficients and diffusion coefficients was examined with an existing one-dimensional vertical transport model for the unsaturated zone. Model calculations indicate that the common practice of assuming saturated partition coefficients apply to unsaturated conditions should be avoided to obtain accurate predictions of volatile contaminant transport.

Walter, T., H. J. Ederer, C. Forst, and L. Stieglitz 2000. Sorption of selected polycyclic aromatic hydrocarbons on soils in oil-contaminated systems. Chemosphere 41:387-397.
Reference ID: 76
Keywords: adsorption behaviour/desorption/distribution/hydrocarbon/methods/models/PAH/partitioning/sorption/vapor/vapor sorption
Notes: Vapor sorption
Abstract: The adsorption and desorption behaviour of selected polycyclic aromatic hydrocarbons (PAHs) on different soils was investigated by static and dynamic methods. On the basis of a system including the four phases of soil, water, oil adsorbed and oil in emulsion, a model for the description of the adsorption behaviour in the presence of oil was developed. In systems without oil a similar partitioning behaviour in the batch and column experiments was observed for all PAHs. Thus the distribution coefficients can be calculated from the octanol/water coefficient of the aromatic compounds and the organic carbon content of the soils. The presence of a lipophilic phase had a significant influence on the sorption of the PAHs, usually resulting in a drastic decrease of adsorption with increasing oil content in the system. For the oil-contaminated system the modelling of the adsorption behaviour enabled a more detailed interpretation of the experimental observations as well as the calculation of the sorption behaviour for the PAHs from characteristic parameters of the components involved. (C) 2000 Elsevier Science Ltd. All rights reserved

Zytner, R. G. 1994. Sorption of Benzene, Toluene, Ethylbenzene and Xylenes to Various Media. Journal of Hazardous Materials 38:13-126.
Reference ID: 79
Keywords: benzene/BTEX/desorption/hydrocarbon/p/partition coefficient/sorption/toluene/vapor/vapor sorption
Notes: Vapor sorption
Abstract: The sorption and desorption characteristics of the major components of gasoline were determined for five media; sandy loam soil, organic top soil, clay soil, peat moss and granular activated carbon (GAC). Emphasis was placed on the sorption of benzene, toluene, ethylbenzene and xylenes (BTEX), the aromatic hydrocarbons contained in gasoline. The results showed that the Freundlich isotherm satisfactorily described the sorption and desorption of dissolved BTEX on the media tested. The organic carbon content of the media was an important factor in both sorption and desorption, with the order of sorption preference being GAC, peat moss, organic top soil, clay soil and sandy

loam soil. The soil-water partition coefficient (K(oc)) for the BTEX compounds and Total BTEX suggests that the BTEX compounds will migrate quickly through soil, with benzene being the fastest followed by toluene, m-, p- and o-xylenes and ethylbenzene

Kristensen, A.H., P. Loll, M.G. Møller, L. Mortensen, K. Henriksen and P. Møldrup. Forudsætninger for naturlig nedbrydning af oliestoffer i den umættede zone under typiske danske forhold. ATV vintermøde, 185-193. 2011
Reference ID: 342
Keywords: degradation/key factors/nutrients/oxygen/heterogeneity/soil layering

B 3.3: Indirekte kvantitative metoder

Aichberger, H., M. Hasinger, R. Braun, and A. P. Loibner 2005. Potential of preliminary test methods to predict biodegradation performance of petroleum hydrocarbons in soil. Biodegradation 16:115-125.
Reference ID: 273
Keywords: BIODEGRADATION/BIOREMEDIATION/bioventing/columns/concentration/contamination/degradation/degradation rates/first-order rate constants/hydrocarbon/laboratory experiments/lysimeter/methods/monitoring/petroleum/remediation/respiration/ZONE
Notes: Indirect quantitative method
Abstract: Preliminary tests at different scales such as degradation experiments (laboratory) in shaking flasks, soil columns and lysimeters as well as in situ respiration tests (field) were performed with soil from two hydrocarbon contaminated sites. Tests have been evaluated in terms of their potential to provide information on feasibility, degradation rates and residual concentration of bioremediation in the vadose zone. Sample size, costs and duration increased with experimental scale in the order shaking flasks - soil columns - lysimeter - in situ respiration tests, only time demand of respiration tests was relatively low. First-order rate constants observed in degradation experiments exhibited significant differences between both, different experimental sizes and different soils. Rates were in line with type and history of contamination at the sites, but somewhat overestimated field rates particularly in small scale experiments. All laboratory experiments allowed an estimation of residual concentrations after remediation. In situ respiration tests were found to be an appropriate pre-testing and monitoring tool for bioventing although residual concentrations cannot be predicted from in situ respiration tests. Moreover, this method does not account for potential limitations that might hamper biodegradation in the longer term but only reflects the actual degradation potential when the test is performed

Allen, J. P., E. A. Atekwana, E. A. Atekwana, J. W. Duris, D. D. Werkema, and S. Rossbach 2007. The microbial community structure in petroleum-contaminated sediments corresponds to geophysical signatures. Applied and Environmental Microbiology 73:2860-2870.
Reference ID: 12
Keywords: AQUIFER/BACTERIA/BIOREMEDIATION/degradation/DIVERSITY/DNA/geoelectrical properties/geoelectrical signatures/groundwater/hydrocarbon/LIQUIDS/microbial communities/monitoring/NAPL/ORGANIC-

ACIDS/petroleum/PLUME/PROBABLE-NUMBER/RIBOSOMAL-RNA/spatial variation
Notes: Indirect quantitative method
Abstract: The interdependence between geoelectrical signatures at underground petroleum plumes and the structures of subsurface microbial communities was investigated. For sediments contaminated with light non-aqueous-phase liquids, anomalous high conductivity values have been observed. Vertical changes in the geoelectrical properties of the sediments were concomitant with significant changes in the microbial community structures as determined by the construction and evaluation of 16S rRNA gene libraries. DNA sequencing of clones from four 16S rRNA gene libraries from different depths of a contaminated field site and two libraries from an uncontaminated background site revealed spatial heterogeneity in the microbial community structures. Correspondence analysis showed that the presence of distinct microbial populations, including the various hydrocarbon-degrading, syntrophic, sulfate-reducing, and dissimilatory-iron-reducing populations, was a contributing factor to the elevated geoelectrical measurements. Thus, through their growth and metabolic activities, microbial populations that have adapted to the use of petroleum as a carbon source can strongly influence their geophysical surroundings. Since changes in the geophysical properties of contaminated sediments parallel changes in the microbial community compositions, it is suggested that geoelectrical measurements can be a cost-efficient tool to guide microbiological sampling for microbial ecology studies during the monitoring of natural or engineered bioremediation processes

Atekwana, E. A., D. D. Werkema, J. W. Duris, S. Rossbach, E. A. Atekwana, W. A. Sauck, D. P. Cassidy, J. Means, and F. D. Legall 2004. In-situ apparent conductivity measurements and microbial population distribution at a hydrocarbon-contaminated site. Geophysics 69:56-63.
Reference ID: 13
Keywords: aerobic/BACTERIA/BIODEGRADATION/CRUDE-OIL/degradation/GEOCHEMICAL EVOLUTION/geoelectrical properties/GROUND-WATER/microbial communities/models/ORGANIC-ACIDS/PLUME/PROBABLE-NUMBER/PROBABLE-NUMBER PROCEDURE/SPILL/ZONE
Notes: Indirect quantitative method
Abstract: We investigated the bulk electrical conductivity and microbial population distribution in sediments at a site contaminated with light nonaqueous-phase liquid (LNAPL). The bulk conductivity was measured using in-situ vertical resistivity probes; the most probable number method was used to characterize the spatial distribution of aerobic heterotrophic and oil-degrading microbial populations. The purpose of this study was to assess if high conductivity observed at aged LNAPL-impacted sites may be related to microbial degradation of LNAPL. The results show higher bulk conductivity coincident with LNAPL-impacted zones, in contrast to geoelectrical models that predict lower conductivity in such zones. The highest bulk conductivity was observed to be associated with zones impacted by residual and free LNAPL. Data from bacteria enumeration from sediments close to the resistivity probes show that oil-degrading microbes make up a larger percentage (5-55%) of the heterotrophic microbial community at depths coincident with the higher conductivity compared to similar to5% at the uncontaminated location. The coincidence of a higher percentage of oil-degrading microbial populations in zones of higher bulk conductivity suggests that the higher conductivity in these zones may result from increased fluid con-

ductivity related to microbial degradation of LNAPL, consistent with geochemical studies that suggest that intrinsic biodegradation is occurring at the site. The findings from this study point to the fact that biogeochemical processes accompanying biodegradation of contaminants can potentially alter geoelectrical properties of the subsurface impacted media

Barber, C., G. B. Davis, D. Briegel, and J. K. Ward 1990. Factors controlling the concentration of methane and other volatiles in groundwater and soil-gas around a waste site. Journal of Contaminant Hydrology 5:155-169.
Reference ID: 190
Keywords: concentration/groundwater/methane/soil gas
Notes: Indirect quantitative method

Davis, G. B., C. D. Johnston, B. M. Patterson, C. Barber, and M. Bennett 1998. Estimation of Biodegradation Rates Using Respiration Tests During In Situ Bioremediation of Weathered Diesel NAPL. Ground Water Monitoring and Remediation 18:123-132.
Reference ID: 166
Keywords: BIODEGRADATION/BIOREMEDIATION/NAPL/respiration
Notes: Indirect quantitative method

Davis, G. B., M. G. Trefry, and B. M. Patterson. Petroleum and solvent vapours: Quantifying their behaviour, assessment and exposure. A report to the Western Australian Department of Environment. 2004. CSIRO. (GENERIC)
Ref Type: Report
Ref ID: 7
Keywords: assessment/barometric pressure/carbon dioxide/chorinated solvent/degradation rates/depth profile/field study/groundwater contamination/health risk/hydrocarbon/investigation techniques/modeling/models/monitoring/NAPL/oxygen/oxygen consumption rates/petroleum/soil contamination/unsaturated zone/vapour/vapour behaviour/vapour migration
Notes: Indirect quantitative method

Davis, G. B., J. L. Rayner, M. G. Trefry, S. J. Fisher, and B. M. Patterson 2005. Measurement and modeling of temporal variations in hydrocarbon vapor behavior in a layered soil profile. Vadose Zone Journal 4:225-239.
Reference ID: 4
Keywords: assessment/BIODEGRADATION/carbon dioxide/degradation rates/depth profile/fate/hydrocarbon/modeling/modeling of degradation/models/monitoring/N2/NAPL/oxygen/soil physical properties/temporal variation/unsaturated zone/vapor/vapour/VOCs/ZONE
Notes: Indirect quantitative method
Abstract: Reproduced from Vadose Zone Journal. Published by Soil Science Society of America. All copyrights reserved. Fine-scale measurement of gasoline vapors, major gases (O-2, CO2, N-2, and CH4), residual nonaqueous phase liquid (NAPL) gasoline, and soil physical properties has allowed detailed assessment of the role of soil layering and seasonal variability on hydrocarbon vapor fate and biodegradation. In this study we conducted coring and static depth profile monitoring at the end of summer and end of winter for a layered sandy vadose zone in Perth, Western Australia. Transient on-line monitoring of vapors and O-2 was also performed with in situ multilevel volatile organic compound

(VOC) and O-2 probes. For high soil moisture contents at the end of winter, vapors were shown to accumulate beneath a compacted, cemented layer approximately 0.3 m below the ground surface, and O-2 penetrated only to depths of 0.4 m below ground. At the end of summer, when soil moisture was lower, O-2 penetrated to depths of up to 1.5 m, and hydrocarbon vapors remained at or below this depth. Regardless of seasonal changes, sharp separations were seen between the depth of O-2 penetration from the ground surface and the depth of penetration of the vapors upward the hydrocarbon-contaminated zone. Modeling of steady-state O-2 profiles indicated that a number of simple O-2 consumption models apply, including point-sink, distributed zero-order, or distributed first-order models, each leading to different biodegradation rates. Combining independent data with modeling helped determine the most appropriate model, and hence estimates of O-2 consumption and hydrocarbon biodegradation. Also, reliable estimates of the biodegdegradation radation rate could only be calculated after consideration of the layered features

Davis, G. B., B. M. Patterson, and M. G. Trefry 2006. Typical Behaviour of Petroleum and Solvent Vapours: Updating our Understanding from Australian Field Investigations. (Anonymous,). CSIRO Land and Water.
Reference ID: 6
Keywords: chorinated solvent/field study/groundwater/petroleum/vapor/vapour/vapour behaviour/vapour migration
Notes: Indirect quantitative method

Davis, G. B., B. M. Patterson, and M. G. Trefry 2009. Evidence for Instantaneous Oxygen-Limited Biodegradation of Petroleum Hydrocarbon Vapors in the Subsurface. Ground Water Monitoring and Remediation 29:126-137.
Reference ID: 1
Keywords: aerobic/aerobic biodegradation/aerobic degradation/assessment/BIODEGRADATION/carbon dioxide/concentration/degradation rates/depth profile/diffusion/diffusion coefficient/diffusive processes/hydrocarbon/modeling of degradation/monitoring/organic compounds/oxygen/petroleum/transport/transport processes/vapor/vapour/vapour intrusion/vapour migration/VOCs
Notes: Indirect quantitative method
Abstract: Petroleum hydrocarbon vapors biodegrade aerobically in the subsurface. Depth profiles of petroleum hydrocarbon vapor and oxygen concentrations from seven locations in sandy and clay soils across four states of Australia are summarized. The data are evaluated to support a simple model of biodegradation that can be used to assess hydrocarbon vapors migrating toward built environments. Multilevel samplers and probes that allow near-continuous monitoring of oxygen and total volatile organic compounds (VOCs) were used to determine concentration depth profiles and changes over time. Collation of all data across all sites showed distinct separation of oxygen from hydrocarbon vapors, and that most oxygen and hydrocarbon concentration profiles were linear or near linear with depth. The low detection limit on the oxygen probe data and because it is an in situ measurement strengthened the case that little or no overlapping of oxygen and hydrocarbon vapor concentration profiles occurred, and that indeed oxygen and hydrocarbon vapors were largely only coincident near the location where they both decreased to zero. First-order biodegradation rates determined from all

depth profiles were generally lower than other published rates. With lower biodegradation rates, the overlapping of depth profiles might be expected, and yet such overlapping was not observed. A model of rapid (instantaneous) reaction of oxygen and hydrocarbon vapors compared to diffusive transport processes is shown to explain the important aspects of the 13 depth profiles. The model is simply based on the ratio of diffusion coefficients of oxygen and hydrocarbon vapors, the ratio of the maximum concentrations of oxygen and hydrocarbon vapors, the depth to the maximum hydrocarbon source concentration, and the stoichiometry coefficient. Whilst simple, the model offers the potential to incorporate aerobic biodegradation into an oxygen-limited flux-reduction approach for vapor intrusion assessments of petroleum hydrocarbon compounds

Davis, G. B., B. M. Patterson, and M. G. Trefry. Biodegradation of Petroleum Hydrocarbon Vapours: Report for CRC CARE. 2009. CSIRO Land and Water. (GENERIC)
Ref Type: Report
Ref ID: 8
Keywords: aerobic degradation/attenuation/BIODEGRADATION/exposure reduction/hydrocarbon/modeling/oxygen/petroleum/vapor/vapour/vapour intrusion
Notes: Indirect quantitative method

Davis, G. B., M. G. Trefry, and B. M. Patterson. Petroleum vapour model comparison. 2009. CRCCare. (GENERIC)
Ref Type: Report
Ref ID: 15
Keywords: BIODEGRADATION/models/petroleum/pore gas/risk assessment/vapour/vapour behaviour/vapour intrusion
Notes: Indirect quantitative method

Deyo, B. G., G. A. Robbins, and G. K. Binkhorst 1993. Use of Portable Oxygen and Carbon-Dioxide Detectors to Screen Soil-Gas for Subsurface Gasoline Contamination. Ground Water 31:598-604.
Reference ID: 2
Keywords: aerobic/aerobic degradation/anarobic degradation/BIODEGRADATION/carbon dioxide/contamination/degradation/degradation zones/EXPERIMENTATION/hydrocarbon/monitoring/oxygen/soil gas/soil temperature/temporal variation/vapor/VAPOR DETECTION INSTRUMENTS/vapour/ZONE
Notes: Indirect quantitative method
Abstract: The field screening of soil gas CO2 and O2 using portable instruments is shown to be useful for indirectly detecting and delineating subsurface gasoline contamination. Shallow (< 50 cm) soil gas surveys performed at a site of subsurface gasoline contamination in Connecticut indicated a good correlation between elevated CO2, depleted O2, and total hydrocarbon vapor anomalies. CO2 and O2 anomalies were also found to be spatially coincident with the area of known subsurface gasoline leakage. Soil gas CO2 levels ranged from 0.2 to 18.7 volume percent, whereas O2 levels ranged from 20.8 to 0.5 volume percent. The gases exhibited a nearly constant inverse correlation except near the source of contamination. In this area, CO2 generation from anaerobic degradation of hydrocarbons likely caused a decrease in the observed CO2 and O2 correlation. This suggests that the ratio of soil gas CO2 to

O2 may be useful to delineate aerobic and anaerobic degradation zones, the latter being in the vicinity of highly contaminated areas. Periodic sampling of seven permanent soil gas probes over a 17-month period indicated significant seasonal variations in CO2 and O2. When the soil was warmest during the summer, the CO2 reached a maximUM and O2 reached a minimum. The opposite was observed during the winter when the soil achieved its minimum temperature. These observations most likely reflect changes in microbial acitivity in response to subsurface temperature variations. Further, hydrocarbon vapor levels were observed to decrease by several orders of magnitude to nondetectable levels during the winter months. Although CO2 and O2 anomalies were also diminished during the winter months, they were still readily detectable. These observations indicate that soil gas surveying for subsurface gasoline leakage may be enhanced by monitoring CO2 and O2

Laubacher, R. C., P. Bartholomae, P. Velasco, and H. J. Reisinger 1997. An Evaluation of the Vapor Profile in the Vadose Zone above a Gasoline Plume. (Anonymous,).
Reference ID: 11
Keywords: attenuation/carbon dioxide/case study/depth profile/GROUNDWATER/groundwater/hydrocarbon/modeling/oxygen/PLUME/remediation/vapor/vapour/vapour transport/ZONE
Notes: Indirect quantitative method

Lee, C. H., J. Y. Lee, J. Y. Cheon, and K. K. Lee 2001. Attenuation of petroleum hydrocarbons in smear zones: A case study. Journal of Environmental Engineering-Asce 127:639-647.
Reference ID: 5
Keywords: AQUIFER/AQUIFERS/attenuation/barometric pressure/BIODEGRADATION/BIOREMEDIATION/carbon dioxide/case study/concentration/contamination/degradation/degradation rates/depth profile/GEOLOGIC MEDIA/GROUNDWATER/groundwater/groundwater contamination/hydrocarbon/models/NATURAL ATTENUATION/oxygen/oxygen consumption rates/petroleum/soil contamination/spatial variation/temporal variation/toluene/unsaturated zone/water table fluctuation/ZONE
Notes: Indirect quantitative method
Abstract: Soil and ground water in a shallow aquifer were contaminated by petroleum hydrocarbons, mostly comprised of toluene. The degrees of soil and ground-water contamination were closely correlated. The vertical profile of soil contamination showed an exponential or semilinear decrease both upward and downward from the mean water table, and this was closely related to water table fluctuation. Vertical and seasonal variations in the concentrations of petroleum hydrocarbon contaminants and their degradation products were analyzed in detail. Total natural attenuation rate and the contribution of biodegradation to the rate were estimated. Biodegradation was found to be an effective attenuation process at this site

Lundegard, P. D. Soil Gas Behavior Beneath a Residential Building. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 10
Keywords: benzene/depth profile/methane/natural ventilation/near-

slab/nitrogen/oxygen/oxygen transport/pressure gradients/soil gas/sub-slab/underpressure/vapor/vapour behaviour
Notes: Indirect quantitative method

McNeel, P. J. and V. Dibley 1997. Case study comparisons of vapor inhalation risk estimates: ASTM RBCA model predictions vs site specific soil vapor data. (Anonymous,).
Reference ID: 9
Keywords: case study/chorinated solvent/concentration/groundwater/health risk/hydrocarbon/models/petroleum/prediction/release/risk assessment/transport/vapor/vapour/vapour flux/vapour transport
Notes: Indirect quantitative method
Abstract: The American Society for Testing and Materials (ASTM) Standard E-1739, Risk-Based Corrective Action Applied at Petroleum Release Sites (RBCA), offers a streamlined methodology for selecting and implementing cost-effective corrective action for petroleum hydrocarbon release sites. ASTM is also currently developing the Standard Guide for Risk Based Corrective Action which extends the RBCA process to include a wide range of chemicals of concern. Comparing the results derived from the RBCA vapor transport models with field data has underscored the extremely conservative nature of the RBCA inhalation pathway models. Two case studies are described in this paper which compare exposure point concentration and human health risk estimated from the RBCA vapor transport models and actual measurements of soil vapor concentrations and soil vapor flux.

Muchitsch, N. Laenvej, Glesborg. Monitering af naturlig nedbrydning af benzin i den umættede zone. Afsluttende afrapportering. OM-SAG 8585-47-9165. 2009. NIRAS Allerød. (GENERIC)
Ref Type: Report
Ref ID: 312
Keywords: BTEX/carbon dioxide/degradation/degradation rates/monitoring/MTBE/NATURAL ATTENUATION/natural degardation/oxygen/pore gas/unsaturated zone/ZONE
Notes: Indirect quantitative method

NIRAS. Videncenter for jordforurening - Projekteringsparametre. Nedbrydningsrate, umættet zone. 2009.
Ref Type: Internet Communication
Ref ID: 275
Keywords: carbon dioxide/degradation/degradation rates/depth profile/determination of degradation rates/field assessment/methods/oxygen/soil gas/unsaturated zone/ZONE
Notes: Indirect quantitative method

Patterson, B. M. and G. B. Davis 2009. Quantification of Vapor Intrusion Pathways into a Slab-on-Ground Building under Varying Environmental Conditions. Environmental Science & Technology 43:650-656.
Reference ID: 3
Keywords: advection/aerobic/aerobic biodegradation/BIODEGRADATION/concentration/contamination/degradation/diffusion/hexan/hydrocarbon/molecular diffusion/monitoring/oxygen/pathways/soil gas/transport/vapor/vapour/vapour flux/vapour intrusion/VOCs
Notes: Indirect quantitative method
Abstract: Potential hydrocarbon-vapor intrusion pathways into a build-

ing through a concrete slab-on-ground were investigated and quantified under a variety of environmental conditions to elucidate the potential mechanisms for indoor air contamination. Vapor discharge from the uncovered open ground soil adjacent to the building and subsequent advection into the building was unlikely due to the low soil-gas concentrations at the edge of the building as a result of aerobic biodegradation of hydrocarbon vapors. When the building's interior was under ambient pressure, a flux of vapors into the building due to molecular diffusion of vapors through the building's concrete slab (cyclohexane 11 and methylcyclohexane 31 mg m(-2) concrete slab day(-1)) and short-term (up to 8 h) cyclical pressure-driven advection of vapors through an artificial crack (cyclohexane 4.2 x 10(3) and methylcyclohexane 1.2 x 10(4) mg m(-2) cracks day(-1)) was observed. The average subslab vapor concentration under the center of the building was 25,000 A L-1. Based on the measured building's interior vapor concentrations and the building's air exchange rate of 0.66 h(-1), diffusion of vapors through the concrete slab was the dominant vapor intrusion pathway and cyclical pressure exchanges resulted in a near zero advective flux. When the building's interior was under a reduced pressure (-12 Pa), advective transport through cracks or gaps in the concrete slab (cyclohexane 340 and methylcyclohexane 1100 mg m(-2) cracks day(-1)) was the dominant vapor intrusion pathway

Pearce, K. and W. A. Pretorius 1998. A bioventing feasibility test to aid remediation strategy. Water Sa 24:5-9.
Reference ID: 274
Keywords: BIODEGRADATION/BIOREMEDIATION/bioventing/case study/hydrocarbon/in situ/microorganisms/monitoring/MONITORING WELLS/oxygen/permeability/remediation/soil gas
Notes: Indirect quantitative method
Abstract: A case study is presented where the feasibility of bioventing was assessed for the remediation of a petroleum-contaminated site. This was achieved through the determination of the radius of influence of a single vent well, the soil gas permeability of the site and the oxygen utilisation rate of the in situ micro-organisms. The on-site test used one vent well and three monitoring wells. A radius of influence of 9.5 m was determined. A soil gas permeability of 3.8 Darcy was measured. The oxygen utilisation of 1.32% (v/v) O-2/h indicated that an active microbial population existed in situ. The theoretical biodegradation rate was calculated to be 752 mg hydrocarbon (based on hexane)/kg soil-month. Based on these results, bioventing was found to be a feasible bioremediation option for cleanup of the site, provided that other soil conditions were suitable for biological activity

Poulsen, M. and A. Damborg 1990. Fordeling og transport i umættet og mættet zone. (Anonymous,).
Reference ID: 189
Keywords: chorinated solvent/partitioning/transport/unsaturated zone/ZONE
Notes: Indirect quantitative method

Roggemans, s., C. L. Bruce, P. C. Johnson, and R. L. Johnson. Vadose Zone Natural Attenuation Of Hydrocarbon Vapors: An Empirical Assessment Of Soil Gas Vertical Profile Data. (december 2001 no. 15). 2001. American Petroleum Institute. (GENERIC)
Ref Type: Report

Ref ID: 14
Keywords: assessment/attenuation/BIODEGRADATION/hydrocarbon/modeling/NATURAL ATTENUATION/soil gas/unsaturated zone/vapor/vapour flux/vapour transport/ZONE
Notes: Indirect quantitative method

B 3.4: Fanemodellering i umættet zone

Baehr, A. L. 1987. Selective Transport of Hydrocarbons in the Unsaturated Zone Due to Aqueous and Vapor-Phase Partitioning. Water Resources Research 23:1926-1938.
Reference ID: 276
Keywords: contamination/diffusive processes/groundwater/groundwater contamination/hydrocarbon/LIQUIDS/migration/modeling/numerical simulation/partitioning/PLUME/plume migration/transport/unsaturated zone/vapor/vapour/VOCs/ZONE
Notes: Plume mapping and inverse modeling
Abstract: Long-term groundwater contamination can result from vapors and solutes emanating from organic liquids spilled in the unsaturated zone. The mathematical modeling analysis presented in this paper demonstrates for gasoline-range hydrocarbons, and other volatile organics commonly spilled, that diffusive transport in the unsaturated zone is a significant transport mechanism which can cause aqueous and vapor plumes to spread away from the immiscible liquid source, resulting in increasing groundwater contaminating potential. An analytical solution to a one-dimensional version of the' transport model allows for the definition of a retardation coefficient which is dependent on phase-partitioning coefficients and moisture content. Significant differences in migration rates should be anticipated between hydrocarbons. A numerical solution was developed for a radially symmetric version of the model defining transport for a multiconstituent contaminant like gasoline. Differences in anticipated migration rates between aromatic and nonaromatic hydrocarbons was clearly demonstrated. A simulation based on the composition of an actual gasoline revealed that aromatic constituents, although constituting a fraction of the initial gasoline composition, completely defined the groundwater contaminating potential. this potential changes in time as constituents are selectively removed from the unsaturated zone. Further, the groundwater contaminating potential is q~ite sensitive to the ground surface boundary characterization.

Bonroy, J., J. van de Steene, R. van de Velde, G. van Eatvelde, H. Verplancke, F. Verfailie, and G. Boucneau 2007. Monitored Natural Attenuation of Domestic Fuel Oil in the Unsaturated Zone. (Anonymous,).
Reference ID: 277
Keywords: aerobic/aerobic biodegradation/attenuation/BIODEGRADATION/BIOREMEDIATION/bioventing/concentration/contamination/gas transport/modeling/monitored natural attenuation/N2/NATURAL ATTENUATION/PLUME/remediation/transport/unsaturated zone/ZONE
Notes: Plume mapping and inverse modeling
Abstract: The natural attenuation of domestic fuel oil in the unsaturated zone was examined in a small scale remediation study. Domestic fuel oil was spilled in the 1980s from two 25,000 litre underground storage tanks. The bulk of the contamination was detected at 3 meter below land surface with maximum domestic fuel oil concentration of 7,700 mg

kg-1 in 2003. The unsaturated zone of the site consisted predominantly of fineto medium-grained sand with intermittent layers of dense clay. Monitored natural attenuation remediation was approved as a first choice remediation technique by the Flemish Public Waste Company, with bioventing as an alternative option if cleanup levels cannot be met within a period of four years starting from February 2005. The goal of the study was to quantify and predict the biodegradation reaction rates from measured O2, CO2 and N2 concentrations in the soil air using a steady state gas transport model. Decreasing TPH concentrations measured over time are indicating a shrinking contaminant plume. Evidence of aerobic biodegradation was demonstrated by the monitored O2 and CO2 concentrations, which showed a higher O2 consumption and CO2 production in the contaminated zone compared to the non-contaminated zone. From calculated biodegradation rates, the remediation time by monitored natural attenuation was estimated to be 4 years to reach a target concentration of 600 mg kg-1.

Chaplin, B. P., G. N. Delin, R. J. Baker, and M. A. Lahvis 2002. Long-Term Evolution of Biodegradation and Volatilization Rates in a Crude Oil-Contaminated Aquifer. Bioremediation Journal 6:237-255.
Reference ID: 278
Keywords: aerobic/aerobic biodegradation/attenuation/BIODEGRADATION/concentration/CRUDE-OIL/gas transport/hydrocarbon/inverse modeling/modeling/NATURAL ATTENUATION/numerical simulation/PLUME/SPILL/substrate/transport/unsaturated zone/volatilization/ZONE
Notes: Plume mapping and inverse modeling
Abstract: Volatilization and subsequent biodegradation near the water Table make up a coupled natural attenuation pathway that results in significant mass loss of hydrocarbons. Rates of biodegradation and volatilization were documented twice 12 years apart at a crude-oil spill site near Bemidji, Minnesota. Biodegradation rates were determined by calibrating a gas transport model to O2, CO2, and CH4 gas-concentration data in the unsaturated zone. Reaction stoichiometry was assumed in converting O2 and CO2 gas-flux estimates to rates of aerobic biodegradation and CH4 gas-flux estimates to rates of methanogenesis. Model results indicate that the coupled pathway has resulted in significant hydrocarbon mass loss at the site, and it was estimated that approximately 10.52 kg/day were lost in 1985 and 1.99 kg/day in 1997. In 1985 3% of total volatile hydrocarbons diffusing from the floating oil were biodegraded in the lower 1 m of the unsaturated zone and increased to 52% by 1997. Rates of hydrocarbon biodegradation above the center of the floating oil were relatively stable from 1985 to 1997, as the primary metabolic pathway shifted from aerobic to methanogenic biodegradation. Model results indicate that in 1997 biodegradation under methanogenenic conditions represented approximately one-half of total hydrocarbon biodegradation in the lower 1 m of the unsaturated zone. Further downgradient, where substrate concentrations have greatly increased, total biodegradation rates increased by greater than an order of magnitude from 0.04 to 0.43 g/m2-day. It appears that volatilization is the primary mechanism for attenuation in early stages of plume evolution, while biodegradation dominates in later stages.

