SV-415

Development of a Numerical Simulator
for LNAPL Weathering

Final report

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Samenvatting
Bodemverontreinigingen met olieachtige producten komen veel voor en er gaat een langdurige bedreiging van uit wanneer die olie als puur product in de bodem voorkomt, bijvoorbeeld als drijflaag. De olie fungeert dan als bron van waaruit continue levering van verontreinigingen richting het grondwater plaatsvindt. Het is bekend dat die levering vanuit de bron in de loop der tijd verandert en vermindert ten gevolge van verweringsprocessen. Het komt erop neer dat verschillende oliecomponenten verschillend oplossen met als gevolg dat de meest oplosbare componenten het eerst zullen verdwijnen. Wat overblijft is een bron met een toenemend gehalte aan relatief immobiele componenten.
Deze verandering in afgifte wordt tot nu toe niet meegenomen bij het omgaan met bodemverontreinigingen en er zijn geen computermodellen om die verandering in afgifte naar het grondwater te bepalen. Dit onderzoek heeft geleid tot de ontwikkeling van de computercode RT3D-OW die succesvol is getest op een drietal testlocaties.

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Abstract
Contaminated sites with oil like products are among the most common contamination types. If these products are present as a NAPL (Non-Aqueous Phase Liquid), the contamination poses a long-term threat to the environment. The oil will act as a source from which contamination continuously emanates to the groundwater. The emission of pollutants into the groundwater changes with time as a result of weathering processes.

In particular, the volatilisation and dissolution rates of these components are different. For example, the more soluble and volatile components (e.g. benzene) will be mobilised first, leaving behind a NAPL with increased mole fractions of less mobile compounds. It is, therefore, expected that the release of contaminants from the oil will decrease with time. This changing source function is presently not regarded when dealing with subsurface oil contamination.
This research has conducted to the development of the computer code RT3D-OW that has been tested successfully on three test locations.

Keywords

| **Controlled terms** | **Uncontrolled terms** |
| contamination, dissolution, source function, modelling | NAPL, floating layer, oilweathering, residual oil |

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CONTENS

SUMMARY

Development of a Numerical Simulator for LNAPL Weathering

Introduction
The source areas at most contaminated sites consist of mixtures of organic contaminants. All these components have their own physical properties such as solubility. This means that the emission into the groundwater will initially be dominated by the most soluble components. Eventually these components will become depleted, resulting in change of concentration of the source area. This means that release of components into the groundwater will change with time. This time dependent emission of pollutants into the groundwater is not included in current solute transport models.

One of the conclusions of the BEVER project A5 was that in order to implement policies such as stable end situations, it is paramount to have tools capable of evaluate and predict the risk of spreading of subsurface contamination. This report describes the development of such a tool for multi-component source areas.

Conceptual model and numerical code
After an extensive evaluation of existing models it was decided to take the widely used RT3D code as a starting point. RT3D is a finite-difference numerical model for simulation of 3-D, multi-species, reactive transport in saturated porous media. A new module, describing the transfer between a source area and the ambient groundwater was implemented in this code.

Light-Non-Aqueous Phase Liquids can reside in the subsurface as either continuous floating lenses, submersed in the capillary fringe and discontinuous droplets of oil, trapped in the pore space. These two configurations have varying contaminant release mechanisms:

1) A floating lens contains oil at high saturation and flowing of water through that layer is impeded (see figure S1). This means that the mass-transfer occurs at the boundary of the continuous oil body. The migration of the pollutants away from the interface is governed by the transverse dispersivity.
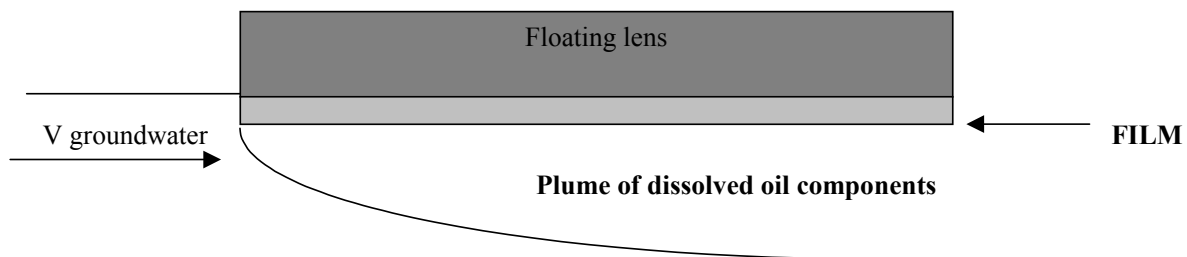
Fig. S1.   Sketch of a plume originated in a pool zone.

2) Due to the much higher water-LNAPL interface, the aqueous concentrations in this zone can be assumed to be at chemical equilibrium. Solubilization occurs when water migrates through this zone and the solutes are moved away by advection.

For both cases, we applied Raoult's law to allow for the solubilization of multiple components. The resulting code is very versatile and generic with respect to input data. The composition of the source and the groundwater can either be specified in fractions of for example mineral oil or individual components. Important is that the data pertaining to the LNAPL and the groundwater match.

Test case Bemidji

The new code RT3D-OW is tested by modelling some basic scenario's followed by a validation on field data originated from the field site Bemidji (USA). The results of the basic runs give a good insight in the dissolution process (see figure S2). The most soluble oil components will dissolve first resulting in a reduction of their relative concentration in the oil phase.

During the modelling of the Bemidji case, several scenario's were calculated in order to give a sensitivity analyses and to try to fit the calculation results on the measured results. It was concluded that mass transfer from a continuous oil body is a slower process compared to mass transfer from residual oil. This is because the residual oil has a larger contact area with the surrounding groundwater. In many situations, the aqueous concentration will therefore be determined mostly by the thickness of this zone. This results also in a higher aqueous concentration in the plume. As a whole, the weathering of oil is a slow process. Within the time modelled (15 years) no more than several per cent of the total mass is dissolved.
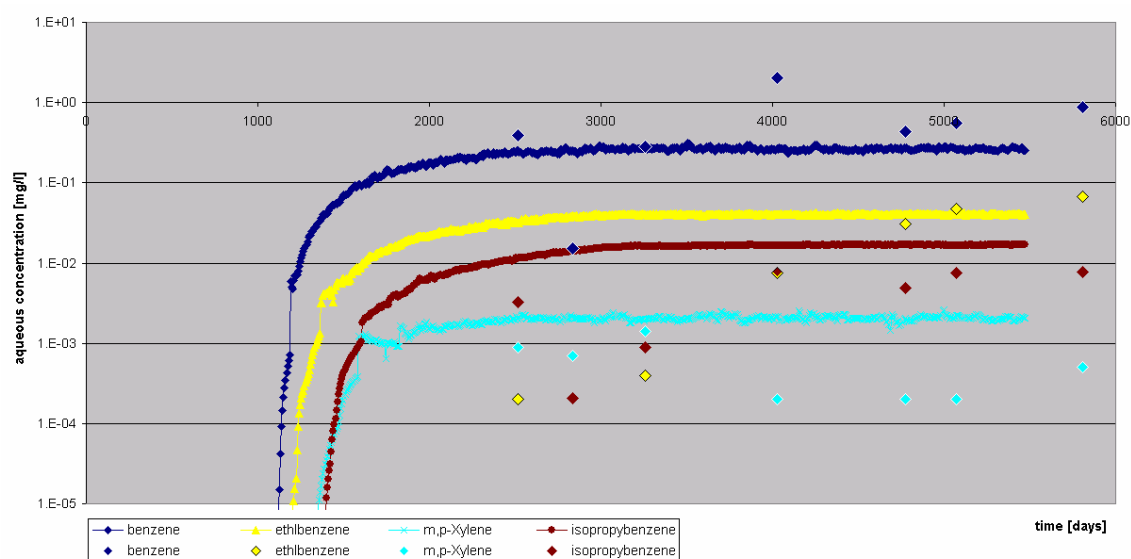
Fig. S2. Modelling results (continues) for 4 components plotted on the field measurements (dots) on a single monitoring location at Bemidji.

Subsequent adjustment of both aerobic and anaerobic constants and the initial oxygen concentration showed a high sensitivity because it is possible to simulate a wide range of plume concentrations and volumes. For the Bemidji case a best fit on the measurements was found at two monitoring locations using biodegradation rates within acceptable ranges.

Two demonstration sites

After the successful test at the Bemidji site, two Dutch sites were selected. One (site 1) consisted of an oil contamination while the second (site 2) was contaminated with diesel oil.

For the two Dutch sites we adopted the TPHCWG fractionation method to obtain representative input data with respect to the composition of the source. This method assumes that aliphatic compounds with similar gas chromatography (GC) retention times have similar properties such as water solubility. The same holds for aromatics. This allows for the allocation of the individual oil components to an oil fraction, to which a representative aqueous solubility can be assigned. Because relationships, between the GC retention times and the solubility, are different for aliphatic and aromatic compounds, it was necessary to separate these two kinds of chemical species before the separate GC analyses.

A test of this method against a similar technique, developed by TTE, showed for two wells that the overall pattern of all samples was comparable. Our analysis however showed a higher proportion of aliphatic components.

Site I
A total of 22 samples extracted from this site were analysed. Some of these samples indicated LCCCO as the contaminant, while another sample indicated more a middle distillate such as a diesel. This was attributed to the presence of multiple source area's originating from different spills.

Groundwater simulations at this site showed that all water was draining towards a local drain within about 3 years. The results also show that degradation of contaminants in the groundwater has a positive effect upon depletion of oil components within the NAPL phase. Subsequently, an initial oil saturation of 10 % was introduced in an area, resembling the actual contaminated site. As the rate of transfer of the discontinuous droplets is much higher than that of the floating layer, ground concentrations are determined predominately by the residual zone.

During 20 years, only the concentrations of two smaller fractions of the more water-soluble aromatics decreased at a well in the vicinity of the drain. All other fraction remained at the same level. This shows that leaching of a source area takes a long time, even when floating layers are not considered. Comparison between the simulations and the measured concentrations corroborated the presence of multiple spills.

Site II
A total of 14 oil samples have been analysed from this site. The GC tracers showed a somewhat elevated level of aromatic components, compared to a fresh diesel sample, which indicates a degree of biodegradation.

For the autonomous development, the combined system of sewage and drainage in the built up urban area adjacent to the site is one critical outflow boundary. Modelling results show that for autonomous development without biodegradation, concentrations of mineral oil are above the target value. If biodegradation is occurring at this site then the plume is confined to the area nearby the floating layer.

The contribution of dissolution from the pool to the mass transport is negligible compared to the contribution of the residual oil in the smear zone. However, the presence of the floating layer in the real world situation is relevant, it causes the replenishment of the smear zone (containing residual oil) through fluctuation of the groundwater level.

Biodegradation also influences the vertical spreading of the plume. However without biodegradation results show concentrations above the target value are already present in the principle aquifer and within 10 years from now, concentrations of mineral oil above the intermediate value for mineral oil are expected.

Based on these results decisions can be made as to what kind of remediation action, if any, is needed at site II. It is unlikely that excavation would be an effective method as a plume of contamination has already developed. Results indicate that further research and perhaps stimulation of NA may be the most suitable approach.

General
It can be concluded that the extended numerical code gives the opportunity to determine the weathering of residual NAPL in the subsoil.

As the code describes (in a simplified way) several important processes associated with oil and other mixed LNAPL contamination, various possible applications can be identified:

1. to provide insight in the physical processes affecting emissions of contaminants from multi-component source areas. What happens to groundwater concentrations when we remove 90 % of the oil contamination?
2. Optimisation and interpretation of possible measurement schemes in the vicinity of the oil contamination source. Where can we take samples, which tell us whether or not natural attenuation is efficient?
3. Simulation of various remedial schemes, What needs to be don in order to reach a stationary end situation. Do we need to remove the source?
4. Identifying sources which have the highest impact on receptors. How long does it take for the contamination to reach the limits of the site and what do we need to do to avoid that?

Areas for future research to increase the applicability of the code will necessarily have to include quantitative experimental lab. Work and field measurements, supported by numerical modelling. Possible areas of focus could be:

- the description of natural attenuation by a first-order biodegradation concept;
- assigning biodegradation constants to fractions of multi-component oils.

SAMENVATTING

Ontwikkeling van een modelcode voor de bronfunctie van olieachtige bodemverontreinigingen naar de omgeving

Inleiding

De brongebieden van de meeste verontreinigde locaties bestaan uit een mengsel van organische contaminanten. Al deze bestanddelen hebben allemaal hun eigen fysieke eigenschappen, zoals oplosbaarheid. Dit betekent dat de lozing in het grondwater in het begin voor het overgrote deel bestaat uit de sterkst oplosbare bestanddelen. Uiteindelijk zijn deze bestanddelen uitgeput, wat leidt tot veranderingen in de concentratie van de bronlocatie. Dit betekent dat de afgifte van bestanddelen aan het grondwater naar verloop van tijd verandert. Deze tijdsafhankelijke afgifte van verontreinigende stoffen aan het grondwater is niet opgenomen in de huidige transportmodellen voor opgeloste stoffen.

Een van de conclusies van het BEVER-project A5 was dat het voor het toepassen van beleid en stabiele eindoplossingen van essentieel belang is dat men beschikt over de middelen die nodig zijn om het risico van verspreiding van bodemverontreiniging te evalueren en voorspellen. In dit rapport wordt de ontwikkeling beschreven van een dergelijk hulpmiddel voor bronlocaties met diverse componenten.

Conceptmodel en numerieke code

Na een uitgebreide evaluatie van bestaande modellen werd besloten om de veelgebruikte RT3D-code als uitgangspunt te nemen. RT3D is een eindige-differentie numeriek model voor simulatie van 3-D, meersoortig reactief transport in verzadigde poreuze media. Er werd een nieuwe module aan deze code toegevoegd, waarin de overdracht tussen een bronlocatie en het omliggende grondwater wordt beschreven.

Lichte vloeistoffen in een niet-waterige fase (LNAPL's) kunnen zich in de grond bevinden als ononderbroken drijflagen in de capillaire zone, of als afzonderlijke oliedruppeltjes die gevangen zitten in de poriënruimte. Deze twee verschillende opbouwen zorgen voor verschillende uitstroommechanismes voor contaminanten:

1) een drijflaag bevat een hoge verzadiging olie en het doorstromen van water door deze laag wordt gehinderd (zie figuur S1). Dit betekent dat de stoftransport plaatsvindt langs de rand van het ononderbroken olielichaam. De verplaatsing van de verontreinigende stoffen vanaf het grensvlak vindt plaats via de transversale dispersiviteit.
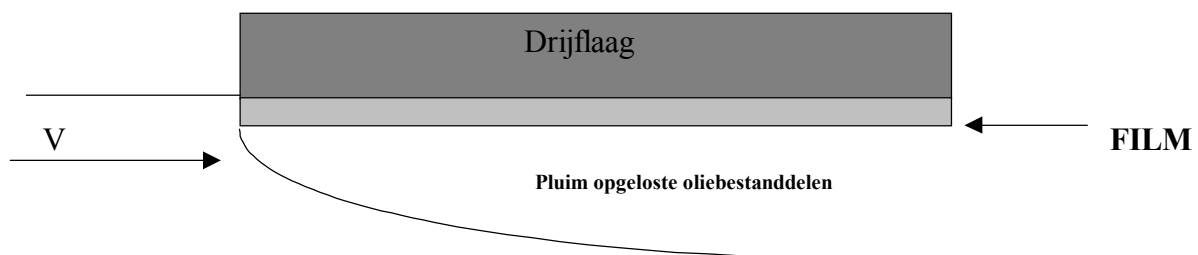
Fig. S1.   Tekening van een pluim ontstaan in een kernzone.

2) Als gevolg van het veel hogere grensvlak tussen water en LNAPL's, kan worden aangenomen dat de waterige concentraties in deze zone chemisch in evenwicht zijn. Het oplosbaar worden treedt op als het water zich door deze zone verplaatst en de opgeloste stoffen worden afgevoerd door middel van advectie.

In beide gevallen hebben we de wet van Raoult toegepast om rekening te houden met het oplosbaar worden van meervoudige componenten.

De resulterende code is zeer veelzijdig en algemeen toepasbaar als het gaat om invoergegevens. De samenstelling van de bron en het grondwater kan ofwel worden gespecificeerd in fracties van bijvoorbeeld minerale olie of in afzonderlijk componenten. Belangrijk is wel dat de gegevens met betrekking tot de LNAPL en het grondwater overeenkomen.

Proef Bemidji

De nieuwe code RT3D-OW is getest door een model te maken van een aantal basisscenario's, gevolgd door een validatie met behulp van veldgegevens van de veldlocatie Bemidji (VS). De resultaten van de basisuitvoeringen geven een goed inzicht in het oplosproces. De sterkst oplosbare oliebestanddelen lossen als eerste op, wat leidt tot een verlaging van hun relatieve concentratie in de oliefase.