Christensen, A. G., P. Kjeldsen, and E. Lassen 2007. Undersøgelse af fyringsolies transport og nedbrydning i den umættede zone. (Anonymous,).
Reference ID: 279

Keywords: BTEX/diffusion/inverse modeling/modeling/PLUME/R-UNSAT/transport/ZONE
Notes: Plume mapping and inverse modeling
Abstract: På to feltlokaliteter forurenet med fyringsolie er der gennemført en detaljeret kortlægning af forureningsspredningen og det geokemiske aftryk efter den biologiske nedbrydning af olie-stoffer. Det kan på baggrund af de målte vertikale og horisontale koncentrationsgradienter i poreluften for både ilt og kuldioxid konkluderes, at der sker en kontinuerlig nedbrydning af kulbrinter i den umættede zone. Jævnlige poreluftmålinger henover året indikerer, at der altid er aerobe forhold i jorden, men at der sker meget store svingninger i iltindholdet. Diffusion er for begge undersøgte feltlokaliteter den væsentligste transportmekanisme – og afgørende for både transporten af ilt ind i den olieforurenede jord samt den modsatrettede transport af den dannede kuldioxid fra den aerobe nedbrydning af oliestofferne. Der ses også en begrænset horisontal spredning af flygtige kulbrinter (BTEX) som følge af nedbrydning og diffusion. Laboratorieforsøgene med forurenet jord fra de to lokaliteter bekræfter, at specielt de flygtige stoffer som f.eks. BTEX nedbrydes relativt hurtigt. De bestemte 1.ordens aerobe nedbrydnings-rater er i god overensstemmelse med publicerede værdier fra andre felt- og laboratorieforsøg.
Modelberegninger med modellen R-UNSAT har klart demonstreret, at der selv for relativt lave 1.ordens nedbrydningsrater af f.eks. BTEX-forbindelser kan opnås en reduktion af koncen-trationen på 10-1000 gange under transporten fra kilden og ned til grundvandet, samt en væsentlig begrænsning af både den horisontale og vertikale spredning ved diffusion. Det er også vist, at der kan ske en markant ændring i oliens sammensætning over tid, og at denne ældningsproces har betydning for, hvilken udvaskning der kan forventes fra f.eks. en restfor-urening. Med det anvendte modelværktøj er det muligt at beregne reduktionen igennem den umættede zone, og det er fundet, at de mest følsomme parametre ved beregningen er ned-brydningsraten, tykkelsen af den umættede zone under kilden samt jordarten og den aktuelle vandmætning.

Christophersen, M., M. M. Broholm, H. Mosbaek, H. K. Karapanagioti, V. N. Burganos, and P. Kjeldsen 2005. Transport of hydrocarbons from an emplaced fuel source experiment in the vadose zone at Airbase V ae rlose, Denmark. Journal of Contaminant Hydrology 81:1-33.
Reference ID: 156
Keywords:
CFC/concentration/degradation/diffusion/groundwater/groundwater flow/hydrocarbon/inverse modeling/modeling/monitoring/NAPL/PLUME/soil gas/toluene/tracer/transport/unsaturated zone/vapour/ZONE
Notes: Plume mapping and inverse modeling
Abstract: An emplaced hydrocarbon source field experiment was conducted in the relatively homogeneous sandy geology of the vadose zone at Airbase V ae rlose, Denmark. The source (10.2 1 of NAPL) consisted of 13 hydrocarbons (n-, iso- and cyclo-alkanes and aromates) and CFC-113 as a tracer. Monitoring in the 107 soil gas probes placed out to 20 m from the centre of the source showed spreading of all the compounds in the pore air and all compounds were measured in the pore air within a few hours after source emplacement. Seven of the fourteen compounds were depleted from the source within the 1 year of monitoring. The organic vapours in the pore air migrated radially from the source. The CFC-113 concentrations seemed to be higher in the deeper soil gas probes compared with the hydrocarbons, indicating a high loss of CFC-

113 to the atmosphere and the lack of degradation of CFC-113. For the first days after source emplacement, the transport of CFC- 113, hexane and toluene was successfully simulated using a radial gas-phase diffusion model for the unsaturated zone. Groundwater pollution caused by the vadose zone hydrocarbon vapours was only detected in the upper 30 cm of the underlying groundwater and only during the first 3 months of the experiment. Only the most water-soluble compounds were detected in the groundwater and concentrations decreased sharply with depth (approximately one order of magnitude within 10 cm depth) to non-detect at 30 cm depth. The groundwater table varied more than 1 m within the measurement period. However that did not influence the direction of the groundwater flow. Approximately 7 months after source emplacement the groundwater table rose more than 1 m within 1 month. That did not cause additional pollution of the groundwater. (c) 2005 Elsevier B.V. All rights reserved

Franzmann, P. D., W. J. Robertson, L. R. Zappia, and G. B. Davis 2002. The role of microbial populations in the containment of aromatic hydrocarbons in the subsurface. Biodegradation 13:65-78.
Reference ID: 169
Keywords: BACTERIA/benzene/contamination/degradation/fate/groundwater/hydrocarbon/inverse modeling/modeling/oxygen/petroleum/PLUME/remediation/sulfate reduction/toluene/transport/vapour/ZONE
Notes: Plume mapping and inverse modeling
Abstract: A survey of soil gases associated with gasoline stations on the Swan Coastal Plain of Western Australia has shown that 20% leak detectable amounts of petroleum. The fates of volatile hydrocarbons in the vadose zone at one contaminated site, and dissolved hydrocarbons in groundwater at another site were followed in a number of studies which are herein reviewed. Geochemical evidence from a plume of hydrocarbon-contaminated groundwater has shown that sulfate reduction rapidly developed as the terminal electron accepting process. Toluene degradation but not benzene degradation was linked to sulfate reduction. The sulfate-reducing bacteria isolated from the plume represented a new species, Desulfosporosinus meridiei. Strains of the species do not mineralise (1)4C-toluene in pure culture. The addition of large numbers of cells and sulfate to microcosms did stimulate toluene mineralisation but not benzene mineralisation. Attempts to follow populations of sulfate-reducing bacteria by phospholipid signatures, or Desulfosporosinus meridiei by FISH in the plume were unsuccessful, but fluorescently-labeled polyclonal antibodies were successfully used. In the vadose zone at a different site, volatile hydrocarbons were consumed in the top 0.5 m of the soil profile. The fastest measured rate of mineralisation of C-14-benzene in soils collected from the most active zone (6.5 mg kg(-1) day(-1)) could account for the majority of the flux of hydrocarbon vapour towards the surface. The studies concluded that intrinsic remediation by subsurface microbial populations in groundwater on the Swan Coastal Plain can control transport of aromatic hydrocarbon contamination, except for the transport of benzene in groundwater. In the vadose zone, intrinsic remediation by the microbial populations in the soil profile can contain the transport of aromatic hydrocarbons, provided the physical transport of gases, in particular oxygen from the atmosphere, is not impeded by structures

Gaganis, P., P. Kjeldsen, and V. N. Burganos 2004. Modeling natural attenuation of multicomponent fuel mixtures in the vadose zone: Use of field data and evaluation of biodegradation effects. Vadose Zone Journal 3:1262-1275.
Reference ID: 257
Keywords: assessment/attenuation/BIODEGRADATION/columns/concentration/contamination/fate/inverse modeling/modeling/NATURAL ATTENUATION/PLUME/risk assessment/transport/ZONE
Notes: Plume mapping and inverse modeling
Abstract: Data from a controlled fuel source emplacement field experiment were used to explore the potential for predictive modeling using an approximate model and parameters from laboratory-scale studies, and to quantify the effects of biodegradation on the natural attenuation of volatile organic compound (VOC) mixtures in the vadose zone. The application of a species grouping technique is investigated in an attempt to reduce the computational cost for predicting the fate of multicomponent mixtures with a minimum loss in accuracy. We show how several difficulties in vadose zone transport modeling may be reasonably well overcome by simplifications that are supported by field data and sensitivity calculations. The estimated case-specific field-scale biodegradation values for the majority of mixture compounds were found to fall within the range of biodegradation rate constants determined from experiments performed in columns that were filled the field soil. A sensitivity analysis showed that using the upper or lower bounds of literature values for the biodegradation constants had a negligible effect on gas concentrations at the early stages of the contamination process, when contaminant concentrations were still high. This is a very encouraging result regarding the usefulness of model calculations in risk assessment procedures

Hers, I., J. Atwater, L. Li, and R. Zapf-Gilje 2000. Evaluation of vadose zone biodegradation of BTX vapours. Journal of Contaminant Hydrology 46:233-264.
Reference ID: 19
Keywords: advection/benzene/BIODEGRADATION/carbon dioxide/concentration/degradation/degradation rates/diffusion/fate/hydrocarbon/inverse modeling/methods/modeling/models/monitoring/organic compounds/oxygen/oxygen transport/PLUME/sorption/toluene/transport/transport processes/unsaturated zone/vapour/vapour transport/VOCs/ZONE
Notes: Plume mapping and inverse modeling
Abstract: Soil vapour transport to indoor air is an important potential exposure pathway at many sites impacted by subsurface volatile organic compounds (VOCs). The inclusion of biodegradation in vadose zone transport models for benzene, toluene and xylene (BTX) and fuel hydrocarbons has been proposed; however, there is still significant uncertainty regarding biodegradation rates and the local effects of buildings or ground surface cover on fate and transport processes. The objective of this study was to evaluate biodegradation processes through comprehensive monitoring at a site contaminated with BTX and model simulation. Study methods included extensive vertical profiling of BTX vapour and light gas (oxygen and carbon dioxide) concentrations and moisture content, and semi-continuous monitoring of oxygen and pressure below a building floor slab. Significant vadose zone biodegradation over a relatively small depth interval was observed. Based on the ob-

served soil vapour profile, first-order biodegradation rates were estimated by fitting an analytical solution fur diffusion and biodecay to the data. Degradation rates were found to compare well to other reported laboratory and field data. A two-dimensional (2-D) numerical model incorporating vapour-phase diffusion, advection, sorption and biodegradation was used to simulate the effect of a building floor slab on transport processes. Model results demonstrate the sensitivity of vapour-phase BTX and oxygen transport to partial barriers to diffusion (e.g. building foundation) and highlight the importance of using a model that ties biodecay to oxygen availability. In addition, depressurization within a building and advective transport is shown to have a potentially significant effect on BTX late, in soil below. (C) 2000 Elsevier Science B.V. All rights reserved

Hohener, P., N. Dakhel, M. Christophersen, M. Broholm, and P. Kjeldsen 2006. Biodegradation of hydrocarbons vapors: Comparison of laboratory studies and field investigations in the vadose zone at the emplaced fuel source experiment, Airbase Vaerlose, Denmark. Journal of Contaminant Hydrology 88:337-358.
Reference ID: 35
Keywords: aerobic/aerobic biodegradation/attenuation/benzene/BIODEGRADATION/degradation/degradation rates/hydrocarbon/inverse modeling/kinetics/microbial communities/migration/modeling/models/NATURAL ATTENUATION/organic compounds/petroleum/PLUME/reactive transport/transport/unsaturated zone/vapor/VOCs/ZONE
Notes: Plume mapping and inverse modeling
Abstract: The natural attenuation of volatile organic compounds (VOCs) in the unsaturated zone can only be predicted when information about microbial biodegradation rates and kinetics are known. This study aimed at determining first-order rate coefficients for the aerobic biodegradation of 13 volatile petroleum hydrocarbons which were artificially emplaced as a liquid mixture during a field experiment in an unsaturated sandy soil. Apparent first-order biodegradation rate coefficients were estimated by comparing the spatial evolution of the resulting vapor plumes to an analytical reactive transport model. Two independent reactive numerical model approaches have been used to simulate the diffusive migration of VOC vapors and to estimate degradation rate coefficients. Supplementary laboratory column and microcosm experiments were performed with the sandy soil at room temperature under aerobic conditions. First-order kinetics adequately matched the lab column profiles for most of the compounds. Consistent compound-specific apparent first-order rate coefficients were obtained by the three models and the lab column experiment, except for benzene. Laboratory microcosm experiments lacked of sensitivity for slowly degrading compounds and underestimated degradation rates by up to a factor of 5. Addition of NH_3 vapor was shown to increase the degradation rates for some VOCs in the laboratory microcosms. All field models suggested a significantly higher degradation rate for benzene than the rates measured in the lab, suggesting that the field microbial community was superior in developing benzene degrading activity. (c) 2006 Elsevier B.V. All rights reserved

Karapanagioti, H. K., P. Gaganis, V. N. Burganos, and P. Hohener 2004. Reactive transport of volatile organic compound mixtures in the unsaturated zone: modeling and tuning with lysimeter data. Environmental Modelling & Software 19:435-450.

Reference ID: 280
Keywords: attenuation/concentration/groundwater/inverse modeling/lysimeter/modeling/organic compounds/petroleum/PLUME/reactive transport/solubility/SPILL/transport/unsaturated zone/VOCs/volatility/ZONE
Notes: Plume mapping and inverse modeling
Abstract: Petroleum products involve mixtures of different volatile organic compounds (VOCs) that may represent a risk for groundwater after a spill to the unsaturated zone. However, the majority of the published approaches and codes for unsaturated zone modeling handle only either a single or a limited number of compounds in order to cope with the complexity of processes involved in VOC attenuation. This work aimed at simulating complex VOC scenarios using a grouping procedure, which results in the definition of a small number of effective pseudospecies with carefully specified effective properties. Grouping criteria are developed for a hypothetical scenario that involves a mixture of seven VOCs with properties covering a wide range of values. These criteria are assessed through a comparison of group-based calculations with rigorous calculations using the individual components. Groups of species with similar solubility resulted in concentration profiles that compared very satisfactorily with the rigorous results. The approach is validated with data from a large-scale lysimeter experiment. The simulation results compare satisfactorily with the experimental data for several days and for the vast majority of the mixture components. The agreement was significantly improved when temporally varying solubility values were used, justified by the difference in the compound volatility and the concomitant alteration of the VOC mixture composition with time. (C) 2003 Elsevier Ltd. All rights reserved

Lahvis, M. A. and A. L. Baehr 1996. Estimation of rates of aerobic hydrocarbon biodegradation by simulation of gas transport in the unsaturated zone. Water Resources Research 32:2231-2249.
Reference ID: 24
Keywords: aerobic/aerobic biodegradation/aerobic degradation/BIODEGRADATION/bioventing/calibration/carbon dioxide/concentration/degradation/distribution/gas transport/geoelectrical signatures/groundwater/hydrocarbon/inverse modeling/migration/modeling/models/oxygen/petroleum/PLUME/plume stabilization/remediation/SPILL/transport/unsaturated zone/vapour flux/volatilization/ZONE
Notes: Plume mapping and inverse modeling
Abstract: The distribution of oxygen and carbon dioxide gases in the unsaturated zone provides a geochemical signature of aerobic hydrocarbon degradation at petroleum product spill sites. The fluxes of these gases are proportional to the rate of aerobic biodegradation and are quantified by calibrating a mathematical transport model to the oxygen and carbon dioxide gas concentration data. Reaction stoichiometry is assumed to convert the gas fluxes to a corresponding rate of hydrocarbon degradation. The method is applied at a gasoline spill site in Galloway Township, New Jersey, to determine the rate of aerobic degradation of hydrocarbons associated with passive and bioventing remediation field experiments. At the site, microbial degradation of hydrocarbons near the water table limits the migration of hydrocarbon solutes in groundwater and prevents hydrocarbon volatilization into the unsaturated zone. In the passive remediation experiment a site-wide degradation rate estimate of 34,400 g yr(-1) (11.7 gal. yr(-1)) of hydrocarbon was obtained by model calibration to carbon dioxide gas concentration

data collected in December 1989. In the bioventing experiment, degradation rate estimates of 46.0 and 47.9 g m(-2) yr(-1) (1.45 x 10(-3) and 1.51 x 10(-3) gal. ft.(-2) yr(-1)) of hydrocarbon were obtained by model calibration to oxygen and carbon dioxide gas concentration data, respectively. Method application was successful in quantifying the significance of a naturally occurring process that can effectively contribute to plume stabilization

Anonymous. Overview of BioVapor. 2009.
Ref Type: Slide
Ref ID: 238
Keywords: aerobic biodegradation/BIODEGRADATION/modeling/models
Notes: Modeling

Anonymous, 9999. 1-dimensional modeling of volatilization and dissolution of kerosene in the unsaturated zone at flughafen Niedergörsdorf.
Reference ID: 235
Keywords: dissolution/kerosene/modeling/NAPL/unsaturated zone/volatilization/ZONE
Notes: Modeling

Battistelli, A. 2003. MODELING THE BIODEGRADATION OF ORGANIC CONTAMINANTS WITH TMVOCBIO. (Anonymous,).
Reference ID: 82
Keywords: aerobic degradation/anarobic degradation/BIODEGRADATION/chorinated solvent/groundwater contamination/hydrocarbon/metabolism/microorganisms/migration/modeling/soil contamination/substrate/TMVOC/VOCs
Notes: Modeling

Battistelli, A. 2008. Modeling multiphase organic spills in coastal sites with TMVOC V.2.0. Vadose Zone Journal 7:316-324.
Reference ID: 86
Keywords: AQUIFER/AQUIFERS/CRUDE-OIL/groundwater/migration/modeling/NAPL/organic compounds/PLUME/plume migration/SPILL/TMVOC/transport
Notes: Modeling
Abstract: Contaminant spills are frequently encountered in coastal sites where many industrial plants are located. Refineries and petrochemical plants are often built close to the sea for easy transport of crude oil and final by-products. The migration of organic compounds spilled in the subsurface of coastal sites can be influenced by the effects of seawater intrusion in the aquifers discharging to the sea. An improved version of TMVOC, belonging to the TOUGH2 family of numerical reservoir simulators, can model the migration of multicomponent organic mixtures under multiphase conditions accounting for the effects of sodium chloride dissolved in the aqueous phase. The thermophysical properties of groundwater as a function of temperature, pressure, and salinity are evaluated following the basic approach used for saline brines in EWASG, a specialized thermodynamic module of TOUGH2 originally developed to model geothermal reservoirs. Simulations of a multicomponent organic spill using a two-dimensional vertical numerical model show the effects of seawater intrusion on the distribution of contaminants within the aquifer. The effects of the construction of an impervious wall on the nonaqueous phase liquid (NAPL) plume migration, as a

means to contain the spreading of plume toward the sea, are also investigated

Dakhel, N., G. Pasteris, D. Werner, and P. Hohener 2003. Small-volume releases of gasoline in the Vadose Zone: Impact of the additives MTBE and ethanol on groundwater quality. Environmental Science & Technology 37:2127-2133.
Reference ID: 90
Keywords: aerobic/AQUIFER/benzene/BIODEGRADATION/concentration/diffusion/fate/groundwater/hydrocarbon/lysimeter/modeling/MTBE/petroleum/SPILL/unsaturated zone/vapor/ZONE
Notes: Modeling
Abstract: A controlled gasoline spill experiment was performed under outdoor conditions typical for winter in temperate regions to study the fate of methyl tert-butyl ether (MTBE), ethanol, benzene, and selected other petroleum hydrocarbons. Artificial gasoline containing MTBE and ethanol (5% w/w of each) was placed at a defined depth into a 2.3 m thick unsaturated zone of alluvial sand overlying a gravel aquifer in a lysimeter. During an initial period of 41 days without recharge, MTBE and hydrocarbon vapors migrated by vapor-phase diffusion to groundwater, while ethanol vapors were naturally attenuated. In a subsequent period of 30 days with 5-mm daily recharge, all soluble compounds including ethanol were transported to the groundwater. Ethanol disappeared concomitantly with benzene and all other petroleum hydrocarbons except isooctane from the aerobic groundwater due to biodegradation. MTBE persisted for longer than 6 months at concentrations larger than 125 000 mug L-1. No evidence for MTBE biodegradation was found, whereas >99.6% of ethanol removal from the lysimeter was due to biodegradation. It is concluded that MTBE-free gasoline would be less harmful for groundwater resources and that ethanol is an acceptable substitute

DeVaull, G. Basics of vapor intrusion modeling. 2002. (GENERIC)
Ref Type: Slide
Ref ID: 236
Keywords: aerobic/BIODEGRADATION/modeling/vapor/vapour intrusion
Notes: Modeling

Falta, R. W., I. Javandel, K. Pruess, and P. A. Witherspoon 1989. Density-Driven Flow of Gas in the Unsaturated Zone Due to the Evaporation of Volatile Organic-Compounds. Water Resources Research 25:2159-2169.
Reference ID: 85
Keywords: density-driven flow/evaporation/modeling/organic compounds/unsaturated zone/VOCs/ZONE
Notes: Modeling

Friedel, M. J. 2005. Coupled inverse modeling of vadose zone water, heat, and solute transport: calibration constraints, parameter nonuniqueness, and predictive uncertainty. Journal of Hydrology 312:148-175.
Reference ID: 95
Keywords: calibration/concentration/inverse modeling/modeling/models/parameter nonuniqueness/prediction/predictive uncertainty/transport/transport equation/unsaturated zone/ZONE
Notes: Modeling

Abstract: In this study, an inverse methodology is presented and used to evaluate the effect that calibration of a synthetic artificial recharge model, constrained by different combinations of measurements (pressure head, temperature, and concentration), has on estimated vadose zone model parameter-value nonuniqueness and predictive water, heat, and solute transport uncertainty. Several findings are arrived at following model calibration and predictive analysis. First, composite scaled sensitivities revealed that all calibration measurement combinations contributed to the estimation of 30 water, beat, and solute transport parameters by inverting a set of vadose zone transport equations that were coupled explicitly through dependent variables and implicitly through parameters and fluid properties. Second, despite excellent model quality and perfect match of simulated-to-measured dependent field variables, the limitations in information content of field measurements used to constrain the calibration process promoted correlation among parameters; correlation among parameters promoted parameter nonuniqueness; and parameter nonuniqueness promoted predictive uncertainty. Consequently, simulations by transport models calibrated against field information represent a single realization associated with some quantifiable range of predictive uncertainty. Third, a primary reduction in uncertainty was achieved by increasing the number of calibration-constraint measurements, but reductions in uncertainty appeared restricted implying a practical limit to parameterization detail. Fourth, for a fixed number of measurements, a less prominent reduction in the range of predictive uncertainty could be realized through selective use of measurement types to constrain the calibration process. Therefore, field measurement types used to constrain the calibration process should be matched to target predictions. Fifth, because correlation among parameters contributes to predictive uncertainty, it may be possible to further reduce predictive uncertainty by estimating parameters that also minimize the largest eigenvalue in the normalized eigenvector matrix. Published by Elsevier B.V

Johnson, P. C. IDENTIFICATION OF CRITICAL PARAMETERS FOR THE JOHNSON AND ETTINGER (1991) VAPOR INTRUSION MODEL. 2003. American Petroleum Institute. (GENERIC)
Ref Type: Report
Ref ID: 91
Keywords: Johnson and Ettinger (1991) model/modeling/models/vapor/vapour migration
Notes: Modeling

Lahvis, M. A. and A. L. Baehr 1999. Transport of methyl tert-butyl ether (MTBE) and hydrocarbons to ground water from gasoline spills in the unsaturated zone. (Anonymous,).
Reference ID: 87
Keywords: GROUND-WATER/hydrocarbon/modeling/MTBE/SPILL/transport/unsaturated zone/ZONE
Notes: Modeling

Lahvis, M. A. Evaluation of Small-Volume Releases of Ethanol-Blended Gasoline at UST Sites. 2003. American Petroleum Institute. (GENERIC)
Ref Type: Report
Ref ID: 89
Keywords: benzene/BIODEGRADATION/GROUND-WA-

TER/groundwater/migration/modeling/MTBE/transport/UST/ZONE
Abstract: In anticipation of widespread use of ethanol (EtOH) as a replacement for methyl tert-butyl ether (MTBE), transport modeling was applied to predict potential effects on ground water from small-volume releases of EtOH-blended gasoline (gasohol) in the vadose zone. In particular, mass loading rates (fluxes) and travel times of EtOH andbenzene to ground water were evaluated as a function of soil type, biodegradation rate, ground-water infiltration rate, and depth to ground water. Model results indicate that migration of EtOH in the vadose zone is limited to less than 100 cm from the source for releases occurring in coarse-grained soil (sand) assuming highly conservative biodegradation- and infiltration-rate approximations. In fine-grained soil (sandy clay), EtOH transport is limited to less than 50 cm under equivalent biodegradation and infiltration conditions. In addition, the presence of EtOH in gasoline does not significantly affect benzene transport and mass loading to ground water. Travel times to ground water may be more than an order of magnitude greater for EtOH than for benzene depending primarily on the soil type, biodegradation rate, and depth to ground water. Collectively, the model results indicate that EtOH and benzene impacts on ground water from small-volume releases of EtOH-blended gasoline in the vadose zone are not expected to be significant unless the release occurs near the water table (< 100 cm) or, in the case of benzene, its biodegradation is limited.
Notes: Modeling

Lahvis, M. A. Evaluation of potential vapor transport to indoor air associated with small-volume releases of oxygenated gasoline in the zadose zone. 2005. American Petroleum Institute. (GENERIC)
Ref Type: Report
Ref ID: 92
Keywords: modeling/transport/unsaturated zone/vapor/vapour intrusion/ZONE
Notes: Modeling

Lahvis, M. A. Maximum potential impacts of tertiary butyl alcohol (TBA) on groundwater from small-volume releases of ethanol-blended gasoline in the vadose zone. 2005. American Petroleum Institute. (GENERIC)
Ref Type: Report
Ref ID: 94
Keywords: groundwater/modeling/MTBE/TBA/transport/ZONE
Notes: Modeling

Rivett, M. O. 1995. Soil-Gas Signatures from Volatile Chlorinated Solvents - Borden Field Experiments. Ground Water 33:84-98.
Reference ID: 97
Keywords: Borden field site/chorinated solvent/contamination/diffusion/distribution/GROUND-WATER/groundwater/groundwater contamination/modeling/NAPL/PLUME/soil gas/soil gas signatures/transport/volatilization/ZONE
Notes: Modeling
Abstract: Field experiments have been conducted at the Borden research site to evaluate the widely applied soil-gas survey method. In particular, the ability of surveys to delineate DNAPL chlorinated solvent sources and associated ground-water plumes has been investigated. Field experiments indicated that dissolved-phase plumes from DNAPL pools or residual located about a meter or more below the water table are

unlikely to be directly detected by soil-gas surveys. Soil-gas plumes observed at real sites are attributed to volatilization of source material in the vadose zone and consequent formation of very shallow interface zone ground-water contamination that is able to partition to the soil gas as it transports downgradient. The distribution of DNAPL sources and dissolved-phase plumes deeper in the ground-water zone may often bear little resemblance to the shallow interface zone ground-water plume above, and hence the location of this deeper contamination will remain highly difficult to identify by soil-gas surveys. Field observations are confirmed with simple analytical 1-D diffusion modeling and the implications of the results to the practice of soil-gas surveys at contaminated sites indicated

Schneider, W. and H. Stöfen 9999. Relevanz des Quellterms bei der Sickerwasserprognose. Bodenschutz.
Reference ID: 98
Keywords: modeling
Notes: Modeling

Seely, G. E., R. W. Falta, and J. R. Hunt 1994. Buoyant Advection of Gases in Unsaturated Soil. Journal of Environmental Engineering-Asce 120:1230-1247.
Reference ID: 84
Keywords: advection/density/diffusion/laboratory experiments/LIQUIDS/methane/modeling/molecular diffusion/organic compounds/permeability/soil gas/transport/vapor
Notes: Modeling
Abstract: In unsaturated soil, methane and volatile organic compounds can significantly alter. the density of soil gas and induce buoyant gas flow. A series of laboratory experiments was conducted in a two-dimensional, homogeneous sand pack with gas permeabilities ranging from 110 to 3,000 darcy. Pure methane gas was injected horizontally into the sand and steady-state methane profiles were measured. Experimental results are in close agreement with a numerical model that represents the advective and diffusive components of methane transport. Comparison of simulations with and without gravitational acceleration permits identification of conditions where buoyancy dominates methane transport. Significant buoyant flow requires a Rayleigh number greater than 10 and an injected gas velocity sufficient to overcome dilution by molecular diffusion near the source. These criteria allow the extension of laboratory results to idealized field conditions for methane as well as denser-than-air vapors produced by volatilizing nonanaqueous phase liquids trapped in unsaturated soil

Silka, L. R. 9999. Simulation of vapor transport through the unsaturated zone - interpretation of soil-gas surveys. unknown.
Reference ID: 96
Keywords: diffusive processes/groundwater contamination/modeling/oil gas/soil contamination/soil gas/transport/unsaturated zone/vapor/VOCs/ZONE
Notes: Modeling

Srinivasan, V., T. P. Clement, and K. K. Lee 2007. Domenico solution - Is it valid? Ground Water 45:136-146.
Reference ID: 93
Keywords: analytical model/analytical solution/dispersivity/Domenico solution/GROUND-WATER/longitudonal dispersiv-

ity/modeling/models/transport
Notes: Modeling
Abstract: The Domenico solution is widely used in several analytical models for simulating ground water contaminant transport scenarios. Unfortunately, many textbook as well as journal article treatments of this approximate solution are full of empirical statements that are developed without mathematical rigor. For this reason, a rigorous analysis of this solution is warranted. In this article, we present a mathematical method to derive the Domenico solution and explore its limits. Our analysis shows that the Domenico solution is a true analytical solution when the value of longitudinal dispersivity is zero. For nonzero longitudinal dispersivity values, the Domenico solution will introduce a finite amount of error. We use an example problem to quantify the nature of this error and suggest some general guidelines for the appropriate use of this solution

Troldborg, M., P. J. Binning, S. Nielsen, P. Kjeldsen, and A. G. Christensen 2009. Unsaturated zone leaching models for assessing risk to groundwater of contaminated sites. Journal of Contaminant Hydrology 105:28-37.
Reference ID: 81
Keywords: analytical solution/assessment/attenuation/concentration/degradation/diffusion/ground water/leaching/modeling/models/risk assessment/sorption/transport/transport equation/unsaturated zone/ZONE
Notes: Modeling
Abstract: Risk assessments of sites contaminated with organic contaminants are typically conducted using models that ignore gas phase transport in the unsaturated zone. Here a general approach to developing analytical solutions to multiphase transport is presented. The approach is based on a combined gas and aqueous phase contaminant transport equation. The equation has the same general form as the standard advection-diffusion equation for which many analytical solutions have been derived. Four new analytical solutions are developed using this approach: a three-dimensional solution accounting for infiltration, lateral gas diffusion, sorption and degradation; a simple one-dimensional screening model, and two one-dimensional radial gas diffusion models for use in simulating volatile organic contaminant diffusion in unsaturated soils with an impermeable cover. The models show that both degradation and diffusion are important mechanisms for attenuation of contaminant concentrations at the water table. Finally, model results are compared with field data to illustrate the applicability of the solutions in risk assessment. (C) 2008 Elsevier B.V. All rights reserved