Tijdens het maken van het model voor de locatie Bemidji, werden verschillende scenario's berekend om een gevoeligheidsanalyse te geven en om te proberen de calculatieresultaten overeen te laten komen met de gemeten resultaten. Er werd vastgesteld dat het stoftransport vanaf een ononderbroken olielichaam een trager proces is dan stoftransport vanaf residuele olie. Dit komt doordat de residuele olie een groter contactoppervlak heeft met het omringende grondwater. In veel gevallen wordt de waterige concentratie dan ook hoofdzakelijk bepaald door de dikte van deze zone. Dit levert eveneens een hogere waterige concentratie in de pluim op. Als geheel is de verwering van olie een traag proces. Binnen de in het model verwerkte tijd (15 jaar) is niet meer dan enkele procenten van de totale stof opgelost.
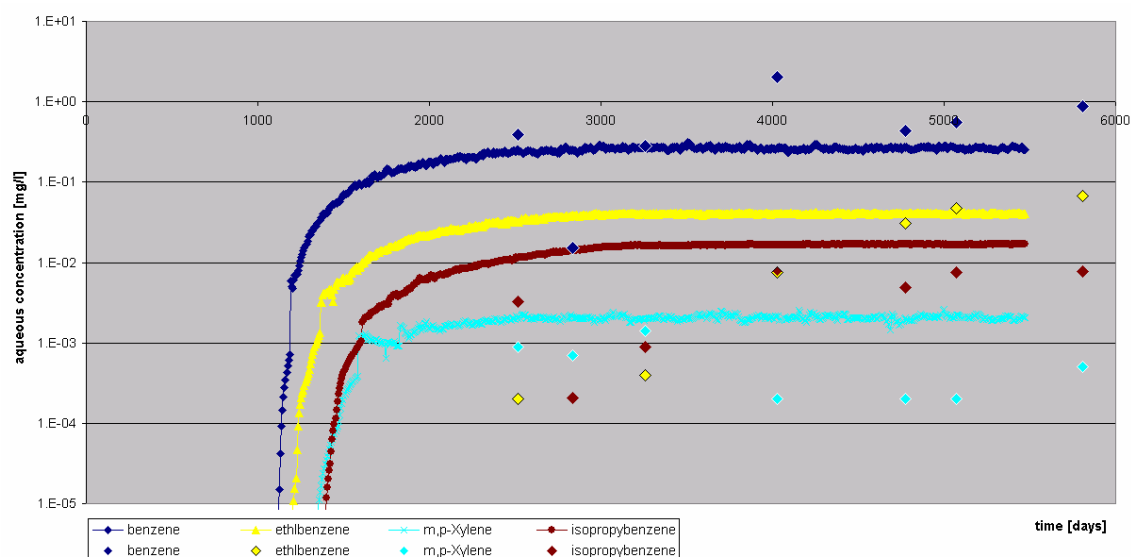
Fig. S2. Modelresultaten (doorgetrokken) voor 4 componenten afgezet tegen de veldmetingen (stippen) op één controlelocatie te Bemidji.

Verdere aanpassing van zowel aërobe als anaërobe constanten en de oorspronkelijke zuurstofconcentratie gaven een hoge gevoeligheid te zien, aangezien het mogelijk is om een grote verscheidenheid aan pluimconcentraties en –volumes te simuleren. Voor de Bemidji-locatie werd de beste aansluiting op de metingen gevonden op twee controlelocaties waarbij sprake was van biodegradatiesnelheden binnen acceptabele grenzen.

Twee demonstratielocaties
Na de succesvolle test op de Bemidji-locatie werden twee Nederlandse locaties gekozen. Eén locatie (locatie 1) was met olie vervuild, op de andere (locatie 2) was sprake van vervuiling met dieselolie.

Voor de twee Nederlandse locaties kozen we de TPHCWG-fractioneringsmethode om representatieve invoerdata te verkrijgen met betrekking tot de samenstelling van de bron. Bij deze methode wordt aangenomen dat alifatische verbindingen met gelijke gaschromatografie-retentietijden (GC) gelijkwaardige eigenschappen hebben, zoals oplosbaarheid in water. Hetzelfde geldt voor aromaten. Op deze manier kunnen de individuele oliecomponenten worden toegepast op een oliefragment, waaraan een representatieve oplosbaarheid in water kan worden toegekend. Aangezien de relatie tussen de GC-retentietijden en de oplosbaarheid verschillend is voor alifatische en aromatische verbindingen, moesten deze twee verschillende chemische soorten worden gescheiden voor de afzonderlijke GC-analyses.
Een test van deze methode tegen een vergelijkbare techniek, ontwikkeld door TTE, toonde aan dat voor twee bronnen het algehele patroon van alle monsters vergelijkbaar was. Onze analyse toonde echter een groter aandeel alifatische verbindingen aan.

Locatie I
In totaal werden 22 monsters van deze locatie genomen en geanalyseerd. Een aantal van deze monsters wees op LCCCO (lichte katalytisch gekraakte omloopolie) als de verontreinigende stof, terwijl een ander monster meer in de richting wees van een middeldistillaat als diesel. Dit werd toegeschreven aan de aanwezigheid van meerdere bronlocaties afkomstig van verschillende lozingen.

Grondwatersimulaties op deze locatie wezen uit dat al het water binnen ongeveer 3 jaar wegliep naar een plaatselijke drain. De resultaten wijzen er bovendien op dat degradatie van contaminanten in het grondwater een positief effect heeft op de depletie van oliebestanddelen in de NAPL-fase (niet met water mengbare fase). Vervolgens werd er op een locatie gezorgd voor een oorspronkelijke olieverzadiging van 10%, ter nabootsing van de feitelijke verontreinigde locatie. Aangezien de overdrachtsnelheid van de losse druppeltjes veel hoger is dan die van de drijflaag, worden de grondconcentraties grotendeels bepaald door de residuele zone.

Gedurende 20 jaar namen alleen de concentraties van twee kleinere gedeelten van de beter in water oplosbare aromaten bij een bron in de nabijheid van de drain af. Alle andere gedeelten bleven op hetzelfde niveau. Dit toont aan dat het uitlogen van een bronlocatie lang duurt, ook als de drijflagen buiten beschouwing worden gelaten. Een vergelijking tussen de simulaties en de gemeten concentraties bevestigde de aanwezigheid van meerdere vervuilingen.

Locatie II
Van deze locatie zijn in totaal 14 oliemonsters geanalyseerd. De GC-indicatoren lieten een iets verhoogd niveau aromatische bestanddelen zien, in vergelijking met een nieuw dieselmonster, wat wijst op een bepaalde mate van biologische afbraak.

Voor de autonome ontwikkeling is het gecombineerde systeem van riolering en ontwatering in het aangrenzende bebouwde stedelijke gebied een uiterste uitstroomgrens. Modelresultaten geven aan dat voor autonome ontwikkeling zonder biologische afbraak, de concentraties van minerale olie boven de doelwaarde liggen. Als er op deze locatie biologische afbraak optreedt dan wordt de pluim beperkt tot het gebied dichtbij de drijflaag.

De bijdrage van oplossing van de kern in de richting van het stoftransport is verwaarloosbaar in vergelijking met de bijdrage van de residuele olie in de smeerzone. De aanwezigheid van de

drijflaag in de werkelijke situatie is echter wel relevant; deze zorgt voor de aanvulling van de smeerzone (die residuele olie bevat) als gevolg van fluctuering van het grondwaterniveau.

Ook biodegradatie is van invloed op de verticale verspreiding van de pluim. Zonder biodegradatie wijzen de resultaten er echter op dat concentraties boven de doelwaarde al aanwezig zijn in de belangrijkste waterhoudende laag, en binnen 10 jaar worden er concentraties minerale olie ver-wacht die boven de tussenwaarde voor minerale olie liggen.

Op basis van deze resultaten kunnen beslissingen worden genomen over welke saneringsmaat-regelen er, indien nodig, moeten worden genomen op locatie II. Het is onwaarschijnlijk dat uit-graving een effectieve methode is, aangezien er zich reeds een verontreinigingspluim heeft ontwikkeld. De resultaten geven aan dat verder onderzoek en mogelijk een stimulering van NA de meest geschikte benadering vormen.

Algemeen
Er kan worden geconcludeerd dat de uitgebreide numerieke code de mogelijkheid biedt om de verwering van de residuele NAPL in de ondergrond te bepalen.
Aangezien met de code (op een vereenvoudigde manier) verschillende belangrijke processen worden beschreven die te maken hebben met olie en andere gemengde LNAPL-verontreiniging, zijn er verschillende toepassingen mogelijk:
1. Inzicht bieden in de fysieke processen die van invloed zijn op de emissie van verontreinigen-de stoffen vanuit bronlocaties met meerdere componenten. Wat gebeurt er met concentraties in het grondwater als we 90% van de olieverontreiniging verwijderen?
2. Optimalisering en interpretatie van mogelijke meetschema's in de nabijheid van de oliever-ontreiniginsbron. Waar kunnen we monsters nemen die ons laten zien of natuurlijke niveau-reductie goed werkt of niet?
3. Simulatie van verschillende saneringsplannen, wat moet er gedaan worden om een stabiele eindsituatie te bereiken. Moeten we de bron verwijderen?
4. Bronnen identificeren die de grootste invloed hebben op receptoren. Hoe lang duurt het voordat de verontreiniging de grenzen van de locatie bereikt en wat moeten we doen om dit te voorkomen?

Gebieden voor toekomstig onderzoek voor het vergroten van de toepasbaarheid van de code moeten noodzakelijkerwijs een kwantitatief onderzoekslaboratorium omvatten. Werk en veldme-tingen ondersteund door numerieke modellen. Mogelijke toepassingsgebieden zouden kunnen zijn:
- de beschrijving van natuurlijke niveaureductie middels een eerste-orde biodegradatiecon-cept;
- biodegradatie-constanten toewijzen aan gedeelten van meercomponenten-oliën.

CHAPTER 1

INTRODUCTION

1.1 **Subject**

Subsurface contamination with petroleum products such as gas condensate, kerosine, diesel and creosote is among the most common subsurface contamination types. If these products are present as a NAPL (Non-Aqueous Phase Liquid), the contamination poses a long-term threat to the environment. In this report, we will only regard LNAPL (Light Non-Aqueous Phase Liquids, here also referred to as "oil"). The oil will act as a source from which contamination continuously emanates to the groundwater (figure 1).
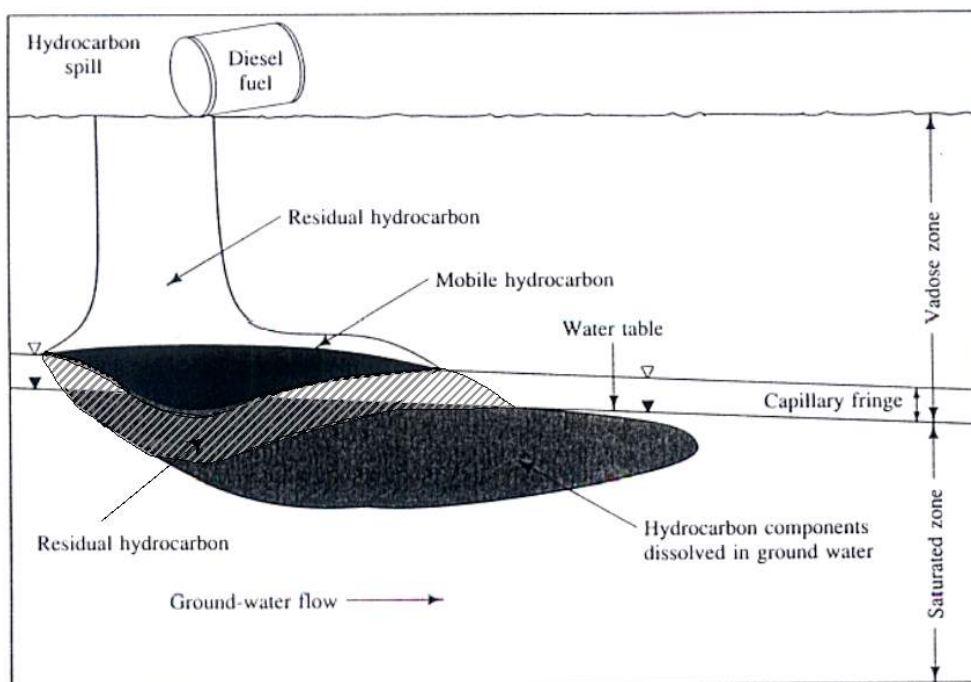
Fig. 1.   Subsurface distribution of an LNAPL spill. After: Fetter [1993].

Recently, the report of BEVER project A5 has been released. In this report, a "stable end situation" is considered to occur when (i) spreading of contaminants from the source has stopped or (ii) release from the contaminant source and natural attenuation (NA) are in balance. If the conclusions from this report are translated into new policy, it is important to have the right tools to be able to quantitatively evaluate and predict the risk of spreading of subsurface oil contamination. The current project aims at developing these tools by developing a numerical simulator for weathering of oil contaminants in the subsurface.

1.2 **Problem definition**

In most risk assessment studies, the oil is considered to be of constant composition and thus to have constant properties. This would be true only if the oil phase contains one single component. However, oil is often composed of many components with various properties. In particular, the volatilisation and dissolution rates of these components are different. Thus, in NAPL with a heterogeneous composition like petroleum derived LNAPL, the release of components to the ground water will change as a function of time because of "weathering". For example, the more soluble

and volatile components (e.g. benzene) will be mobilised first, leaving behind a NAPL with increased mole fractions of less mobile compounds. It is, therefore, expected that the release of contaminants from the oil will decrease with time.

This changing emission from the oil phase is presently not regarded when dealing with subsurface oil contamination. Besides that, there are no public computer codes available that model the relation between the systematic change of the composition of the oil phase and the emission of dissolved oil from the organic phase.

1.3 Goals of the project and the project approach

The general objective of this project is:

> *The development and demonstration of a computer code describing the emission from a multi component LNAPL contamination to groundwater.*

The project is divided into 6 phases.

1. General Survey
    Characterisation of the relation between (1) the composition of a multi component LNAPL contaminant in the source zone and (2) dissolved in groundwater downstream of the source zone. A better understanding of the most important processes will focus the development of the computer code on those processes instead of giving to much effort to processes of minor or no importance. This knowledge will lead the process of constructing the conceptual model. Part of this activity is also to do some initial fieldwork. The fieldwork was undertaken at two study sites, one with an LNAPL with an industrial product and one LNAPL with diesel fuel. The oil source was characterised, as well as the organic constituents in the ground water downstream of the LNAPL in order to try and interpret the weathering processes that dominate locally.

2. Overview of the existing model approaches
    In the field of research on source behaviour some model codes exists, each made with another objective, other scales, other assumptions or based upon other concepts. Some of the institutes, who develop a code, do not give permission to others to use the code. This project will use as much knowledge as possible, therefor an overview is generated of the existing models, used concepts etc.

3. Development of a computer code
    The computer code will describe the change in source function of oil as a result of oil weathering as a function of time. Based upon the knowledge from phase 1 and 2 the conceptual model with all important processes will be made complete. The conceptual model will be used as a guide to actually program the modelling code RT3D-OW, based on the existing code RT3Dv2.5.

4. Validation of the computer code
    Part of the validation process is the modelling of a series of imaginary scenario's to be able to do some basic validation. Besides that, a well defined field experiment will be selected to actually validate the code. The existing field data will give the input to the weathering model and the results will be compared with the field measurement.

5. Development of a user friendly code
    The goal of the project is to develop a code that can be used by others in a user friendly environment. Therefore the code is developed in a way it van be used in the well known modelling shell GMS. GMS can be used to manage the input as well as the output of RT3D-OW.

6. Demonstration of the integrated computer code
    In this phase, 2 field experiments are used to demonstrate the code. The future development of the plume is described and if there is information about the initial composition of the oil, the present situation can be modelled and compared to field measurements.

1.4   Composition of the consortium

The consortium of the SKB project *Modelcode* consist of:

Party	Contact
TNO-NITG	Mr. C. Hofstee
TU Delft	Mr. S.M. Hassanizadeh
Ingenieursbureau Gemeentewerken Rotterdam	Ms. P. Timmerman
GeoDelft	Mr. G.A.M. van Meurs
Shell Global Solutions	Mr. W. Vrieling
Shell Nederland Raffinaderij BV	Mr. R.A.A. Hetterschijt
SBNS	Mr. D.H.A. Veltkamp
Gemeentelijk Havenbedrijf Rotterdam	Mr. J.G. Meijer
Provincie Limburg	Mr. F.L. Martens
Provincie Noord-Holland	Mr. F. de Graaf
Provincie Zuid-Holland	Mr. F. van der Ham

1.5   Content of this report

The second chapter of the report starts with a systematic overview of existing model codes, describing the area of application and the model concepts used in the process of developing. The modelling concept that is used in the development of the new code RT3D-OW is presented in chapter 3. As part of the code development process, the code was validated using the field site Bemidji (USA) which is described in chapter 4. Chapter 5 describes the TPHCWG fractionation approach that is used to obtain representative properties of the multi-component oil phase in order to be able to model the oil weathering. The modelling code is demonstrated at two field sites, described in chapter 6 and 7 respectively. The report ends with an evaluation of results in chapter 8 and the conclusions and recommendations in chapter 9.

CHAPTER 2

BACKGROUND INFORMATION ON EXISTING MODELLING CODES

During the last few decades, significant numbers of numerical simulators of flow and transport in the subsurface have been developed across the globe. The majority of these models are research tools intended for use by individual research groups or researchers. They are not well documented, not properly tested, and/or not meant for "public" distribution. In short, they are not suitable for use by others. Many models have been developed for and used by the petroleum community and are not directly suitable for environmental applications. In general, existing models describing flow and transport in porous media can be divided into four major groups:

Group 1. Single-phase multi-component transport models.
These are models for simulating (multiple) plumes of contaminants spreading within a saturated porous medium. The pollutants are assumed to be already dissolved in water and either entering the medium through a boundary or simply being present in some source area. The flow field is either assumed to be known or calculated by means of a flow model, such as MODFLOW. In addition to dispersion and advection, processes such as adsorption and sometimes biodegradation are included. These models do not simulate transport in the unsaturated zone or the presence of a pure NAPL phase. Because the flow of ground water can be described by a linear equation, and because properties in the saturated zone tend to show little spatial variation, the grid sizes used can be of the order of 50-100 m, unless sharp gradients in for example the piezometric head exist (e.g. near extraction wells).

Group 2. Variably water-saturated multi-component transport models.
These models include transport in the unsaturated zone and possible movement of the ground water table. Here again, the pollutants are assumed to be already dissolved in the water phase. The presence of a pure NAPL phase is not "allowed". In addition to dispersion, advection, and sometimes biodegradation, volatilisation of dissolved components and diffusion in the gas phase is commonly included in these models.

Group 3. Mobile water/immobile NAPL transport models.
In these models, two phases (water and oil) or three phases (water, oil and air) may be present. Only the flow of water is modelled. Air movement is neglected, the NAPL phase is assumed to be immobile, and the NAPL is assumed to consist of a single component (or the change in NAPL composition is neglected). Thus, in these transport models, in addition to dispersion, advection, adsorption, and sometimes biodegradation (and volatilisation), the dissolution of contaminants from the NAPL phase is commonly included. The NAPL phase is simply assumed to be present in a certain area of the domain. Its formation is not modelled.

Group 4. Multiphase flow and multi-component transport models.
This is the most complex group of models. The flow of two or more immiscible phases (water, oil and air) is modelled, and transport of many components is included. Often, the NAPL phase is assumed to be a single component. So, only transport in the water phase (and possibly in the air phase) is simulated. Examples are STOMP (developed by PNNL) and UTCHEM (developed by the University of Austin). The latter also includes biodegradation options. The equations used in these models have a highly non-linear nature. Because of this non-linearity, and because variables such as saturation and permeabilities show very large spatial variations, the grid sizes in multifluid models are very small (in the order of 1 cm).

Because of the differences in grid sizes, 3-D simulations of multiphase flow in the subsurface are usually restricted to perhaps a single field, whereas ground water can be modelled at a regional scale. In other words, it is possible to model the fate and transport of an oil plume at the regional scale, whereas the simulation of the oil infiltration which led to that plume has to be made for a much smaller area. Because of the great complexity of the various governing and constitutive relationships involved in the modelling of multifluid flow and the associated computer requirements, simplifying assumptions are often required. One approach, which is currently used in for example the STOMP simulator, is to assume that the NAPL consists of a single component. This means that the actual oil infiltration, transport and redistribution can be modelled, but that subsequent preferential dissolution of the various compounds and thus weathering of the oil phase cannot be described.

Modelling of the behaviour of an oil spill at an actual site is thus complicated by two major factors: (i) the inability of the multifluid simulator to deal with multicomponent NAPL, and (ii) the complications associated with linking two modelling approaches with very different grid sizes.

The objective of this project was to develop a numerical simulator, which falls within Group 3 (see above). However, as far as we know, the models in Group 3 have assumed the NAPL phase to be either a single component, or the change in NAPL composition has been neglected. Therefore, they cannot model weathering of the oil phase. In the simulator we will develop, we shall consider a multi-component oil phase and include its change of composition.

The new code can be used in combination with existing models in Group 4 (see figure 2), which can simulate the infiltration and final spatial distribution of the oil contamination after a spill. The new simulator subsequently describes the mass-transfer between the stagnant multi-component NAPL and the ground water, oil weathering and the fate and transport of the plume. Such a model will be suitable to determine stable end situations for contaminated soils and aquifers.
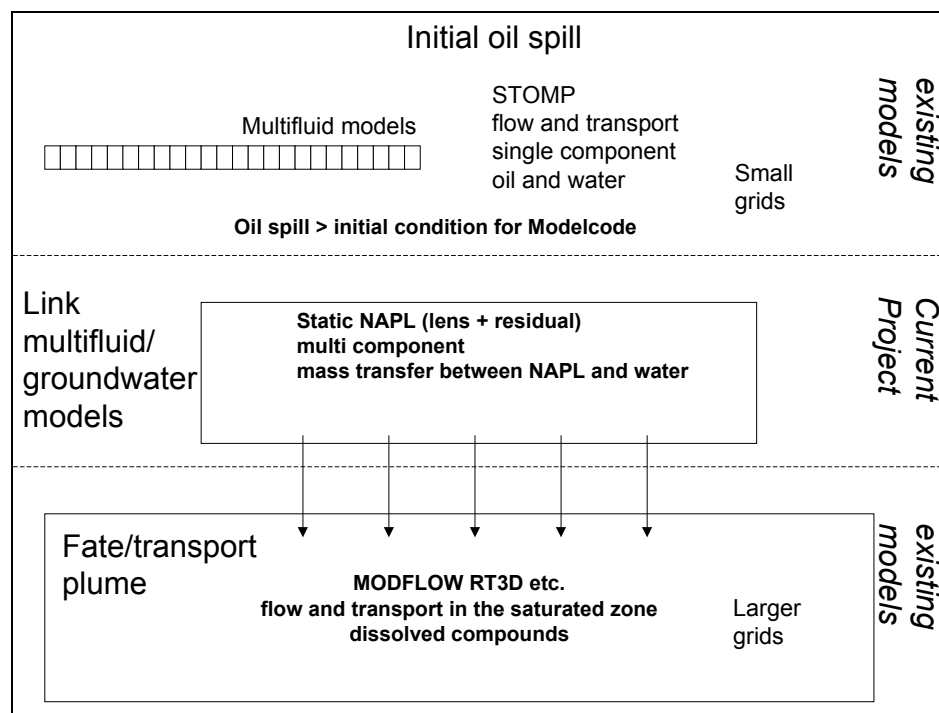

Fig. 2.   Schematic representation of the role of the designed numerical simulator, in relation to existing models.

CHAPTER 3

CONCEPTION MODEL AND IMPLEMENTATION INTO RT3D

Our working hypothesis has been to use the RT3D computer code as the basis for the model code. RT3D (Reactive Transport in 3 Dimensions) has been developed at Pacific Northwest National Laboratories (PNNL), Richland, WA, USA [Clement et al., 1998]. Full details can be found at the RT3D home page:http://www.bioprocess.pnl.gov/rt3d.htm.

Based on the classification as given in chapter **Fout! Verwijzingsbron niet gevonden.**, RT3D is a group II model that does not include a NAPL phase. RT3D is a finite-difference numerical code for simulation of three-dimensional, multi-species, single-phase, reactive transport in saturated porous media. The flow field needs to be provided as the solution of a (finite difference) groundwater flow package such as MODFLOW. RT3D includes seven built-in kinetic reaction modules. Other (more complex) reaction mechanisms may also be specified by the user through a number of generic user-defined modules. This is a powerful option provided in the RT3D code. Under this option, the user has the choice of defining any type of reaction kinetics.

Values of reaction parameters, as well as spatially variable and/or constant parameters can be specified via the reaction package input files with the extension *.RCT. These 6 parameters must be given for all modelled components (oil fractions):
- pure phase solubility;
- aerobic degradation rate;
- anaerobic degradation rate;
- stochiometric values;
- molecular weight;
- specific weight.

For a full description about the format and location of the necessary input, we refer to the RT3D-OW manual.

3.1 **The mineral oil source area**

Whenever a spill of oil occurs, it will migrate as a separate phase through the vadose zone. Initially, the oil is wetting the water-air interface and displaces air. It therefore behaves as a secondary wetting phase. Once the organic phase reaches the capillary fringe (water-saturated zone above the groundwater table), it has to displace water before it can migrate deeper into the subsurface. Now it behaves as a distinct non-wetting fluid, which needs to exceed the capillary entry pressure before it can proceed. As the density of the oil is less than that of water, the entry pressure at some depth below the top of the capillary fringe no longer will be exceeded and the mobile phase can only migrate in the lateral direction. The result is an immobile floating lens of oil, which is usually submersed in the capillary fringe. This oil body consists of an interconnected phase. Due to the high oil saturation in this part of the subsurface, it is a virtually impermeable zone for the aqueous phase.

In case of a lowering of the groundwater table during for example a draught, the floating lens will follow the descending groundwater. When the groundwater rises again, the mobile (continuous) oil will migrate upwards leaving behind a zone of water-enclosed discontinuous oil blobs, which are trapped in the pore space. The oil saturation in this so-called smearing zone is typically in the order of about 0.1-0.2. This means that the permeability of the groundwater is hardly affected in this zone.

Overall the source area consists of a floating lens overlying a smearing zone which down to lowest groundwater level since the occurrence of the spill.
Although the smearing zone and the floating layer are not connected, they will be reconnected and the oil exchanged during the following descend of the groundwater table.

Extensions to the RT3D code allow for the modelling of the mass transfer of components from the oil to the ground water. Two different situations will be accommodated: (i) the oil is present in the form of a pool floating on the ground water table; (ii) the oil is present in a residual form below the ground water table. The residual situation is created when the pool oil is smeared out by temporal changes of the ground water level. Processes of mass transfer for the two situations are modelled by different mechanisms in the code, as described below.

3.2   Mass transfer from residual oil

Where the groundwater is in contact with residual oil, the mass transfer can be described by a first order kinetic relation as proposed by Miller and Mayer [1996] (see also figure 3).

$$S_h = \frac{kd^2}{D_m} = A + B \operatorname{Re}^m (\phi s)^n$$

where S_h stands for the dimensionless Sherwood number, ϕ for porosity, s for saturation, k for NAPL-aqueous interface transfer coefficient (1/T), d for particle diameter (L), D_m for molecular diffusion coefficient (L^2/T) and A and B are empirical parameters (-). Re stands for the Reynolds number:

$$\operatorname{Re} = \frac{v^w \rho_w d}{\mu_w},$$

where v stands for flow velocity (L/T), ρ_w (M/L^3) and μ_w (ML^{-1} T^{-1}) for the density and dynamic viscosity of the aqueous phase, respectively.
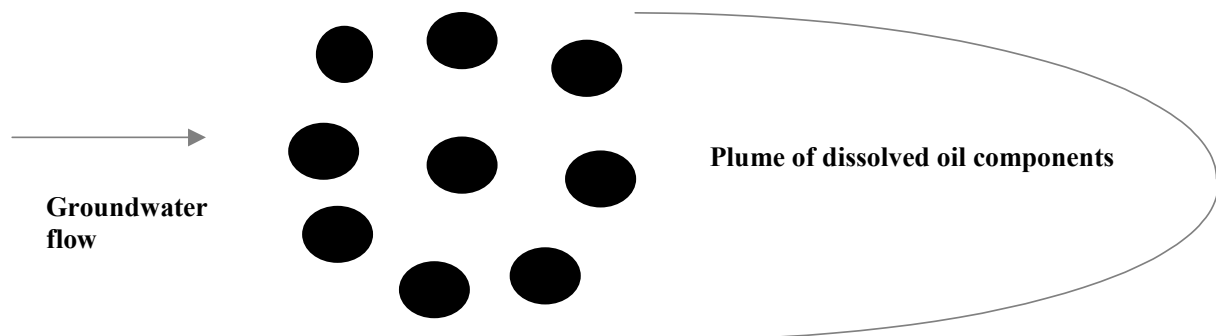
Fig. 3.   Sketch of a plume originated in a zone of residual oil.

The mass transfer co-efficient is written as a function of the Sherwood Number, which is time dependent. Raoult's law defines the time dependent partition coefficient in this relation. For the mass transfer relation and the different time dependent coefficient, a new Fortran module was programmed which can be added easily to the RT3D code as part of the reaction package.

3.3 Mass transfer from a pool

The mass transfer from a floating pool is described as follows (see also figure 4). We assume that a stagnant film of water surrounds the pool. The film is assumed to be in chemical equilibrium with the pool, i.e. the concentrations of the NAPL (oil) components in the film are assumed to be related to the concentrations of the components in the pool by Raoult's law:

$$S_i = S_i^* X_i$$

where S stands for aqueous solubility, S^* stands for equilibrium solubility and X is the mole fraction of component I in the oil phase.

Then, the transfer of components from the film to the flowing groundwater is assumed to occur through lateral dispersion:

$$J = D_t \frac{\partial C}{\partial x}$$

where J stands for the dispersive mass flux ($ML^{-2}T^{-1}$), D_l denotes the effective lateral hydrodynamic dispersion coefficient (L^2T^{-1}), C is the concentration (ML^{-3}) and x is the spatial coordinate (L).
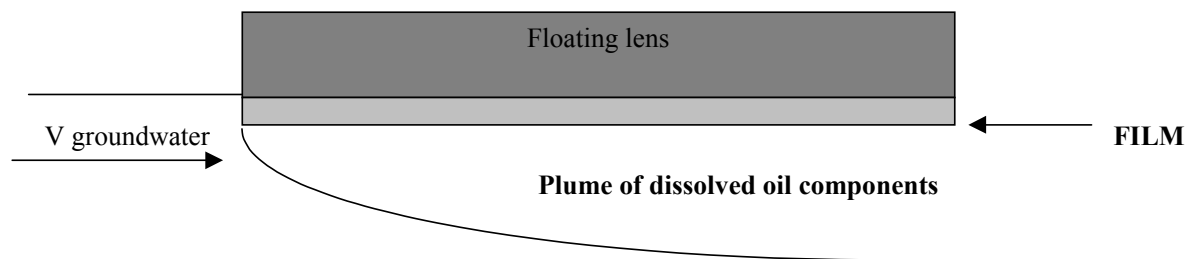
Fig. 4. Sketch of a plume originated in a pool zone.

The RT3D computer code consists of a main program and a large number of highly independent subroutines, called modules, which are grouped in a series of "packages". Each of these packages deals with a single aspect of the transport simulation. For modelling the mass transfer from the pool, we modified the dispersion package. The two upper layers of the computational grid of the aquifer model were used to model the pool and the film.

The RCT-package (Reactive Chemical Transport) is used to identify the cells of these layers (see also the RT3D-OW manual). This is done by assigning the value –3 for a film cell and -4 for a pool cell. In the subroutine SSM3RP of the SSM-package this input value is then translated to a value in the array ICBUND which is used throughout the package to identify special cells such as constant concentration cells. Then, from the cells indicated as film cells, a dispersive (or diffusive) flux to the groundwater is computed. Therefore, three actions have to take place in the subroutine DSP3SV of the dispersion package:
- for the second layer, no dispersion has to be computed if the cell does not belong to the film;
- for the third layer, no dispersion at the upper boundary has to be calculated if the cell is not below a film cell;
- the new concentration in the pool cell has to be calculated.

In the user-defined module in the reaction package, the equilibrium concentration in the film cell will be calculated.

TESTS AND VALIDATION OF RT3D-OW AT BEMIDJI SITE

In order to test the code RT3D-OW, several scenario runs were executed. Besides that, field measurements were used to validate the code. The objective of this process is to test if the code is capable of simulating the dominant processes at a field site where weathering of a subsurface oil contamination is known to have occurred? The field measurements for the validation process originate from a comprehensive study on the Bemidji site (USA).

4.1   Basic tests

Several model scenarios were simulated as a first test of the numerical simulator. For this test a simple 3D groundwater model was built with the same configuration as the first example problem from the RT3D manual. The site is a part a confined aquifer (10 m thick) with a flow gradient of 1/500 m.