Vogele, T. J., A. Kulresthra, J. J. Nitao, and K. Lee. Simulation of Soil Vapor Extraction at Building 518 Lawrence Livermore National Laboratory Livermore Site. 1996. (GENERIC)
Ref Type: Report
Ref ID: 83
Keywords: diffusion/heterogeneous media/modeling/NUFT/remediation/SVE/TCE/unsaturated zone/vapor/VOCs
Notes: Modeling

Walter, G. R., A. M. Geddis, R. Murray, and H. W. Bentley. Vapor Phase Transport as a Groundwater Contamination Process at Arid Landfill Sites. 9999. (GENERIC)
Ref Type: Unpublished Work

Ref ID: 88
Keywords: calibration/capillary fringe/contamination/diffusion/dispersion/groundwater/groundwater contamination/groundwater flow/halogenated VOCs/landfill/modeling/molecular diffusion/monitoring/organic compounds/PLUME/soil gas/transport/transport processes/vapor/vapour transport/VOCs/ZONE
Abstract: The occurrence of halogenated volatile organic compounds (HVOCs) in groundwater beneath several municipal solid waste landfills in Tucson, Arizona in the absence of significant liquid phase movement has suggested that vapor phase transport may be the principal process transporting HVOCs from the vadose zone into the water table. The results of mathematical modeling of these transport processes were used to evaluate their relative importance under site specific conditions. The processes considered included molecular diffusion and mechanical dispersion through the capillary fringe and the effects of a falling water table on mass transport. Calibration of the mathematical model against soil gas and groundwater monitoring data indicated that mechanical dispersion due to natural groundwater flow is sufficient to result in groundwater plumes of HVOCs exceeding maximum contaminant levels. A falling water table further increases mass transport from the vadose zone to the water table through advective transport of dissolved HVOCs.
Notes: Modeling

Maier, U. 2004. Modeling of Natural Attenuation in Soil and Groundwater. Der Geowissenschaftlichen Fakultät der Eberhard -Karls- Universität Tübingen.
Reference ID: 307
Keywords: attenuation/groundwater/inverse modeling/modeling/NATURAL ATTENUATION
Notes: Inverse modeling

B 3.5: Isotopteknikker

Aravena, R. Use of Isotope Methods in Unsaturated Zones Studies. 9999. (GENERIC)
Ref Type: Report
Ref ID: 64
Keywords: CSIA/diffusion/groundwater contamination/hydrocarbon/isotope analysis/isotope techniques/methods/unsaturated zone/vapour intrusion/VOCs/ZONE
Notes: Isotope techniques

Bouchard, D., D. Hunkeler, P. Hohener, R. Aravena, P. Kjeldsen, and M. Broholm 2007. Assessment of Biodegradation of Organic Contaminants in the Unsaturated Zone Using Isotopes. (Anonymous,).
Reference ID: 281
Keywords: assessment/BIODEGRADATION/BIOREMEDIATION/isotope analy-

sis/isotope techniques/unsaturated zone/ZONE
Notes: Isotope techniques

Bouchard, D., D. Hunkeler, P. Gaganis, R. Aravena, P. Hohener, M. M. Broholm, and P. Kjeldsen 2008. Carbon isotope fractionation during diffusion and biodegradation of petroleum hydrocarbons in the unsaturated zone: Field experiment at Vaerlose airbase, Denmark, and modeling. Environmental Science & Technology 42:596-601.
Reference ID: 63
Keywords: BIODEGRADATION/diffusion/hydrocarbon/isotope analysis/isotope techniques/modeling/organic compounds/petroleum/SPILL/unsaturated zone/vapor/VOCs/volatilization/ZONE
Notes: Isotope techniques
Abstract: A field experiment was conducted in Denmark in order to evaluate the fate of 13 volatile organic compounds (VOCs) that were buried as an artificial fuel source in the unsaturated zone. Compound-specific isotope analysis showed distinct phases in the C-13/C-12 ratio evolution in VOC vapors within 3 m from the source over 114 days. At day 3 and to a lesser extent at day 6, the compounds were depleted in C-13 by up to -5.7%o with increasing distance from the source compared to the initial source values. This trend can be explained by faster outward diffusion of the molecules with C-12 only compared to molecules with a C-13. Then, the isotope profile leveled out, and several compounds started to become enriched in C-13 by up to 9.5 parts per thousand with increasing distance from the source, due to preferential removal of the molecules with C-12 only, through biodegradation. Finally, as the amount of a compound diminished in the source, a C-13 enrichment was also observed close to the source. The magnitude of isotope fractionation tended to be larger the smaller the mass of the molecule was. This study demonstrates that, in the unsaturated zone, carbon isotope ratios of hydrocarbons are affected by gas-phase diffusion in addition to biodegradation,which was confirmed using a numerical model. Gas-phase diffusion led to shifts in delta C-13 >1 parts per thousand during the initial days after the spill, and again during the final stages of source volatilization after >75% of a compound had been removed. In between, diffusion has less of an effect, and thus isotope data can be used as an indicator for hydrocarbon biodegradation

Bouchard, D., P. Hohener, and D. Hunkeler 2008. Carbon Isotope Fractionation During Volatilization of Petroleum Hydrocarbons and Diffusion Across a Porous Medium: A Column Experiment. Environmental Science & Technology 42:7801-7806.
Reference ID: 282
Keywords: benzene/BIODEGRADATION/concentration/diffusion/diffusion coefficient/hydrocarbon/isotope fractionation/isotope techniques/monitoring/organic compounds/petroleum/unsaturated zone/vapor/VOCs/volatilization/ZONE
Notes: Isotope techniques
Abstract: The study focuses on the effect of volatilization, diffusion, and biodegradation on the isotope evolution of volatile organic compounds (VOCs) in a 1.06 m long column filled with alluvial sand. A liquid mixture of 10 VOCs was placed at one end of the column, and measurements of VOC vapor concentrations and compound-specific isotope ratios (delta C-13) were performed at the source and along the column. Initially, the compounds became depleted in C-13 by up to -4.8

parts per thousand along the column axis, until at 26 h, uniform isotope profiles were observed for most compounds, which is expected for steady-state diffusion. Subsequently, several compounds (n-pentane, benzene, n-hexane) became enriched in C-13 throughout the column. For the same compounds, a significant decrease in the source vapor concentration and a gradual enrichment of C-13 by up to 5.3 parts per thousand at the source over a period of 336 h was observed. This trend can be explained by a larger diffusive mass flux for molecules with light isotopes compared to those with a heavy isotope, which leads to a depletion of light isotopes in the source. The isotope evolution of the source followed closely a Rayleigh trend and the obtained isotope enrichment factor corresponded well to the ratio between the diffusion coefficients for heavy and light molecules as expected based on theory. In contrast to diffusion, biodegradation had generally only a small effect on the isotope profiles, which is expected because in a diffusion-controlled system the isotope shift per decrease of mass flux is smaller than in an advection-controlled system. These findings open interesting perspectives for monitoring source depletion with isotope and have implications for assessing biodegradation and source variability in the unsaturated zone based on isotopes

Bouchard, D. 9999. Use of stable isotope analysis to assess biodegradation of volatile organic compounds in the unsaturated subsurface.
Reference ID: 252
Keywords: BIODEGRADATION/isotope analysis/isotope techniques/organic compounds/unsaturated zone/VOCs
Notes: Isotope techniques

Coffin, R. B., J. W. Pohlman, K. S. Grabowski, D. L. Knies, R. E. Plummer, R. W. Magee, and T. J. Boyd 2008. Radiocarbon and stable carbon isotope analysis to confirm petroleum natural attenuation in the vadose zone. Environmental Forensics 9:75-84.
Reference ID: 283
Keywords: attenuation/concentration/degradation/hydrocarbon/isotope analysis/isotope techniques/methane/monitoring/NATURAL ATTENUATION/petroleum/soil gas/ZONE
Notes: Isotope techniques
Abstract: Co-2 and CH4 radiocarbon and stable carbon isotope ratios were used to assess natural attenuation at a fuel-contaminated soil site at the Norfolk Navy Base, Norfolk, VA (USA). Soil gas samples were collected spatially over a monitoring network in October 2002 and in March 2003. CO2 and CH4 from regions with high petroleum concentrations were 14 C-depleted relative to uncontaminated areas. (14) C-depleted methane suggested methanogenic hydrocarbon degradation. The difference in CO2 age between background and plume-influenced areas indicated that approximately 90% of the CO2 at the latter was petroleum derived making contaminant the primary source of carbon for the microbial assemblage

Conrad, M. E., A. S. Tempeton, P. F. Daley, and L. varez-Cohen 1999. Isotopic evidence for biological controls on migration of petroleum hydrocarbons. Organic Geochemistry 30:843-859.
Reference ID: 284
Keywords: aerobic/aerobic degradation/BIODEGRADATION/BIOREMEDIATION/C14/concentration/degradation/dissolution/groundwater/hydrocarbon/intrinsic bioremediation/isotope techniques/migration/organic compounds/organic mat-

ter/pathways/petroleum/PLUME/soil gas
Notes: Isotope techniques
Abstract: The isotopic compositions of potential metabolic byproducts of petroleum hydrocarbon biodegradation in soil gas and groundwater samples from a shallow plume of aviation gas (AVGAS) were analyzed to assess levels and pathways of intrinsic bioremediation occurring at the site. Gasoline range organic compounds (GROs) in soil gas samples from the original source area were low (<1000 ppm), but GRO levels under an adjacent, asphalt-covered parking lot exceeded 100,000 ppm. Soil gas CH4 was > 20% in the central part of the plume and correlated well with GRO concentrations. The C-14 contents of the CH4, associated soil gas CO2 and dissolved inorganic carbon compounds (DIC) in the groundwater were all less than 0.1 times modern, indicating they were primarily formed from degradation of AVGAS and not other potential carbon sources such as degradation of natural organic matter or dissolution of carbonate shells. The delta D and delta(13)C values of the CH4 indicate that it was produced via acetate fermentation. The delta(13)C values of CO2 and DIC in the central part of the plume were high, suggesting that a large fraction of the CO2 in that area was also produced by acetate fermentation. At the down-gradient edges of the plume, CH4 levels dropped to zero and the delta(13)C values of CO2 were much lower (-26 parts per thousand), indicating that aerobic degradation of the AVGAS was dominant in this area. Beyond the down-gradient edges of the plume, the C-14 contents of both groundwater DIC and soil gas CO2 were significantly below modern levels, implying that most of the carbon there was derived from hydrocarbons and had migrated beyond the edge of the plume. These data show that methanogenic activity in the central part of the plume was slowly degrading the AVGAS, but aerobic activity at the edges of the plume was effectively limiting migration of the hydrocarbons. (C) 1999 Elsevier Science Ltd. All rights reserved

Conrad, M. E. and D. J. DePaolo 2004. Carbon isotopic evidence for biodegradation of organic contaminants in the shallow vadose zone of the Radioactive Waste Management complex. Vadose Zone Journal 3:143-153.
Reference ID: 65
Keywords: BIODEGRADATION/C14/carbon dioxide/concentration/hydrocarbon/isotope techniques/management/monitoring/MONITORING WELLS/organic compounds/pore gas/ZONE
Notes: Isotope techniques
Abstract: Waste material buried in drums in the shallow subsurface at the Radioactive Waste Management Facility (RWMC) of the Idaho National Engineering and Environmental Laboratory (INEEL) consignificant amounts of organic compounds, including lubricating oils and chlorinated solvents. Carbon dioxide concentrations in pore gas samples from monitoring wells in the vicinity of the disposal are three to five times higher than the concentrations in nearby background wells. The stable C isotope ratios (delta(13)C values) of CO2 from the disposal pits averaged 2.4% less than CO2 from the background wells, indicating that the elevated CO2 concentrations around the pits were derived from source materials with delta(13)C values in the range of -24 to -29parts per thousand. These delta(13)C values are typical of lubricating oils, but higher than most solvents. The radiocarbon (C-14) contents of CO2 across most of the site were significantly elevated above modern concentrations due to reactor blocks buried in a subsurface vault at the site. However, several samples collected from the high-CO2 zone the far

side of the RWMC from the reactor blocks had very low C-14 contents (<0.13 times modern), confirming production from lubricating oils manufactured from fossil hydrocarbons. The magnitude of the CO2 anomaly observed at the site is consistent with intrinsic biodegradation rates on the order of 0.5 to 3.0 t C yr(-1)

Gray, J.R., Coulome, G.L., Gandhi, D., Wilson, R.D., Mackay, D.M., Lollar, B.S.. Carbon and Hydro-gen isotope fractionation during biodegradation of methyl tert-Butyl ether. Environ. Sci. Technology 36(9), 1931-1938, 2002.
Reference ID: 319

Hunkeler, D.N., Andersen,N.,Aravena, R., Bernasconi, S.M., and Butler, J. Hydrogen and carbon iso-tope fractionation during aerobic biodegradation of benzene. Environmental science and technology. 35. 3462-3467, 2001.
Reference ID: 320

Hunkeler, D.N. Personlig kommunikation. 2011.
Reference ID: 321

Meckenstock, R.U., Morasch, B., Griebler, C., Richnow, H.H. Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated aquifers. Journal of contaminant hydrology 75, 215-255, 2004.
Reference ID: 318

Ririe, G. T. Case study - Santa Maria. 9999. (GENERIC)
Ref Type: Slide
Ref ID: 251
Keywords: carbon dioxide/case study/depth profile/isotope techniques/oxygen/soil gas
Notes: Isotope techniques

B 3.6: Push-pull test

Addy, K., D. Q. Kellogg, A. J. Gold, P. M. Groffman, G. Ferendo, and C. Sawyer 2002. In situ push-pull method to determine ground water denitrification in riparian zones. Journal of Environmental Quality 31:1017-1024.
Reference ID: 291
Keywords: AQUIFER/AQUIFERS/GROUNDWATER/management/nitrate/PLUME/Push-pull tests/tracer/ZONE
Notes: Push-pull tests
Abstract: To quantify ground water denitrification in discrete locations of riparian aquifers, we modified and evaluated an in situ method based on conservative tracers and N-15-enriched nitrate. Ground water was "pushed" (i.e., injected) into a mini-piezometer and then "pulled" (i.e., extracted) from the same mini-piezometer after an incubation period. This push-pull method was applied in replicate mini-piezometers at two Rhode Island riparian sites, one fresh water and one brackish water. Conservative tracer pretests were conducted to determine incubation periods, ranging from 5 to 120 h, to optimize recovery of introduced plumes. For nitrate push-pull tests, we used two conservative tracers, sulfur hexafluoride and bromide, to provide insight into plume recovery. The two conservative tracers behaved similarly. The dosing solutions were amended with N-15-enriched nitrate that enabled us to quantify the mass of denitrification gases generated during the incubation pe-

riod. The in situ push-pull method detected substantial denitrification rates at a site where we had previously observed high denitrification rates. At our brackish site, we found high rates of ground water denitrification in marsh locations and minimal denitrification in soils fringing the marsh. The push-pull method can provide useful insights into spatial and temporal patterns of denitrification in riparian zones. The method is robust and results are not seriously affected by dilution or degassing from ground water to soil air. In conjunction with measurements of ground water flowpaths, this method holds promise for evaluating the influence of site and management factors on the ground water nitrate removal capacity of riparian zones

Gomez, K., G. Gonzalez-Gil, M. H. Schroth, and J. Zeyer 2008. Transport of methane and noble gases during gas push-pull tests in variably saturated porous media. Environmental Science & Technology 42:2515-2521.
Reference ID: 285
Keywords: Ar/DESIGN/dissolution/flow rate/gas push-pull test/methane/numerical simulation/partitioning/pore water/Push-pull tests/saturation/tracer/transport
Notes: Push-pull tests
Abstract: The gas push-pull test (GPPT) is a single-well gas-tracer method to quantify in situ rates of CH4 oxidation in soils. To improve the design and interpretation of GPPT field Experiments, gas component transport during GPPTs was examined in abiotic porous media over a range of water saturations (0.0 <= S-W <= 0.61). A series of GPPTs using He, Ne, and Ar as tracers for CH4 were performed at two injection/extraction gas flow rates (similar to 200 and similar to 700 mL min(-1)) in a laboratory tank. Extraction phase breakthrough curves and mass recovery curves of the gaseous components became more similar at higher S-w as water in the pore space restricted diffusive gas-phase transport. Diffusional fractionation of the stable carbon isotopes of CH4 during the extraction period of GPPTs also decreased with increasing S-w (particularly when S-w > 0.42). Gas-component transport during GPPTs was numerically simulated using estimated hydraulic parameters for the porous media and no fitting of data for the GPPTs. Numerical simulations accurately predicted the relative decline of the gaseous components in the breakthrough curves, but slightly overestimated recoveries at low S-w (<= 0.35) and underestimated recoveries at high S-w (>= 0.49). Comparison of numerical simulations considering and not considering air-water partitioning indicated that removal of gaseous components through dissolution in pore water was not Significant during GPPTs, even at S-w = 0.61. These data indicate that Ar is a good tracer for CH4 physical transport over the full range of Sw studied, whereas, at S-w > 0.61, any of the tracers could be used. Greater mass recovery at higher Sw raises the possibility to reduce gas flow rates, thereby extending GPPT times in environments such as tundra soils where low activity due to low temperatures may require longer test times to establish a quantifiable difference between reactant and tracer breakthrough curves

Gomez, K. E., G. Gonzalez-Gil, A. Lazzaro, and M. H. Schroth 2009. Quantifying methane oxidation in a landfill-cover soil by gas push-pull tests. Waste Management 29:2518-2526.
Reference ID: 286
Keywords: aerobic/concentration/first-order rate constants/gas push-pull test/isotope fractionation/landfill/methane/Push-pull tests/tracer
Notes: Push-pull tests

Abstract: Methane (CH4) oxidation by aerobic methanotrophs in landfill-cover soils decreases emissions of landfill-produced CH4 to the atmosphere. To quantify in situ rates of CH4 oxidation we performed five gas push-pull tests (GPPTs) at each of two locations in the cover soil of the Lindenstock landfill (Liestal, Switzerland) over a 4 week period. GPPTs consist of the injection of a gas mixture containing CH4, O-2 and noble gas tracers followed by extraction from the same location. Quantification of first-order rate constants was based upon comparison of breakthrough curves of CH4 with either At or CH4 itself from a subsequent inactive GPPT containing acetylene as an inhibitor of CH4 oxidation. The maximum calculated first-order rate constant was 24.8 +/- 0.8 h(-1) at location 1 and 18.9 +/- 0.6 h(-1) at location 2. In general, location 2 had higher background CH4 concentrations in vertical profile samples than location 1. High background CH4 concentrations in the cover soil during some experiments adversely affected GPPT breakthrough curves and data interpretation. Real-time PCR verified the presence of a large population of methanotrophs at the two GPPT locations and comparison of stable carbon isotope fractionation of CH4 in an active GPPT and a subsequent inactive GPPT confirmed that microbial activity was responsible for the CH4 oxidation. The GPPT was shown to be a useful tool to reproducibly estimate in situ rates of CH4 oxidation in a landfill-cover soil when background CH4 concentrations were low. (C) 2009 Elsevier Ltd. All rights reserved

Gonzalez-Gil, G., M. H. Schroth, and J. Zeyer 2007. Transport of methane and noble gases during gas push-pull tests in dry porous media. Environmental Science & Technology 41:3262-3268.
Reference ID: 287
Keywords: advection/aerobic/Ar/concentration/diffusion/first-order rate constants/flow rate/gas push-pull test/methane/microorganisms/numerical simulation/Push-pull tests/tracer/transport
Notes: Push-pull tests
Abstract: A field method called the gas push-pull test (GPPT) was previously developed and tested for the in situ quantification of aerobic methane (CH4) oxidation by soil microorganisms. The GPPT consists of an injection followed by extraction of reactant and tracer gases into and out of the soil. Quantification of microbial activities from GPPTs requires insight in the transport of reactant and tracer gases under diverse field conditions. We investigated how the transport of different tracer gases (He, Ne, and Ar) compares to that of the reactant gas CH4 during GPPTs conducted in a well-defined, dry porous media that mimicked an open system. Transport of gaseous components during GPPT is mainly driven by advection resulting from injection and extraction and diffusion driven by concentration gradients. Regardless of the advective component (selected injection/extraction, flow rates 0.2-0.8 L min(-1)), diffusion was the dominant transport mechanism for gaseous components. This resulted in dissimilar transport of CH4 and the tracers He and Ne. Numerical simulations of GPPTs showed that similar transport of these components is only achieved at very high injection/extraction rates that, in practice, are not feasible since they would imply extremely short duration times of GPPTs to allow for consumption of a measurable amount of reactant(s) by soil microorganisms. However, Ar transport was similar to that of CH4. Hence, Ar may be a good tracer provided that it is injected at high concentrations (e.g., >25% [v/v]) to overcome its background concentration in soil air. Using moderate injection/extraction rates (e. g., 0.6 L min(-1)) with injected

volumes of 10-30 L will result in GPPT durations of 1-3 h, which would suffice to attain a measurable consumption of reactant(s) in soils having relatively high (e. g., first-order rate constants > 0.3 h-1) microbial activities

Gonzalez-Gil, G., M. H. Schroth, K. Gomez, A. Papritz, and J. Zeyer 2008. Diffusional and microbial isotope fractionation of methane during gas push-pull tests. Geochimica et Cosmochimica Acta 72:2115-2124.
Reference ID: 255
Keywords: AQUIFER/case study/diffusion/gas push-pull test/isotope fractionation/laboratory experiments/methane/microorganisms/modeling/molecular diffusion/numerical simulation/Push-pull tests/tracer/transport/transport processes/unsaturated zone/ZONE
Notes: Push-pull tests
Abstract: A field method called gas push-pull test (GPPT) was previously developed for in-situ quantification of methane (CH4) oxidation by soil microorganisms. We examined whether natural-abundance stable carbon-isotope analysis of CH4, a common approach used to measure in-situ bioconversions, could be used as a quantitative tool to complement the GPPT method. During GPPTs strong isotope fractionation of CH4 due to molecular diffusion can occur. This effect was observed in laboratory experiments regardless of the GPPTs' advective component (i.e., for different injection/extraction rates). Numerical simulations showed that if a GPPT is applied in soils with low microbial CH4 oxidation activities, isotope fractionation may be dominated by molecular diffusion rather than by consumption. Because diffusional and microbial isotope fractionation of CH4 occur simultaneously during a GPPT, CH4 isotope data alone from a single GPPT cannot be used to assess the bioconversion process. However, microbial fractionation may be estimated if the extent of diffusional fractionation is known. This can be achieved either by conducting two sequential GPPTs, with microbial activity being inhibited in the second test, or by estimating physical transport processes via co-injected tracers' gas analysis. We present a case study, in which we re-analyzed GPPTs previously performed in the unsaturated zone above a petroleum-contaminated aquifer. At this field site the combination of sequential GPPTs, stable carbon-isotope analysis of CH4, and a modeling approach, which considers diffusion and microbial CH4 oxidation, was a powerful tool to estimate in situ both apparent Michaelis-Menten kinetic constants and the microbial kinetic isotope effect. (c) 2008 Elsevier Ltd. All rights reserved

Haggerty, R., M. H. Schroth, and J. D. Istok 1998. Simplified method of "push-pull" test data analysis for determining in situ reaction rate coefficients. Ground Water 36:314-324.
Reference ID: 294
Keywords: AQUIFER/concentration/dispersivity/in situ/monitoring/porosity/Push-pull tests/tracer/transport
Notes: Push-pull tests
Abstract: The single-well, "push-pull" test method is useful for obtaining information on a wide variety of aquifer physical, chemical, and microbiological characteristics. A push-pull test consists of the pulse-type injection of a prepared test solution into a single monitoring well followed by the extraction of the test solution/ground water mixture from the same well. The test solution contains a conservative tracer and one or more reactants selected to investigate a particular process. During the extraction phase, the concentrations of tracer, reactants, and pos-

sible reaction products are measured to obtain breakthrough curves for all solutes. This paper presents a simplified method of data analysis that can be used to estimate a first-order reaction rate coefficient from these breakthrough curves. Rate coefficients are obtained by fitting a regression line to a plot of normalized concentrations versus elapsed time, requiring no knowledge of aquifer porosity, dispersivity, or hydraulic conductivity. A semi-analytical solution to the advective-dispersion equation is derived and used in a sensitivity analysis to evaluate the ability of the simplified method to estimate reaction rate coefficients in simulated push-pull tests in a homogeneous, confined aquifer with a fully-penetrating injection/extraction well and varying porosity, dispersivity, test duration, and reaction rate. A numerical flow and transport code (SUTRA) is used to evaluate the ability of the simplified method to estimate reaction rate coefficients in simulated push-pull tests in a heterogeneous, unconfined aquifer with a partially penetrating well. In all cases the simplified method provides accurate estimates of reaction rate coefficients; estimation errors ranged from 0.1 to 8.9% with most errors less than 5%. In an example application, the method is used to estimate reaction rate coefficients for a microbiological process (denitrification) using data from field push-pull tests performed in a petroleum-contaminated, unconfined alluvial aquifer

Schroth, M. H., J. D. Istok, and R. Haggerty 2001. In situ evaluation of solute retardation using single-well push-pull tests. Advances in Water Resources 24:105-117.
Reference ID: 299
Keywords: AQUIFER/AQUIFERS/dispersivity/distribution/in situ/methods/numerical simulation/Push-pull tests/retardation factor/sorption/transport
Notes: Push-pull tests
Abstract: More efficient methods are needed for the in situ evaluation of solute sorption to aquifer sediments. The objective of this study was to develop a simplified method for estimating retardation factors for injected solutes from "push-pull" test extraction phase breakthrough curves (BTCs). Sensitivity analyses based on numerical simulations were used to evaluate the method performance for a variety of test conditions. Simulations were conducted for varying retardation factors, aquifer parameters and injection phase durations, for tests performed under nonideal transport conditions such as nonlinear equilibrium and linear nonequilibrium sorption, and for a test performed in a physically heterogeneous aquifer. Predicted retardation factors showed errors less than or equal to 14% in tests performed under ideal transport conditions (physically homogeneous aquifer with spatially uniform dispersivity that does not vary from solute to solute, spatially uniform linear equilibrium sorption). The method performed more poorly for solutes with large retardation factors ($R > 20$) and for tests conducted under nonideal transport conditions, and is expected to perform poorly in aquifers with highly heterogeneous sorption. In an example application, we used the method to estimate the distribution coefficient for Sr-85 using data from a field test performed by Pickens JF, Jackson RE, Inch KJ, Merritt WF. (Water Resour Res 1981;17:529-44). Reasonable agreement was found between distribution coefficients obtained using the simplified method of estimation and those obtained by Pickens et al. (1981). (C) 2000 Elsevier Science Ltd. All rights reserved

Schroth, M. H. and J. D. Istok 2005. Approximate solution for solute transport during spherical-flow push-pull tests. Ground Water 43:280-284.