Test 1
Using this hydrological model, dissolution of BTEXI (Benzene, Toluene, Ethylbenzene, m,p-Xylene, o-Xylene, Iso-propylbenzene) from residual oil was simulated over two years, assuming first order aerobic and anaerobic bio-degradation in the aqueous phase. Changes of concentration with time of the different components are displayed in figure 5.
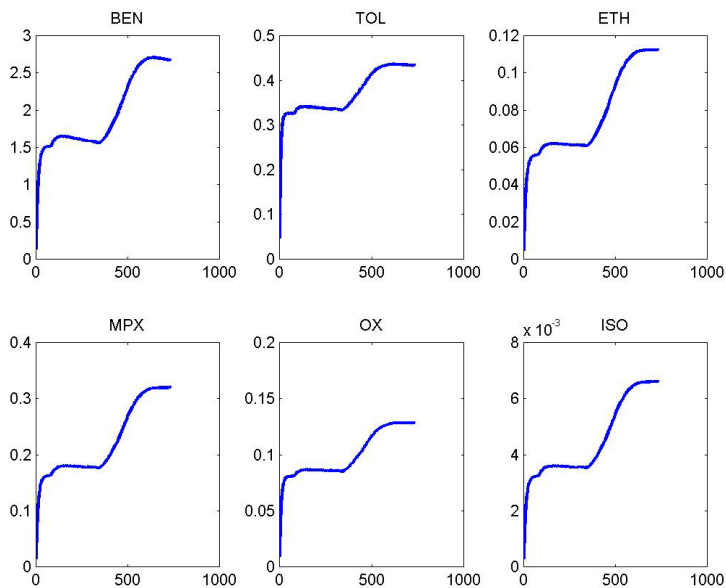
Fig. 5.   Simulated concentrations (mg/L) versus time (days) using anaerobic and aerobic degradation for Benzene (BEN), Toluene (TOL), Ethylbenzene (ETH), m,p-Xylene (MPX), o-Xylene (OX) and Iso-propylbenzene (ISO).

The typical change of concentration in time after approximately 450 days is due to the initial amount of oxygen. The concentrations are increasing when the aerobic biodegradation stops due to lack of oxygen. Without modelling the aerobic biodegradation at all, the development of the concentration in time misses the initial 'dip' and immediately increases towards the level reached after 600 days.

Test 2

The modelling of dissolution of just one or two component gives more insight in the processes that take place and the modelling results. The residual oil now consists of only one component. In this case the concentration of this component in the *oil phase* should stay at the same level as the initial value and after the residual is completely depleted this concentration drops to zero (see figure 6). Because of the decrease of saturation and groundwater flow, the aqueous concentration is decreasing as well.
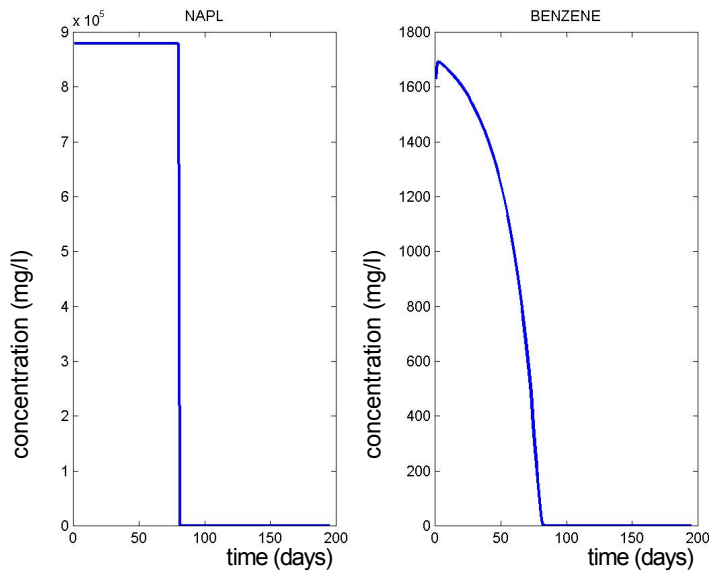
Fig. 6.   Simulated benzene concentration in NAPL and dissolved benzene concentration as function of time.

Test 3

This test has the same configuration as the second one. The residual oil consists of 2 components. The solubility of the first component is 1000 times greater than the solubility of the second component. Concentration in both NAPL phase and aqueous phase are presented in figure 7.

Because of a dominant massflux of component 1 to the aqueous phase, the relative NAPL concentration of the second component will increase in time. After the complete dissolution of contaminant 1 (after > 400 days) the NAPL concentration of component 2 stays constant (see test 2) until the residual is completely depleted. At that moment the concentration drops to zero.

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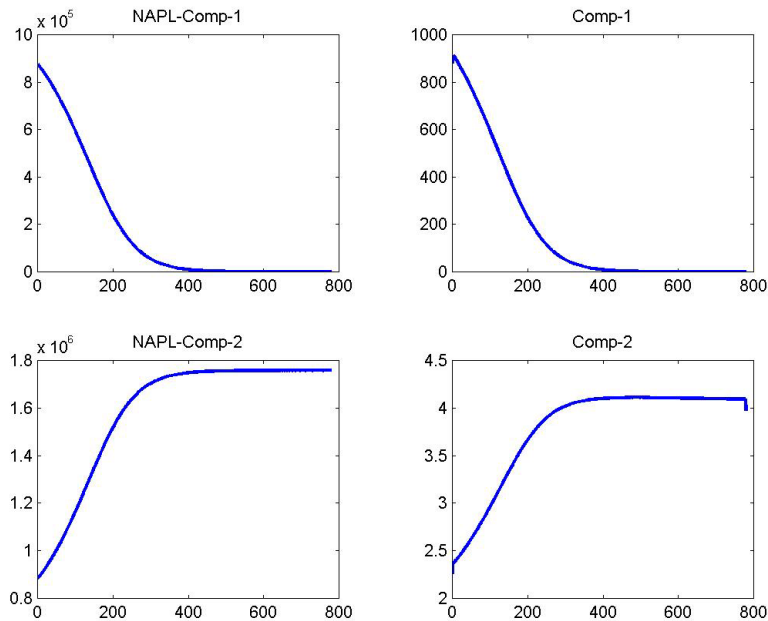
Fig. 7.   Simulated concentrations of two components with different solubilities in NAPL and dissolved in water (mg/L) as function of time (days).

4.2   Description of Bemidji site and contamination

On August 20, 1979, the land surface and shallow subsurface on a remote site near the town of Bemidji, Minnesota (USA), became contaminated when a crude oil pipeline burst. After cleanup efforts were completed in 1980, 400,000 l of crude oil remained in the unsaturated zone and near the water table (see figure 8 and 9). Because of a fluctuation of the groundwater table at the Bemidji site, it is expected that a residual zone will be formed in times of a high groundwater table.

For more details about the site and the contamination, we refer to the USGS Bemidji Crude-Oil Research Project website at: http://mn.water.usgs.gov/bemidji/.
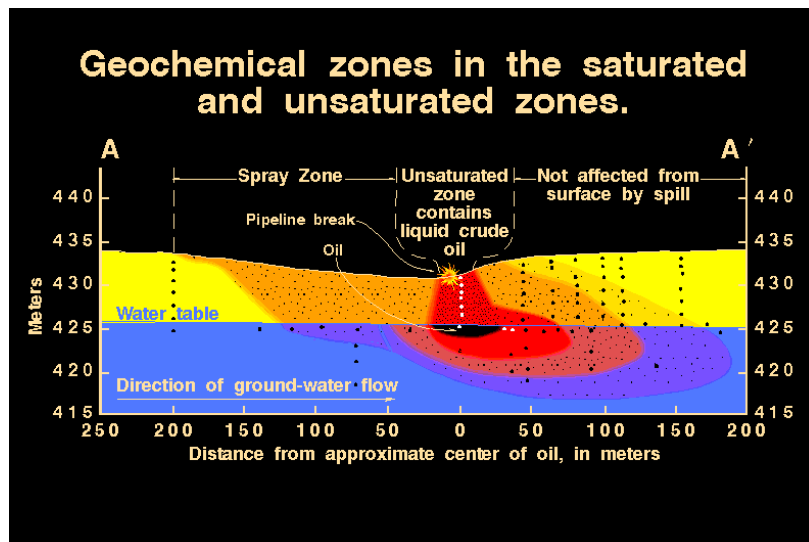
Fig. 8.   Cross-section of subsurface of Bemidji showing the distribution of contamination.

The initial parameters for the modelling are derived from a publication on inverse modelling by Essaid [2001] at the Bemidji site (see table 1).

Table 1.   Initial conditions Bemidji case.

NAPL component	Oil concentration	Biodegradation	
	Pool/residual (mg/l)	Anaerobic (day^{-1})	Aerobic (day^{-1})
benzene	2050	1.3e-003	4,3E-02
toluene	2050	6.8e-002	,, ,,
Ethylbenzene	1496	7.1e-004	,, ,,
m&p – xylene	1989	2.5e-003	,, ,,
o – xylene	1081	2.80e-002	,, ,,
Isopropylbenzene	596	0.0	,, ,,

4.3   General findings concerning the Bemidji case

Before actually validating the code some preliminary test were carried out with the Bemidji case model to gain more insight in the weathering process. This paragraph summarises these findings.

- Mass transfer from a continuous oil body is a slower process compared to mass transfer from residual oil. This is because the residual oil has a larger contact area with the surrounding groundwater. In many situations, the aqueous concentration will therefore be determined mostly by the thickness of this zone. This results also in a higher aqueous concentration in the plume.
- The mass transfer from residual oil is directly related to the decrease of the concentration in the residual oil. This decrease is faster in a residual oil than in a pool. A higher mass transfer from a residual oil towards the plume results in plume front that travels further.
- Weathering of oil is a slow process compared to biodegradation. Within the time modelled (15 years) no more than several % of the total mass is dissolved.
- Mass transfer from a pool in combination with a groundwater flow causes differences in oil concentration in the longitudinal direction op the pool. Oil concentration in the downstream part of the pool will decrease slowly compared to that in the upstream parts because of lower concentration gradients between the oil and water phase.
- Whether or not modelling the process of aerobic biodegradation has a strong impact on the results. When modelling both anaerobic and aerobic biodegradation, the plume volume will be strongly reduced.

4.4   Model Validation

In the period between 1986 and 1995 concentration measurements were performed in several filters at different depths in and around the plume originating at the north pool (see figure 9). During this period of 10 years there were only 4 to 8 moments of measurement. Analyses of the data sometimes show large annual fluctuations in the aqueous concentrations. Although 8 data points in 10 year (with a fluctuating character) are not sufficient to observe the concentration pattern in detail, a general trend can be found (see measured data in figure 10).
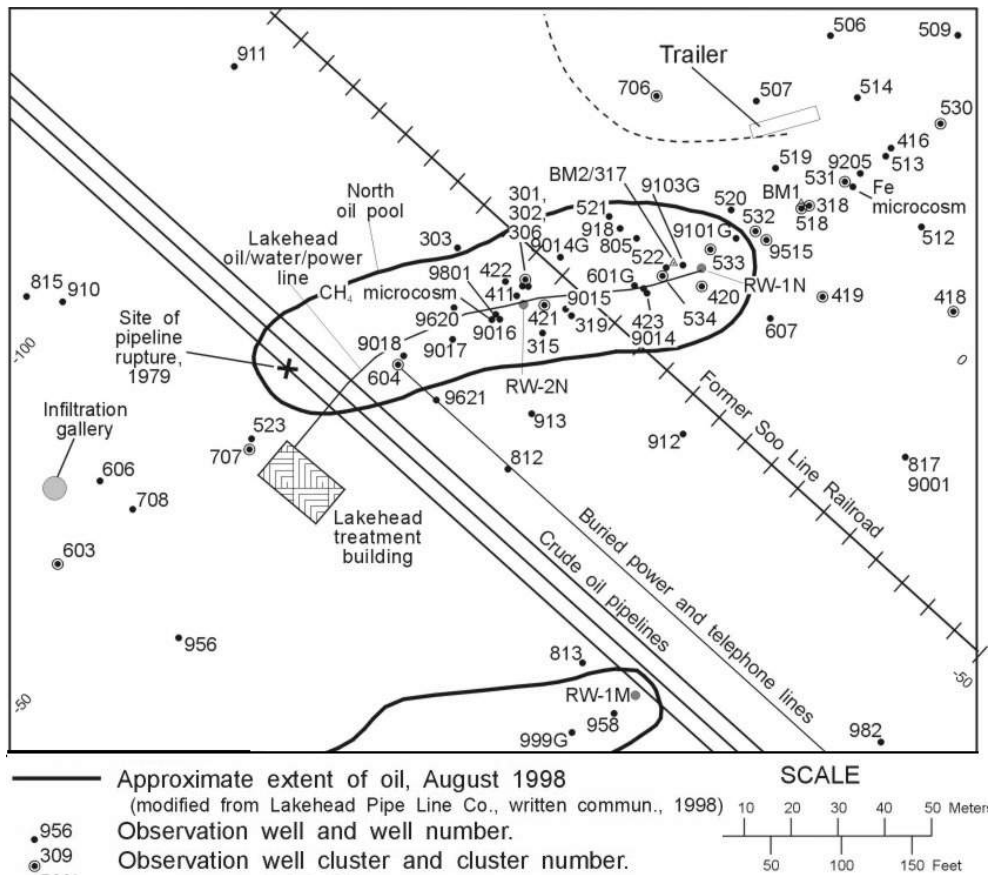
Fig. 9.   Overview of the Bemidji site showing the North pool contour and monitoring well locations.

A first model simulation was performed using many assumed input parameters and the always uncertain first-order biodegradation constants. In spite of that, the model simulates aqueous concentrations that reasonable close to measured concentration at about 60 m from the tail of the oil body.

A rather good fit on the field data is possible by changing the degradation parameters within acceptable ranges as found in Essaid *et al.* [2001]

Adjustment of biodegradation rates results in a best fit of both modelled and measured concentrations and is shown in figure 10. These new biodegradation rates are mainly on the low site of the estimated range. Subsequent adjustment of both aerobic and anaerobic constants and the initial oxygen concentration showed that it is possible to simulate almost any concentration at any location.
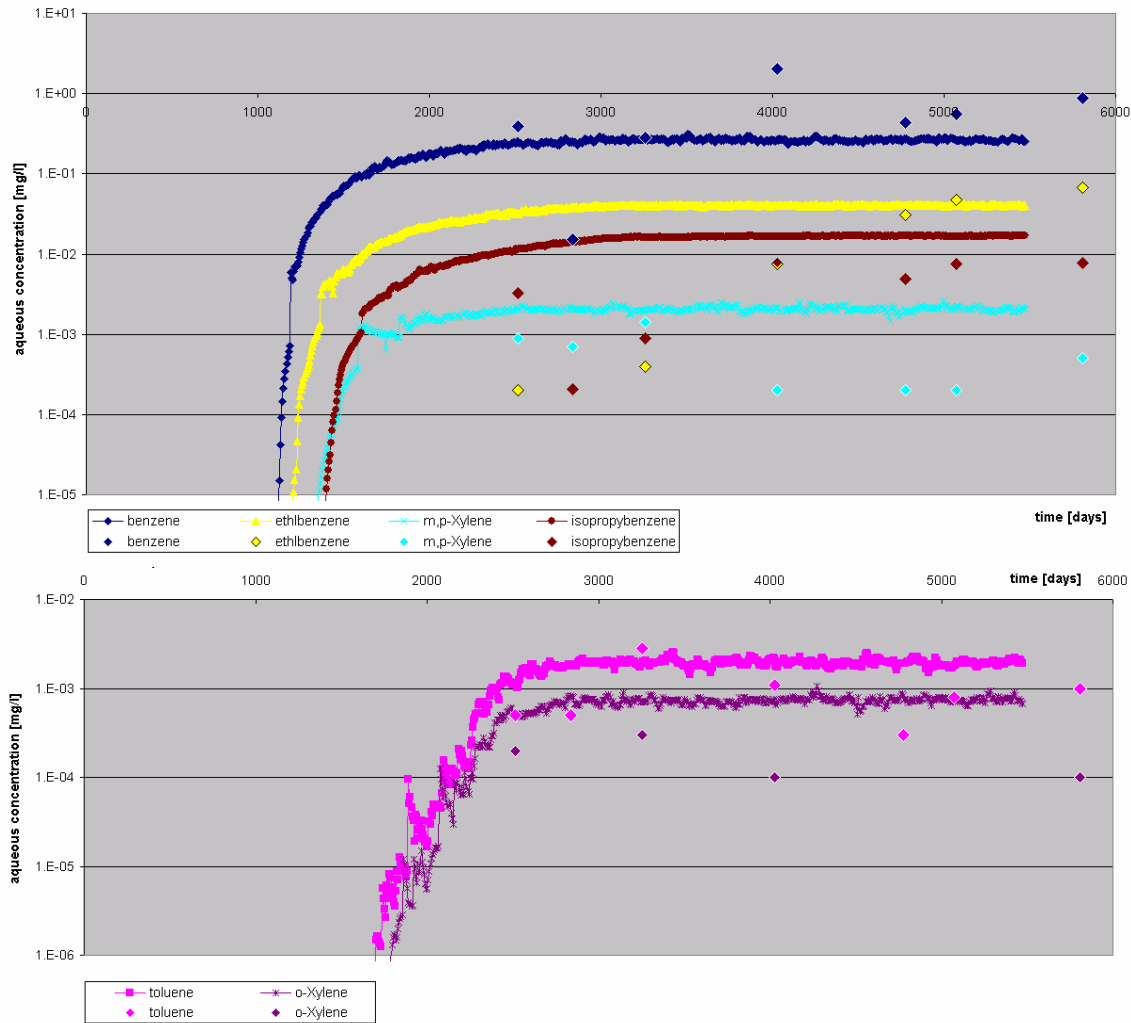
Fig. 10.   Modelling results (continues) for 6 components plotted on the field measurements (dots) on a single monitoring location.

The field data for Benzene (dark blue) show strong fluctuations but the calculated values fit rather well. Looking at the calculated concentrations of Ethylbenzene, it shows a quicker break through than measured. However, after some 5000 days the concentrations get to the same concentration level. Based on the measurements it is not clear if the trend in concentration will continue after 5.000 days. If concentrations increase towards 10.000 days, the calculated concentrations will lose fit with the measurements.

Calculated concentrations for Isopropylbenzene and m,p-Xylene are slightly higher than the field data.

In the basic run, no Toluene and o-Xylene did reach the presented observation point. One reason can be that the model generates too much biodegradation. The anaerobic degradation rated for these components was reduced as part of the sensitivity analyses giving better results.

Simulated results also indicate that the emissions from an oil lens and even from the residual zone remain virtually constant. The 'stable end situation' can therefore only be reached when the source area has largely been removed, when dilution is taken place or when natural attenuation or some other plume treatment is used.

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Overall, the new code showed to be capable of simulating weathering of subsurface oil in a residual as well as a pure ("pool") form and well as the subsequent fate and transport of the multi-component plume.

CHAPTER 5

CHARACTERISATION OF THE MULTI-COMPONENT OIL PHASE

To obtain representative properties of the multi-component oil phase at both sites, we adopted the TPHCWG fractionation approach (Weisman [1998], Potter [1998]). In short, this fraction assumes that aliphatic compounds with similar gas chromatography (GC) retention times have similar physical properties such as water solubility and saturated vapour pressure. The same holds for aromatic compounds. This allows for the allocation of the individual oil components to an oil fraction, to which a representative aqueous solubility can be assigned. Because relationships, between the GC retention times and the solubility, are different for aliphatic and aromatic compounds, it was necessary to separate these two kinds of chemical species before the separate GC analyses.

5.1 Analytical procedure and quantification of mineral oil fractions

A schematic overview of the procedure for soil samples is given in figure 11. Since the sampling and the fractionation step may cause significant evaporation the method is not suitable for the quantification of volatile components (< n-C10).

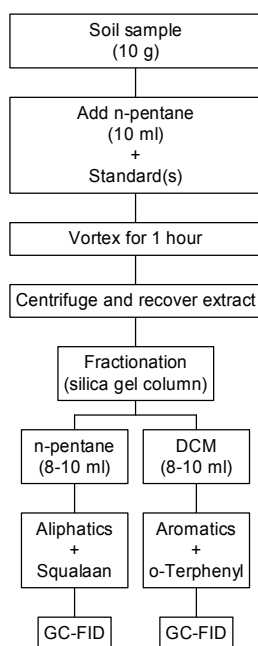Fig. 11.   Schematic overview of the analytical procedure.

For the quantification of the fractions the external standard method has been used. This method is based upon the determination of the response factor (RF). The surface areas of the standard (Ai), as measured on the GC-FID are plotted against the concentrations Ci and after linear regression the slope determines the <RF> value.

$$< RF > = Ai / Ci$$

where:

<RF> = response factor, in ml/μg
Ai = peak area for the standard i
Ci = concentration of the standard i, in μg/ml

This response factor has been determined for the aliphatic fraction as well as for the aromatic fraction:

<RF>aliphatic = 0.699 ml/ μg
<RF>aromatic = 0.475 ml/ μg

The mineral oil content in soil and sediment is given by the formula below:

$$C = A * v * f / <RF> * G$$

where:

C = concentration mineral oil in mg/kg d.s.
A = peak area of the sample
v = volume of the end extract in ml
f = dilution factor (if applicable)
<RF> = response factor, in ml/μg
G = amount in g d.s. extracted sample material, recalculated on a dry weight basis

This formula has been applied for both the aliphatic and the aromatic fractions. The total mineral oil content of a sample is calculated as the sum of both fractions.
In the chromatograms 7 aliphatic (F-1 to F-7) and 5 aromatic (F-8 to F-12) fractions are defined. The exact definition of these fractions is given in table 2. Note that the subdivision into the different fractions is somewhat different for both sites.

Table 2. Definition of the aliphatic and aromatic fractions and water solubilities for two Sites.

Site I					
Aliphatic		S_{water} (μg/l)	Aromatic		S_{water} (μg/l)
F-1	< EC 10	0.427	F-8	< EC 11	50.7
F-2	EC10-EC12	0.034	F-9	EC11-EC13	15.1
F-3	EC12-EC14	0.003	F-10	EC13-EC15	5.8
F-4	EC14-EC16	2.1E-04	F-11	EC15-EC18	1.7
F-5	EC16-EC18	1.7E-05	F-12	EC18-EC23	0.2
F-6	EC18-EC21	7.2E-07			
F-7	EC21-EC25	8.5E-09			
Site II					
Aliphatic		S_{water} (μg/l)	Aromatic		S_{water} (μg/l)
F-1	< EC 10	0.427	F-8	< EC 11	50.7
F-2	EC10-EC12	0.034	F-9	EC11-EC14	11.9
F-3	EC12-EC14	0.003	F-10	EC14-EC16	3.5
F-4	EC14-EC16	2.1E-04	F-11	EC16-EC19	1.1
F-5	EC16-EC18	1.7E-05	F-12	EC19-EC22	0.2
F-6	EC18-EC20	1.3E-06			
F-7	EC20-EC22	1.1E-07			

5.2   Comparison with TTE analyses

The Three Engineers (TTE) has carried out an oil characterisation at Site 1on two samples from well A01037 and A02057, respectively using their oil characterisation method [TTE project C0221, 2002]. The positions of the wells are shown in figure 12. TNO-NITG has analysed three samples from well A01037 and two samples from well A02057. A detailed comparison between the analytical results is not possible since no further details are provided on the analytical procedures carried out by TTE. Furthermore, no information is given with respect to sample depths and no chromatograms are provided. In order to allow for a comparison of the data, the subdivision into aliphatic and aromatic classes has been modified somewhat to meet the classification as reported by TTE.
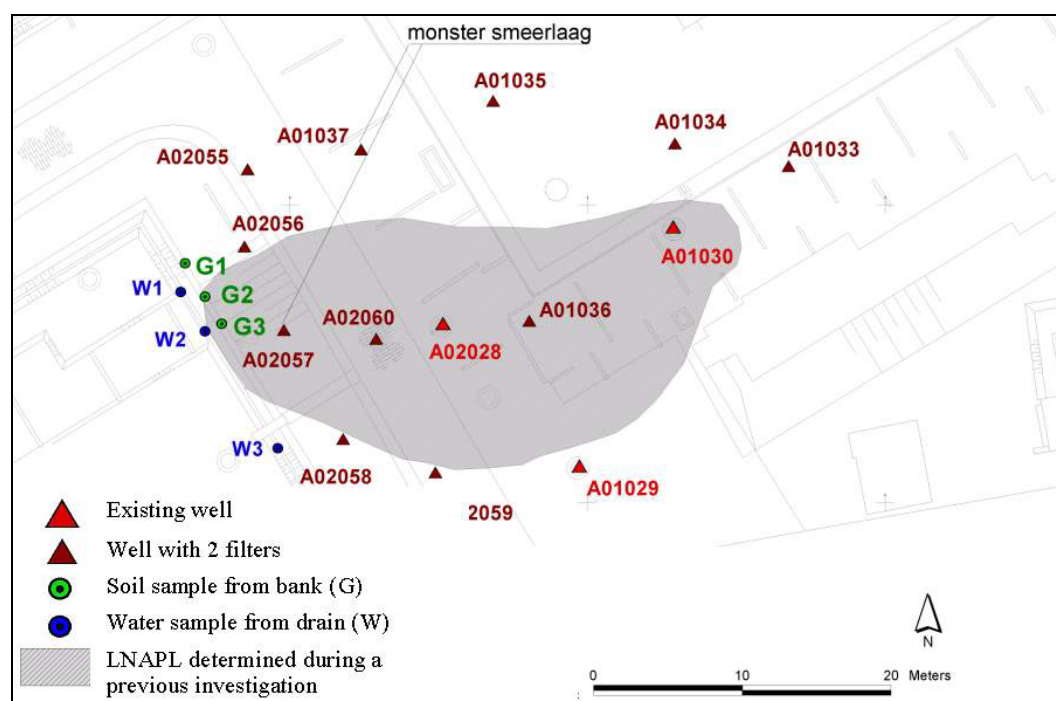
Fig. 12.   Monitoring locations used at Site 1.

Table 3 gives the results as deduced from both analytical procedures. TTE concluded that the composition of the oil fraction in both samples is more or less similar. They reported that sample A01037 consists for 92 percent of (poly)aromatic components, whereas samples A02057 consists for 83 percent of (poly)aromatic components. The NITG results show a relatively wide variation. For well A01037 the proportion of the aromatic fraction ranges from 64 to 76 percent and in well A02057 it ranges from 43 to 63 percent. The results are also illustrated in figure 13. In general the samples analysed by NITG have a significantly higher proportion of aliphatic components. Yet, the overall pattern of all samples is comparable. For comparison the characteristics for the LCO product have also been added. LCO appears to have an intermediate position in the diagram. The cause for the observed differences is not clearly understood. Some possible explanations may include: different samples or sampling, different analytical procedures or differences in preservation.

In general aliphatic components are more readily degradable than (poly)aromatic components. This phenomenon may also be interpreted for the current samples. From the results as given in **Fout! Verwijzingsbron niet gevonden.** and in figure 13 it can be concluded that the relative proportion of aliphatic components decreases with increasing depth.

Table 3.   Summary of the analytical results of TTE and TNO-NITG.

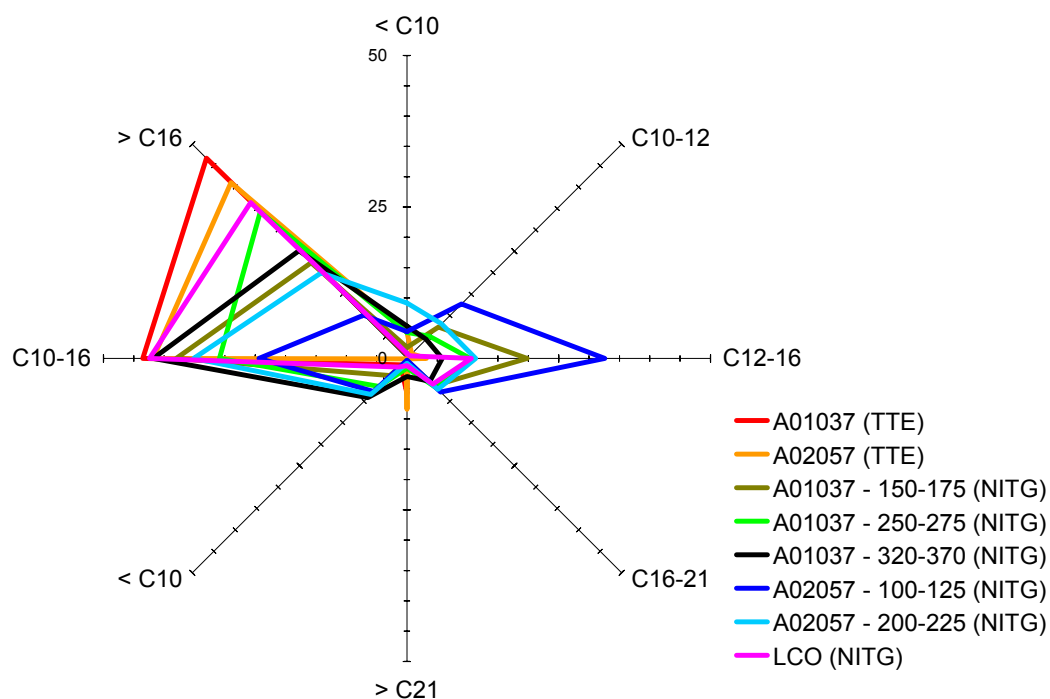|	Aliphatic					Aromatic				
	< C10	C10-12	C12-16	C16-21	> C21	< C10	C10-16	> C16	Aliphatic %	Aromatic %
A01037 (TTE)	0.7	1.2	0.6	0	5.8	1.5	43.5	46.7	8.3	91.7
A02057 (TTE)	4.3	1.1	3.2	0.1	8.4	0.1	41.8	41	17.1	82.9
A01037 – 150-175 (NITG)	1.8	7.4	19.8	6.4	0.4	4.0	38.0	22.3	35.7	64.3
A01037 – 250-275 (NITG)	4.3	5.2	10.4	6.9	1.6	6.5	30.9	34.2	28.4	71.6
A01037 – 320-370 (NITG)	5.3	4.5	5.8	5.3	3.0	9.1	41.8	25.2	23.9	76.1
A02057 – 100-125 (NITG)	4.5	12.7	32.6	7.8	0.3	7.7	24.4	10.1	57.9	42.1
A02057 – 200-225 (NITG)	9.1	8.0	11.3	7.2	0.8	8.4	35.1	20.0	36.5	63.5

Fig. 13.   Comparison of the aliphatic and aromatic fractions of the wells A01037 and A02057 as analysed by TTE and NITG.

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CHAPTER 6

APPLICATION OF THE CODE AT THE SITE I

6.1   Introduction

The extended computer code RT3D-OW is applied to Site I. In the past the subsoil is contaminated due to an oil spill. In the subsoil the oil behaves as a LNAPL. The following activities are carried out:
- Constructing a conceptual site model;
- Constructing a groundwater flow model of the location;
- Collecting samples from soil and groundwater;
- Analysing the collected samples;
- Constructing a model for the transfer of contaminants dissolved in the oil phase to the groundwater and taking fate and migration in the groundwater into account.

In this chapter the word 'block' or 'blocks' is often used, which is actually the same as 'oil fraction'.

6.2   Extension of the code RT3D

The computer code RT3D is extended with a routine in which the transfer of components dissolved in the NAPL phase to the groundwater is described. Raoult's law describes this transfer. This means that the concentration in the aqueous phase (the groundwater) is in equilibrium with the concentration in the NAPL phase. The product of the molar fraction in the NAPL phase and the solubility determine this aqueous equilibrium concentration.

For the description of weathering, two different phenomena are distinguished. In the first one a floating layer of NAPL is present just above the vadose zone. In the second one the NAPL phase is present as a residual phase: small droplets of NAPL are kept in place due to capillary forces. The rate of transfer of the second one is higher due to the larger surface across which dissolution to the water phase takes place. Therefore, for the Shell Case transfer from the residual NAPL phase is considered.

The numerical implementation is carried out by TU-Delft. After implementation, GeoDelft has tested the code for a residual situation. Also the code is tested for a situation for which also the original code of RT3D is used. These tests succeeded.

6.3   Site investigation

Samples from soil and groundwater are collected from the location. Groundwater samples were analysed directly. However, the soil samples were stored. The groundwater samples are analysed on several specific compounds: Mineral Oil, Volatile Oil, Aromatics and PAH. The soil samples are analysed with the method of oil characterisation called TPHCWG. Based upon the properties of the compounds, the results are presented as Blocks (oil fractions) with an Equivalent Carbon (EC) number.