Reference ID: 297
Keywords: analytical solution/AQUIFER/numerical simulation/Push-pull tests/transport
Notes: Push-pull tests
Abstract: An approximate analytical solution to the advection-dispersion equation was derived to describe solute transport during spherical-flow conditions in single-well push-pull tests. The spherical-flow case may be applicable to aquifer tests conducted in packed intervals or partially penetrating wells. Using results of two-dimensional numerical simulations, we briefly illustrate the applicability of the derived spherical-flow solution and provide a comparison with its cylindrical-flow counterpart. Good agreement between simulated extraction-phase breakthrough curves and the spherical-flow solution was found when the length of the injection/extraction region was small compared to both aquifer thickness and maximum solute frontal position at the end of the injection phase. On the other hand, discrepancies between simulated breakthrough curves and the spherical-flow solution increased with increasing anisotropy in hydraulic conductivities. Several inherent limitations embedded in its derivation such as assumptions of isotropy and homogeneity warrant the cautious use of the spherical-flow solution

Schroth, M. H. and J. D. Istok 2006. Models to determine first-order rate coefficients from single-well push-pull tests. Ground Water 44:275-283.
Reference ID: 300
Keywords: AQUIFER/first-order rate constants/models/nitrate/numerical simulation/Push-pull tests
Notes: Push-pull tests
Abstract: Push-pull tests (PPTs) have been successfully employed to quantify various microbially mediated processes in the subsurface. Current models for determining first-order rate coefficients (k) from PPTs assume complete and instantaneous mixing of injected test solution in the portion of the aquifer investigated by the test, i.e., the system is treated like a well-mixed reactor. Here we present two alternative models to estimate k that are based on different mixing assumptions, i.e., plug-flow and variably mixed reactor models. Rate coefficients estimated by the models were compared using a sensitivity analysis and numerical simulations of PPTs. Results indicated that all models yielded reasonably accurate k estimates (errors < 13%), while best accuracy (errors < 1%) was obtained using the variably mixed reactor model. The well-mixed reactor model generally overestimated true (simulation input) k values, whereas true k values were consistently underestimated by the plug-flow reactor model. However, estimates of k obtained with the latter models bracketed true k values in all cases. As the variably mixed reactor model is more difficult to apply, we suggest using the well-mixed and plug-flow reactor models to obtain intervals for k estimates that will encompass true k values with high certainty. In an example application, we used all models to reanalyze a published PPT data set to obtain k estimates for nitrate consumption in a petroleum-contaminated aquifer. Similar results were obtained for all three models (relative differences < 10% between k estimates), indicating that all three models are robust tools for estimating k values from PPT experimental data

Snodgrass, M. F. and P. K. Kitanidis 1998. A method to infer in situ reaction rates from push-pull experiments. Ground Water 36:645-650.
Reference ID: 301

Keywords: advection/concentration/DESIGN/dispersion/GROUND-WATER/in situ/methods/models/Push-pull tests/sorption/tracer/transport/ZONE
Notes: Push-pull tests
Abstract: A method to evaluate first-order and zero-order in situ reaction rates from a push-pull test is presented. A single-well push-pull test starts with the rapid injection of a well-mixed slug containing a known quantity of a conservative tracer and a reactive solute into the saturated zone, The slug is then periodically extracted and sampled from the same well. For zero- or first-order reactions, in the absence of sorption and assuming negligible background concentrations, these measurements can be used to evaluate reaction rate coefficients directly. The method does not involve computer-based solute transport models and requires no knowledge of regional ground water now or hydraulic parameters, The method performs well when the dominate processes are advection, dispersion, and zero- or first-order irreversible reactions. Regional now velocities must be sufficiently low such that the slug stays within the area of the well during the sampling phase, In the case of zero-order reactions, results using the method proposed here are compared with those obtained through the traditional method of calibrating a computer-based transport model. The two methods give similar estimates of the reaction rate coefficient, The method is general enough to work with a broad range of push-pull experiment designs and sampling techniques

Urmann, K., G. Gonzalez-Gil, M. H. Schroth, M. Hofer, and J. Zeyer 2005. New field method: Gas push-pull test for the in-situ quantification of microbial activities in the vadose zone. Environmental Science & Technology 39:304-310.
Reference ID: 253
Keywords: AQUIFER/first-order rate constants/gas push-pull test/groundwater/in situ/methane/microbial processes/oxygen/Push-pull tests/tracer/ZONE
Notes: Push-pull tests
Abstract: Quantitative information on microbial processes in the field is important. Here we propose a new field method, the "gas push-pull test" (GPPT) for the in-situ quantification of microbial activities in the vadose zone. To evaluate the new method, we studied microbial methane oxidation above an anaerobic, petroleum-contaminated aquifer. A GPPT consists of the injection of a gas mixture of reactants (e.g., methane, oxygen) and nonreactive tracer gases (e.g., neon, argon) into the vadose zone and the subsequent extraction of the injection gas mixture together with soil air from the same location. Rate constants of gas conversion are calculated from breakthrough curves of extracted reactants and tracers. In agreement with expectations from previously measured gas profiles, we determined first-order rate constants of 0.68 h(-1) at 1.1 m below soil surface and 2.19 h(-1) at 2.7 m, close to the groundwater table. Co-injection of a specific inhibitor (acetylene) for methanotrophs showed that the observed methane consumption was microbially mediated. This was confirmed by increases of stable carbon isotope ratios in methane by up to 42.6parts per thousand. In the future, GPPTs should provide useful quantitative information on a range of microbial processes in the vadose zone

B 3.7: Diffusiv emitter test

Rose, M. B., M. Thomsen, P. Kjeldsen, and N. Tuxen 2007. Spredning af TCE i den umættede zone under en industrigrund. (Anonymous,).
Reference ID: 288
Keywords: CFC/chorinated solvent/TCE/tracer/tracer experiment/unsaturated zone/ZONE
Notes: Diffusiv emitter test

B 3.8: Dual Point Degradation test

Loll, P., A.H. Kristensen, P. Larsen, K. Henriksen and C. Larsen. In situ test til dokumentation af nedbrydning i umættet zone. ATV vintermøde, 285-295. 2011.
Reference ID: 343
Keywords: Dual Point Degradation test/DPD-test/in-situ/rate estimation/unsaturated zone

Loll, P., Kristensen, A.H., Larsen, P., Nielsen, J.L., og Henriksen, K. Nye metoder til dokumentation af naturlig nedbrydning af oliestoffer i den umættede zone. Udkast til miljøprojekt – under udarbejdelse. 2011.
Reference ID: 344
Keywords: Dual Point Degradation test/DPD-test/in-situ/rate estimation/unsaturated zone/qPCR/diversity analysis

B 3.9: Nedbrydningsrater

Anonymous. Bioaktivitetstest - aerob nedbrydning af olie. 2002.
Ref Type: Slide
Ref ID: 240
Keywords: aerobic degradation/bioactivity test/bioaktivitetstest/degradation/degradation rates
Notes: Degradation rates

Davis, R. An analysis of subsurface vapor attenuation data ffrom petroleum hydrocarbon sites. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 243
Keywords: attenuation/degradation/degradation rates/hydrocarbon/petroleum/vapor/vapour
Notes: Degradation rates

Davis, R. OUST - soil gas DB analysis. 9999. (GENERIC)
Ref Type: Slide
Ref ID: 244
Keywords: benzene/degradation/degradation rates/first-order rate constants/modeling/soil gas
Notes: Degradation rates

Davis, R. V. Bio-attenuation of petroleum hydrocarbon vapors in the subsurface - update on studies and proposed screening criteria for the vapor intrusion pathway. 2009. (GENERIC)
Ref Type: Slide
Ref ID: 242

Keywords: bioattenuation/BioVapor/degradation/degradation rates/field study/henry's constant/hydrocarbon/models/NAPL/petroleum/vapor/vapour/vapour intrusion
Notes: Degradation rates

DeVaull, G. Microcosm analyses in applied monitored natural attenuation of MTBE and TBA. 2006. (GENERIC)
Ref Type: Slide
Ref ID: 212
Keywords: attenuation/degradation/degradation rates/monitored natural attenuation/MTBE/NATURAL ATTENUATION/TBA
Notes: Degradation rates

DeVaull, G. MTBE / TBA Biodegradation Rates. 2007. (GENERIC)
Ref Type: Slide
Ref ID: 303
Keywords: BIODEGRADATION/degradation/degradation rates/MTBE/TBA
Notes: Degradation rates

DeVaull, G. Exclusion distance screening criteria. 2009. (GENERIC)
Ref Type: Slide
Ref ID: 241
Keywords: degradation/degradation rates/exclusion distance/modeling/NAPL/petroleum/vapor/vapour/vapour intrusion
Notes: Degradation rates

Devaull, G. E., R. A. Ettinger, J. P. Salanitro, and J. B. Gustafson 1997. Benzene, toluene, ethylbenzene, and xylenes (BTEX) degradation in vadose zone soils during vapor transport: First-order rate constants. (Anonymous,).
Reference ID: 74
Keywords: benzene/BTEX/degradation/degradation rates/diffusive processes/first-order rate constants/groundwater/hydrocarbon/kinetics/monod-type kinetics/petroleum/toluene/transport/vapor/ZONE
Notes: Degradation rates

Klenk, I. D. Transport of volatile organic compounds (VOC's) from soil-gas to groundwater. 2000. (GENERIC)
Ref Type: Report
Ref ID: 73
Keywords: aerobic degradation/capillary fringe/chorinated solvent/conceptual models/Crank-Nicolson/degradation/degradation rates/diffusion/dispersion/dispersivity/field study/groundwater/henry's constant/modeling/numerical simulation/organic compounds/oxygen/prediction/R-UNSAT/risk assessment/soil gas/transport/unsaturated zone/vapour processes/VOCs/volatilization
Notes: Degradation rates

Lahvis, M. A. Evaluation of 1st-order biodegradation rates of benzene for VI risk assessment at petroleum-hydrocarcon sites. 9999. (GENERIC)
Ref Type: Pamphlet
Ref ID: 239
Keywords: assessment/benzene/BIODEGRADATION/degradation/degradation

rates/first-order rate constants/risk assessment
Notes: Degradation rates

B 3.10: Metoder

Avshalom, B., Lazarovitch, N., Kurtzman, D. and Dahan, O. In-fluence of intensive agriculture in greenhouse on groundwater quality. Abstract. 2011. Manuscript under preparation.
Ref ID: 326

Baram, S. and Dahan, O. Pollutant transport through clayey va-dose zone underlying dairy farm waste lagoons. Abstract. 2011. Manuscript under preparation.
Ref ID: 327

Baldwin, C. K., B. L. Hall, and R. R. Dupont. *IN SITU* INSTRUMENTATION FOR EVALUATING AIR INJECTION REMEDIATION TECHNOLOGIES. 9999. (GENERIC)
Ref Type: Unpublished Work
Ref ID: 75
Keywords: air sparging/concentration/GROUND-WATER/in-well aeration/methods/monitoring/oxygen/remediation/unsaturated zone/ZONE
Abstract: An instrumentation system consisting of driven well-points, instrumentation bundles, and discrete sampling has been developed for monitoring subsurface conditions during the operation of air injection remediation systems. The driven well points provide intimate contact reducing the impact on the remediation process. The instrumentation bundles afford continuous monitoring of subsurface conditions. The saturated zone bundle provides information on dissolved oxygen, temperature, and ground water displacement for use in defining the volume of influence of air injection systems in the saturated zone. The vadose zone bundle provides data on changes in oxygen concentrations and temperature. Both bundles allow discrete sampling for laboratory analysis. Criteria for sensor evaluation and laboratory testing protocols used for sensor evaluation are discussed. Also included are a description of the bundle housing and well-point layout at a field site.
Notes: Methods

Dahan, O., B. Tatarsky, Y. Enzel, C. Kulls, M. Seely, and G. Benito. Dynamics of flood water infiltra-tion and ground water recharge in hyperarid desert. Ground Water 46:450–461, 2008.
Ref ID: 322

Dahan, O., Y. Shani, Y. Enzel, Y. Yechieli, and A. Yakirevich. Direct measurements of floodwater infiltration into shallow allu-vial aquifers. J. Hydrology 344:157–170, 2007.
Ref ID: 325

Dahan, O., Mandelbaum, R., and Ronen, Z. Optimization of remediation conditions using vadose zone monitoring technology . Abstract. 2011. Manuscript under preparation.
Ref ID: 328

Dahan, O., Nativ, R., Adar, E. M., Berkowitz, B. and WeisbrodB, N. On Fracture Structure and Prefer-ential Flow in Unsaturated Chalk. Ground Water, 38: 444–451. doi: 10.1111/j.1745-6584.2000.tb00231.x, 2000.
Ref ID: 329

Dahan, O., Nativ, R., Adar, E. and Berkowitz, B. A Measurement System to Determine Water Flux and Solute Transport Through Fractures in the Unsaturated Zone. Ground Water, 36: 444–449, 1998.
Ref ID: 330

Dahan, O., R. Nativ, E. M. Adar, B. Berkowitz, and Z. Ronen Field observation of flow in a fracture intersecting unsaturated chalk, Water Resour. Res., 35(11), 3315–3326, doi:10.1029/1999WR900198. 1999.
Ref ID: 331

Dahan, O., R. Talby, Y. Yechieli, E. Adar, N. Lazarovitch, and Y. Enzel 2009. In Situ Monitoring of Water Percolation and Solute Transport Using a Vadose Zone Monitoring System. Vadose Zone Journal 8:916-925.
Reference ID: 311
Keywords: methods/migration/monitoring/pore water/tracer/transport/ZONE
Notes: Methods
Abstract: Water percolation and tracer migration through the vadose zone underneath an ephemeral channel were studied using a vadose zone monitoring system (VMS) and application of a multitracer test. The VMS included flexible time-domain reflectometry (FTDR) probes for continuous tracking of water content profiles, and vadose zone sampling ports (VSPs) for frequent sampling of the deep vadose pore water at multiple depths. The VMS was installed directly under an infiltration pond with several infiltration rings containing a traceable solution. Water content measurements by the FTDR probes allowed detailed visualization of the vadose wetting process; VSP samples allowed the establishment of tracer breakthrough curves at various depths. Flow velocities and fluxes were calculated from both the wetting process and the tracer breakthrough curves. The multitracer experiment revealed an unsteady flow pattern strongly affected by the layered structure of the sediments. The tracer breakthrough curves indicated domination of a mobile-immobile flow mechanism controlling contaminant migration across the vadose zone. The experimental setup demonstrated the ability of the VMS to provide real-time monitoring of water flow and contaminant transport in the vadose zone

Dahan, O. and S. Bones. VADOSE-ZONE MONITORING SYSTEM - KEY TO GROUNDWATER PROTECTION AND OPTIMIZATION OF REMEDIATION CONDITIONS. 9999. (GENERIC)
Ref Type: Pamphlet
Ref ID: 310
Keywords: groundwater/methods/monitoring/remediation
Notes: Methods

Dahan O, Bones S. Vadose-zone monitoring as a key to groundwater protection and optimization of remediation strategies. 2010.
Ref Type: Slide
Ref ID: 317

Keywords: groundwater/monitoring/remediation/methods
Notes: Methods

Davis, G. B., B. M. Patterson, and J. Wright. Field assessment of vapours. 2009. CRC Care. (GENERIC)
Ref Type: Report
Ref ID: 193
Keywords: assessment/field assessment/field study/guidance/methods/vapour/vapour behaviour/vapour intrusion/vapour migration/VOCs
Notes: Methods

Hartman, B. Field techniques and strategies for documenting bioattenuation. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 234
Keywords: bioattenuation/documentation of degradation/field techniques/hydrocarbon/methods/soil gas
Notes: Methods

Kjærgaard, M. Prøvetagning af porevand i umættet zone. Et litteraturstudie. 540. 2000. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 192
Keywords: gravitation sampler/MACRO/methods/models/pore water/samplings methods/transport/unsaturated zone/vacumm sampler/vapour transport/ZONE
Abstract: Ofte overvurderes risikoen for, at en jordforurening påvirker grundvandsressourcen, fordi man estimerer en for stor porevæskekoncentrationen. Miljøstyrelsen har derfor iværksat dette studie af metoder til prøvetagning af porevand. Sugeceller, passive prøvetagere, vandig ekstraktion, centrifugering samt beregning efter fugacitetsprincippet vurderes at være potentielt egnede metoder over for de stoffer, for hvilke der findes grundvandskvalitetskriterier. Der kræves dog betydelig metodeudvikling
Notes: Methods

Kjærgaard, M. Bestemmelse af forureningskoncentrationen i mobilt porevand i den umættede zone. 1224. 2008. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 191
Keywords: concentration/lysimeter/methods/monitoring/pore gas/pore water/unsaturated zone/ZONE
Notes: Methods

NEW YORK STATE DEPARTMENT OF HEALTH. Guidance for Evaluating Soil Vapor Intrusion in the State of New York. 2006. New York State Department of Health. (GENERIC)
Ref Type: Report
Ref ID: 194
Keywords: field assessment/guidance/indoor air quality/remediation/vapor/vapour intrusion
Abstract: This document provides guidance on identifying and addressing existing and potential human exposures to contaminated subsurface vapors associated with known or suspected volatile chemical contamination. The guidance is applicable anywhere a soil vapor intrusion in-

vestigation is warranted in the State of New York.
Notes: Methods

Rimon, Y., O. Dahan, R. Nativ, and S. Geyer. Water percolation through the deep vadose zone and groundwater recharge: Pre-liminary results based on a new vadose zone monitoring system. Water Re-sour. Res. 43:W05402, 2007.
Ref ID: 323

Rimon, Y., Nativ. R., and Dahan, O., Physical and Chemical Evidence for Pore-Scale Dual-Domain Flow in the Vadose Zone. Vadose Zone J. Vol. 10, 2011.
Ref ID: 324

B 3.10.1 Tracermetoder

Cameron, R. J., J. C. Evans, M. D. Johnson, and T. L. Liikala. Summary of Hanford Subsurface Air Flow and Extraction (SAFE) Activities for Fiscal Year 2002. 2002. Pacific Northwest National Laboratory. (GENERIC)
Ref Type: Report
Ref ID: 206
Keywords: AQUIFER/assessment/capillary fringe/groundwater/hydrocarbon/methods/remediation/risk assessment/tracer/transport/unsaturated zone/vapour
Notes: Tracer methods

Divine, C. E., J. E. McCray, L. M. W. Martib, W. J. Blanford, D. J. Blitzer, M. L. Brusseau, and T. B. Boving 2004. Partitioning tracer tests as a remediation metric: Case study at naval amphibious base little creek, Virginia Beach, Virginia. Remediation Journal 14:7-32.
Reference ID: 55
Keywords: case study/concentration/DESIGN/distribution/LIQUIDS/methods/NAPL/partitioning/partitioning tracer test/PLUME/PLUME/pore gas/remediation/saturation/tracer
Notes: Tracer methods
Abstract: The partitioning tracer test (PTT) is a characterization tool that can be used to quantify the porespace saturation (S_N) and spatial distribution of dense nonaqueous phase liquids (DNAPLs) in the subsurface. Because the method essentially eliminates data interpolation errors by directly measuring a relatively large subsurface volume, it offers significant promise as a remediation metric for DNAPL-zone remediation efforts. This article presents, in detail, the design and results of field PTTs conducted before and after a DNAPL-zone treatment at the Naval Amphibious Base Little Creek, Virginia Beach, Virginia. The results from different tracers yield a relatively large range in S_N estimates, indicating notable uncertainty and presenting significant challenges for meaningful interpretation. Several potential interpretation methods are presented, resulting in an estimated DNAPL removal range of 15 to 109 L. While this range is large, it is consistent with the DNAPL removal (30 L) determined from analysis of effluent concentration measurements collected during the remediation efforts. At this site, the initial and final S_N values are low, and the relatively inconsistent performance of the various tracers indicates that these levels are near the lower prac-

tical quantification limit for these PTTs; however, the effective lower quantification limit for these tests is unknown. Generally, an understanding of lower quantification limits is particularly important for interpretation of post-remediation PTTs because S_N values are likely to be low (due to remediation efforts) and the S_N estimated from the PTT may be used to predict long-term dissolved plume behavior and assess associated environmental risk. Partitioning tracer test quantification limits are test-specific, as they are dependent on a variety of factors including analytical uncertainty, tracer breakthrough characteristics, and tracer data integration techniques. The results of this case study indicate that methods for estimating lower quantification limits for field PTTs require further development. © 2004 Wiley Periodicals, Inc.

Jones, K. 2009. USING ATMOSPHERIC NOBLE GASES AND SF6 AS INDICATORS FOR TRANSPORT AND REACTION PROCESSES IN HYDROCARBON CONTAMINATED SEDIMENTS.
Reference ID: 207
Keywords: advection/AQUIFER/Ar/attenuation/BIODEGRADATION/concentration/diffusion/diffusion coefficient/fate/free phase/gas transport/hydrocarbon/methods/migration/modeling/N2/partitioning/pressure gradients/tracer/transport/ZONE
Notes: Tracer methods
Abstract: Naturally occurring contaminant attenuation processes are investigated in a petroleum-hydrocarbon contaminated shallow aquifer, near Bemidji, MN. At this site, the biodegradation of hydrocarbons operates mostly under methanogenic conditions and generates CO2 and CH4. The main objectives of this study are to determine whether the full suite of noble gases, including He, Ne, Ar, Kr, and Xe, can be used to further delineate the fate of contaminants in the saturated and vadose zones and to identify mass transfer processes between these two compartments. Noble gases are sampled in the field and analyzed by way of an extraction line and mass spectrometry. In the vadose zone, gas consumption and production will induce pressure gradients, causing advective gas transport, which can be identified through concentration gradients of the inert gases. Noble gas data collected at the Bemidji site confirms the occurrence of advective gas transport, providing verification for previous field investigations and modeling that focused on Ar and N2 as gas tracers. In addition, the present study reveals that heavier noble gases provide the strongest signal for identifying reaction-induced gas advection in the vadose zone, as a result of their lower diffusion coefficients. The biogenic addition of gas to the saturated zone promotes gas exsolution and bubble formation, which can be marked in the source zone by the depletion of dissolved noble gas concentrations in relation to atmospheric values. Modeling results support the hypothesis that ebullition, the buoyancy-driven upward migration of gas bubbles, is taking place locally in the source zone. The flux of gas across the water table, as a result of ebullition, is estimated at 0.177Lm-2day-1. Ebullition is further investigated under laboratory closed system conditions. Results indicate that both atmospherically derived Ar and injections of SF6 can be used as tracers for ebullition. However, the partitioning of gas tracers into free-phase hydrocarbons limits the applicability of gas tracer injections. An oil-gas partitioning experiment is carried out to assess the feasibility of SF6 as a tracer in hydrocarbon contaminated settings. The results suggest that partitioning of SF6 into oil is extensive, with a dimensionless oil-gas partitioning coefficient of 0.73.

Weeks, E. P., D. E. Earp, and G. M. Thompson 1982. Use of Atmospheric Fluorocarbons F-11 and F-12 to Determine the Diffusion Parameters of the Unsaturated Zone in the Southern High-Plains of Texas. Water Resources Research 18:1365-1378.
Reference ID: 54
Keywords: diffusion/methods/tracer/unsaturated zone/ZONE
Notes: Tracer methods

Wiedemeier, T. H., M. A. Swanson, J. T. Wilson, D. H. Kampbell, R. N. Miller, and J. E. Hansen 1996. Approximation of biodegradation rate constants for monoaromatic hydrocarbons (BTEX) in ground water. Ground Water Monitoring and Remediation 16:186-194.
Reference ID: 302
Keywords: analytical solution/AQUIFER/attenuation/benzene/BIODEGRADATION/BIOREMEDIATION/BTEX/concentration/dispersion/dissolution/fate/GROUNDWATER/hydrocarbon/intrinsic bioremediation/methods/modeling/models/monitoring/MONITORING WELLS/NATURAL ATTENUATION/PLUME/sorption/SPILL/toluene/tracer/transport/volatilization
Notes: Tracer methods
Abstract: Two methods were used to approximate site-specific biodegradation rates of monoaromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes [BTEX]) dissolved in ground water. Both use data from monitoring wells and the hydrologic properties of the aquifer to estimate a biodegradation rate constant that can be used in ground water solute fate and transport models. The first method uses a biologically recalcitrant tracer in the ground water associated with the hydrocarbon plume to normalize changes in concentration of BTEX under anaerobic conditions; attenuation of the tracer is attributed to dilution, sorption, and/or volatilization. Attenuation of BTEX in excess of the attenuation of the tracer is attributed to biodegradation, although other processes may affect the observed rate. The second method assumes that the plume has evolved to a dynamic steady-state equilibrium. A one-dimensional analytical solution to the advection-dispersion equation is used to extract the rate of attenuation that would be necessary to produce a steady-state plume of the configuration found at the site. Attenuation is attributed largely to biodegradation because the analytical solution removes the effects of sorption and dispersion and volatilization is assumed to be minimal. Neither method fully accounts for the effects of continuing dissolution of BTEX in the source area or nonlinear sorption. Therefore, the rates cannot be attributed fully to biodegradation, but still are useful for ground water contaminant fate and transport modeling. The methods were applied to a data set from a JP-4 jet fuel spill at Hill Air Force Base, Utah. In estimates along two separate flow paths, natural attenuation rates for BTEX ranged from 0.006 to 0.038 day (-1), with most rates near 0.02 day(1). The rate for benzene ranged from 0.025 to 0.038 day (1). The rates of attenuation of individual BTEX compounds as estimated by the two methods were in close agreement. For an individual compound, the rate estimated using the second method was at most 36 percent greater than, but usually within 20 percent of, the rate estimated using the first method, suggesting that intrinsic bioremediation was the dominant process that attenuated BTEX

B 3.11: Nedbrydning

B 3.11.1 Naturlig nedbrydning

Atlas. R.M. Microbial degradation of petroleum hydrocarbons : an environmental perspective. Micro-biological reviews. 45(1):180-209, 1981.
Reference ID: 332

Baehr, A. L. and M. L. Fischer 9999. Overview of research on the transport, microbial degradation, and remediation of hydrocarbons at a subsurface gasoline-spill site in Galloway township, New Jersey. unknown.
Reference ID: 33
Keywords: aerobic degradation/anarobic degradation/capillary zone/degradation/degradation rates/degradation zones/geochemistry/groundwater contamination/hydrocarbon/natural degradation/remediation/SVE/transport/transport processes/unsaturated zone/vapour transport/ventilation
Notes: Natural degradation

Baker, R. J., A. L. Baehr, and M. A. Lahvis 2000. Estimation of hydrocarbon biodegradation rates in gasoline-contaminated sediment from measured respiration rates. Journal of Contaminant Hydrology 41:175-192.
Reference ID: 37
Keywords: aerobic/BIODEGRADATION/capillary zone/carbon dioxide/concentration/degradation/degradation rates/hydrocarbon/natural degradation/nitrogen/oxygen/respiration/toluene/vapor/ZONE
Notes: Natural degradation
Abstract: An open microcosm method for quantifying microbial respiration and estimating biodegradation rates of hydrocarbons in gasoline-contaminated sediment samples has been developed and validated. Stainless-steel bioreactors are filled with soil or sediment samples, and the vapor-phase composition (concentrations of oxygen (O-2), nitrogen (N-2), carbon dioxide (CO2), and selected hydrocarbons) is monitored over time. Replacement gas is added as the vapor sample is taken, and selection of the replacement gas composition facilitates real-time decision-making regarding environmental conditions within the bioreactor. This capability allows for maintenance of field conditions over time, which is not possible in closed microcosms. Reaction rates of CO2 and O-2 are calculated from the vapor-phase composition time series. Rates of hydrocarbon biodegradation are either measured directly from the hydrocarbon mass balance, or estimated from CO2 and O-2 reaction rates and assumed reaction stoichiometries. Open microcosm experiments using sediments spiked with toluene and p-xylene were conducted to validate the stoichiometric assumptions. Respiration rates calculated from O-2 consumption and from CO2 production provide estimates of toluene and p-xylene degradation rates within about +/-50% of measured values when complete mineralization stoichiometry is assumed. Measured values ranged from 851.1 to 965.1 g m(-3) year(-1) for toluene, and 407.2-942.3 g m(-3) year(-1) for p-xylene. Contaminated sediment samples from a gasoline-spill site were used in a second set of microcosm experiments. Here, reaction rates of O-2 and CO2 were measured and used to estimate hydrocarbon respiration rates. Total hydrocarbon reaction rates ranged from 49.0 g m(-3) year(-1) in uncontaminated (background) to 1040.4 g m(-3) year(-1) for highly contaminated sediment, based on CO2 production data. These rate estimates were similar to those obtained independently from in situ CO2 vertical gradient and flux determinations at the field site. In these experiments, aerobic conditions were maintained in the microcosms by using air as the replacement gas, thus preserving the ambient aerobic environment

of the subsurface near the capillary zone. This would not be possible with closed microcosms. (C) 2000 Elsevier Science B.V. All rights reserved

Bezerra, S. M. C. and R. G. Zytner 9999. Bioventing of Gasoline-Contaminated Soil: Some Aspects for Optimization. unknown.
Reference ID: 32
Keywords: bioventing/contamination/degradation/groundwater/groundwater contamination/hydrocarbon/microorganisms/natural degradation/prediction/remediation/soil contamination/soil vapour extraction/SVE/vapour
Notes: Natural degradation
Abstract: Underground storage tank leakage is a concern in North America because gasoline contaminated soil can cause significant groundwater contamination. São Paulo (Brazil) has leakage rates similar to North America. The typical in-situ remediation process is soil vapour extraction (SVE), but experience shows that tailing usually occurs. Bioventing is an innovative technology to address tailing in the remediation of contaminated sites, where natural occurring hydrocarbon degrading microorganisms are stimulated. The drawback is the prediction of time needed for bioventing to reach site closure. Encouraging laboratory results have not always translated into similar outcomes in the field. One reason for this inconsistency is the scale-dependent phenomenon that influences the process. Research is being conducted to develop correlations that incorporate a variety of factors including soil type, contaminant composition, and nutrient composition. These correlations will assist in better predicting the necessary time to reach site closure.

Brauner, J. S. and M. Killingstad. In situ Bioremediation of Petroleum Aromatic Hydrocarbons. 1996. (GENERIC)
Ref Type: Internet Communication
Ref ID: 38
Keywords: aerobic degradation/BIOREMEDIATION/BTEX/degradation/electron acceptor/electron tower/groundwater contamination/hydrocarbon/natural degradation/petroleum/redox conditions
Notes: Natural degradation

Christensen, A. G. Projekt om umættet zone - undersøgelse af fyringsolies transport og nedbrudning i den umættede zone. 2006. (GENERIC)
Ref Type: Report
Ref ID: 306
Keywords: degradation/field study/natural degradation/transport/unsaturated zone/ZONE
Notes: Natural degradation

Dibble, J.T. and Bartha, R., 1979. Leaching aspects of oil sludge biodegradation in soil. Soil Science 127, 365-370.
Ref ID: 341

DMR. Upublicerede data. 2011.
Ref ID: 336

Downey, D.C., Hinchee, R.E., og Miller, R.N. Cost-Effective Remediation and Closure of Petroleum-Contaminated Sites. Battelle Press, Columbus,

Ohio. ISBN 1-57477-071-3. 1999.
Ref ID: 340

Downey, D. C. and F. L. Hall. Using soil gas surveys to determine bioventing feasibility and natural attenuation potential. 9999. (GENERIC)
Ref Type: Report
Ref ID: 250
Keywords: attenuation/bioventing/degradation/NATURAL ATTENUATION/natural degradation/soil gas
Notes: Natural degradation

Grathwohl, P., D. Halm, A. Bonilla, M. Broholm, V. Burganos, M. Christophersen, R. Comas, P. Gaganis, I. Gorostiza, P. Hohener, P. Kjeldsen, and H. van der Sloot. Guideline for groundwater risk assessment at contaminated sites (GRACOS). 2003. (GENERIC)
Ref Type: Report
Ref ID: 249
Keywords: assessment/BIODEGRADATION/capillary fringe/degradation/diffusion/diffusion limited desorption/DOC/groundwater/guidance/heavy metals/leaching/modeling/NAPL/natural degradation/raoult's law/risk assessment/toxicity/unsaturated zone/VOCs
Notes: Natural degradation

Hansen, L., S. Waisner, D. Ringelberg, H. Fredrickson, R. Wade, R. Bajpai, and J. Talley. Gasoline Alley, Fort Drum Bioremediation Evaluation, Area 1595, Phase I and Phase II. 2000. (GENERIC)
Ref Type: Report
Ref ID: 53
Keywords: BIOREMEDIATION/columns/degradation/hydrocarbon/microbial processes/microorganisms/natural degradation/remediation
Notes: Natural degradation

Hinchee, R. E. and S. K. Ong 1992. A Rapid Insitu Respiration Test for Measuring Aerobic Biodegradation Rates of Hydrocarbons in Soil. Journal of the Air & Waste Management Association 42:1305-1312.
Reference ID: 31
Keywords: aerobic/aerobic biodegradation/aerobic degradation/assessment/BIODEGRADATION/bioventing/carbon dioxide/degradation/degradation rates/hydrocarbon/in situ/In-situ method/methods/monitoring/natural degradation/oxygen/petroleum/remediation/respiration/soil contamination/unsaturated zone/ventilation/ZONE
Notes: Natural degradation
Abstract: An in situ test method to measure the aerobic biodegradation rates of hydrocarbons in contaminated soil is presented. The test method provides an initial assessment of bioventing as a remediation technology for hydrocarbon-contaminated soil. The in situ respiration test consists of ventilating the contaminated soil of the unsaturated zone with air and periodically monitoring the depletion of oxygen (O2) and production of carbon dioxide (CO2) over time after the air is turned off. The test is simple to implement and generally takes about four to five days to complete. The test was applied at eight hydrocarbon-contaminated sites of different geological and climatic conditions. These sites were contaminated with petroleum products or petroleum fuels, except for two sites where the contaminants were primarily poly-

cyclic aromatic hydrocarbons. Oxygen utilization rates for the eight sites ranged from 0.02 to 0.99 percent O2/hour. Estimated biodegradation rates ranged from 0.4 to 19 mg/kg of soil/day. These rates were similar to the biodegradation rates obtained from field and pilot studies using mass balance methods. Estimated biodegradation rates based on O2 utilization were generally more reliable (especially for alkaline soils) than rates based on CO2 production. CO2 produced from microbial respiration was probably converted to carbonate under alkaline conditions

Konopka, A. and R. Turco 1991. Biodegradation of Organic-Compounds in Vadose Zone and Aquifer Sediments. Applied and Environmental Microbiology 57:2260-2268.
Reference ID: 30
Keywords: AQUIFER/BIODEGRADATION/C14/capillary fringe/degradation/degradation rates/microbial processes/natural degradation/organic compounds/sorption/unsaturated zone/ZONE
Notes: Natural degradation
Abstract: The microbial processes that occur in the subsurface under a typical Midwest agricultural soil were studied. A 26-m bore was installed in November of 1988 at a site of the Purdue University Agronomy Research Center. Aseptic collections of soil materials were made at 17 different depths. Physical analysis indicated that the site contained up to 14 different strata. The site materials were primarily glacial tills with a high carbonate content. The N, P, and organic C contents of sediments tended to decrease with depth. Ambient water content was generally less than the water content, which corresponds to a -0.3-bar equivalent. No pesticides were detected in the samples, and degradation of added C-14-labeled pesticides (atrazine and metolachlor) was not detected in slurry incubations of up to 128 days. The sorption of atrazine and metolachlor was correlated with the clay content of the sediments. Microbial biomass (determined by direct microscopic count, viable count, and phospholipid assay) in the tills was lower than in either the surface materials or the aquifer located at 25 m. The biodegradation of glucose and phenol occurred rapidly and without a lag in samples from the aquifer capillary fringe, saturated zone, and surface soils. In contrast, lag periods and smaller biodegradation rates were found in the till samples. Subsurface sediments are rich in microbial numbers and activity. The most active strata appear to be transmissive layers in the saturated zone. This implies that the availability of water may limit activity in the profile

Kristensen, A. H. 2009. NATURLIG NEDBRYDNING I LAGDELT UMÆTTET ZONE. (Anonymous,).
Reference ID: 204
Keywords: degradation/hydrocarbon/natural degradation/soil properties/unsaturated zone/ZONE
Notes: Natural degradation
Abstract: Naturlig nedbrydning af kulbrinter i umættet zone afhænger af de jordfysiske forhold, der
styrer transporten af ilt og gasformig forurening. Rambøll har sammen med Oliebranchens
Miljøpulje og Aalborg Universitet undersøgt hvordan potentialet for naturlig nedbrydning,
under optimale betingelser i laboratoriet, varierer i jordprøver fra en dyb, lagdelt umættet zone
forurenet med benzin og diesel. Resultaterne viste, at vandindholdet i de

forskellige
lagdelinger var en indikator for lokale iltforhold og dermed potentialet for aerob nedbrydning.
Desuden blev det vist, at nedbrydningspotentialet var tæt forbundet med den enkelte
jordprøves tekstur i rækkefølgen: gruset moræneler > finsand > fugtig kalk. Resultaterne taler
for, at risikovurderinger i lagdelt geologi bør inddrage naturlig nedbrydning på en måde, der
tager hensyn til lagdelingernes forskellige biologiske og fysiske egenskaber. Geologiske
modeller bør derfor medtage information, der gør det muligt, at vurdere nedbrydningspotentialets rumlige variation.