A total of 22 samples has been analysed according to the analytical procedure described in the previous section. Figure 14 shows the comparison between four LNAPL samples and the LCO (pure product). The composition of three LNAPL samples is almost identical to LCO, the sample from well A01030 is significantly different. This well is situated at the north-eastern part of the

LCO NAPL contour as drawn by 'Oranjewoud' during an earlier study. The LNAPL as encountered in this well shows the characteristics of a middle distillate such as diesel oil (see figure 14)
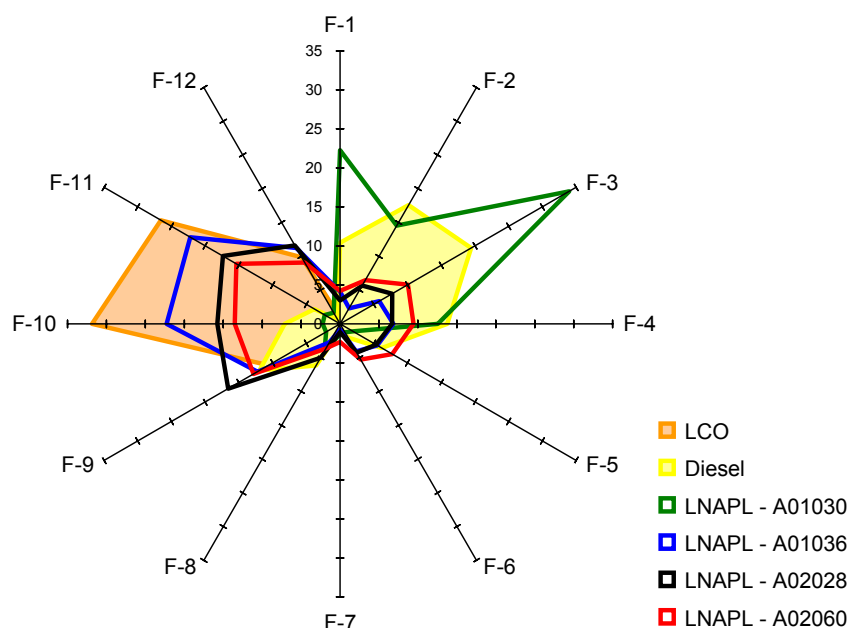
Fig. 14.   Comparison of the LNAPL samples with a LCO and a diesel sample.
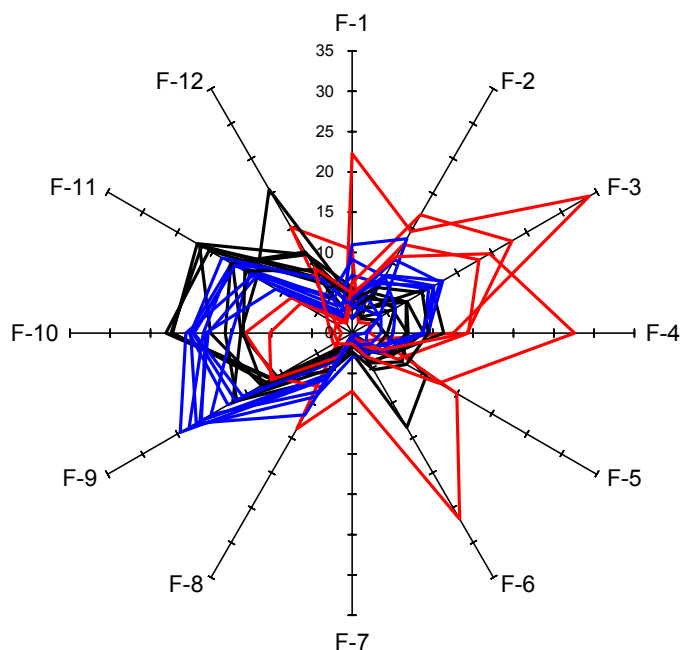
Fig. 15.   Composition of the samples in relative amounts (percentages) Site 1. See **Fout! Verwijzingsbron niet gevonden.** for explanation of the codes.

In figure 15 the composition of all samples is plotted on the basis of the 12 different fractions. Three different groups of samples can be differentiated on the basis of the 12 fractions. One group, indicated in red on figure 15 has a highly aliphatic character. The other two groups are more aromatic (indicated in blue and black on figure 15). The differentiation of these two aromatic groups is arbitrary and mainly based on a dominance on either the F-9 axis or the F-10/F-11 axes. This implies that the group of samples indicated by the black line in figure 15 is com-

posed of a slightly heavier aromatic fraction as compared to the samples represented by the blue lines. No definite geographic differentiation can be made on the basis of these groups, yet the samples represented by the blue line appear to be restricted to the western side of the location. The aliphatic character of the 5 samples indicated by the red line is confirmed by the ratio of the aliphatic to aromatic components (see figure 16). Although encountered at different depth intervals all three groups are present in well A02060, situated in the central part of the LNAPL contour.

Fig. 16.   Ratio of aliphatic to aromatic components in the samples of Site 1.
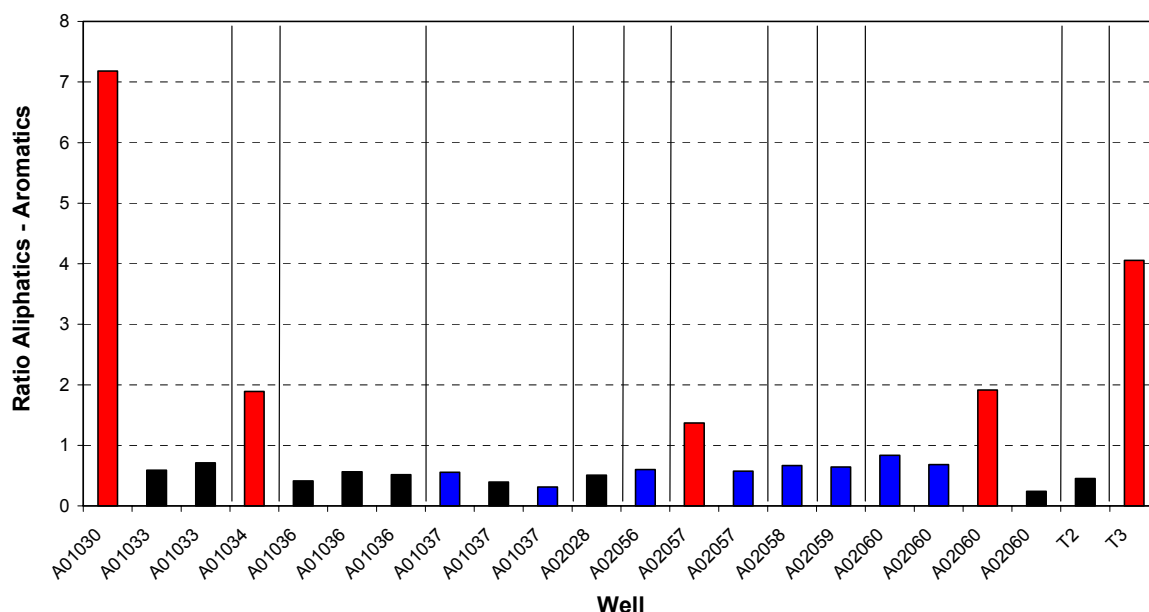
The results of the groundwater samples do not exceed solubility of the respective compounds. However, the concentrations found in the soil samples do exceed solubility of the soil moisture and a realistic value for adsorption onto the soil particles. Therefore, also the oil phase needs to be present in the samples. Based upon soil and fluid (NAPL-phase and aqueous phase) properties, the concentration of each Block dissolved in the NAPL phase is generated. The area in which NAPL phase is present in the soil samples is larger then expected. Also the vertical section in which the NAPL phase is present is larger. This, and also the observation of saturation exceeding 100%, was attributed to the disturbed soil cores from which the samples were taken.

A variation in the degree of oil saturation is found. Even values above 100 %. No conclusion can be drawn about the composition of the oil and the position of the sample relative to the groundwater table.

Also a few oil samples are taken from the floating layer. The characteristic measured with the GC showed differences with the composition of LCCCO (one of) the originally spilled product(s). Therefore, it can be concluded that in the past also other products were spilled.

6.4   Weathering of oil

Several preliminary calculations are carried out. In these calculations simplified circumstances are present for the oil composition (two versus six Blocks), characteristics of the groundwater flow (uniform flow in a confined layer versus unconfined flow to the drain) and soil properties (neither adsorption nor biodegradation versus adsorption/desorption and biodegradation). The objec-

tive of these calculations is to control the results. For this control, knowledge is used about the behaviour of leaching of components from the oil phase.

For two Blocks of components (figure 17 and figure 18), the initial concentration in the aqueous phase agrees with Raoult's law (**Fout! Verwijzingsbron niet gevonden.**). During depletion of the Block with the highest solubility, the concentration of the remaining Block in the NAPL phase asymptotically approaches the value for the density of the NAPL phase (figure 17), whereas the concentration in the aqueous phase agrees with solubility (figure 18).
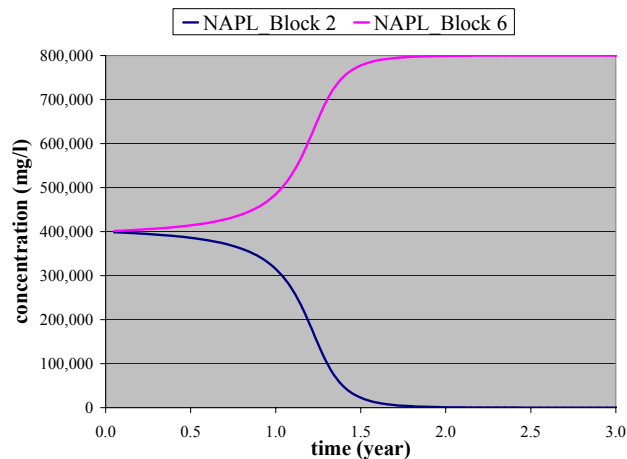
Fig. 17.   Development in time of the concentration in the NAPL phase when only two blocks are modelled.
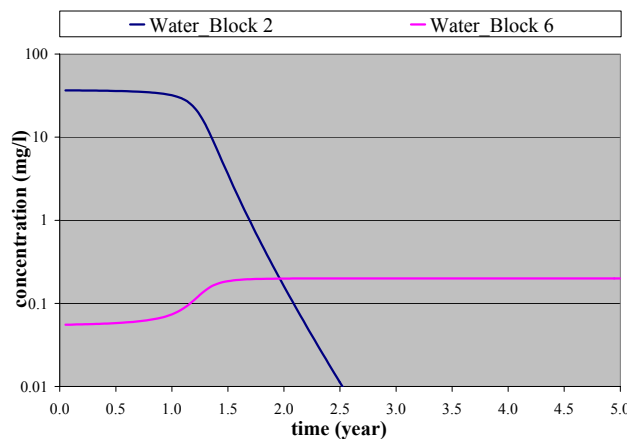
Fig. 18.   Development in time of the concentration in the water phase in the source area when only two blocks are modelled.

6.5   **Demonstration at Site 1**

6.5.1   *Small spill*
Subsequently several of the circumstances at the industrial location are taken into account. To gain information about the character of transfer of oil components, the initial distribution in the NAPL phase is taken in agreement with the composition of LCCCO: (one of) the original spilled product(s).

With the TPHCWG method the following Blocks of components of LCCCO are distinguished:

- Block 1: Aliphatcs
- Block 2: Aromatics with EC-number < 11
- Block 3: Aromatics with EC-number 11 - < 13
- Block 4: Aromatics with EC-number 13 - < 15
- Block 5: Aromatics with EC-number 15 - < 18
- Block 6: Aromatics with EC-number 18 - < 23

Initially about 500 litre of residual oil was assumed to be present. The results are shown in figure 19. The calculated initial concentration in the aqueous phase is in agreement with Raoult's law. From the results it can be concluded that the initial concentration in the NAPL phase only plays a minor role in the order of depletion. Leaching of Blocks of components out of the NAPL phase is dominated by its solubility (figure 19). For this situation, the Aromatics with a lower EC-number are depleted within a time period of about fifteen years (figure 19). After thirty years, only Block 1 (the Aliphatics), Block 5 and Block 6 (the longer Aromatics) are present (figure 19).
Due to the low solubility of the Aliphatics (lower than the trigger value of one microgram per litre) and the low concentration of Block 5 in the NAPL phase, no risk of migration is related with it. However, the concentration of Block 6 is above this trigger value. Looking to the plume in the groundwater of Block 6 shows that the plume already became stationary due to degradation in the aqueous phase. The results also show that degradation of contaminants in the groundwater has a positive effect upon depletion of Blocks of components within the NAPL phase.
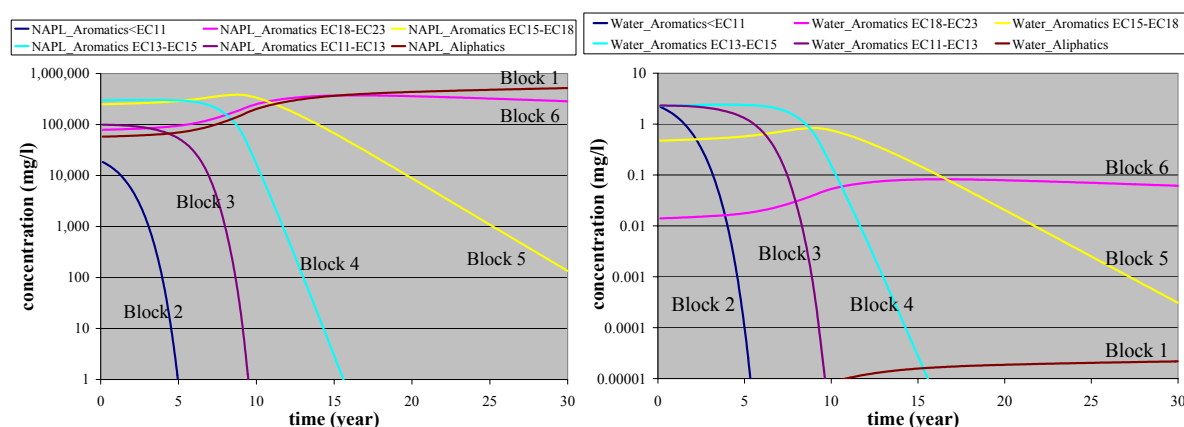
Fig. 19.   Development in time of the concentration in the NAPL phase (LCCCO) and in the water phase in the source.

A comparison is made between the temporal behaviour calculated for distribution of the constituents in the NAPL-phase and the results derived from the measurements of the soil samples (figure 20). Comparison shows that the results derived from the soil samples show enrichment of Block 2 and Block 3 compared with the composition of LCCCO. However, the results calculated show only depletion of Block 2, Block 3 and Block 4 and no enrichment. In all soil samples enrichment for Block 1 (Aliphatics) has taken place. This is in agreement with the calculations. This comparison indicates that also another type of oil contributes to the NAPL phase. Therefore, the spilled product not only includes LCCCO. In figure 20 also information is given about the relative position of the depth of the soil sample compared with the groundwater level: The red dashed line within figure 20. However, no relationship is found between this relative position and the distribution of the constituents dissolved in the NAPL-phase.

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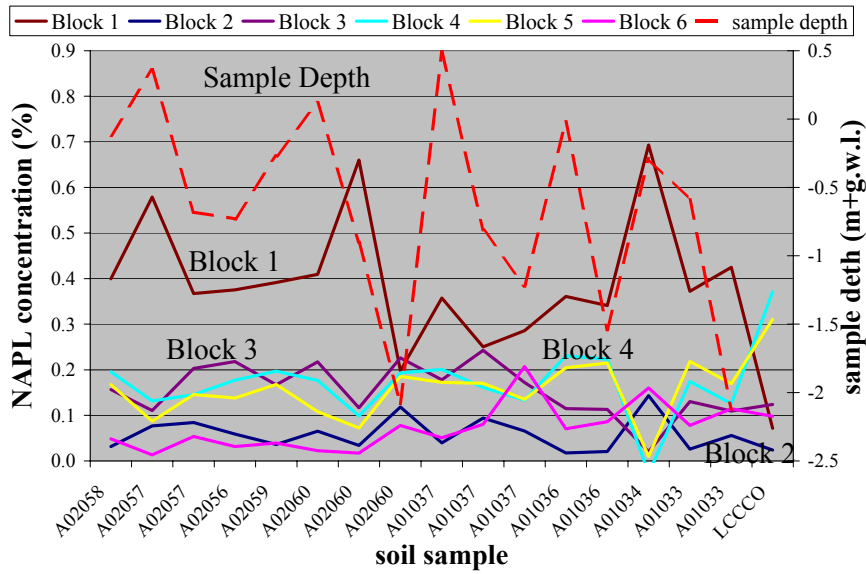
Fig. 20.   Concentration in the NAPL phase of each Block in the NAPL phase measured in soil samples and compared with LCCCO.

6.5.2   *Larger spill*

For the actual situation two calculations are carried out (see figure 21 and 22). In the first calculation the residual oil phase is represented as a conservative tracer. The results show that within a restricted time period of about three years, the tracer is removed from the subsoil due to the extraction by a local drain.

In the second calculation initially residual oil is present. The approximate oil saturation was set to 10 %. The area of residual oil is in agreement with the site observation. To analyse the numerical results, at several locations observation points are introduced: at the location of the drain (OP1), at a distance of one third of the extension of the residual area (OP2) and near the border of the residual area upstream of the groundwater (OP3). The calculation is carried out for a time period of twenty years.

Fig. 21.   (a) Concentration of each Block in the NAPL phase within the residual zone at OP2 (b) Contribution of each Block to the density of the NAPL at the position of OP2.

Fig. 22.   (a) Concentration (logarithmic scale) of each Block in the water phase within the residual zone in OP2.(b) Concentration (linear scale) of the Aromatic Blocks in the water phase in OP2.

The results show that in the vicinity of the drain (OP1), only the concentrations of the two smaller Blocks of Aromatics are declining. The others more or less remain at a constant level. The concentration of all t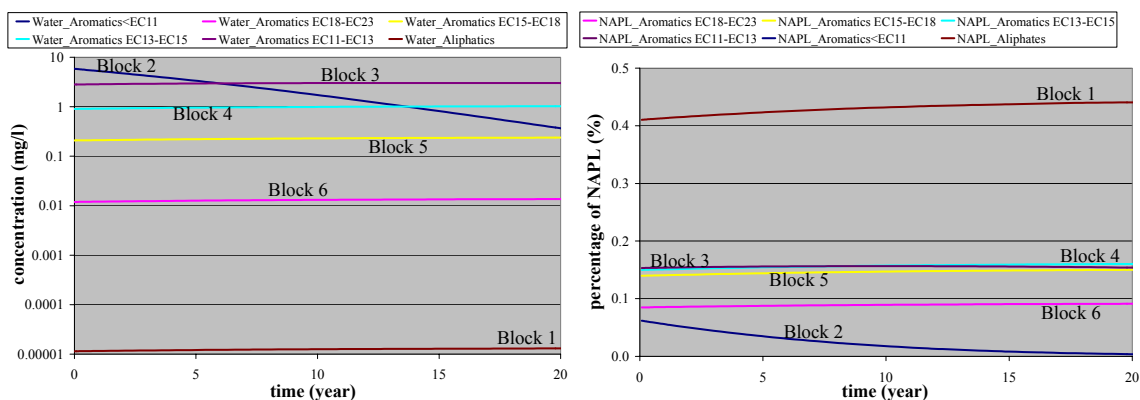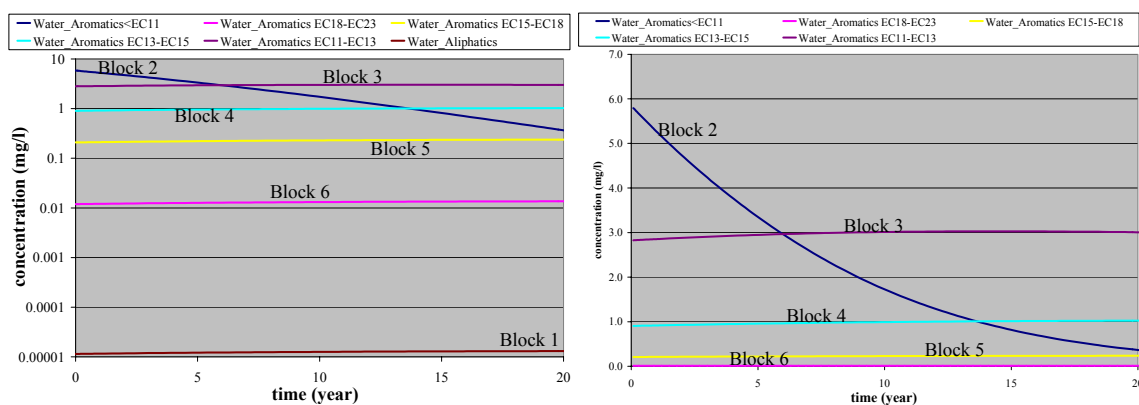he Blocks of Aromatics are above one microgram per litre. Due to its development, it is expected that after thirty years, only the concentration of Block 2 becomes below this trigger value. Within the residual area (OP2), again only the concentration of Block 2 is declining. Obviously, this is caused by a comparable development in time of the concentration in the NAPL phase of Block 2. Near the border of the residual area (OP3), are comparable with the results in OP2.

As a control for the numerical administration of the phenomenon of leaching, the total concentration of the Blocks of components dissolved in the NAPL phase can be used. For all calculations, this total concentration remains equal to the density of the NAPL phase.

6.6   Conclusions

It can be concluded that the extended numerical code gives the opportunity to determine the weathering of residual NAPL in the subsoil. As a consequence, information about the temporal behaviour of the concentration in the water phase within the residual zone becomes available. This behaviour can be compared with formal regulations about the risk of migration.

Taking into account the properties of the current situation at the location of Shell, it can be concluded that for relatively small oil spills of about 500 litre having the characteristics of LCCCO, natural processes will deplete the NAPL within a time period of thirty years. Whenever, the amount of spilled product is larger, much more time is needed before weathering of the oil results in a concentration in the water phase which is below environmental standards.

6.7   Recommendations

To stimulate further acceptance of the extended computer code RT3D-OW, several additional activities are recommended. The recommendations belong to the numerical code RT3D-OW, to the capability to characterise the composition of oil present in groundwater as well as in soil samples and to further research.

6.7.1   Numerical code RT3D-OW
The standard code RT3D-OWv2.5 gives the opportunity to analyse the mass balance for all modelled oil fractions. Due to the increasing complexity when weathering of the oil phase is taken into account, it is not possible to test the conservation of mass with the standard mass balance

ance output. However, for judging the reliability of the numerical results, it is recommended to extend the numerical code with of RT3D-OW with the capability to generate this information.

The current version of the numerical code RT3D-OW does not have the capability to deliver output of the degree of saturation of the NAPL phase. Therefore, it was not possible to generate the temporal behaviour of the depletion of the NAPL phase. It is recommended to extend the numerical code with this facility.

Numerical time steps are limited by the dynamics of fate and migration in the subsoil. Whenever other phenomena, such as weathering or depletion of the NAPL phase, are taken into account the effects of these phenomena upon the numerical time step needs to be expressed explicitly.

6.7.2 *Characterisation of the samples*
Within this project the soil samples were characterised by the method of TPHCWG and the groundwater samples by a traditional analytical technique. Due to the difference in characterisation, the results can hardly be compared, especially whenever multiple phases are present in the samples. Therefore, oil characterisation needs also to become a tool for the distribution of the concentration of the constituents within a groundwater sample.

Beside the results of an oil characterisation also the concentration of several specific compounds needs to become available, especially for assessing the risks related to fate and migration of petroleum products in the groundwater.

To apply the method of TPHCWG to groundwater samples, an extraction method needs to be used (or developed) which requires larger water samples. In order to improve the accuracy of the derivation of the distribution of constituents in the NAPL phase from the analytical results of a soil sample, a few recommendations can be formulated. It is recommended to have also information about the density and the organic matter (organic carbon) content of the soil sample. As soon as it is expected that also pure NAPL is present within the sample, it is recommended to fractionate the three phases (oil, water and solid material).

6.7.3 *Further research*
Depletion of the NAPL phase results in a change in the contribution of the various constituents to the density of the NAPL. Due to his change also several physical properties of the NAPL changes. Among them are the viscosity and the rate of transfer to the aqueous phase. Further experimental research is needed whether or not these phenomena are significant enough to implement into the modelling. Generally spoken, it is recommended to carry out laboratory experiments to verify the transfer phenomena which form the foundation of the numerical modelling.

CHAPTER 7

APPLICATION OF THE CODE AT SITE II

7.1   Introduction

Within the project 'Development of a Numerical Simulator for LNAPL Weathering', a prototype of the numerical simulator has been developed. On the one hand, the robustness of the model code and the user-friendliness of the user interface have been tested, on the other hand the model results have been judged in terms of plausibility and usefulness as compared to the conventional approach to mass transport simulation.

The purpose of the simulator is to predict the development of plumes of groundwater contamination from floating LNAPL layers resulting from terrestrial spills. The source area is either a floating oil lens and/or a groundwater zone containing residual LNAPL. The emission into the groundwater system from the source area is supposed to vary with the composition of the oil. This composition changes over time, due to preferential volatilisation and dissolution of components. The usefulness of the simulator is demonstrated by showing the relevance of reliable results of transport simulation within a conceptual framework of soil management decisions.

7.2   Site investigation

The research site is situated in the Netherlands. From 1968 until present, the site has been used for diesel tank storage. In 2001 the site is investigated. The results from this indicated that a floating layer of contamination remained at the site, further the investigation defined the extent of the oil plume. The floating layer is estimated to cover an area of 620 m^2. On the basis of the previous use of the site and chromatogram results it is expected that diesel oil is still present.

A total of 15 samples have been analysed from this site. Soil, water and oil samples from site II were analysed following an analytical procedure which was developed specifically for this project, and which was based on the work of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) in combination with NEN-method. Whereas NEN shows that the hydrocarbons fractions C12 – C22 are present in the highest concentrations, the TPHCWG gives more specific results as it divides the HC's in smaller subsets and we see that EC 12 – 14 and EC 14 – 16 are the predominant EC classes.

All samples containing detectable amounts of hydrocarbons show very similar aliphatic GC traces. These consist of a complex mixture of hydrocarbons in the range C8-20, with a number of relatively high peaks which are probably branched or isoprenoid alkanes. These GC traces are typical for a biodegraded diesel. Fresh diesel contains abundant n-alkanes [Morrison, 2000]. Biodegradation of hydrocarbons occurs in a particular order, with the n-alkanes being degraded first [Connan, 1984]. Figure 23 shows a comparison of the LNAPL sample with a fresh diesel sample on the basis of the aliphatic and aromatic fractions as defined for this site (see table 2). This analysis demonstrates that the LNAPL most likely consists of a (bio)degraded diesel.
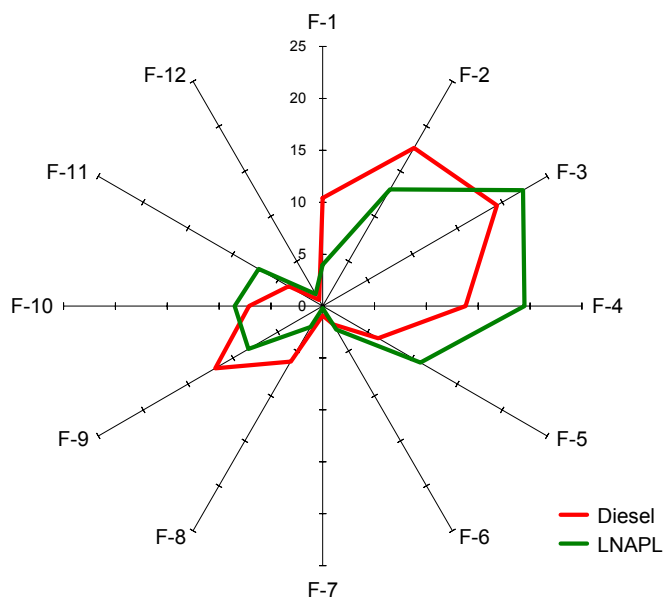
Fig. 23.   Comparison of the LNAPL from Site II with a fresh diesel sample.
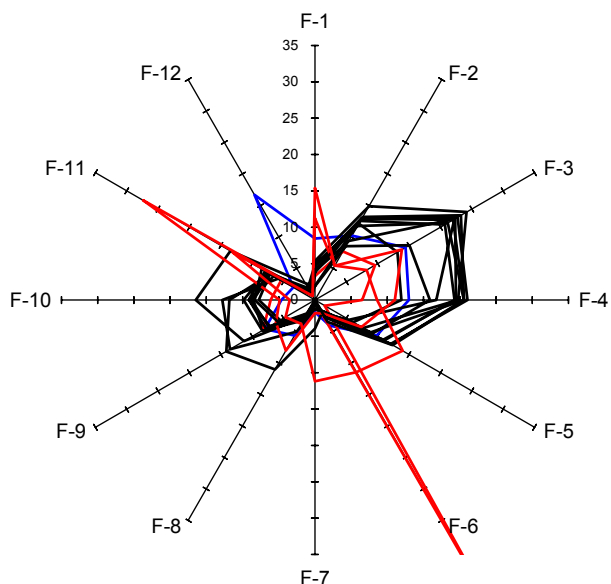
Fig. 24.   Comparison of all samples from Site II on the basis of the aliphatic and aromatic fractions.

Figure 24 shows the composition of all samples. Most samples fall within the area designated as a weathered diesel.

The amounts of mineral oil in the soil samples range from 25-339 mg/g (wet) soil.
The relative amounts show that these weathered diesel samples are very aliphatic, with amounts of aromatic components as low as 1-3 %. Fresh diesel consists for ca. 24 % of aromatic components [Morrison, 2000]. It is conceivable that, along with biodegradation of n-alkanes, loss of aromatic components has occurred through water washing (probably in combination with biodegradation).

The diesel analysed within this project is slightly more aromatic and consists for approximately 30 % of aromatic components. Four samples show a somewhat different composition (indicated

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in red in figure 24). This includes the water sample (indicated in blue in figure 24), which has a relatively high proportion of heavy aromatics.

In summary, the contamination situation at the shunting yard seems to be relatively simple, with indications for only one original product (diesel), which was also the expected product based on historical information form this site.

7.3   **Conceptual framework**

In the weathering process, oil is transported by the groundwater from the source area (containing residual oil) towards a hydrological outflow boundary (see figure 25).
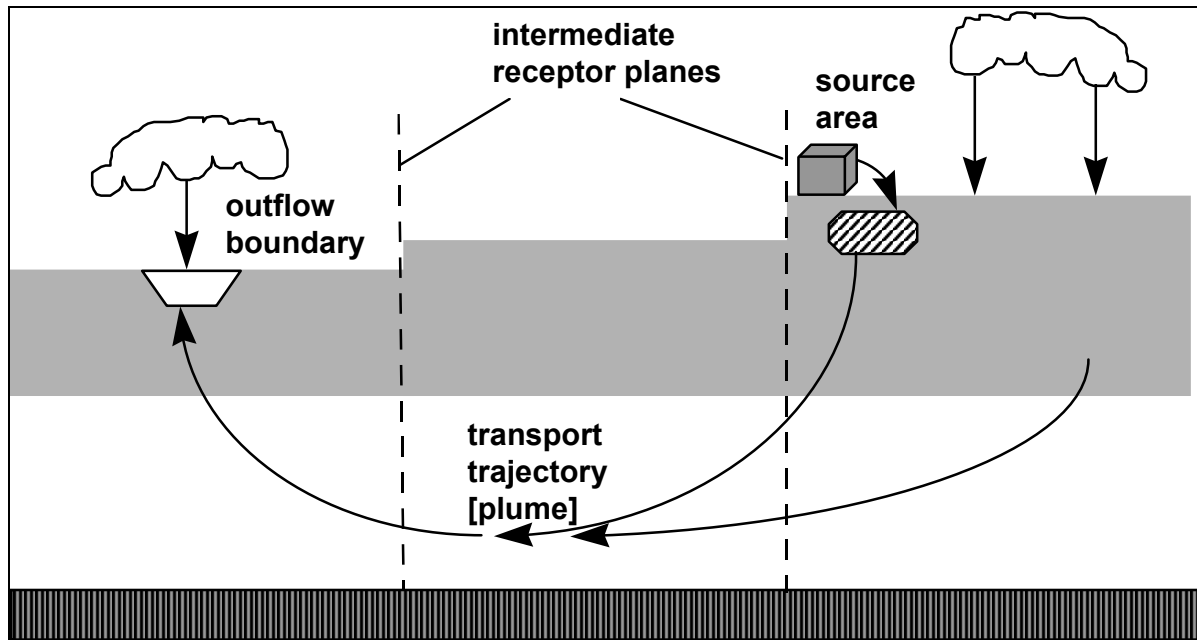
Fig. 25.   Conceptual model for transport of mobile groundwater pollution.

The time required for the contaminated water to reach this boundary (t_{max}) provides a logical time scale to describe the transport process. The maximum volume occupied by contaminated groundwater (V_{max}) in this autonomous development scenario provides the spatial scale. We postulate that the maximum possible concentration (C_{max}) arrives at the outflow boundary after t_{max}. With the simulator, the development of the groundwater concentration at the outflow boundary (the breakthrough curve) can be determined.
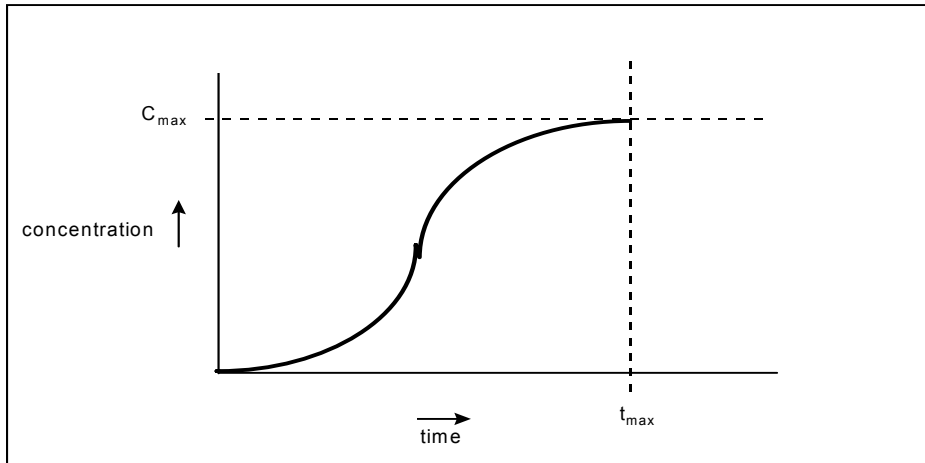
Fig. 26.   Breakthrough curve for conservative transport.