Lahvis, M. A., A. L. Baehr, and R. J. Baker 1999. Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions. Water Resources Research 35:753-765.
Reference ID: 36
Keywords: aerobic/aerobic biodegradation/aerobic degradation/attenuation/benzene/BIODEGRADATION/capillary zone/carbon dioxide/concentration/degradation/first-order rate constants/gas transport/groundwater/hydrocarbon/kinetics/migration/NATURAL ATTENUATION/natural degradation/oxygen/soil gas/SPILL/toluene/transport/unsaturated zone/vapor/volatilization/ZONE
Notes: Natural degradation
Abstract: Aerobic biodegradation and volatilization near the water table constitute a coupled pathway that contributes significantly to the natural attenuation of hydrocarbons at gasoline spill sites. Rates of hydrocarbon biodegradation and volatilization were quantified by analyzing vapor transport in the unsaturated zone at a gasoline spill site in Beaufort, South Carolina. Aerobic biodegradation rates decreased with distance above the water table, ranging from 0.20 to 1.5 g m(-3) d(-1) for toluene, from 0.24 to 0.38 g m(-3) d(-1) for xylene, from 0.09 to 0.24 g m(-3) d(-1) for cyclohexene, from 0.05 to 0.22 g m(-3) d(-1) for ethylbenzene, and from 0.02 to 0.08 g m(-3) d(-1) for benzene. Rates were highest in the capillary zone, where 68% of the total hydrocarbon mass that volatilized from the water table was estimated to have been biodegraded. Hydrocarbons were nearly completely degraded within 1 m above the water table. This large loss underscores the importance of aerobic biodegradation in limiting the transport of hydrocarbon vapors in the unsaturated zone and implies that vapor-plume migration to basements and other points of contact may only be significant if a source of free product is present. Furthermore, because transport of the hydrocarbon in the unsaturated zone can be limited relative to that of oxygen and carbon dioxide, soil-gas surveys conducted at hydrocarbon-spill sites would benefit by the inclusion of oxygen- and carbon-dioxide-gas concentration measurements. Aerobic degradation kinetics in the unsaturated zone were approximately first-order. First-order rate constants near the water table were highest for cyclohexene (0.21-0.65 d(-1)) and nearly equivalent for ethylbenzene (0.11-0.31 d(-1)), xylenes (0.10-0.31 d(-1)), toluene (0.09-0.30 d(-1)), and benzene (0.07-0.31 d(-1)). Hydrocarbon mass loss rates at the water table resulting from the coupled aerobic biodegradation and volatilization process were determined by extrapolating gas transport rates through the capillary zone. Mass loss rates from groundwater were highest for toluene (0.20-0.84 g

m(-2) d(-1)), followed by xylenes (0.12-0.69 g m(-2) d(-1)), cyclohexene (0.05-0.15 g m(-2) d(-1)), ethylbenzene (0.02-0.12 g m(-2) d(-1)), and benzene (0.01-0.04 g m(-2) d(-1)). These rates exceed predicted rates of solubilization to groundwater, demonstrating the effectiveness of aerobic biodegradation and volatilization as a combined natural attenuation pathway

Lundstedt, S. Analysis of PAHs and their transformation products in contaminated soil and remedial processes. 2003. (GENERIC)
Ref Type: Report
Ref ID: 208
Keywords: accelerated solvent extraction/accumulation/BIOREMEDIATION/bioslurry/concentration/degradation/for,ation/hydrocarbon/metabolites/methods/natural degradation/oxidation products/oxy-PAHs/PAH/remediation/transformation
Abstract: Soil that is heavily contaminated with polycyclic aromatic hydrocarbons (PAHs) is often found at the sites of former gasworks and wood-impregnation plants. Since PAHs are toxic these sites represent a hazard to human health and the environment, and therefore they need to be treated, preferably by a method that destroys the contaminants, and thus eliminates the problem permanently. However, during biological and chemical degradation of PAHs other toxic compounds may be formed. If these transformation products are sufficiently persistent they could potentially accumulate during remedial processes. In the work underlying this thesis the degradation and transformation of PAHs were studied in three remedial processes: *viz.* a pilot-scale bioslurry reactor, microcosms with wood-rotting fungi and lab-scale treatments with Fenton's reagent. A group of transformation products referred to as oxygenated-PAHs (oxy-PAHs) was found to be particularly important, as these compounds are toxic and were shown to be relatively persistent in the environment. The oxy-PAHs were, for instance, found at significant concentrations in the gasworks soil used in most of the studies. This soil was highly weathered and had therefore been depleted of the more readily degradable compounds. In addition, experiments in which earthworms were exposed to the gasworks soil showed that the oxy-PAHs were more easily taken up in living organisms than PAHs. To facilitate the studies, new extraction and fractionation methods were developed. For instance, pressurized liquid extraction (PLE) was investigated for its reliability and efficiency to extract PAHs and oxy-PAHs from soil. Furthermore, a selective PLE-method was developed that can simultaneously extract and separate the PAHs and oxy-PAHs into two different fractions. This was accomplished by adding a chromatographic material (silica or Florisil) to the extraction cell. Under certain conditions all three remedial processes resulted in increasing amounts of oxy-PAHs in the soil. For example, 1-acenaphthenone and 4-oxapyrene-5-one accumulated in the bioslurry reactor. Similarly, in the soil inoculated with a white-rot fungus 9-fluorenone, benzo[*a*]anthracene-7,12-dione, 4-hydroxy-9-fluorenone and 4-oxapyrene-5-one accumulated. Finally, in an ethanol-Fenton treatment the concentration of some PAH-quinones increased in the soil. The results show that it might be necessary to monitor oxy-PAHs as well as PAHs during the remediation of PAH-contaminated sites. Otherwise, the soil may be considered detoxified too early in the process. In the long term it would be desirable to include analyses with sufficient marker compounds to follow the possible production and elimination of the oxy-PAHs. However, until such compounds can be identified it is suggested that contaminated soil should be screened for oxy-PAHs in general. The selective PLE-method presented

in this thesis could be a useful tool for this.
Notes: Natural degradation

Newman, W. A. and K. D. Barr 1997. Assessment of natural rates of unsaturated zone hydrocarbon bioattenuation. (Anonymous,).
Reference ID: 34
Keywords: assessment/barometric pressure/bioattenuation/BIOREMEDIATION/bioventing/degradation/degradation rates/hydrocarbon/in situ/molecular diffusion/NATURAL ATTENUATION/natural degradation/oxygen/unsaturated zone/ZONE
Notes: Natural degradation

Peargin, T. The significance of hydrocarbon biodegradation: Interpreting observations of hydrocarbon and oxygen behavior above shallow LNAPL source. 9999. (GENERIC)
Ref Type: Unpublished Work
Ref ID: 210
Keywords: BIODEGRADATION/degradation/hydrocarbon/NAPL/natural degradation/oxygen
Notes: Natural degradation

Pedersen, S. R. and H. U. Sø 2004. Nedbrydning af kulbrintet i den umættede zone.
Reference ID: 305
Keywords: batch test/degradation/hydrocarbon/modeling/natural degradation/partitioning/phase distribution/transport/unsaturated zone/ZONE
Notes: Natural degradation

Pejter, H. M. 2006. Transport and degradation of heating oil in soil - a soil column study.
Reference ID: 304
Keywords: BIODEGRADATION/columns/degradation/groundwater contamination/heating oil/natural degradation/PAH/risk assessment/soil contamination/transport
Notes: Natural degradation

Rambøll. Upublicerede data. 2011.
Reference ID: 335

US EPA. Bioventing Principles andPractice. Volume II: Bioventing Design. 1995. US EPA. (GENERIC)
Ref Type: Report
Ref ID: 205
Keywords: bioventing/degradation/DESIGN/natural degradation
Notes: Natural degradation

Zytner, R. G. 2002. Organic compounds in unsaturated soil.
Reference ID: 209
Keywords: adsorption/behaviour/BIOREMEDIATION/degradation/fate/hydrocarbon/isotherms/modeling/NAPL/natural degradation/organic compounds/residual saaturation of NAPL/soil vapour extraction/soil-water partition coefficient/sorption/supercritical fluid extraction/unsaturated zone/volatilization:SVE
Notes: Natural degradation

B 3.11.2 Stimuleret nedbrydning

Loll, P., C. Larsen, and K. Henriksen 2007. Stimuleret biologisk nedbrydning af fyringsolie - feltresultater der viser muligheder og brgrænsninger. (Anonymous,).
Reference ID: 289
Keywords: BIOREMEDIATION/carbon dioxide/degradation/field study/hydrocarbon/OM/oxygen/remediation/stimulated degradation/stimulation/ventilation/ZONE
Notes: Stimulated degradation
Abstract: På en villasag i Give gennemfører DMR A/S, på vegne af Topdanmark Forsikring via Olie-branchens Miljøpulje, en afværge der er baseret på stimuleret biologisk nedbrydning af fy-ringsolie. Der er tale om et spild af fyringsolie som er beliggende i et velafgrænset jordvolu-men af en 3 meter dyb umættet zone bestående af sand. Afværgen er baseret på infiltration af olienedbrydende mikroorganismer og næringssalte, samt aktiv ilttilførsel til behandlingszonen via ventilation. Der er etableret en afværgeboring nedstrøms behandlingsområdet, til sikring af hydraulisk kontrol med forureningen og det infiltrerede næringsberigede vand. De gennem-førte tiltag samt hovedresultater, problemer og perspektiver præsenteres i indlægget.

Loll, P., C. Larsen, K. Henriksen, and P. Brask. Bio-nedbrydning af fyringsolieforurening. Vand og jord . 2007. (GENERIC)
Ref Type: Magazine Article
Ref ID: 290
Keywords: benzene/BIODEGRADATION/BTEX/degradation/remediation/stimulated degradation
Abstract: Når der går hul på fyringsolieinstallationerne skal der ofte bortgraves betydelige jordmængder. Stimuleret biologisk nedbrydning har været foreslået til oprensning uden opgravning, men denne artikel viser, at metoden kun har begrænsede anvendelsesmuligheder.
Notes: Stimulated degradation

B 3.12: Parallelle strategier for mættet zone

Broholm, M., M. Christophersen, C. Westergaard, H. C. L. Hansen, D. L. Baun, L. Andersen, N. Hansen, D. Hunkeler, K. E. Klint, and H. Skou. Vurdering af naturlig nedbrydning af tjærestoffer i grundvand. Ringe Tjære- og Asfaltfabrik, Ringe, Fyn. 2009. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 203
Keywords: assessment/degradation/natural degardation/remediation/risk assessment/stimulation/tar/ZONE
Notes: Parallel strategies for saturated zone

Cunningham, J. A., H. Rahme, G. D. Hopkins, C. Lebron, and M. Reinhard 2001. Enhanced in situ bioremediation of BTEX contaminated groundwater by combined injection of nitrate and sulfate. Environmental Science & Technology 35:1663-1670.
Reference ID: 292
Keywords: AQUIFER/attenuation/benzene/BIODEGRADATION/BIOREMEDIATION/BTEX/degradation/distribution/electron acceptor/groundwater/hydrocarbon/NATURAL ATTENUATION/nitrate/remediation/sulfate reduction/ZONE
Notes: Parallel strategies for saturated zone
Abstract: Enhancement of in situ anaerobic biodegradation of BTEX compounds was demonstrated at a petroleum-contaminated aquifer in Seal Beach, CA. Specifically, combined injection of nitrate and sulfate into the contaminated aquifer was used to accelerate BTEX removal as compared to remediation by natural attenuation. An array of multi-level sampling wells was used to monitor the evolution of the in situ spatial distributions of the electron accepters and the BTEX compounds. Nitrate was utilized preferentially over sulfate and was completely consumed within a horizontal distance of 4-6 m from the injection well; sulfate reduction occurred in the region outside the denitrifying zone. By combining injection of both nitrate and sulfate, the total electron acceptor capacity was enhanced without violating practical considerations that limit the amount of nitrate or sulfate that can be added individually. Degradation of total xylene appears linked to sulfate utilization, indicating another advantage of combined injection versus injection of nitrate alone. Benzene degradation also appears to have been stimulated by the nitrate and sulfate injection close to the injection well but only toward the end of the 15-month demonstration. The results are consistent with the hypothesis that benzene can be biodegraded anaerobically after other preferentially degraded hydrocarbons have been removed

Hageman, K. J., J. A. Field, J. D. Istok, and M. H. Schroth 2003. "Forced mass balance" technique for estimating in situ transformation rates of sorbing solutes in groundwater. Environmental Science & Technology 37:3920-3925.
Reference ID: 293
Keywords: AQUIFER/concentration/dispersivity/groundwater/in situ/modeling/Push-pull tests/retardation factor/transformation/transport/transport processes/ZONE
Notes: Parallel strategies for saturated zone
Abstract: A method for estimating in situ transformation rates of sorbing solutes in groundwater is presented. The method utilizes a novel data processing technique called "forced mass balance" (FMB) to remove the effects of transport processes from reactant and product con-

centrations measured during single-well, "push-pull" tests. The effectiveness of the FMB technique was evaluated by quantifying errors in derived rates obtained by applying FMB to simulated push-pull test data generated by a numerical model. Results from simulated tests indicated that errors in derived rates increase as the test duration, groundwater velocity, and ratio of reactant to product retardation factors increase. In addition, errors in derived rates increase as the reaction rate constant and aquifer dispersivity decrease. As a demonstration, the FMB technique was used to derive an in situ reductive dechlorination rate for trichlorofluoroethene (TCFE) using data from a field push-pull test. Error analyses indicated that the in situ TCFE transformation rate was underestimated by a factor of 1.1-2. Thus, the FMB technique makes it possible to estimate in situ transformation rates of sorbing solutes and when FMB is coupled with computer modeling to estimate errors in derived in situ rates

Istok, J. D., J. A. Field, and M. H. Schroth 2001. In situ determination of subsurface microbial enzyme kinetics. Ground Water 39:348-355.
Reference ID: 295
Keywords: aerobic/AQUIFER/concentration/field study/in situ/kinetics/microbial processes/models/petroleum/respiration/substrate/transformation/ZONE
Notes: Parallel strategies for saturated zone
Abstract: The single-well, push-pull test has been used in previous field studies to measure in situ zero- and first-order rates for aerobic and anaerobic microbial respiration in the saturated zone. In this paper we demonstrate that the test can also be used to obtain more generalized descriptions of the kinetics of microbially mediated enzymatic reactions. Laboratory and field tests were performed with the model enzyme substrate p-nitrophenyl-beta -D-glucopyranoside (PNG). During a push-pull test, injected PNG is hydrolyzed in situ to p-nitrophenol (PNP); the rate of PNP production is taken as a measure of the beta -glucosidase activity expressed by indigenous microorganism. Laboratory tests were performed in physical aquifer models packed with natural aquifer sediment; field tests were performed in a shallow unconfined alluvial aquifer at a petroleum contaminated site. The laboratory and field tests demonstrate that it is possible to compute the in situ rate of PNP production as a function of PNG concentration using only data from a single push-pull test. These data can then be used to estimate the Michaelis-Menton kinetic parameters V-max and K-m for the hydrolysis reaction. This approach potentially extends the range of applicability of the push-pull test approach for use in determining kinetic parameters for a wide range of microbial processes in situ. These could include the broad class of substituted nitrophenyl substrates used to assay other enzyme systems, as well as microbially mediated redox reactions that occur during contaminant transformations

Kjærgaard, M. and J. P. Ringsted. Naturlig nedbrydning af miljøfremmede stoffer i jord og grundvand - Et litteraturstudium af 1.-ordens nedbrydningshastigheder
af miljøfremmede stoffer for hvilke der er fastsat et kvalitetskriterium i jord eller grundvand. Miljøprojekt nr. 408. 1998. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 202
Keywords: degradation/first-order rate constants/ZONE
Notes: Parallel strategies for saturated zone

Newell, C. J., H. S. Fifai, J. T. Wilson, J. A. Connor, J. A. Aziz, and M. P. Suarez. Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies. 9999. US EPA. (GENERIC)
Ref Type: Report
Ref ID: 201
Keywords: attenuation/first-order rate constants/MNA/monitored natural attenuation/NATURAL ATTENUATION/ZONE
Notes: Parallel strategies for saturated zone

Reinhard, M., S. Shang, P. K. Kitanidis, E. Orwin, G. D. Hopkins, and C. A. Lebron 1997. In situ BTEX biotransformation under enhanced nitrate- and sulfate-reducing conditions. Environmental Science & Technology 31:28-36.
Reference ID: 296
Keywords: AQUIFER/benzene/BTEX/groundwater/in situ/kinetics/nitrate/toluene/tracer/transformation/ZONE
Notes: Parallel strategies for saturated zone
Abstract: In situ anaerobic biotransformation of BTEX (benzene, toluene, ethylbenzene, o-xylene, and m-xylene) was investigated under enhanced nitrate- and sulfate-reducing conditions. Controlled amounts of BTEX compounds added to slugs of treated groundwater were released into a gasoline-contaminated aquifer at Seat Beach, CA. In a series of studies, the slugs, 470-1700 L in volume, were released into the aquifer through a multi-port injection/extraction well and were subsequently withdrawn over a 2-3-month period. To evaluate unamended in situ conditions, the injectate was treated with granular activated carbon (GAC) and augmented with bromide as a tracer. To evaluate nitrate- and sulfate-reducing conditions,the injectate was also deionized and augmented with 200-300 mu g/L BTEX, nitrate or sulfate, and background electrolytes. Under unamended conditions, transformation appeared to be limited to the slow removal of toluene and m,p-xylene (i.e., sum of m+p-xylene). Under nitrate-reducing conditions, toluene, ethylbenzene, and m-xylene were transformed without a lag phase in less than 10 days, and o-xylene was transformed in 72 days. Under sulfate-reducing conditions, toluene, m-xylene and o-xylene were completely transformed in less than 50 days, and ethylbenzene was removed in 60 days. Benzene appeared to be removed under sulfate-reducing conditions, but the trend was pronounced only at some levels. A two-dimensional model is presented for the evaluation of reactive solute behavior in such slug tests. For compounds that are transformed without a fag phase, zero-order kinetics appears to be more applicable than first-order kinetics

Schroth, M. H., J. D. Istok, G. T. Conner, M. R. Hyman, R. Haggerty, and K. T. O'Reilly 1998. Spatial variability in in situ aerobic respiration and denitrification rates in a petroleum-contaminated aquifer. Ground Water 36:924-937.
Reference ID: 298
Keywords: aerobic/AQUIFER/concentration/hydrocarbon/in situ/oxygen/petroleum/PLUME/Push-pull tests/respiration/ZONE
Notes: Parallel strategies for saturated zone
Abstract: An extensive series of single-well, push-pull tests was performed to quantify horizontal and vertical spatial variability in aerobic respiration and denitrification rates in a petroleum-contaminated aquifer, The results indicated rapid consumption of injected O-2 or NO3- in shallow and deep test intervals across a large portion of the site, Computed first-order rate coefficients for aerobic respiration ranged from

0.15 to 1.69 h(-1) in the shallow test interval, and from 0.08 to 0.83 h(-1) in the deep test interval. The largest aerobic respiration rates occurred on the upgradient edge of the contaminant plume where concentrations of petroleum hydrocarbons and dissolved O-2 were relatively high. Computed first-order rate coefficients for denitrification ranged from 0.09 to 0.42 h(-1) in the shallow test interval, and from 0.11 to 0.28 h(-1) in the deep test interval. The largest denitrification rates occurred on the downgradient edge of the plume where hydrocarbon concentrations were relatively high but dissolved oxygen concentrations were small. The rates reported here represent maximal rates of aerobic respiration and denitrification, as supported by high concentrations of electron accepters in the injected test solutions. Production of dissolved CO2 during aerobic respiration and denitrification tests provided evidence that O-2 and NO3- consumption was largely due to microbial activity. Additional evidence for microbial NO3- consumption was provided by reduced rates of NO3- consumption when dissolved O-2 was injected with NO3-, and by increased N2O production when C2H2 was injected with NO3-.

B 3.13: Diverse litteratur

American Petroleum Institute. Assessing the signifiance of subsurface contaminant vapor migration to enclosed spaces, site-specific alternatives to generic estimates. 1998. American Petroleum Institute. (GENERIC)
Ref Type: Report
Ref ID: 186
Keywords: migration/vapor
Notes: XXXX

Anonymous. Influence of bioattenuation on vapor intrusion into buildings - model simulations using semi-analytical one-dimensional model. 2006. Golder Associates. (GENERIC)
Ref Type: Report
Ref ID: 130
Keywords: aerobic degradation/bioattenuation/BIODEGRADATION/BTEX/hydrocarbon/J&E-BIO model/modeling/petroleum/semi-analytic/transport/vapor/vapour intrusion/vapour migration
Notes: XXXX

Anonymous. Rehabilitation of the former camide landfill, Horsley Park. 2006. Centre for Water & Waste Technology (CWWT). (GENERIC)
Ref Type: Report
Ref ID: 254
Keywords: biofiltration/gas interception trench/landfill/monitoring/vapour migration
Notes: XXXX

Abreu, L. D. V. and P. C. Johnson 2006. Simulating the effect of aerobic biodegradation on soil vapor intrusion into buildings: Influence of degradation rate, source concentration, and depth. Environmental Science & Technology 40:2304-2315.
Reference ID: 27
Keywords: aerobic/aerobic biodegradation/attenuation/benzene/BIODEGRADATION/degradation/hydrocarbon/oxygen/transport/vapor

Notes: XXXX
Abstract: Steady-state vapor intrusion scenarios involving aerobically biodegradable chemicals are studied using a three-dimensional multi-component numerical model. In these scenarios, sources of aerobically biodegradable chemical vapors are placed at depths of 1-14 m beneath a 10 m x 10 m basement or slab-on-grade construction building, and the simultaneous transport and reaction of hydrocarbon and oxygen vapors are simulated. The results are presented as Johnson and Ettinger attenuation factors alpha (predicted indoor air hydrocarbon concentration/source vapor concentration), and normalized contour plots of hydrocarbon and oxygen concentrations. In addition to varying the vapor source depth, the effects of source concentration (2-200 mg chemical/L vapor) and oxygen-limited first-order reaction rates 10.018-1.8 h(-1)) are studied. Hydrocarbon inputs were specific to benzene, although the relevant properties are similar to those for a range of hydrocarbons of interest. Overall, the results suggest that aerobic biodegradation could play a significant role in reducing vapor intrusion into buildings (decreased (alpha-values) relative to the no-biodegradation case, with the significance of aerobic biodegradation increasing with increasing vapor source depth, decreasing vapor source concentration, and increasing first-order biodegradation rate. In contrast to the no-biodegradation case, differences in foundation construction can be significant in some settings. The significance of aerobic biodegradation is directly related to the extent to which oxygen is capable of migrating beneath the foundation. For example, in the case of a basement scenario with a 200 mg/L vapor source located at 3 m bgs, oxygen is consumed before it can migrate beneath the foundation, so the attenuation factors for simulations with and without aerobic biodegradation are similar for all first-order rates studied. For the case of a 2 mg/L vapor source located at 8 m bgs, the oxygen is widely distributed beneath the foundation, and the attenuation factor for the biodegradation case ranges from about 3 to 18 orders-of-magnitude less than that for the no-biodegradation case

Amos, R. T. and D. W. Blowes 2008. Versatile direct push profiler for the investigation of volatile compounds near the water table. Water Resources Research 44.
Reference ID: 150
Keywords: AQUIFER/DESIGN/petroleum/SPILL/ZONE
Notes: XXXX
Abstract: The collection of representative samples of dissolved volatile compounds requires particular care to ensure that degassing does not occur during sampling, particularly for sites where the water table is deep. Furthermore, the investigation of physical and chemical processes involving volatile components can be enhanced by collecting vadose zone gas samples above the water table and collecting water samples very close to the water table. Here we describe the design and operation of a direct push profiler that allows the collection of gas and water samples from one hole. The profiler is capable of collecting water samples close to the water table and preserves the integrity of the samples collected from below deep water tables with respect to volatile compounds. The versatility of the profiler is due to the incorporation of a small-diameter bladder pump into the tip of a Waterloo profiler. Laboratory testing shows that samples collected from 10 cm below the water table and at 9 m depth below ground surface show no signs of degassing. Field measurements made at a petroleum spill site near Bemidji, Minnesota, provide a comparison of profiler results to samples collected from an existing well cluster, demonstrating the ability of the profiler to ob-

tain representative samples under field conditions. Furthermore, the field tests demonstrate the utility of the direct push profiler in terms of obtaining high-resolution, high-quality data through the vadose zone and into the upper few meters of the aquifer

Ashley, R. P., D. N. Lerner, and J. W. Lloyd 1994. Distribution and Degradation of Diesel Oil in the Unsaturated Zone Following An Oil-Spill on A Chalk Aquifer. Journal of Hydrology 159:43-59.
Reference ID: 158
Keywords: AQUIFER/AQUIFERS/degradation/dissolution/evaporation/methods/migration/remediation/unsaturated zone/ZONE
Notes: XXXX
Abstract: In 1976, there occurred a substantial loss of diesel oil from a storage facility at Royston in eastern England. The site is on the outcrop of the important Chalk aquifer, which is protected by an unsaturated zone 24-30 m thick. In 1986, a cored borehole was drilled through the site of the spillage to investigate the fate of the contaminants. The core samples were analysed by physical and chemical methods to determine the physical structure of the rock, and the characteristics and distribution of the oil. The chemically analysed samples included pore water extracts, scrapings from fracture surfaces, and non-fracture (matrix) samples. The results indicate that oil accumulated within a few millimetres of major fissure surfaces, and entry into the rock matrix was limited by the small size of pores and the presence of water. Oil may also have migrated along microscopic channels away from the major fissures. There was no evidence of downward migration of oil since the initial phase of movement. The adoption of certain assumptions regarding degradation, evaporation and dissolution processes allows the estimation of oil depletion caused by these processes. Physical weathering and degradation were found to have been extensive, but highly variable. Both processes occurred on the major fissure surfaces but, in the matrix, degradation appears to have been restricted. The conclusions have implications for the investigation and remediation of fissured Chalk aquifers contaminated by oil

Azadpour-Keeley, A., J. W. Keeley, H. H. Russell, and G. W. Sewell 2001. Monitored natural attenuation of contaminants in the subsurface: Applications. Ground Water Monitoring and Remediation 21:136-143.
Reference ID: 159
Keywords: attenuation/degradation/GROUNDWATER/modeling/monitoring/NATURAL ATTENUATION/PLUME
Notes: XXXX
Abstract: In recent years there has been increasing interest in the application of passive technologies to reduce or remove contaminants from the subsurface environment including soil and ground water. In most cases, the impetus for this interest lies in a perceived savings compared with more traditional remedial alternatives. In a few cases, the infrastructure at contaminated sites, such as buildings, paved areas, and utilities, makes the use of conventional remedial measures difficult and expensive. To demonstrate that natural processes are effective in reaching established goals, it is necessary to determine that transformation processes are taking place at a rate that is protective of human health and the environment and that these processes will continue for an acceptable period of time. The basic conditions that must be present to confirm natural attenuation processes are taking place are discussed along with the

behavior of contaminated plumes, monitoring requirements, data analysis, rates of degradation, and mathematical modeling

Bekins, B. A., I. M. Cozzarelli, E. M. Godsy, E. Warren, H. I. Essaid, and M. E. Tuccillo 2001. Progression of natural attenuation processes at a crude oil spill site: II. Controls on spatial distribution of microbial populations. Journal of Contaminant Hydrology 53:387-406.
Reference ID: 154
Keywords: AQUIFER/attenuation/benzene/concentration/CRUDE-OIL/dissolution/hydrocarbon/NATURAL ATTENUATION/SPILL/toluene/transport/ZONE
Notes: XXXX
Abstract: A multidisciplinary study of a crude-oil contaminated aquifer shows that the distribution of microbial physiologic types is strongly controlled by the aquifer properties and crude oil location. The microbial populations of four physiologic types were analyzed together with permeability, porewater chemistry, nonaqueous oil content, and extractable sediment iron. Microbial data from three vertical profiles through the anaerobic portion of the contaminated aquifer clearly show areas that have progressed from iron-reduction to methanogenesis. These locations contain lower numbers of iron reducers, and increased numbers of fermenters; with detectable methanogens. Methanogenic conditions exist both in the area contaminated by nonaqueous oil and also below the oil where high hydrocarbon concentrations correspond to local increases in aquifer permeability. The results indicate that high contaminant flux either from local dissolution or by advective transport plays a key role in determining which areas first become methanogenic. Other factors besides flux that are important include the sediment Fe(II) content and proximity to the water table. In locations near a seasonally oscillating water table, methanogenic conditions exist only below the lowest typical water table elevation. During 20 years since the oil spill occurred, a laterally continuous methanogenic zone has developed along a narrow horizon extending from the source area to 50-60 in downgradient. A companion paper [J. Contain. Hydrol. 53, 369-386] documents how the growth of the methanogenic zone results in expansion of the aquifer volume contaminated with the highest concentrations of benzene, toluene. ethylbenzene. and xylenes. (C) 2001 Elsevier Science B.V. All rights reserved

Berry, K. A. T. and D. L. Burton 1997. Natural attenuation of diesel fuel in heavy clay soil. Canadian Journal of Soil Science 77:469-477.
Reference ID: 160
Keywords: attenuation/contamination/hydrocarbon/methods/NATURAL ATTENUATION/petroleum
Notes: XXXX
Abstract: petroleum hydrocarbons in the extractable fraction decreased rapidly in a heavy clay soil contaminated with diesel fuel at 5000 mg kg(-1) demonstrating natural attenuation. Natural attenuation rates for untilled soil were estimated using two distinct extraction and analysis methods, the Oil & Grease Content (O&G) (US EPA 418.1; ASTM D 95) and extractable organics (EO) (EPA 3520B; EPA 8000A). The time to 50% decrease (t(1/2)) in the fraction varied with extraction method, Oil & Grease Content (11 d) and Extractable Organics (26 d). Complete attenuation appeared to have occurred after 74 d as Extractable Organic values for soil extracts were below the detection limit (5 mu g g(-1)). An enzyme-linked immunosorbant assay (ELISA) was also used to

monitor the hydrocarbons present in the soil. This also effectively demonstrated the near-complete disappearance of the hydrocarbons but was not quantitative. Soil microbial biomass carbon (chloroform fumigation-extraction) and surface CO2 flux measurements did not show any significant impact of diesel contamination or tillage in the active microbial population. This observation serves to demonstrate the applicability of natural attenuation as a remedial strategy for heavy clay soils contaminated with diesel fuel of the type used in this study

Bhupathiraju, V. K., P. Krauter, H. Y. N. Holman, M. E. Conrad, P. F. Daley, A. S. Templeton, J. R. Hunt, M. Hernandez, and L. varez-Cohen 2002. Assessment of in-situ bioremediation at a refinery waste-contaminated site and an aviation gasoline contaminated site. Biodegradation 13:79-90.
Reference ID: 161
Keywords: BIODEGRADATION/BIOREMEDIATION/carbon dioxide/degradation/groundwater/hydrocarbon/methane/methods/oxygen/petroleum/soil gas/ZONE
Notes: XXXX
Abstract: A combination of geochemical, microbiological and isotopic methods were used to evaluate in-situ bioremediation of petroleum hydrocarbons at one site contaminated with refinery waste and a second site contaminated with aviation gasoline at Alameda Point, California. At each site, geochemical and microbiological characteristics from four locations in the contaminated zone were compared to those from two uncontaminated background locations. At both sites, the geochemical indicators of in-situ biodegradation included depleted soil gas and groundwater oxygen, elevated groundwater alkalinity, and elevated soil gas carbon dioxide and methane in the contaminated zone relative to the background. Radiocarbon content of methane and carbon dioxide measured in soil gas at both sites indicated that they were derived from hydrocarbon contaminant degradation. Direct microscopy of soil core samples using cell wall stains and activity stains, revealed elevated microbial numbers and enhanced microbial activities in contaminated areas relative to background areas, corroborating geochemical findings. While microbial plate counts and microcosm studies using soil core samples provided laboratory evidence for the presence of some microbial activity and contaminant degradation abilities, they did not correlate well with either contaminant location, geochemical, isotopic, or direct microscopy data

Boopathy, R. 2004. Anaerobic biodegradation of no. 2 diesel fuel in soil: a soil column study. Bioresource Technology 94:143-151.
Reference ID: 162
Keywords: attenuation/BIODEGRADATION/BIOREMEDIATION/columns/degradation/electron acceptor/hydrocarbon/metabolism/NATURAL ATTENUATION/nitrate/petroleum/SPILL/ZONE
Notes: XXXX
Abstract: Soil and sediments are contaminated with petroleum hydrocarbons in many parts of the world. Anaerobic degradation of petroleum hydrocarbon is very relevant in removing oil spills in the anaerobic zones of soil and sediments. This research investigates the possibility of degrading no. diesel fuel under anaerobic conditions. Anaerobic packed soil columns were used to simulate and study in situ bioremediation of soil contaminated with diesel fuel. Several anaerobic conditions were evaluated in soil columns, including sulfate reducing, nitrate reducing, methanogenic, and mixed electron acceptor conditions. The objectives

were to determine the extent of diesel fuel degradation in soil columns under various anaerobic conditions and identify the best conditions for efficient removal of diesel fuel. Diesel fuels were degraded significantly under all conditions compared to no electron supplemented soil column (natural attenuation). However, the rate of diesel degradation was the highest under mixed electron acceptor conditions followed in order by sulfate reducing, nitrate reducing, and methanogenic conditions. Under mixed electron acceptor condition 8 No of diesel fuel was degraded within 3 10 days. While under sulfate reducing condition 54.5% degradation of diesel fuel was observed for the same period. This study showed evidence for diesel fuel metabolism in a mixed microbial population system similar to any contaminated field sites, where heterogeneous microbial population exists. (C) 2004 Elsevier Ltd. All rights reserved

Capuano, R. M. and M. A. Johnson 1996. Geochemical reactions during biodegradation vapor-extraction remediation of petroleum contamination in the vadose zone. Ground Water 34:31-40.
Reference ID: 163
Keywords: BIODEGRADATION/BIOREMEDIATION/BTEX/concentration/contamination/DESIGN/evaporation/hydrocarbon/lysimeter/pathways/petroleum/remediation/unsaturated zone/vapor/ZONE
Notes: XXXX
Abstract: Hydrocarbon concentrations in soil water and vapor are generally used to evaluate the progress of biodegradation and vapor extraction of petroleum contamination in the unsaturated zone. This study shows that changes in the inorganic composition of vadose zone water samples can be used to evaluate the reactions that occur in the unsaturated zone during such a remediation effort. Chemical analyses were completed on water samples collected from alluvial sediments contaminated with diesel fuel and gasoline at the Gallatin Farmers Cenex, Belgrade, Montana. The samples were collected from 7 suction lysimeters for 3 months after fertilization, but before vapor extraction, and then for 6 months following the start of vapor extraction, The geochemical reaction progress code SOLMINEQ.88 is used to calculate the aqueous equilibria in the samples and to simulate possible reaction pathways. Reduction in TPH and BTEX concentrations indicated that biodegadation of the petroleum began after fertilization, prior to vapor extraction, and continued after the start of vapor extraction, SO4=, HCO3-, pH, and P-CO2 show large systematic variations with both time and depth. These variations are independent of evaporation, mixing, sample extraction time, and soil moisture content and thus appear to be a direct consequence of bioremediation and vapor extraction. P-CO2 is found to be a measure of the effectiveness of vapor extraction. The chemical mass transfer calculations also show that if vapor extraction occurs alone removing CO2 from solution without coupling of a process to buffer the solution pH, large amounts of carbonate minerals could precipitate, significantly reducing sediment permeability. These data suggest that analyses of inorganic compounds in lysimeter samples can be used to evaluate geochemical changes during vadose zone remediation and can be used to improve remediation design

Choi, J. W. and J. A. Smith 2005. Geoenvironmental factors affecting organic vapor advection and diffusion fluxes from the unsaturated zone to the atmosphere under natural conditions. Environmental Engineering Science 22:95-108.

Reference ID: 155
Keywords: diffusion/organic compounds/transport/unsaturated zone/vapor/VOCs/water table fluctuation/ZONE
Notes: XXXX
Abstract: This study investigates the importance of various geoenvironmental conditions such as depth to water table, gas permeability, water-table fluctuations, moisture content. and temperature on the advection and diffusion fluxes of volatile organic compounds (VOCs) from the unsaturated zone to the atmosphere under natural conditions. A one-dimensional gas-flow and organic-vapor transport model was used to simulate vapor fluxes under sinusoidal atmospheric pressure changes with an amplitude of 300 N m(-2). The diffusion fluxes were generally greater than the advection fluxes by several orders of magnitude. The thickness of the vadose zone and gas permeability have a relatively significant effect on the advection fluxes at land surface compared to their effect on diffusion fluxes. Increasing the thickness of the vadose zone up to 30 m causes advection fluxes to increase. Increasing the gas permeability of the vadose zone Up to 10(-12) m(2) also increases the advection flux. Further increases of vadose-zone thickness or gas permeability do not cause significant additional increases in advection flux. Water-table fluctuations as small as 0.1 m affect the advection fluxes as significantly as the atmospheric pressure changes. Moisture content effects not only advection flux but also diffusion flux during sinusoidal atmospheric pressure changes. Daily temperature variations also have a significant effect on the fluxes. Heterogeneity in gas permeability and moisture content impacts advection and diffusion fluxes at land surface

Cohen, B. A., L. R. Krumholz, H. K. Kim, and H. F. Hemond 1995. In-Situ Biodegradation of Toluene in A Contaminated Stream .2. Laboratory Studies. Environmental Science & Technology 29:117-125.
Reference ID: 164
Keywords: BIODEGRADATION/degradation/field study/laboratory experiments/toluene
Notes: XXXX
Abstract: In-situ biodegradation rates for a stream contaminated with toluene (< 350 mu g/L) were determined in laboratory experiments and compared to those determined in field studies within the same stream reported in the previous paper. The biodegradation rate constant obtained in batch studies (shake-flasks, 0.06-0.16 m/h) was comparable to the in-situ rate constant obtained in field studies (0.08-0.40 m/h) at similar temperature while the rate constant from column studies was only 2% of the in-situ rate constant. This data showed that the batch studies were better indicators oi in-situ biodegradation and also more accurately reflected field conditions. Streambed surfaces were responsible for virtually all degradation, with sediments and rocks providing the most important (> 95%)compartmental contributions. Rates determined in batch studies under winter conditions were 11-14% of rates determined under summer conditions. Batch,studies of mineralization rates determined with [U-C-14]toluene indicate that mineralization rates were 23% of biodegradation rates. The remaining toluene was converted to soluble intermediates (l5%) land 62% was taken up as biomass or converted to other insoluble material. Our results support the assertion that biodegradation was the most important environmental sink for toluene, with 70% of the toluene loss due to biodegradation over the studied stream reach

Davis, G. B., T. R. Power, D. Briegel, and B. M. Patterson 1998. BTEX vapour biodegradation rates in the vadose zone: initial estimates. (Anonymous,).
Reference ID: 16
Keywords: BIODEGRADATION/BTEX/degradation rates/depth profile/groundwater/hydrocarbon/modeling/oxygen/oxygen consumption rates/remediation/unsaturated zone/vapour/ZONE
Notes: XXXX

De Visscher, A., D. Thomas, P. Boeckx, and O. Van Cleemput 1999. Methane oxidation in simulated landfill cover soil environments. Environmental Science & Technology 33:1854-1859.
Reference ID: 185
Keywords: assessment/columns/kinetics/landfill/methane/oxygen/soil gas/stimulation/ZONE
Notes: XXXX
Abstract: A considerable fraction of the methane that is produced by landfills is oxidized by its covering soil before it can reach the atmosphere. This process was studied in soil columns that simulate landfill cover soil environments. The methane uptake was followed as a function of time. In soils of agricultural origin, a maximum value of 10.7 mot m(column)(-2) d(-1) was observed. Mixing sugar beet leaves with the soil led to a temporary stimulation of the methane oxidation rate, whereas a wheat straw amendment led to permanent stimulation. Soil originating from a real landfill cover oxidized on the order of 15 mol m(column)(-2) d(-1), the highest value found in the literature to date. The soil gas composition was studied as a function of depth. With a new hatch incubation technique, methane oxidation kinetics were determined in samples taken from the soil column. By combining this kinetic data with the soil gas composition data, the actively methane oxidizing zone in the soil column could be determined and an in situ assessment of oxygen limitation could be performed. Methane oxidation takes place mainly in the Pop 30 cm of the covering soil

Delin, G. N. and W. N. Herkelrath 2005. Use of soil moisture probes to estimate ground water recharge at an oil spill site. Journal of the American Water Resources Association 41:1259-1277.
Reference ID: 152
Keywords: calibration/CRUDE-OIL/GROUND-WATER/SPILL/unsaturated zone/water table fluctuation/ZONE
Notes: XXXX
Abstract: Soil moisture data collected using an automated data logging system were used to estimate ground water recharge at a crude oil spill research site near Bemidji, Minnesota. Three different soil moisture probes were tested in the laboratory as well as the field conditions of limited power supply and extreme weather typical of northern Minnesota: a self-contained reflectometer probe, and two time domain reflectometry (TDR) probes, 30 and 50 cm. long. Recharge was estimated using an unsaturated zone water balance method. Recharge estimates for 1999 using the laboratory calibrations were 13 to 30 percent greater than estimates based on the factory calibrations. Recharge indicated by the self-contained probes was 170 percent to 210 percent greater than the estimates for the TDR probes regardless of calibration method. Results indicate that the anomalously large recharge estimates for the self-contained probes are not the result of inaccurate measurements of volumetric moisture content, but result from the presence of crude oil, or bore-hole leakage. Of the probes tested, the 50 cm long TDR probe

yielded recharge estimates that compared most favorably to estimates based on a method utilizing water table fluctuations. Recharge rates for this probe represented 24 to 27 percent of 1999 precipitation. Recharge based on the 30 cm. long horizontal TDR probes was 29 to 37 percent of 1999 precipitation. By comparison, recharge based on the water table fluctuation method represented about 29 percent of precipitation

Dror, I., Z. Gerstl, R. Prost, and B. Yaron 2002. Abiotic behavior of entrapped petroleum products in the subsurface during leaching. Chemosphere 49:1375-1388.
Reference ID: 167
Keywords: attenuation/concentration/dissolution/distribution/fate/GROUNDWATER/hydrocarbon/NATURAL ATTENUATION/petroleum/solubility/transport/unsaturated zone/vapor/ZONE
Notes: XXXX
Abstract: Petroleum products are generally volatile hydrocarbon mixtures. These mixtures may contaminate land surfaces, the unsaturated zone and ground waters at numerous sites and thus represent a long-term source of environmental subsurface pollution. Based on laboratory and field evidence obtained by our research groups and others we emphasize in the present review paper the effect of leaching on the abiotic processes controlling the fate of volatile petroleum hydrocarbon mixtures (VPHMs) in the soil environment. The modification of petroleum hydrocarbon mixtures due to changes in the soil water content is considered the result of a "leaching phenomenon". The experimental evidence of VPHM behavior in the porous media is linked to four major processes: retention, redistribution and attenuation in the subsurface, and dissolution in the soil water. Once VPHMs reach the soil surface, their residual concentration and composition is influenced by the amount and quality of the leaching water. The transport and natural attenuation of the VPHMs in the unsaturated zone is affected by the amount and rate of leaching. Since VPHM are a mixture of volatile and non-volatile hydrocarbons whose components differ by several orders of magnitude in their vapor pressure and water solubility, their fates in the soil environment under leaching will be diverse too. This will influence the temporal concentrations of the VPHM components and their distributions with depth, as vapors, solutes, or water-immiscible solutions. Wetting the soil before or after the VPHMs reach it, differentially affects the abiotic processes governing petroleum products behavior into the porous media. (C) 2002 Elsevier Science Ltd. All rights reserved

English, C. W. and R. C. Loehr 1991. Degradation of Organic Vapors in Unsaturated Soils. Journal of Hazardous Materials 28:55-63.
Reference ID: 132
Keywords: benzene/BIODEGRADATION/BIOREMEDIATION/degradation/fate/modeling/organic compounds/sorption/sorption coefficient/TCE/unsaturated zone/vapor/VOCs
Notes: XXXX
Abstract: To predict the fate of volatile organic compounds (VOCs) in unsaturated soil, it is necessary to understand the physical and chemical processes that occur in the soil system. Two important removal mechanisms of organic vapors in soil are sorption and biodegradation. Modeling efforts to describe the removal of organic vapors in soil require constitutive relationships that are developed from laboratory data. This pa-

per reports measurements of removal coefficients for three VOCs in a fine sandy loam soil. Sorption coefficients and degradation removal rates were determined from batch reactors for three compounds: benzene, trichloroethylene (TCE) and o-xylene. Results indicate organic vapors are sorbed and then removed by biodegradation in the unsaturated soil system. This information has potential for use in the bioremediation of soils contaminated with VOCs and for impacting decisions on air emissions, regulatory limits and on-site controls

Essaid, H. I., I. M. Cozzarelli, R. P. Eganhouse, W. N. Herkelrath, B. A. Bekins, and G. N. Delin 2003. Inverse modeling of BTEX dissolution and biodegradation at the Bemidji, MN crude-oil spill site. Journal of Contaminant Hydrology 67:269-299.

Reference ID: 153

Keywords: aerobic/aerobic degradation/benzene/BIODEGRADATION/BTEX/concentration/conceptual models/CRUDE-OIL/degradation/degradation rates/dissolution/GROUND-WATER/groundwater/hydrocarbon/inverse modeling/modeling/models/oxygen/PLUME/prediction/solubility/SPILL/toluene/transport

Notes: XXXX

Abstract: The U.S. Geological Survey (USGS) solute transport and biodegradation code BIOMOC was used in conjunction with the USGS universal inverse modeling code UCODE to quantify field-scale hydrocarbon dissolution and biodegradation at the USGS Toxic Substances Hydrology Program crude-oil spill research site located near Bemidji, MN. This inverse modeling effort used the extensive historical data compiled at the Bemidji site from 1986 to 1997 and incorporated a multicomponent transport and biodegradation model. Inverse modeling was successful when coupled transport and degradation processes were incorporated into the model and a single dissolution rate coefficient was used for all BTEX components. Assuming a stationary oil body, we simulated benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene (BTEX) concentrations in the oil and ground water, respectively, as well as dissolved oxygen. Dissolution from the oil phase and aerobic and anaerobic degradation processes were represented. The parameters estimated were the recharge rate, hydraulic conductivity, dissolution rate coefficient, individual first-order BTEX anaerobic degradation rates, and transverse dispersivity. Results were similar for simulations obtained using several alternative conceptual models of the hydrologic system and biodegradation processes. The dissolved BTEX concentration data were not sufficient to discriminate between these conceptual models. The calibrated simulations reproduced the general large-scale evolution of the plume, but did not reproduce the observed small-scale spatial and temporal variability in concentrations. The estimated anaerobic biodegradation rates for toluene and o-xylene were greater than the dissolution rate coefficient. However, the estimated anaerobic biodegradation rates for benzene, ethylbenzene, and m,p-xylene were less than the dissolution rate coefficient. The calibrated model was used to determine the BTEX mass balance in the oil body and groundwater plume. Dissolution from the oil body was greatest for compounds with large effective solubilities (benzene) and with large degradation rates (toluene and o-xylene). Anaerobic degradation removed 77% of the BTEX that dissolved into the water phase and aerobic degradation removed 17%. Although goodness-of-fit measures for the alternative conceptual models were not significantly different, predictions made with the models were quite variable. (C) 2003 Elsevier Science B.V. All rights reserved

Fine, P. and B. Yaron 1993. Outdoor Experiments on Enhanced Volatilization by Venting of Kerosene Component from Soil. Journal of Contaminant Hydrology 12:355-374.
Reference ID: 168
Keywords: kerosene/OM/organic matter/retention/soil properties/volatilization
Notes: XXXX
Abstract: The effect of soil properties on the retention of kerosene in soils, at equilibrium and under venting, was studied. Eleven soils were studied, which represent a wide range of chemical properties and mechanical composition. The retention of kerosene in dry soils ranges from 3.5 to 18.1 mL/(100 g), and was related linearly to clay, silt and organic matter (OM) contents. A coarsely-aggregated dry vertisol (2-5 mm aggregates) retained half as much kerosene as its finely-aggregated (<2 mm) counterpart. Moisture content had a strong inverse effect on kerosene retention. The soil factors that inversely affected kerosene retention also enhanced kerosene stripping by venting. Of these, soil aggregation and porosity were the most important. In addition, kerosene volatilized faster and more completely from an initially moist soil, as compared with an initially dry soil. Differential volatilization of lighter components of kerosene changed the chemical composition of the residue in the soil substantially, as compared with the initial composition

Fischer, M. L., A. J. Bentley, K. A. Dunkin, A. T. Hodgson, W. W. Nazaroff, R. G. Sextro, and J. M. Daisey 1996. Factors affecting indoor air concentrations of volatile organic compounds at a site of subsurface gasoline contamination. Environmental Science & Technology 30:2948-2957.
Reference ID: 17
Keywords: concentration/contamination/degradation/field study/indoor air quality/organic compounds/soil gas/transport/ventilation/VOCs
Notes: XXXX
Abstract: We report a field study of soil-gas transport of volatile organic compounds (VOCs) into a building at a site contaminated with gasoline. High VOC concentrations (30-60 g m(-3)) were measured in soil gas 0.7 m below the building. Measured indoor air concentrations were similar to 10(6) lower due to a sharp gradient in soil-gas VOC concentrations between 0.1 and 0.7 m (a factor of similar to 10(3)) and the dilution of soil gas entering the building by wind-driven building ventilation (a factor of similar to 10(3)), Measurements of soil physical and biological characteristics indicate that a partial physical barrier to vertical transport in combination with microbial degradation can explain the gradient. While these factors are likely to be important to varying degrees at other sites contaminated with VOC, we conclude that (1) the results of this study cannot be directly applied to estimate indoor air quality at other sites without the risk of incurring significant errors and instead that (2) future attempts to estimate VOC transport into buildings should be made with careful attention to the identification and separation of physical and biotic effects

Franzmann, P. D., L. R. Zappia, T. R. Power, G. B. Davis, and B. M. Patterson 1999. Microbial mineralisation of benzene and characterisation of microbial biomass in soil above hydrocarbon-contaminated groundwater. Fems Microbiology Ecology 30:67-76.
Reference ID: 18

Keywords: benzene/concentration/groundwater/hydrocarbon/oxygen
Notes: XXXX
Abstract: Rates of microbial mineralisation of benzene were measured in a soil profile above gasoline-contaminated groundwater. The fastest mineralisation rate of benzene occurred in soil with overlapping concentration gradients of hydrocarbon volatile organic carbon and oxygen, in which neither oxygen nor hydrocarbon volatile organic carbon was at a concentration considered to be rate limiting (13.8% oxygen and 1.1 mg l(-1) hydrocarbon volatile organic carbon). Al our site, the fastest I ate of microbial mineralisation of [C-14]benzene was 83 +/- 13 mu mol kg(-1) day(-1) with a half-life (t(1/2)) of 11+/-1 days in soil from a depth of 0.25 m below the ground surface. Microbial mineralisation rates were slower in soil from a depth of 0.5 m (27+/-6 mol kg(-1) day(-1) t(1/2) = 72+/-16 days) as were mineralisation rates in surface soils (52+/-13 mu mol kg(-1) day(-1), t(1/2) = 26+/-7 days). In the anoxic soils just above the groundwater table, microbial mineralisation rates were extremely slow (0.04+/-0.01 mu mol kg(-1) day(-1) t(1/2) = 173+/-31 years). Microbial biomass at 0.25 m below the ground was comparable to the microbial biomass in surface soils (2.0+/-0.2X10(8) and 1.4+/-0.4X10(8) stationary phase Escherichia coli equivalent cells g(-1) dry wt., respectively). The monounsaturated fatty acids in the phospholipids in the microbiota in soils from 0.25 and 0.5 m below the ground surface were greatly enriched in their trans isomers. As the surface soil microbiota was poor in trans isomers of mono-unsaturated fatty acids and showed no better mineralisation rate than microbes from similar environments that were not previously exposed to hydrocarbons, it would seem likely that aromatic hydrocarbons do not pass through the surface of the soil due to microbial mineralisation in the soil profile. This hypothesis was supported by the absence of hydrocarbon volatile organic carbons in air collected from above the soil surface and a comparison of the measured mineralisation rates with the mass flux of aromatic hydrocarbons. (C) 1999 Federation of European Microbiological Societies. Published by Elsevier Science B.V. All rights reserved

Freijer, J. I., H. deJonge, W. Bouten, and J. M. Verstraten 1997. Assessing mineralization rates of petroleum hydrocarbons in soils in relation to environmental factors and experimental scale. Biodegradation 7:487-500.
Reference ID: 133
Keywords: BIODEGRADATION/concentration/diffusion/diffusion coefficient/hydrocarbon/lysimeter/models/petroleum/transport
Notes: XXXX
Abstract: Mineralization rates of non-volatile petroleum hydrocarbons (HCs) in five different oil-contaminated soils with initial HC contents ranging from 0.1 to 13 g kg(-1) are estimated as a function of environmental factors. The aim of the study is threefold, (i) to study the relevance of environmental factors that may influence the mineralization rate, (ii) to compare mineralization rates estimated in two experiments at different scales, after standardizing them to environmental reference conditions, (iii) to evaluate the CO2 production rate as a measure for the mineralization rate of HCs. Experiments were performed at laboratory scale (30-50 cm(3) soil volume) in closed-jars under constant environmental conditions and in lysimeters (0.81 m(3) soil volume) under dynamic climatic and hydrological conditions. A biodegradation model, coupled to transport models for soil heat, water, and gas dynamics is employed for data interpretation. The transport models are used to simulate the environmental conditions that influence the mineralization rate in the non-steady lysimeter experiments. The results show that

temperature, O-2 concentration and HC content have an effect on the mineralization rates. Water content could not be identified as a direct governing environmental factor. However, an indirect effect of water content is that it influences the effective gas diffusion coefficient in soils. The CO2 production rate seems to be a good quantity to express the mineralization rate of HCs for HC contents > 1 g kg(-1). Measured CO2 production rates standardized to reference conditions are similar for the two different experimental scales. This demonstrates that the usage of biodegradation rates obtained in the laboratory to predict the biodegradation rates under field conditions is sound, as long as the differences in environmental conditions have been taken into account

Gerhardt, R. A. 1984. Landfill Leachate Migration and Attenuation in the Unsaturated Zone in Layered and Nonlayered Coarse-Grained Soils. Ground Water Monitoring and Remediation 4:56-65.
Reference ID: 170
Keywords: attenuation/landfill/leachate/migration/unsaturated zone/ZONE
Notes: XXXX

Gidda, T., W. H. Stiver, and R. G. Zytner 1999. Passive volatilization behaviour of gasoline in unsaturated soils. Journal of Contaminant Hydrology 39:137-159.
Reference ID: 171
Keywords: fate/SPILL/unsaturated zone/volatilization/ZONE
Notes: XXXX
Abstract: Gasoline behaviour in the unsaturated zone is difficult to predict as a number of soil factors, gasoline properties and environmental conditions will determine the eventual fate of a spill. These factors include the diffusive and convective processes that contribute to passive volatilization. To gain a better insight into passive volatilization and how it can impact the clean-up of a contaminated site, batch column experiments were completed. Three soils were tested at varying initial gasoline contents, water contents, and at room and sub-zero temperatures. The results indicate that immiscible phase movement to the surface is a significant contributor to passive volatilization. However, the immiscible phase movement ceases once the gasoline content has dropped below a threshold level. The driving force necessary for immiscible phase movement is maintained by gasoline precipitation at the soil surface. Higher soil water contents inhibited the volatilization of gasoline as water impacted both the diffusive and wicking movement of the gasoline. Sub-zero temperatures reduced volatilization and extended the time to cessation of wicking behaviour. (C) 1999 Elsevier Science B.V. All rights reserved

Grifoll, J. and Y. Cohen 1996. Contaminant migration in the unsaturated soil zone: The effect of rainfall and evapotranspiration. Journal of Contaminant Hydrology 23:185-211.
Reference ID: 172
Keywords: benzene/contamination/diffusion/dispersion/migration/modeling/transport/volatilization/ZONE
Notes: XXXX
Abstract: The potential effect of rainfall and evapotranspiration on contaminant migration in the unsaturated soil zone was studied using a deterministic dynamic modeling approach. The contaminant mass transfer equation was solved along with Richards' equation for water transport

subject to dynamic surface boundary conditions that consider rainfall and evapotranspiration. As an illustration of the effect of rainfall and evapotranspiration on various transport mechanisms, test cases are presented for the transport and volatilization of benzene, 1,1,2,2-tetrachloroethane and methanol for a loam-type soil using self-consistent dynamic rainfall and evapotranspiration weather sequences. The present study suggests that transport mechanisms such as diffusion, dispersion and convection can all be significant, to varying degrees, during various parts of the year. The temporal variability of both the volatilization flux and the amount of chemical remaining in the unsaturated soil zone are significantly impacted by the dynamics of rainfall and the period of initial contamination

Hageman, K. J., J. D. Istok, J. A. Field, T. E. Buscheck, and L. Semprini 2001. In situ anaerobic transformation of trichlorofluoroethene in trichloroethene contaminated groundwater (vol 35, pg 1729, 2001). Environmental Science & Technology 35:2860.
Reference ID: 315
Keywords: groundwater/in situ/transformation
Notes: XXXX