Compared to the breakthrough curve for conservative transport, t_{max} is prolonged and C_{max} is attenuated for reactive contaminants. This combined effect of retardation and (bio-)degradation is called natural attenuation (NA) (see figure 26 and 27).
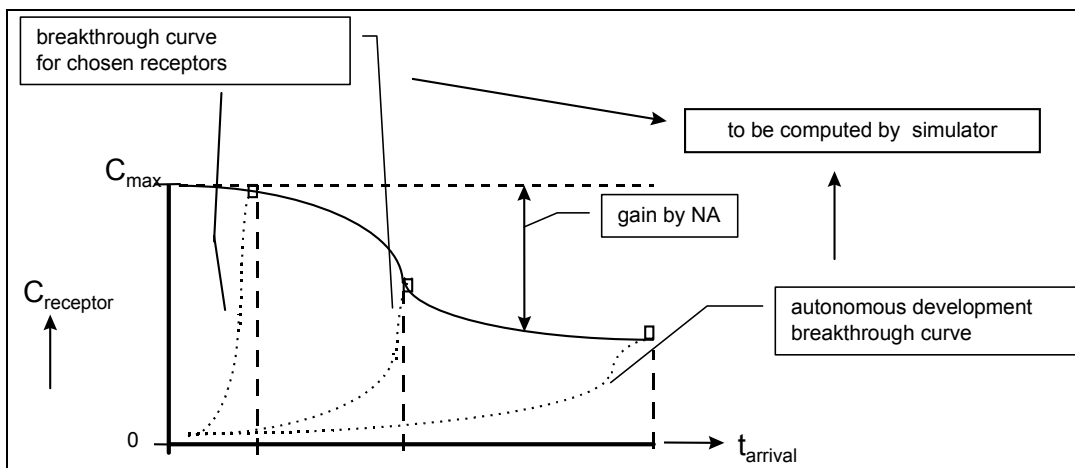
Fig. 27.   Relation between breakthrough time tmax, breakthrough concentration Cmax and natural attenuation.

In terms of risk of exposure, a proper term for the outflow boundary is receptor. In terms of groundwater quality management, a so-called *plane of compliance*, can be defined as the receptor.

For the present situation, we define a stable end situation (SES) as the situation where the volume of contaminated groundwater no longer grows. This volume is defined as the volume where the concentration of one or more components of the oil exceeds a certain critical value (C_{crit}) for intervention.

A chosen receptor plane is associated with a volume V_{crit} and with a corresponding breakthrough curve. This curve, which is produced by the simulator, describes how the concentration develops from 0 to C_{max} in a period ($t_{breakthrough}$). Only a chosen, (limited) concentration is allowed to spread beyond this plane. Various measures can be implemented to ensure that the chosen level is not exceeded.

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NB The ratio of V_{crit} to V_{max} expresses the environmental quality relative to the autonomous development. The area enclosed by the boundary may be considered a bioreactor.

A further decision is required regarding the maximum allowable concentration (C_{crit}) to pass beyond the receptor plane. This decision determines the period available to take these measures (t_{crit}).

NB The value of C_{crit} expresses the level of ambition with respect to the environmental quality outside the plane of compliance (see figure 28).
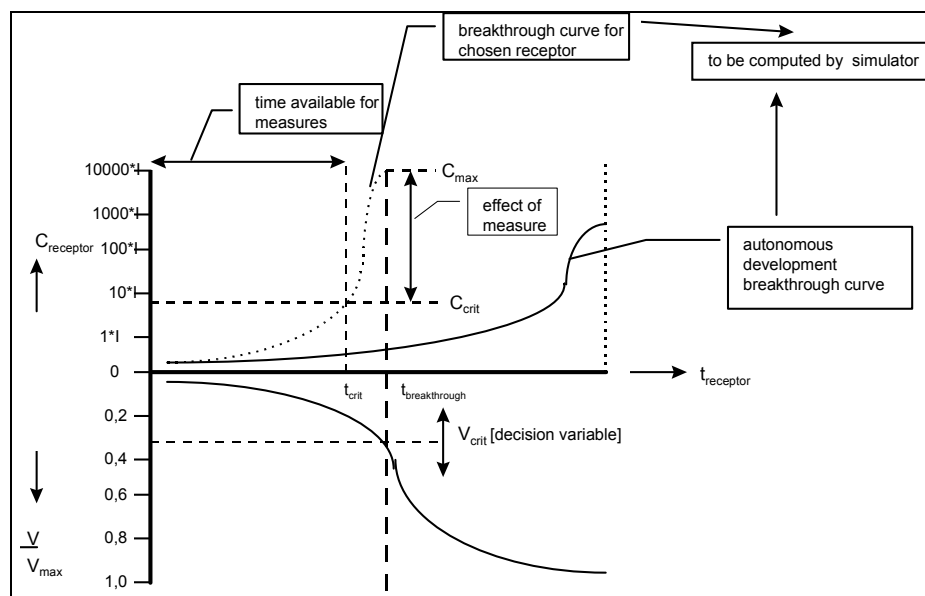
Fig. 28.   Vcrit and Ccrit as decision variables and the resulting latest possible time tcrit for measures.

The moment of intervention determines which measures can be taken. We consider the following types of intervention:

1. elimination of the source zone through isolation or removal by excavation and/or pumping. This is possible only for a relatively short time from the present;
2. pump & treat. This option is always available;
3. stimulation of decay or biodegradation. This may effectively lower C_{max}, thus yielding more time. C_{max} may even be reduced to a level below C_{crit}.

This is not an exhaustive list. However, to demonstrate the use of the simulator these most relevant options suffice.

Using this framework, soil management is translated into spatial planning of the intervention strategy for a given investment level.

For site II, a model has been developed and calibrated. This 3-D model can be used to produce the breakthrough curves and further to expore the options for specific soil management.

7.4   Demonstration at site II

For these simulations two aliphatic EC blocks were used, firstly EC< 11 and secondly EC 14 – 16. Although the low EC fractions were not found at high concentrations in site II, due to the relatively high solubility the shortest group of aliphatic EC's has been modelled (S1). The second aliphatic block (S2) was used in the modelling simulations as this was the most predominant EC at the location. 4 blocks of aromatics were used (S3-S6). Although, aromatic components were measured in low concentrations in relation to the aliphatics, their higher solubility, means that

more dissolution an dispersion can occur making them a wider threat to the environment (see table 4).

Table 4.   Modelled Components.

Block code	Hydrocarbon class
S1	Aliphatics < EC 10
S2	Aliphatics EC 14-16
S3	Aromatics < EC 11
S4	Aromatics EC 11 - 14
S5	Aromatics EC 14 - 16
S6	Aromatics EC 16 - 19

Four simulations will be carried out for the site II:

1. historical reconstruction of the present situation (including calibration);
2. the development from the present situation without biodegradation;
3. as '2' with biodegradation;
4. as '3' removal of 50% of the source area.

The 44 year stress period is based on sub periods of 14 years and 30 years. For the first 14 years the location was influenced by pumping from the 'Waterleiding Maatschappij Overijssel' situated about 500m South-east from the site location. Thus the influence of the pumping for the groundwater flow situation and the spreading of contamination has been simulated by the model.

For the autonomous development scenario, a sensitivity analysis will be carried out with respect to the microbial decay rate constant. This will determine the relevance of NA in environmental management decisions for the site.

The results from the modelling indicate that after the period of 44 years (30 years from now) concentrations of the mineral oil have reached an equilibrium state. In the pool itself concentrations are high (> intervention value) for all the scenarios. For scenario 1 (without biodegradation) the concentration in the plume is around 0.10 mg/l, therefore between the target and the intermediate value for mineral oil.
For scenarios 2 and 3 the concentration of mineral oil in the plume is below the target value of 0.05 mg/l (see table 5)

Table 5.   T$_{(max)}$ for receptors.

Scenario	Receptor	Time for contamination to reach the specified level (years)		
		> target level	> intermediate level	> intervention level
Scenario 1	drains	0	x	x
	principle aquifer	0	10	x
Scenario 2	drains	x	x	x
	principle aquifer	x	x	x
Scenario 3	drains	x	x	x
	principle aquifer	x	x	x

* target, intermediate and intervention levels from 'Leidraad bodembescherming, [1995].

The initial residual oil modelled in the scenarios was mostly (70%) Aliphatics; Block 1 is the low EC group EC< 11, and 'Block 2" which is EC 14-16. Modelling results show that composition of the mobile phase is nearly 100% aromatic (blocks 3 - 6).

Table 6.   Modelling results.

Block code	conc. residual oil (mg/l)	% of total residual oil	conc. in groundwater (mg/l)	% in groundwater
1	63000	28	2.77E-04	0.02
2	95000	42	1.25E-05	0.00
3	14000	6	1.01	76.52
4	27000	12	0.27	20.45
5	16000	7	3.28E-02	2.48
6	10000	4	5.32E-03	0.40

*   conc. residual oil is based on the initial concentration input
**   conc. in groundwater is based on the mobile component concentrations in the pool after the first modelling
     time step (9 days)

The simulation results will be analysed and interpreted in terms of the framework presented in section xx based on the development over time of the following quantities:
1. the plume development;
2. the composition of the oil in the source area. This determines the importance of taking into account weathering of the oil in simulating the development of plumes.

For the contaminant development, the combined system of sewage and drainage in the built up urban area adjacent to the site is one critical outflow boundary (receptor 1). Modelling results show that for autonomous development without biodegradation (scenario1), concentrations of mineral oil are already above the target value. If biodegradation is occurring at this site (scenarios 2 & 3) then the plume is confined to the area nearby the floating layer.

Biodegradation also influences the vertical spreading of the plume, for scenarios 2 and 3 spreading of the plume is restricted to the upper ground layers, and after 30 years from now, no mineral oil is present in the principal aquifer.

However without biodegradation (scenario 1) results show concentrations above the target value are already present in the principal aquifer (receptor 2) and within 10 years from now, concentrations of mineral oil above the intermediate value for mineral oil are expected.

The results suggest that aerobic degradation has already caused a stable situation, i.e. the plume has already reached its maximum volume. The values used for the aerobic degradation rate are an estimate based on the redox potential and oxygen concentrations monitored at the site. The results therefore are indicative of the biodegradation potential of the site. A limited amount of:
-   further site specific information on parameters determining NA;
-   additional modelling
is required to determine with sufficient certainty if the plume has indeed reached its maximum volume, i.e. that the present situation is stable. The effect of recent or likely changes in groundwater flow regime on the conclusion can and should be taken into account.

7.5   Evaluation

In obtaining simulation results we draw the following conclusions with respect to the usefulness:
-   a conceptual framework for soil management decisions is required to decide which simulations to make (if any) and how to interpret the results;
-   the model calibration, based on historical reconstruction, yielded results which reflect the present situation at site II sufficiently well, given the uncertainty in input data;
-   therefore the simulator is a reliable tool for simulation of plume development from a floating layer in combination with a smear zone. A similar instrument has not been freely available to date;

- for site II, decisions relating to soil management can be optimised using model results as indicated in the framework;
- for the LNAPL spilled at site II, no noticeable effect of preferential dissolution is apparent in the floating layer over the 44 year modelling period. As the floating layer is predominantly made up of aliphatics (which have a low solubility) it is likely that a model run for a much longer period would be needed to notice the dissolution difference in the floating layer;
- the contribution of dissolution from the pool to the mass transport is negligible compared to the contribution of the residual oil in the smear zone. However, the presence of the floating layer in the real world situation is relevant, it causes the replenishment of the smear zone (containing residual oil) through fluctuation of the groundwater level;
- a special method of analysing soil and groundwater samples has been recommended for use in this project. This allows a detailed specification of EC-classes. This is an interesting option when <u>all</u> characteristics (physical, chemical and ecotoxicological) of the substances vary much between EC-classes and little within EC-classes.

7.6   **Recommendations**

We recommend the following:
- as an aid to future applications, the choice of EC-classes and the method of determination of the average characteristics (literature sources, lab results, etcetera) could be shared between users of the simulator;
- the mass transport simulator (including the manual) should be made fit for using multiple stress periods. This is required in order to simulate changes in geohydrological regime and/or mass transport, either as a result of external conditions, or as a result of the activation of mitigating measures as part of a management strategy;
- the usefulness of the simulator can be demonstrated further in the process of choosing the soil management strategy for site II. For a given investment level, the minimum plane of compliance may be found. Alternatively, for a given plane of compliance the minimum investment level may be determined. The simulator serves to predict the effect of measures. Technical constraints have to be specified, such as accessibility;
- further optimisation of this strategy may be possible by analyses of the link between characteristics per EC-block and management decision variables and constraints;
- a more extensive manual such as those available for MODFLOW and RT3D would greatly help the user. A section explaining the meaning of input variables in terms of the model concept would be particularly useful.

CHAPTER 8

EVALUATION OF RESULTS

The RT3D-OW code was tested successfully at the Bemidji site in the USA. It was shown that the code is capable of simulating the main processes governing the emission, transport and fate of oil components in the groundwater. Subsequently, the code was applied to two sites in The Netherlands.

In principle the new code can be applied wherever the original RT3D code can be used.

Since the RT3D-OW describes additional processes compared to the original RT3D code, it also requires additional inputdata. These can either be measured or estimated.

Composition and saturation of the oil phase:
The code is generic and can deal with various oil characterisation and individual component input data. Whenever the goal is to link simulations with field measurements it is paramount, to use similar techniques for the oil and the aqueous phase.

For the initial NAPL saturations as a function of position, it is either possible to assume reasonable values based on published experimental data or to measure the values in the field. One way to obtain measured values is to conduct extraction of undisturbed soil sample, followed by an oil characterisation.

The mass transfer between the floating lens and the groundwater is governed by transverse dispersivity. Based on laboratory test, the αt can be assumed to be about 4 mm.

As the code describes (in a simplified way) several important processes associated with oil and other mixed LNAPL contamination, various possible applications can be identified:
1. to provide insight in the physical processes affecting emissions of contaminants from multi component source areas. What happens to groundwater concentrations when we remove 90 % of the oil contamination?
2. Optimization and interpretation of possible measurement schemes in the vicinity of the oil contamination source. Where can we take samples, which tell us whether or not natural attenuation is efficient?
3. Simulation of various remedial schemes, What needs to be done in order to reach a stationary end situation. Do we need to remove the source?
4. Identifying sources which have the highest impact on receptors. How long does it take for the contamination to reach the limits of the site and what action should be taken to avoid that?

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

A simulator (RT3D-OW) was developed which quantitatively evaluates and predicts the spreading of dissolved oil components in groundwater. The pre- and post processing of the code is managed by the existing processing shell GMS. Although the code is based on a simplified description of reality, it is capable of simulating the various aspects of weathering of an immobile subsurface oil phase, contaminant emission from this oil phase and subsequent fate and transport of the plume of dissolved oil components. The RT3D-OW code considers emissions from floating oil lenses as well as from smearing zones (discontinuous oil droplets).

The code is generic and can use data obtained from various measurement techniques and data sets. The composition of the oil phase is described by either individual components or by different fractions, and the transport and fate of these components or fractions is simulated. An advantage is that it is an extension of the commonly used RT-3D code, which means that the various pre- and post processing tools which have been designed for that code can also be used for the code RT3D-OW.

A first test of the code was conducted for the Bemidji site in Minesota, USA. Available data such as the composition of the floating lens and groundwater concentrations were used. Several physical and chemical input parameters were independently estimated or assumed. These included first order biodegradation constants, which were taken from literature, and which are highly uncertain and variable. Even so, the simulation results showed that the calculated concentrations in the groundwater in two wells downstream from the well defined source area, were similar to the measured groundwater concentrations. This means that the code is capable of simulating the main processes governing the emission, transport and fate of oil components in groundwater. In addition, it was shown that biodegradation strongly affects the dimension of the contamination plume. Consequently, a correct description of the presence and consumption of oxygen is essential for the Bemidji site. Simulations also showed that the composition of the continuos oil lens remained almost constant during 15 years of weathering and that the composition of the residual zone changed only slightly. This corroborates the common experience of site managers that dissolution of a source area is a very long term process and that the emissions to the groundwater are mainly from the smearing zone.

Overall, the new code showed to be capable of simulating the weathering of subsurface oil contamination sources (floating lenses as well as residual discontinuous zones) as well as simulating the subsequent fate and transport of the multi-component plume.

Possible future applications of the newly developed code are:
-   to provide insight in the physical processes affecting emissions of contaminants from multi-component source areas;
-   optimisation and interpretation of possible measurement schemes in the vicinity of multi-component contamination sources;
-   simulation of various remediation strategies.

For some of the application it is necessary to get detailed information about the mass balance of the distinguished oil components for specific areas within the model. Until now, there is no mass balance feature available in the standard postprocessor (modelling shell GMS). Therefor it is recommended to extent the numerical code of RT3D-OW or GMS with the capability to generate this information.

Areas for future research to increase the applicability of the code will necessarily have to include quantitative experimental lab work and field measurements, supported by numerical modelling. Possible areas of focus could be:
- the description of natural attenuation by a first-order biodegradation concept;
- assigning biodegradation constants to fractions of multi-component oils.

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