Hess, A., P. Hohener, D. Hunkeler, and J. Zeyer 1996. Bioremediation of a diesel fuel contaminated aquifer: Simulation studies in laboratory aquifer columns. Journal of Contaminant Hydrology 23:329-345.
Reference ID: 134
Keywords: aerobic/AQUIFER/AQUIFERS/BIOREMEDIATION/columns/concentration/DOC/field study/groundwater/hydrocarbon/in situ/petroleum
Notes: XXXX
Abstract: The in situ bioremediation of aquifers contaminated with petroleum hydrocarbons is commonly based on the infiltration of groundwater supplemented with oxidants (e.g., O-2, NO3-) and nutrients (e.g., NH4+, PO43-). These additions stimulate the microbial activity in the aquifer and several field studies describing the resulting processes have been published. However, due to the heterogeneity of the subsurface and due to the limited number of observation wells usually available, these field data do not offer a sufficient spatial and temporal resolution. In this study, flow-through columns of 47-cm length equipped with 17 sampling ports were filled with homogeneously contaminated aquifer material from a diesel fuel contaminated in situ bioremediation site. The columns were operated over 96 days at 12 degrees C with artificial groundwater supple mented with O-2, NO3- and PO43-. Concentration profiles of O-2, NO3-, NO2-, dissolved inorganic and organic carbon (DIC and DOC, respectively), protein, microbial cells and total residual hydrocarbons were measured. Within the first 12 cm, corresponding to a mean groundwater residence time of < 3.6 h, a steep O-2 decrease from 4.6 to < 0.3 mg l(-1), denitrification, a production of DIC and DOC, high microbial cell numbers and a high removal of hydrocarbons were observed. Within a distance of 24 to 40.5 cm from the infiltration, O-2 was below 0.1 mg l(-1) and a denitrifying activity was found. In the presence and in the absence of O-2, n-alkanes were preferentially degraded compared to branched alkanes. The results demonstrate that: (1) infiltration of aerobic groundwater into columns filled with aquifer material contaminated with hydrocarbons leads to a rapid depletion of O-2; (2) O-2 and NO3- can serve as oxidants for the mineralization of hydrocarbons; and (3) the modelling of redox processes in aquifers has to consider denitrifying activity in presence of O-2

Hollender, J., K. Althoff, M. Mundt, and W. G. Dott 2003. Assessing the microbial activity of soil samples, its nutrient limitation and toxic effects of contaminants using a simple respiration test. Chemosphere 53:269-275.
Reference ID: 173
Keywords: attenuation/BIODEGRADATION/BIOREMEDIATION/BTEX/carbon dioxide/contamination/NATURAL ATTENUATION/oxygen/PAH/respiration
Notes: XXXX
Abstract: Eight soil samples from five wells of a former gas plant site differing in the contamination with BTEX and PAHs as well as the nutrient content were investigated by soil respiration measurements. The basal, glucose as well as NH4+ and PO43- induced cumulative oxygen consumption and carbon dioxide production in 72 and 120 h were determined and additionally the maximal turnover rates and the limitation quotients were calculated. Without additional carbon source only one of five investigated samples was clearly nutrient limited. After glucose supplementation four of seven investigated samples showed nutrient limitation that was in accordance with the available ammonium and phosphorous content. BTEX and PAHs did not exhibit an inhibiting effect on the respiration rate. In contrast, BTEX containing samples exhibited the highest oxygen consumption indicating biodegradation of the contaminants. The results show that oxygen consumption and carbon dioxide production as well as the kinetic of these processes are all informative parameters characterizing the whole microbial respiration potential and their nutrient limitation in soil samples. Therefore this fast respirometric method can be used for the decision if further detailed studies of the bioremediation are useful and if nutrient supplementation is recommended to enhance natural attenuation. (C) 2003 Elsevier Ltd. All rights reserved

Huesemann, M. H. 1995. Predictive Model for Estimating the Extent of Petroleum Hydrocarbon Biodegradation in Contaminated Soils. Environmental Science & Technology 29:7-18.
Reference ID: 174
Keywords: BIODEGRADATION/BIOREMEDIATION/concentration/CRUDE-OIL/desorption/distribution/hydrocarbon/petroleum/prediction
Notes: XXXX
Abstract: A series of solid - and slurry-phase soil bioremediation experiments involving different crude oils and refined petroleum products were performed in order to investigate the factors which affect the maximum extent of total petroleum hydrocarbon (TPH) biodegradation. Utilizing a comprehensive petroleum hydrocarbon characterization procedure involving group type separation analyses, boiling point distributions, and hydrocarbon typing by field desorption mass spectroscopy, initial and final concentrations of specified hydrocarbon classes were determined in each of the seven bioremediation treatments. in this study, it was found that the degree of TPH biodegradation was mainly affected by the type of hydrocarbons in the contaminant matrix while the influence of experimental variables such as soil type, fertilizer concentrations, microbial counts, and treatment type (slurry vs land-treatment) on the overall extent of TPH biodegradation appeared to be insignificant. Based on these findings, a predictive algorithm was developed to estimate the extent of TPH biodegradation from the average reduction of 86 individual hydrocarbon cf asses and their respective initial concentrations. Model predictions for gravimetric TPH removals

were in close agreement with analytical results from two independent laboratories

Hupe, K., J. Heerenklage, H. Woyczechowski, S. Bollow, and R. Stegmann 1998. Influence of oxygen on the degradation of diesel fuel in soil bioreactors. Acta Biotechnologica 18:109-122.
Reference ID: 175
Keywords: BIODEGRADATION/bioreactor/degradation/oxygen
Notes: XXXX
Abstract: In fixed-bed bioreactors, the influence of the oxygen content in the inlet air on the biodegradation of diesel fuel in unsaturated soil/compost mixtures was analyzed at 30 degrees C over a period of 7 weeks. Firstly, a wide range from 0 to 80 vol. % O-2 was investigated. Subsequently, the range below 5 vol. % O-2 was examined more closely. Over the whole test period of seven weeks, no significant influence of oxygen could be observed above 1 vol. % O-2 in the inlet air - either on the decrease of the total contaminants or on the total mineralization. Anaerobic conditions should be avoided for the degradation of diesel fuel. During the test period, the courses of CO2 production varied significantly depending on oxygen supply. Furthermore, a model was developed to estimate the total mineralization as a function of oxygen supply. More investigations are recommended in order to test this model for practical application

Istok, J. D., M. D. Humphrey, M. H. Schroth, M. R. Hyman, and K. T. OReilly 1997. Single-well, "push-pull" test for in situ determination of microbial activities. Ground Water 35:619-631.
Reference ID: 314
Keywords: aerobic/AQUIFER/AQUIFERS/carbon dioxide/concentration/contamination/groundwater/in situ/microbial communities/microbial processes/monitoring/nitrate/oxygen/petroleum/respiration/sulfate reduction/tracer/ZONE
Notes: XXXX
Abstract: A single-well, "push-pull" test method is proposed for the in situ determination of microbial metabolic activities in groundwater aquifers. The method consists of the pulse-type injection ("push") of a test solution into the saturated zone of an aquifer through the screen of an existing monitoring well followed by the extraction ("pull") of the test solution/ground-water mixture from the same well. The test solution contains a tracer and one or more reactive solutes selected to investigate specific microbial activities. During the injection phase, the test solution flows radially away from the monitoring well into the aquifer. Within the aquifer, biologically reactive components of the test solution are converted to various products by the indigenous microbial community. During the extraction phase, flow is reversed and solute concentrations are measured to obtain breakthrough curves, which are used to compute the quantities of reactant(s) consumed and/or product(s) formed during the test and reaction rates. Tests were performed to determine rates of aerobic respiration, denitrification, sulfate reduction, and methanogenesis in a petroleum contaminated aquifer in western Oregon. High rates of oxygen, nitrate, nitrite, and hydrogen utilization and nitrite, and carbon dioxide production support the hypothesis that petroleum contamination has resulted in an increase in microbial activity in the anaerobic portion of the site, The results suggest that the push-pull test method should be useful for obtaining quantitative information on a wide range of in situ microbial processes

Jarsjo, J., G. Destouni, and B. Yaron 1994. Retention and Volatilization of Kerosene - Laboratory Experiments on Glacial and Postglacial Soils. Journal of Contaminant Hydrology 17:167-185.
Reference ID: 177
Keywords:
C14/concentration/density/hydrocarbon/hydrophobic/kerosene/laboratory experiments/organic matter/porosity/retention/volatilization/ZONE
Notes: XXXX
Abstract: The influence of environmental conditions and soil characteristics on the retention and volatilisation of kerosene hydrocarbons in soils is investigated through laboratory experiments in six different glacial and post-glacial soils. The soils ranged between 0.55 and 1.80 g cm-3 in density, 29% and 70% in porosity, 0.4% and 28% in organic matter content, and 0% and 51% in clay content. The water retention capacity (WRC) could be estimated on basis of the bulk density and the sand, silt, clay and organic matter contents for many of the soils; for these soils a simple linear relation was identified between WRC and the kerosene retention capacity (KRC). Furthermore, the combined effects of soil porosity and soil moisture content on the KRC were found to be significant and could be quantified by a linear relationship. For moisture contents that can be expected in humid climate zones, the KRC will be relatively low and exhibit small variations between different soils. The effect of temperature on KRC was found to be small. The kerosene volatilisation flux was quantified as a function of time by a power law relationship, based on the initial surface density of kerosene in the soil and the prevailing temperature. The C9-C11 components of the kerosene had selectivities above zero and were thus removed preferentially, while the C14 and C15 components were characterised by negative the soil by increasing the concentration of the C14 and C15 components. The results for the different soil types indicate that the organic matter content of the soil affects the selective volatilisation, possibly through hydrophobic adsorption on surfaces, whereas the clay content appears to be less influential

Kao, C. M. and Y. S. Wang 2001. Field investigation of the natural attenuation and intrinsic biodegradation rates at an underground storage tank site. Environmental Geology 40:622-631.
Reference ID: 178
Keywords: attenuation/benzene/BIODEGRADATION/BTEX/contamination/groundwater/in situ/NATURAL ATTENUATION/PLUME/SPILL/toluene/tracer
Notes: XXXX
Abstract: Contamination of groundwater by petroleum-hydrocarbons is a widespread environmental problem. Natural attenuation is a passive remedial approach to degrade and dissipate contaminants in soil and groundwater. In this study, a mass flux approach was used to calculate the contaminant mass reduction and field-scale decay rate at a gasoline spill site. The mass flux technique is accomplished using the differences in total contaminant mass flux across two cross sections of the contaminant plume. The mass flux calculation shows that up to 88% of the dissolved BTEX (benzene, toluene, ethylbenzene, and xylene isomers) removal was observed by natural attenuation processes. The efficiency of intrinsic biodegradation was evaluated by the in situ tracer method. A first-order decay model was applied for the natural attenuation and intrinsic biodegradation rate calculation. Results reveal that intrinsic biodegradation process was the major cause of the BTEX reduction among the natural attenuation mechanisms, and iron reduction was the domi-

nant biodegradation pattern within the plume. Approximately 87% of the BTEX removal was caused by intrinsic biodegradation processes. The calculated BTEX natural attenuation and intrinsic biodegradation rates were 0.24 and 0.16% 1/day, respectively. Results suggest that natural attenuation mechanisms can effectively contain the plume, and the mass flux method is useful assessing the efficiency of the natural attenuation

Kelly, W. R., G. M. Hornberger, J. S. Herman, and A. L. Mills 1996. Kinetics of BTX biodegradation and mineralization in batch and column systems. Journal of Contaminant Hydrology 23:113-132.
Reference ID: 135
Keywords: AQUIFER/benzene/BIODEGRADATION/columns/kinetics/substrate/toluene
Notes: XXXX
Abstract: Flow-through column and liquid batch experiments were performed in the present study in order to evaluate whether the kinetics of biodegradation reactions of organic contaminants for batch conditions were comparable to those measured under solid-to-solution ratios applicable to aquifer or water-saturated soil systems. The biodegradation of benzene, toluene, and xylene was observed under oxic conditions. Steady-state reaction rates were determined for the biodegradation reactions in the flow-through columns and evaluated using a rate law based on the Monod equation for conditions where bacterial growth is negligible. Calculated rate constants (k(1)) for biodegradation, or substrate disappearance, for sole substrate experiments were 1.32 mmol L(-1) h(-1) for benzene, 1.42 mmol L(-1) h(-1) for toluene, and 0.833 mmol L(-1) h(-1) for xylene. Rate constants were determined for batch experiments using a rate law based on the Monod equation that does account for bacterial growth. The maximum specific growth rate, mu(max), was found to be similar between batch and column experiments, indicating that there were no mass-transport limitations in the columns and that the solid-to-solution ratio was not a significant factor affecting kinetic parameters. There is considerable variability in rate constants for BTX biodegradation reported in the literature, up to two orders of magnitude for mu(max). Rate constants from this study were within the range of published values. For the experiments reported here, rates determined for sole carbon sources could be used to predict the reaction rates of BTX mixtures given some adjustment of cell yields and lag times

Kim, Y., J. Azizian, J. D. Istok, and L. Semprini. Field push-pull test protocol for aerobic cometabolism of chlorinated aliphatic hydrocarbons. ESTCP report 4/21/2005. 2005. Oregon State University
Civil, Construction, and Environmental Engineering Department
Corvallis, OR 97331. (GENERIC)
Ref Type: Report
Ref ID: 316
Keywords: aerobic/field study/hydrocarbon/Push-pull tests
Notes: XXXX

Lee, M. D. and C. M. Swindoll 1993. Bioventing for In-Situ Remediation. Hydrological Sciences Journal-Journal des Sciences Hydrologiques 38:273-282.
Reference ID: 179
Keywords: aerobic/BIOREMEDIATION/bioventing/flow rate/hydrocarbon/in situ/oxygen/remediation/unsaturated zone/ZONE
Notes: XXXX

Abstract: The availability of oxygen generally controls the rate at which aerobic in situ bioremediation proceeds. Bioventing, which couples soil venting with bioremediation, is often the most effective means of supplying oxygen to unsaturated zone soil. Laboratory treatability studies were conducted which showed that bioventing could be successfully applied to compounds ranging from light hydrocarbons, such as gasoline or diesel, to heavier hydrocarbons, such as fuel oils, as well as other volatile and semivolatile compounds. In many cases, the promotion of biological activity through the addition of nutrients and moisture, and optimization of the bioventing flow rates, may achieve greater contaminant reductions than venting alone

Loll, P. and C. Larsen. Anbefalinger til sagsforløb ved in-situ oprensning af jordforurening. Miljøprojekt nr. 1255. 2008. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 313
Keywords: in situ/monitoring/remediation
Notes: XXXX

Lowell, P. S. and B. Eklund 2004. VOC emission fluxes as a function of lateral distance from the source. Environmental Progress 23:52-58.
Reference ID: 188
Keywords: concentration/contamination/migration/modeling/models/PLUME/soil gas/transport/vapor
Notes: XXXX
Abstract: There has been a great deal of recent interest in evaluating the potential for vapor transport from subsurface contamination into nearby buildings. There does not exist, however, any method for calculating whether buildings that are not direct v over the source of contamination may be impacted. For simplicity, typical modeling approaches for estimating vapor migration through soil into buildings assume that the contaminated plume or soil lies directly underneath the building. The models do not take into account the lateral distance, if any, between the source of VOC emissions and the indoor space. This paper presents an approach to calculate diffusion-limited emission fluxes as a function of lateral distance and evaluates the significance of these emissions over relatively short lateral distances from the source. A theoretical, mathematical approach was used. The results show that soil-gas concentration and emission flux are both a decreasing exponential function of the lateral distance from the edge of the contaminant plume. Based on our calculations, the emission flux and the soil-gas concentration are insignificant within a relatively short lateral distance from the source (e.g., 30 m). (C) 2004 American Institute of Chemical Engineers Environ Prog, 23: 52-58, 2004

Lundegard, P. D., P. C. Johnson, and P. Dahlen 2008. Oxygen transport from the atmosphere to soil gas beneath a slab-on-grade foundation overlying petroleum-impacted soil. Environmental Science & Technology 42:5534-5540.
Reference ID: 29
Keywords: advection/concentration/diffusion/field study/in situ/modeling/N2/oxygen/oxygen transport/petroleum/soil gas/transport/vapor
Notes: XXXX
Abstract: Modeling and field study results suggest that, in the case of a building overlying an aerobically biodegradable vapor source (i.e., pe-

troleum-impacted soil), the significance of vapor intrusion into the building depends on the source vapor concentration, the relative position of the vapor source and building, and the rate Of 02 transport from the atmosphere to the soil gas beneath the building. This work quantified the latter at a house having about a 250 m(2) slab-on-grade foundation footprint. It was constructed on 1.5 m of clean fill overlying a petroleum hydrocarbon-impacted soil layer undergoing methanogenesis. Soil gas O-2 and CH4 profiles adjacent to and beneath the foundation were measured and then the soil gas beneath the slab was rapidly displaced with N-2. The natural replenishment of 02 was monitored for 90 days using in situ O-2 sensors, and the responses with time were similar, independent of location. The 02 replenishment rate was about 2500 g-Odd immediately after the N2 flood and then it declined to 200-500 g-Odd over 30 days. Weather events affected the 02 replenishment rate; an increase occurred during a strong wind period (>3 m/s), and a decrease occurred during a heavy rainfall event. The spatial and temporal patterns in the 02 sensor responses and quantified 02 replenishment rates could not be accounted for by simple mechanistic hypotheses involving lateral diffusion or advection through the bulk soil, and instead the data suggest rapid replenishment immediately below the foundation followed by downward diffusion

Malina, G. and J. T. C. Grotenhuis 2000. The role of biodegradation during bioventing of soil contaminated with jet fuel. Applied Biochemistry and Biotechnology 88:59-76.
Reference ID: 180
Keywords: BIODEGRADATION/bioventing/columns/concentration/contamination/desorption/diffusion limited desorption/evaporation/flow rate/kerosene/microorganisms/nitrogen/saturation/sorption/toluene
Notes: XXXX
Abstract: The enhancing removal of kerosene (jet fuel) from contaminated soil during bioventing resulting from biodegradation was compared to the physical removal by evaporation only on bench-scale columns at the controlled temperature of 20 degrees C (+/- 2.5 degrees C). Carbon dioxide-free air and nitrogen were used as flushing gases, at the constant continuous flow rate of 1 dm(3)/h. Kerosene concentrations in soil up to 35000 mg/kg were not toxic for indigenous microbial population. Much slower kerosene biodegradation rates observed for soil from a contaminated site, as compared to soil artificially contaminated with kerosene, were the result of a lower bioavailability of "aged" kerosene, and the presence of compounds that might be persistent or toxic to kerosene-specific degraders. The inhibitory effect of toluene to indigenous microorganisms was found at above 75% of the toluene saturation concentrations in the gas phase. After 29 d, the overall bioventing efficiency was 17-23%, depending on whether CO2 production or O-2 uptake was used for calculations, as compared to the removal of 10% when biodegradation was excluded. The increase in efficiency by 50-100% owing to biodegradation would be more spectacular at lower kerosene concentrations during the "tailing" phase, with diffusion-limited desorption, and much lower evaporation of less volatile constituents. Limitation of bioventing as a result of low bioavailability related to intraparticle sorption of residual contamination is discussed

Margesin, R., A. Zimmerbauer, and F. Schinner 2000. Monitoring of bioremediation by soil biological activities. Chemosphere 40:339-346.
Reference ID: 181

Keywords: BIODEGRADATION/BIOREMEDIATION/hydrocarbon/monitoring/p/respiration
Notes: XXXX
Abstract: An evaluation of soil biological activities as a monitoring instrument for the decontamination process of a mineral-oil-contaminated soil was made using measurements of microbial counts, soil respiration, soil biomass and several enzyme activities. The correlations between these parameters and with the levels of hydrocarbon residues were investigated; the effects of different N- and P-sources on hydrocarbon decontamination and soil biological activities were determined. Inorganic nutrients stimulated hydrocarbon biodegradation but not all biological activities to a significant extent. Biodegradation could be monitored well by soil biological parameters: the residual hydrocarbon content correlated positively with soil respiration, biomass-C (substrate-induced respiration), and with activities of soil dehydrogenase, urease and catalase. Soil lipase activity and the number of hydrocarbon utilizers correlated negatively ($P < 0.0001$) with the remaining hydrocarbon content. (C) 1999 Elsevier Science Ltd. All rights reserved

Mclinn, E. L. and B. W. Rehm 1997. Biodegradation of petroleum hydrocarbons in fractured, unsaturated dolomite at a field site. Ground Water Monitoring and Remediation 17:73-80.
Reference ID: 182
Keywords: BIODEGRADATION/carbon dioxide/fate/GROUND-WATER/hydrocarbon/monitoring/oxygen/petroleum/pore gas/recharge/unsaturated zone/UST/ZONE
Notes: XXXX
Abstract: Gasoline constituents were detected in unsaturated soil and rock during abandonment of a leaky underground storage tank (UST). The unsaturated sequence beneath the former UST consists of 90 feet of silty till. fractured dolomite, and friable sandstone. Pore gas probes were installed in each of the unsaturated units, both in the source area and in a background on-site location. Pore gas samples were collected to evaluate the nature, extent, and fate of residual hydrocarbons in the vadose zone. Pore gas from the till and dolomite in the source area was enriched in petroleum hydrocarbons and carbon dioxide. and was depleted in oxygen, relative to pore gas from the background area. During two years of ground water monitoring at the site, methyl tertiary butyl ether was periodically detected in the ground water beneath the source area as pulses of recharge passed through the unsaturated zone, but no other gasoline constituents were detected. Apparently, the most degradable fraction of the gasoline (aromatic hydrocarbons) is being attenuated in the vadose zone before the water table is reached

Meier-Löhr, M. and G. Batterman 1998. Dissolution and degradation kinetics of BTEX compounds during large scale *in situ* bioremediation applying nitrate as an electron acceptor. (Anonymous,).
Reference ID: 184
Keywords: assessment/BIOREMEDIATION/BTEX/degradation/dissolution/electron acceptor/groundwater/in situ/kinetics/methods/nitrate/remediation
Notes: XXXX
Abstract: Methods and results of mass balance calculations and hydraulic
modelling for the assessment of the efficiency and the degradation kinetics of

a large scale BTEX remediation with nitrate as the predominant electron acceptor, will be presented.

Miljøstyrelsen. Oprydning på forurenede lokaliteter. 6 + 7 (1998). 1998. Miljøstyrelsen. (GENERIC)
Ref Type: Report
Ref ID: 309
Keywords: field assessment/quality criteria/remediation/risk assessment
Notes: Risk assesment

Molins, S. and K. U. Mayer 2007. Coupling between geochemical reactions and multicomponent gas and solute transport in unsaturated media: A reactive transport modeling study. Water Resources Research 43.
Reference ID: 151
Keywords: advection/AQUIFER/AQUIFERS/attenuation/carbon dioxide/diffusion/dissolution/dusty gas model/gas transport/landfill/methane/modeling/organic compounds/oxygen/reactive transport/release/soil gas/SPILL/transport/transport processes/ZONE
Notes: XXXX
Abstract: [1] The two-way coupling that exists between biogeochemical reactions and vadose zone transport processes, in particular gas phase transport, determines the composition of soil gas. To explore these feedback processes quantitatively, multicomponent gas diffusion and advection are implemented into an existing reactive transport model that includes a full suite of geochemical reactions. Multicomponent gas diffusion is described on the basis of the dusty gas model, which accounts for all relevant gas diffusion mechanisms. The simulation of gas attenuation in partially saturated landfill soil covers, methane production, and oxidation in aquifers contaminated by organic compounds (e. g., an oil spill site) and pyrite oxidation in mine tailings demonstrate that both diffusive and advective gas transport can be affected by geochemical reactions. Methane oxidation in landfill covers reduces the existing upward pressure gradient, thereby decreasing the contribution of advective methane emissions to the atmosphere and enhancing the net flux of atmospheric oxygen into the soil column. At an oil spill site, methane oxidation causes a reversal in the direction of gas advection, which results in advective transport toward the zone of oxidation both from the ground surface and the deeper zone of methane production. Both diffusion and advection contribute to supply atmospheric oxygen into the subsurface, and methane emissions to the atmosphere are averted. During pyrite oxidation in mine tailings, pressure reduction in the reaction zone drives advective gas flow into the sediment column, enhancing the oxidation process. In carbonate-rich mine tailings, calcite dissolution releases carbon dioxide, which partly offsets the pressure reduction caused by O-2 consumption

Moyer, E. E., D. W. Ostendorf, R. J. Richards, and S. Goodwin 1996. Petroleum hydrocarbon bioventing kinetics determined in soil core, microcosm and tubing cluster studies. Ground Water Monitoring and Remediation 16:141-153.
Reference ID: 136
Keywords: advection/aerobic/aerobic biodegradation/analytical model/BIODEGRADATION/bioventing/concentration/first-order rate constants/hydrocarbon/in
situ/kinetics/nitrogen/oxygen/petroleum/release/unsaturated
zone/vapor/ZONE
Notes: XXXX

Abstract: Aerobic biodegradation of vapor-phase petroleum hydrocarbons was evaluated in an intact soil core from the site of an aviation gasoline release. An unsaturated zone soil core was subjected to a flow of nitrogen gas, oxygen, water vapor and vapor-phase hydrocarbons in a configuration analogous to a biofilter or an in situ bioventing or sparging situation. The vertical profiles of vapor-phase hydrocarbon concentration in the soil core were determined by gas chromatography of vapor samples. Biodegradation reduced low influent hydrocarbon concentrations by 45 to 92 percent over a 0.6-m interval of an intact soil core. The estimated total hydrocarbon concentration was reduced by 75 percent from 26 to 7 parts per million. Steady-state concentrations were input to a simple analytical model balancing advection and first-order biodegradation of hydrocarbons. First-order rate constants for the major hydrocarbon compounds were used to calibrate the model to the concentration profiles. Rate constants for the seven individual hydrocarbon compounds varied by a factor of 4. Compounds with lower molecular weights, fewer methyl groups, and no quaternary carbons tended to have higher rate constants. the fist-order rate constants were consistent with kinetic parameters determined from both microcosm and tubing cluster studies at the field site

O'Leary, K. E., J. F. Barker, and R. W. Gillham 1995. Remediation of dissolved BTEX through surface application: A prototype field investigation. Groundwater Mon. Rev. 15:99-109.
Reference ID: 138
Keywords: BTEX/remediation
Notes: XXXX

Ostendorf, D. W. and D. H. Kampbell 1991. Biodegradation of Hydrocarbon Vapors in the Unsaturated Zone. Water Resources Research 27:453-462.
Reference ID: 21
Keywords: advection/aerobic/aerobic biodegradation/BIODEGRADATION/capillary fringe/concentration/contamination/degradation/diffusion/hydrocarbon/leaching/modeling/oxygen/porosity/transport/unsaturated zone/vapor/volatilization/ZONE
Notes: XXXX
Abstract: The time-averaged concentration of hydrocarbon and oxygen vapors were measured in the unsaturated zone above the residually contaminated capillary fringe at the U.S. Coast Guard Air Station in Traverse City, Michigan. Total hydrocarbon and oxygen vapor concentrations were observed over a 13-month period. Supplementary gain size, porosity, and moisture content data support the assumption of a uniform, homogeneous site geology which, in view of the planar hydrocarbon source term, abundant oxygen, and sparse data base, is suitable for simple analytical modeling. In the assumed absence of advection, leaching, and transience, the analysis is a straight-forward balance of gaseous diffusion and biological degradation coupled stoichiometrically in the two reacting constituents. Volatilization is shown to be a significant transport mechanism for hydrocarbons at Traverse City, and biodegradation prevents the escape of appreciable contamination to the atmosphere for most locations at this site. Little oxygen is expected to reach the water table because of the aerobic biodegradation process in the unsaturated zone

Ostendorf, D. W., T. H. Schoenberg, E. S. Hinlein, and S. C. Long 2007. Monod kinetics for aerobic biodegradation of petroleum hydrocarbons in unsaturated soil microcosms. Environmental Science & Technology 41:2343-2349.
Reference ID: 20
Keywords: aerobic/aerobic biodegradation/BIODEGRADATION/concentration/hydrocarbon/kinetics/petroleum/saturation/SPILL/substrate/vapor
Notes: XXXX
Abstract: We use Monod kinetics to calibrate previously published data that document the aerobic biodegradation of hydrocarbon vapors in soil microcosms from a weathered petroleum spill site. Monod kinetics offer insight into biodegradation mechanics because they address biomass growth as well as substrate depletion. A blend of five aromatics and five alkanes dose the microcosm sets at four strengths, and a finite difference model describes the response superimposed across the constituent substrates. An observed initial biomass X-O of 125 g biomass/m(3) soil moisture and an endogendous decay rate b of 0.102 day(-1) calibrate all four dosages and agree with heterotrophic plate counts. Common maximum specific growth rates mu(MJ) and half saturation constants K-SJ calibrate each constituent across the four dosages. The biodegradable alkanes exhibit mu(MJ) values ranging from 0.0190 to 0.0996 day(-1), while the aromatic rates vary from 0.0946 to 0.322 day(-1). One of the alkanes (2,2,4-trimethylpentane) is recalcitrant. The half saturation constants range from 0.000083 to 0.000355 g substrate/m(3) soil moisture for the biodegradable alkanes, which imply zero-order kinetics. The aromatic K-SJ values vary from 5.02 to 14.3 g substrate/m(3) soil moisture, and suggest first-order kinetics. The yield Y-J increases with dosage concentration for all the biodegradable constituents, varying from 0.0533 to 1.58 g biomass/g substrate

Pabich, W. J., I. Valiela, and H. F. Hemond 2001. Relationship between DOC concentration and vadose zone thickness and depth below water table in groundwater of Cape Cod, USA. Biogeochemistry 55:247-268.
Reference ID: 139
Keywords: AQUIFER/attenuation/biogeochemical processes/concentration/DOC/groundwater/nitrate/transformation/unsaturated zone/ZONE
Notes: XXXX
Abstract: Changes in concentration of dissolved organic carbon (DOC) reflect biogeochemical processes that determine chemical composition of groundwater and other natural waters. We found that the deeper the vadose zone, the lower the concentration of DOC in groundwater near the water table, indicating that considerable attenuation of surface-derived DOC occurred in the vadose zone. Under vadose zones <1.25 m, DOC concentrations at the surface of the water table ranged to > 20 mg C l(-1), while for vadose zones >5.0 m, DOC never exceeded 2.0 mg C l(-1). DOC concentrations also decreased exponentially with increasing depth below the water table, most notably in the upper two meters, implying continued attenuation in the upper layer of the saturated zone. Ninety-nine percent of the DOC was attenuated by the time the water reached a depth of 19 m below the water table. A strong inverse relationship between DOC and nitrate concentrations suggests that nitrate is depleted where DOC supplies are high, providing evidence that some portion of the DOC losses in groundwater are due to microbial transformations, including denitrification. DOC concentrations in shallow groundwater show considerable spatial variability, but concentra-

tion of DOC at any one site is surprisingly stable over time. The largest source of variation in DOC concentration in groundwater therefore is spatial rather than temporal, suggesting that local heterogeneities play an important role in DOC delivery to shallow groundwater. Our results highlight both the importance of shallow vadose areas in DOC delivery to groundwater and the need to distinguish where samples are collected in relation to flow paths before conclusions are made about mean groundwater DOC concentrations. The substantial losses of DOC in the vadose zone and in shallow depths within the aquifer suggest quite active biogeochemical processes in these boundary environments

Pinkart, H. C., D. B. Ringelberg, J. O. Stair, S. D. Sutton, S. M. Pfiffner, and D. C. White 1995. Phospholipid analysis of extant microbiota for monitoring in situ bioremediation effectiveness. in Monitoring and verification. Bioremedaition. (R. E. Hinchee, G. S. Douglas, and S. K. Ong, Eds.).
Reference ID: 140
Keywords: BIOREMEDIATION/in situ/monitoring
Notes: XXXX

Reilly, T. J., N. S. Fishman, and A. L. Baehr 2009. Effect of Grain-Coating Mineralogy on Nitrate and Sulfate Storage in the Unsaturated Zone. Vadose Zone Journal 8:75-85.
Reference ID: 137
Keywords: concentration/grain size/groundwater/nitrate/pore water/sorption/unsaturated zone/ZONE
Notes: XXXX
Abstract: Unsaturated-zone sediments and the chemistry of shallow groundwater underlying a small (similar to 8-km(2)) watershed were studied to identify the mechanisms responsible for anion storage within the Miocene Bridgeton Formation and weathered Coastal Plain deposits in southern New Jersey. Lower unsaturated-zone sediments and shallow groundwater samples were collected and concentrations of selected ions (including NO3- and SO42-) from 11 locations were determined. Grain size, sorting, and color of the lower unsaturated-zone sediments were determined and the mineralogy of these grains and the composition of coatings were analyzed by petrographic examination, scanning electron microscopy and energy dispersive analysis of x-rays, and quantitative whole-rock x-ray diffraction. The sediment grains, largely quartz and chert (80-94% w/w), are coated with a very fine-grained (<20 mu m), complex mixture of kaolinite, halloysite, goethite, and possibly gibbsite and lepidocrocite. The mineral coatings are present as an open fabric, resulting in a large surface area in contact with pore water. Significant correlations between the amount of goethite in the grain coatings and the concentration of sediment-bound SO42- were observed, indicative of anion sorption. Other mineral-chemical relations indicate that negatively charged surfaces and competion with SO42- results in exclusion of NO3- from inner sphere exchange sites. The observed NO3- storage may be a result of matrix forces within the grain coatings and outer sphere complexation. The results of this study indicate that the mineralogy of grain coatings can have demonstrable effects on the storage of NO3- and SO42- in the unsaturated zone

Ririe, G. T., R. E. Sweeney, and S. J. Daugherty 2002. A comparison of hydrocarbon vapor attenuation in the field with predictions from vapor diffusion models. Soil & Sediment Contamination 11:529-554.
Reference ID: 22
Keywords: attenua-

tion/benzene/bioattenuation/BIODEGRADATION/carbon dioxide/concentration/diffusion/field study/groundwater/hydrocarbon/methane/models/oxygen/prediction/SPILL/transport/vapor/ZONE
Notes: XXXX
Abstract: This study used field data from three sites in Southern California to evaluate vapor phase transport from: (1) free product (diesel and gasoline spill) on groundwater, (2) dissolved benzene (gasoline spill) in groundwater, and (3) hydrocarbon-impacted soil (gasoline spill) in the vadose zone. A sampling program to evaluate the vapor pathway included the following: vertical profile data, minimal purging prior to sample collection, field analysis of data, confirmation of field data using a fixed laboratory analysis, and soil physical properly data. Comparison of hydrocarbon vapor concentrations measured in this field study with those calculated using vapor diffusion models suggest that an additional attenuation factor of between 500 and 35, 000 is needed to account for observed concentrations. Comparison of hydrocarbon profiles with oxygen, carbon dioxide, and methane values is consistent with the interpretation that biodegradation is primarily responsible for the observed attenuation. Therefore, vapor pathway models that do not account for bioattenuation will result in a large overestimation of the risk at spill sites and will not be consistent with field data

Ririe, T. and R. Sweeney 1995. Fate and transport of volatile hydrocarbons in the vadose zone. (Anonymous,).
Reference ID: 131
Keywords: fate/groundwater/hydrocarbon/petroleum/transport/ZONE
Notes: XXXX

Salminen, J. M., P. M. Tuomi, A. M. Suortti, and K. S. Jorgensen 2004. Potential for aerobic and anaerobic biodegradation of petroleum hydrocarbons in boreal subsurface. Biodegradation 15:29-39.
Reference ID: 141
Keywords: aerobic/attenuation/BIODEGRADATION/concentration/degradation/hydrocarbon/in situ/methane/NATURAL ATTENUATION/petroleum/soil gas/ZONE
Notes: XXXX
Abstract: We studied the role of aerobic and anaerobic petroleum hydrocarbon degradation at a boreal, light- weight fuel and lubrication oil contaminated site undergoing natural attenuation. At the site, anoxic conditions prevailed with high concentrations of CH4 (up to 25% v/ v) and CO2 (up to 18% v/ v) in the soil gas throughout the year. Subsurface samples were obtained mainly from the anoxic parts of the site and they represented both the unsaturated and saturated zone. The samples were incubated in microcosms at near in situ conditions (i. e. in situ temperature 8degreesC, aerobic and anaerobic conditions, no nutrient amendments) resulting in the removal of mineral oil (as determined by gas chromatography) aerobically as well as anaerobically. In the aerobic microcosms on average 31% and 27% of the initial mineral oil was removed during a 3- and 4- month incubation, respectively. In the anaerobic microcosms, on average 44% and 15% of the initial mineral oil was removed during a 12- and 10- month anaerobic incubation, respectively, and e. g. n- alkanes from C-11 to C-15 were removed. A methane production rate of up to 2.5 mug CH4 h(-1) g(-1) dwt was recorded in these microcosms. In the aerobic as well as anaerobic microcosms, typically 90% of the mineral oil degraded belonged to the mineral oil fraction

that eluted from the gas chromatograph after C-10 and before C-15, while 10% belonged to the fraction that eluted after C-15 and before C-40. Our results suggest that anaerobic petroleum hydrocarbon degradation, including n- alkane degradation, under methanogenic conditions plays a significant role in the natural attenuation in boreal conditions

Sanders, P. F. and I. Hers 2006. Vapor intrusion in homes over gasoline-contaminated ground water in Stafford, New Jersey. Ground Water Monitoring and Remediation 26:63-72.
Reference ID: 23
Keywords: attenuation/benzene/BTEX/concentration/degradation/GROUNDWATER/groundwater contamination/indoor air quality/MTBE/oxygen/toluene/tracer/vapor/vapour intrusion/ZONE
Notes: XXXX
Abstract: The potential for chemical vapor intrusion from contaminated ground water to the interior of homes was investigated at a site with a leaking underground gasoline storage tank in Stafford Township, New Jersey. This location exhibited conditions favorable to vapor intrusion, with sand soil and a water table depth of 3.3 m. Concentrations of volatile organic chemicals in the ground water were as high as 82 mg/L for total benzene, toluene, ethylbenzene, and xylene (BTEX) and up to 590 mg/L for methyl-t-butyl ether (MTBE). Soil vapor samples at multiple depths were taken adjacent to several homes. Inside the homes, air samples were taken on the main floor, in the basement, and under the foundation slab. Despite high ground water concentrations, only one home had measurable impacts to indoor air quality attributable to some of the ground water contaminants. In this house, the BTEX chemicals were not detected in the basement, indicating a lack of indoor air impacts from the ground water for these chemicals. Oxygen measurements suggested that degradation attenuated these chemicals as they diffused through the vadose zone. However, MTBE, 2,2,4-trimethylpentane (isooctane), and cyclohexane were found in the indoor air. The first two of these chemicals served as gasoline-specific tracers and indicated that vapor intrusion was occurring. Attenuation factors (the ratio of the indoor air concentration to a source soil vapor concentration) for the BTEX chemicals between the ground water and the indoor air were < 1 x 10(-5), and for MTBE was 1.2 x 10(-5). Attenuation factors between the deep-soil vapor and the basement air were as follows: BTEX compounds, < 1 x 10(-5); MTBE, 2.2 x 10(-5); 2,2,4-trimethylpentane, 3.6 x 10(-4); and cyclohexane, 1.2 x 10(-4). Attenuation factors between the subslab vapor and the basement air were 7 to 8 x 10(-3)

Schoefs, O., M. Perrier, D. Dochain, and R. Samson 2003. On-line estimation of biodegradation in an unsaturated soil. Bioprocess and Biosystems Engineering 26:37-48.
Reference ID: 142
Keywords: assessment/BIODEGRADATION/carbon dioxide/concentration/hydrocarbon/kinetics/petroleum
Notes: XXXX
Abstract: The objective of this study was to develop a model-based estimator of biodegradation in unsaturated soil. This would allow real-time assessment of the efficiency of treatment bioprocesses, such as bioventilation and biopile, and eventually permit optimization through the implementation of control strategies. Based on a reduced-order model, an asymptotic observer was designed to estimate on-line the contaminant concentration, using carbon dioxide measurement. Two observer-

based estimators were built to approximate: (1) the specific microbial growth rate; and (2) the biocontact kinetics representing the soil resistance to contaminant biodegradation. State observers and parameter estimators were confronted with the experimental results of biodegradation in microcosms. Hexadecane was used as the model compound, representing petroleum hydrocarbons. Three water contents, corresponding to 20%, 50% and 80% of the water-holding capacity, were tested. The asymptotic observer is able to predict hexadecane depletion with an error on the overall time trajectories of 13%, 8% and 4% for the dry, intermediate and wet soils, respectively, which is acceptable given that all the biokinetic parameters were identified from a biodegradation experiment in liquid phase. The observer-based estimator of the specific microbial growth rate, based on the CO2 measurement, was successfully calibrated using the off-line measurements of hexadecane as validation data, and allowed estimation of the time when biodegradation switched from a microbial to a biocontact limitation. The biocontact kinetics was also identified on-line, using an estimator based on the hexadecane not in biocontact. These results are very encouraging with respect to the potential for on-line assessment of the performance of treatment bioprocesses in unsaturated soils

Shan, C. and D. B. Stephens 1995. An Analytical Solution for Vertical Transport of Volatile Chemicals in the Vadose Zone. Journal of Contaminant Hydrology 18:259-277.
Reference ID: 157
Keywords: advection/analytical solution/concentration/degradation/density/diffusion/dispersion/groundwater/migration/numerical code/partitioning/transport/ZONE
Notes: XXXX
Abstract: An analytical solution is presented for one-dimensional vertical transport of volatile chemicals through the vadose zone to groundwater. The solution accounts for the important transport mechanisms of the steady advection of water and gas, diffusion and dispersion in water and gas, as well as adsorption, and first-order degradation. By assuming a linear, equilibrium partitioning between water, gas and the adsorbed chemical phases, the dependent variable in the mathematical model becomes the total resident concentration. The general solution was derived for cases having a constant initial total concentration over a discrete depth interval and a zero initial total concentration elsewhere. A zero concentration gradient is assumed at the groundwater table. Examples are given to demonstrate the application of the new solution for calculating the case of a non-uniform initial source concentration, and estimating the transport of chemicals to the groundwater and the atmosphere. The solution was also used to verify a numerical code caned VLEACH. We discovered an error in VLEACH, and found that the new solution agreed very well with the numerical results by corrected VLEACH. A simplified solution to predict the migration of volatile organic chemical due to the gas density effect has shown that a high source concentration may lead to significant downward advective gas-phase transport in a soil with a high air-permeability

Song, H. G. and R. Bartha 1990. Effects of Jet Fuel Spills on the Microbial Community of Soil. Applied and Environmental Microbiology 56:646-651.
Reference ID: 143
Keywords: microbial communities/SPILL
Notes: XXXX

Stout, S. A. and P. D. Lundegard 1998. Intrinsic biodegradation of diesel fuel in an interval of separate phase hydrocarbons. Applied Geochemistry 13:851-859.
Reference ID: 144
Keywords: BIODEGRADATION/distribution/groundwater/hydrocarbon/petroleum/saturation/ZONE
Notes: XXXX
Abstract: Emerging acceptance of the limitations of separate phase product recovery has spawned interest in the intrinsic alteration of residual separate phase petroleum products. In this study the geochemical changes in a continuous core through soil containing a separate phase diesel fuel #2 (SPD) in contact with groundwater are investigated. Chemical heterogeneities are shown to exist which can be attributed to weathering, particularly intrinsic biodegradation. The results show that the aliphatic hydrocarbon content is reduced and the delta(13)C ratio of the aliphatic hydrocarbons increased from top to bottom in the core. Both changes are thought to be due to preferential biodegradation of (isotopically lighter) n-alkanes. A slight increase in the relative abundance of shorter chain n-alkanes (<n-C-17) was also observed. The distribution of the dominant aromatic hydrocarbons (C-0-C-3 alkylnaphthalenes) is remarkably consistent throughout the core, although naphthalene is depleted below the oil-water interface. In spite of low oil saturation (S-0), little or no evidence of biodegradation is noted at the uppermost boundary of the SPD. However, intrinsic biodegradation is evident approximately 0.3 m above the oil-water interface in spite of higher S-0. The extent of the chemical changes attributable to biodegradation (described above) gradually increases below the oil-water interface, eventually reaching a maximum at the bottom of the SPD profile (similar to 1.2 m below the interface) where S-0 is again reduced. The relatively higher level of biodegradation observed at and below the oil-water interface may be attributed to the reduced S-0 in this zone. An estimate of the mass reduction in diesel fuel between the uppermost and bottommost parts of the core is calculated to be 23% (by weight), due predominantly to the biodegradation of n-alkanes. (C) 1998 Elsevier Science Ltd. All rights reserved

Sublette, K. L., R. V. Kolhatkar, A. Borole, K. T. Raterman, G. L. Trent, M. Javanmardian, and J. B. Fischer 1997. Intrinsic bioremediation of gas condensate hydrocarbons: Results of over two years of ground water and soil core analysis and monitoring. Applied Biochemical and Biotechnology 63-65:823-834.
Reference ID: 145
Keywords: aerobic/BIOREMEDIATION/gas condensate/GROUNDWATER/hydraulic gradient/hydrocarbon/intrinsic bioremediation/LIQUIDS/monitoring/pathways/soil gas/sulfate reduction
Notes: XXXX
Abstract: Condensate liquids have been found to contaminate soil and ground water at two gas production sites in the Denver Basin operated by Amoco Production Co. These sites have been closely monitored since July 1993 to determine whether intrinsic aerobic or anaerobic bioremediation of hydrocarbons occurs at a sufficient rate and to an adequate end point to support a no-intervention decision. Ground water monitoring, soil gas analysis, and analysis of soil cores suggest that bioremediation is occurring at these sites by multiple pathways, including aerobic oxidation, sulfate reduction, and methanogenesis. Results of

over two years of monitoring of ground water and soil chemistry at these sites are presented to support this conclusion.

Totsche, K. U., I. Kogel-Knabner, B. Haas, S. Geisen, and R. Scheibke 2003. Preferential flow and aging of NAPL in the unsaturated soil zone of a hazardous waste site: implications for contaminant transport. Journal of Plant Nutrition and Soil Science-Zeitschrift fur Pflanzenernahrung und Bodenkunde 166:102-110.
Reference ID: 146
Keywords: accumulation/DIVERSITY/fate/groundwater/LIQUIDS/NAPL/PAH/pathways/permeability/preferential flow/transformation/transport/unsaturated zone/ZONE
Notes: XXXX
Abstract: Flow of non-aqueous phase liquids (NAPL) in the unsaturated zone is thought to be driven by gravity with a dominant vertical flow direction, and lateral spreading to be limited to the gradient of the relative permeabilities. The effect of soil profile build-up, preferential flow, aging, and groundwater level fluctuations is mostly neglected. The objective of our study was to check the effects of such processes on the fate of NAPL in the unsaturated soil zone. At a hazardous waste site, we conducted-a field survey of the unsaturated soil zone and monitored the groundwater for a two year period. We conducted spatially resolved and depth dependent soil sampling and analysis and the evaluation of former ram and core drilling protocols. The samples were analyzed for the 16 EPA PAH and alkanes with GC-MS and GC-FID. C-13-NMR spectroscopy was used to assess structural changes of the NAPL phase. Flow of bulk NAPL along macropores and along preferential permeability structures, like sedimentation discontinuities, are the dominant transport pathways which cause large lateral spreading beyond those expected by the relative permeability gradient. Accumulation of NAPL was found at locations with abrupt textural changes and within the zone of capillary rise. Aging of NAPL results in the depletion in soluble and volatile compounds but also in oxidation and polymerization. It increases the chemical diversity and decreases the mobility of the NAPL. Thus, NAPL flow ceases much earlier than expected from the capillary forces. As chemical transformation is restricted to the NAPL water/air interface, a skin-like thin film is formed which encapsulates and preserves the bulk NAPL from further hardening, limiting contaminant mass transfer from the NAPL to the aqueous phase

Trefry, M. G., J. Öhman, D. S. Whyte, and G. B. Davis 2000. A time-synchronous domain decomposition code for multiphysics systems . (Anonymous,).
Reference ID: 26
Keywords: analytical solution/benzene/black box solver/concentration/heterogeneous media/multiphysics problems/numerical code/partitioning/PDE/prediction/risk assessment/transport/transport processes/vapour/vapour transport/VOCs
Notes: XXXX
Abstract: In assessing risks of exposure to toxic contaminants in environmental systems, the transport dynamics of contaminants through complex heterogeneous media is a key determinant. Quantitative predictions of contaminant concentrations and fluxes are often required for systems involving different classes of physical dynamics and sharply discontinuous material properties. For many volatile contaminants, special conservation laws apply at interfaces between neighbouring system

subdomains. These conservation laws couple dependent variables between the subdomains in a dynamic sense. Within the subdomains, essentially arbitrary physical processes may occur, possibly coupling many dependent variables. We describe the development of a code applicable to such multi-physics problems. The code uses an advanced black box solver as an engine to solve the partial differential equations appropriate to each subdomain. Simple geometric domain decomposition is used to define subdomains. In this first implementation, parallel instances of the solver engine (that is, in each subdomain) communicate synchronously with each other to facilitate time-stepping of the total system solution. The interfacial conservation laws act as constraints to the subdomain solutions, effectively providing dynamic internal boundary conditions. Convergence characteristics of the discretised interface algorithms are discussed in terms of validations against recently derived analytical solutions for diffusion-limited transport in partitioning laminates. Finally, an application of the code to coupled benzene vapour transport in variably saturated porous and permeable media is outlined.

Trefry, M. G., J. Ohman, and G. B. Davis 2001. A simple numerical approach for assessing coupled transport processes in partitioning systems. Applied Mathematical Modelling 25:479-498.
Reference ID: 25
Keywords: analytical solution/numerical code/partitioning/PDE/transport/transport equation/transport processes
Notes: XXXX
Abstract: Recent concepts in the solution of multidomain equation systems are applied to the problem of distinct transport processes coupled over geometrically disjoint domains. The (time dependent) transport equations for the composite system are solved using a simple domain decomposition approach, with parallel implementations of detailed Schwarz balances for the system subdomain interfaces. An existing numerical partial differential equation (PDE) solver is coupled with the interface algorithms to provide a code capable of handling a wide range of dynamical equations within the subdomains. Interface partitioning conditions corresponding to sharply discontinuous Dirichlet constraints. and to (discontinuous) rate-limited Neumann constraints are also incorporated into the code. A variety of transport operators can be handled simply by altering the equation system code block. The code is validated against analytical solutions for representative parabolic transport equations including recent solutions for diffusive transport in partitioning laminates, useful for describing the movement of chemical species in composite materials. The code is then applied to an example problem of coupled multiphase chemical transport in a variably saturated soil column with a low-permeability capping. (C) 2001 Elsevier Science Inc. All rights reserved

Venkatraman, S. N., D. S. Kosson, and J. R. Schuring 1998. Transport and biological fate of toluene in low-permeability soils. Ground Water Monitoring and Remediation 18:105-113.
Reference ID: 147
Keywords: aerobic/BIODEGRADATION/concentration/degradation/degradation rates/diffusion/diffusion coefficient/fate/Millington-Quirk equation/modeling/nitrate/prediction/sorption/toluene/tortuosity/transport/vapor/vapor sorption
Notes: XXXX
Abstract: The effect of simultaneous sorption, diffusion, and biodegra-

dation on the fate and transport of toluene in low-permeability soil formations was examined. A transport model accounting for vapor and liquid sorption, vapor diffusion, and first-order biodegradation was developed to describe the movement of volatile solute in unsaturated soils. Modeling studies were followed with laboratory batch and column studies on fine-grained soil samples obtained from a gasoline-contaminated site. Batch experiments yielded the sorption and diffusion coefficients for generating theoretical solute transport profiles. Column studies were conducted to examine toluene sorption, diffusion, and biodegradation under aerobic and denitrifying conditions. Results from the column studies indicated that vapor sorption onto the soil was minimal due to the high moisture content of the soil. Comparison of model predictions with experimental results indicated that the SASK model, which is based on the resistivity theory, provided a more accurate prediction of the vapor phase tortuosity than the frequently used Millington-Quirk equation. Laboratory results of toluene concentration profiles matched well with the model predictions and yielded degradation rates comparable to those obtained in the field. Column studies, examining toluene biodegradation under aerobic and denitrifying conditions in low-permeability soils, indicated that the presence of excess nitrate in aerobic environments yielded higher solute degradation rates than those observed under exclusively aerobic systems

Wibbe, M. and M. M. Blanke 1999. Aliphatic hydrocarbons in an oil-contaminated soil - Carbon economy during microbiological decontamination. Environmental Science and Pollution Research 6:2-6.
Reference ID: 148
Keywords: BIODEGRADATION/hydrocarbon/microorganisms/nitrate/PAH/PCB/respiration
Notes: XXXX
Abstract: Microbial decontamination of hydrocarbon-polluted soil was paralleled with soil respiration measurements. About 1,500 tons of a loamy top soil were found to be contaminated with approximately 2000 mg/kg of aliphatic hydrocarbons, mainly oleic (C18:1) and linoleic acid (C18:2) found in the vicinity of a linoleum manufacturing and then a car dewaxing plant. The contaminated soil was analysed for dry matter, pH, dehydrogenase activity, electrical conductivity and nutrient content viz. nitrate, phosphorus and potassium, as well as a number of indigenous microbes. The soil was low in salt and nutrients. This paper describes the procedure and measures to decontaminate this bulk soil on site from approx. 2,000 to 500 mg of aliphatic hydrocarbons/kg dry matter by use of a nutrient emulsion, indigenous micro-organisms and aeration over 13 months. This 75% reduction in aliphatic hydrocarbons resulted in a concomitant carbon efflux, measured as soil respiration, and was used to calculate carbon fluxes

Williams, G. M., R. S. Ward, and D. J. Noy 1999. Dynamics of landfill gas migration in unconsolidated sands. Waste Management & Research 17:327-342.
Reference ID: 256
Keywords: advection/aerobic/carbon dioxide/concentration/diffusion/diffusion coefficient/electron acceptor/kinetics/landfill/methane/migration/models/oxygen/permeability/PLUME/porosity/release/remediation/tortuosity/transport/ZONE
Notes: XXXX
Abstract: A gas plume from the Foxhall landfill in Suffolk, UK contains elevated concentrations of methane and carbon dioxide in unsaturated

unconsolidated sands which comprise Pleistocene "Red Crag" deposits. The plume emanates from a relatively restricted zone along one side of the landfill, but extends over 100 m from the site boundary. The reduction in the methane to carbon dioxide ratio with distance and the systematic changes in their carbon and hydrogen stable isotope ratios are evidence of microbially mediated methane oxidation. A one-dimensional advection-diffusion model was used to describe the combined concentration of methane and carbon dioxide in the plume. Diffusion alone underestimated the concentration profile, but a good fit to the data was achieved with an advective flux of 4.5 m yr(-1), indicating that advection due to a pressure gradient from the landfill as well as diffusion should be considered in gas migration modelling. The kinetics of methane oxidation was studied by parameter-fitting a reaction rate into the advection-diffusion equation with first-order decay. A decay constant of -0.063 yr(-1) (half-life 11 yr) produced a poor fit to the methane profile, suggesting that oxidation may not be constant throughout the plume. However, the stable isotope data allowed two rates of oxidation to be inferred. A slow rate of oxidation with a half-life of the order of 4.3 to 7.6 yr was inferred in the centre of the plume where oxygen was absent. A much faster rate with a half-life no longer than 0.76 to 1.21 yr occurred beyond 60 m of the landfill and around the top fringe of the plume where oxygen was present. These rates are considered to reflect the difference between aerobic and anaerobic oxidation, the latter utilizing iron(III) in the sediment as an electron acceptor. The shape of the plume is asymmetrical, indicating a geological control on gas migration. In a two-dimensional model a poor fit to the observed data was obtained when the sand was assumed to be homogeneous and where the gas entered from a restricted part of the landfill boundary. However, a better model was produced by varying the diffusion coefficient in the sands over the range 5 x 10(-7) to 2 X 10(-6) m(2) s(-1) without the need to restrict the zone of gas release along the landfill boundary. Such a range in transport properties could be accounted for by normal variability in the porosity, tortuosity and water content of the sand. The long-term dissipation of the plume assuming only diffusion was predicted to take up to 30 yr for the gas concentration to reduce to 10% of its initial value. However, the plume disappeared within a year after pumping from gas wells in the landfill, indicating chat advection under an imposed pressure gradient was a major control on remediation. This study shows that models can be used to explain landfill gas migration and to infer oxidation rates which can be used to predict gas migration at other sites. However, the need to obtain field data on gas permeabilities and diffusivities will always be a major limitation in predicting gas migration in permeable formations

Wrenn, B. A., J. R. Haines, A. D. Venosa, M. Kadkhodayan, and M. T. Suidan 1994. Effects of Nitrogen-Source on Crude-Oil Biodegradation. Journal of Industrial Microbiology 13:279-286.
Reference ID: 149
Keywords: BIODEGRADATION/CRUDE-OIL/nitrate/oxygen
Notes: XXXX
Abstract: The effects of NH4Cl and KNO3 on biodegradation of light Arabian crude oil by an oil-degrading enrichment culture were studied in respirometers. In poorly buffered sea salts medium, the pH decreased dramatically in cultures that contained NH4Cl, but not in those supplied with KNO3. The ammonia-associated pH decline was severe enough to completely stop oil biodegradation as measured by oxygen uptake. Regular adjustment of the culture pH allowed oil biodegradation to pro-

ceed normally. A small amount of nitrate accumulated in all cultures that contained ammonia, but nitrification accounted for less than 5% of the acid that was observed. The nitrification inhibitor, nitrapyrin, had no effect on the production of nitrate or acid in ammonia-containing cultures. When the culture pH was controlled, either by regular adjustment of the culture pH or by supplying adequate buffering capacity in the growth medium, the rate and extent of oil biodegradation were similar in NH4Cl- and KNO3-containing cultures. The lag time was shorter in pH-controlled cultures supplied with ammonia than in nitrate-containing cultures

B 3.14: Diverse præsentationer

Anonymous. Evaluating the soil vapor intrusion pathway at petroleum release sites in NYS. 9999. (GENERIC)
Ref Type: Slide
Ref ID: 215
Keywords: petroleum/vapor
Notes: Presentations

Abreu, L. and P. Johnson. Modeling the effect of aerobic biodegradation on vapor intrusion. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 216
Keywords: aerobic/aerobic biodegradation/BIODEGRADATION/modeling/vapor/vapour/vapour intrusion
Notes: Presentations

Gallagher, D. Status and application of DTSC's vapor intrusion guidance. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 217
Keywords: guidance/vapor/vapour/vapour intrusion
Notes: Presentations

Hartman, B. Vapor intrusion risk pathway: Practical assessment methods. 2009. (GENERIC)
Ref Type: Slide
Ref ID: 214
Keywords: assessment/methods/pathways/vapor/vapour intrusion
Notes: Presentations

Hopkins, H. Data collection to support sound screening for vapor intrusion to indoor air at petroleum release sites. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 218
Keywords: petroleum/sound screening/vapor/vapour/vapour intrusion
Notes: Presentations

Lahvis, M. A. Type curve approach for assessing potential effects on ground water from small releases of gasoline at UST sites. 2006. (GENERIC)
Ref Type: Slide
Ref ID: 222
Keywords: EtOH/first-order rate constants/GROUNDWATER/groundwater contamination/models/MTB/MTBE/release/TBA/type curve approach/UST
Notes: Presentations

Mchugh, T. Vapor intrusion investigation methods. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 219
Keywords: methods/vapor/vapour/vapour intrusion
Notes: Presentations

Ririe, G. T. Top 10 issuses and workplan. Review-lessons learned. 2009. (GENERIC)
Ref Type: Slide
Ref ID: 211
Notes: Presentations

Ririe, G. T. Case studies to evaluate hydrocarbon vapor attenuation in the vadose zone. 9999. (GENERIC)
Ref Type: Slide
Ref ID: 213
Keywords: attenuation/case study/hydrocarbon/unsaturated zone/vapor/ZONE
Notes: Presentations

Schuver, H., D. Cooper, and H. Dawson. Update on the OSWER vapor intrusion guidance. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 220
Keywords: guidance/vapor/vapour/vapour intrusion
Notes: Presentations

Vescio, J. Update on EPA's petroleum vapor intrusion work group activities. 2005. (GENERIC)
Ref Type: Slide
Ref ID: 221
Keywords: petroleum/vapor/vapour/vapour intrusion
Notes: Presentations

Hinchee, R. E., B. C. Alleman, R. E. Hoeppel, and R. N. Miller 1994. Hydrocarbon bioremediation.
Reference ID: 176
Keywords: BIOREMEDIATION/hydrocarbon
Notes: Book

Rubin, H., N. Narkis, and J. Carberry 1998. Soil and aquifer pollution: non-aqueous phase liquids; contamination and reclamation.
Reference ID: 183
Keywords: AQUIFER/groundwater contamination/LIQUIDS/NAPL/soil contamination
Notes: Book

Resumé

Det overordnede formål med projektet er, på baggrund af et litteraturstudium, at beskrive, hvilke strategier der findes til at dokumentere og kvantificere naturlig nedbrydning af oliestoffer i jordens umættede zone, samt at få belyst, om der findes eller kan udvikles (simple) feltstrategier, der kan sandsynliggøre, at nedbrydning foregår og er tilstrækkelig – og evt. muliggør, at der kan estimeres lokalitetsspecifikke nedbrydningsrater. Endvidere gives der anbefalinger til afprøvning og implementering af metoder/procedurer og måleprogrammer ift. anvendelsen af givne metoder/strategier sammen med JAGG 2.0. Desuden er der i henhold til kommissoriet for projektet, parallelt med litteratursøgningen på strategier/metoder for den umættede zone, indsamlet tilgængelig litteratur for push-pull test i den mættede zone og tilgængelige erfaringsværdier for styrende parametre (næringssalte og ilt) fra den dybere umættede zone på danske lokaliteter.

Miljøministeriet
Miljøstyrelsen

Strandgade 29
DK - 1401 København K
Tlf.: (+45) 72 54 40 00

www. mst.dk