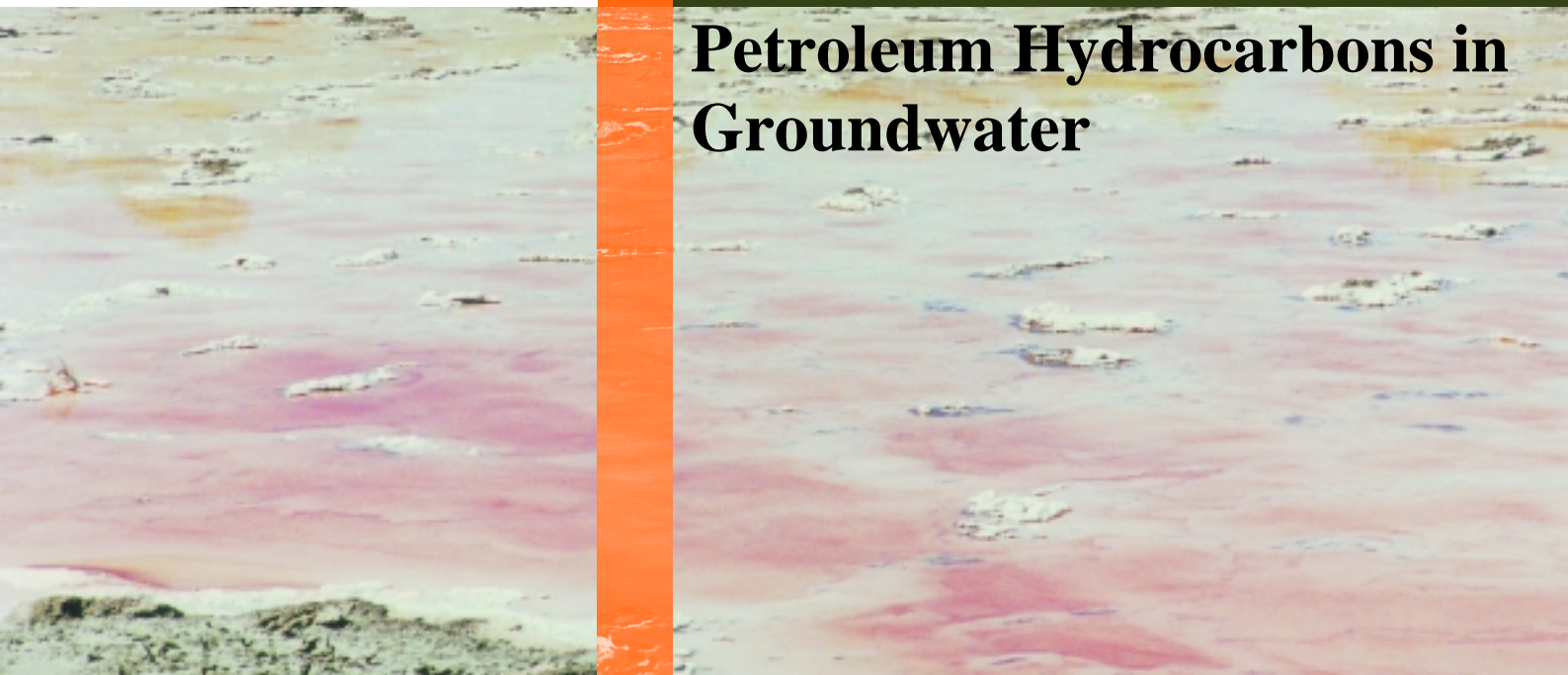# Modelling the Fate of Petroleum Hydrocarbons in Groundwater

EPHC

Environment Protection & Heritage Council

This paper was presented at the Fifth National Workshop on the Assessment of Site Contamination

Proceedings of the Fifth National Workshop on the Assessment of Site Contamination

Editors: Langley A, Gilbey M and Kennedy B

The editors may be contacted through the NEPC Service Corporation for which contact details are provided below.

EPHC Environment Protection and Heritage Council   Incorporating NEPC National Environment Protection Council

Modelling the Fate of Petroleum Hydrocarbons in Groundwater

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ABSTRACT

Models can be powerful tools to aid interpretation of data and for prediction of the fate of contaminants, as in the case of petroleum hydrocarbons in groundwater environments. Here we describe the transport processes that can be more or less dominant at different stages in the 'life' of a petroleum contaminant spill in groundwater, such as advection, dispersion, dissolution from free-phase non-aqueous phase liquid (NAPL), sorption to aquifer material, and biodegradation processes. Consideration of all of these processes may be warranted to provide a comprehensive assessment of the natural attenuation of hydrocarbon compounds in groundwater or for remediation strategy design. Adequate data and a sound conceptual model of plume development and hydrogeochemical response are prerequisites for more comprehensive and realistic modelling. Knowledge of aquifer properties, geochemistry, suitable boundaries of the domain to be studied and indeed the intent of the modelling – all shape the conceptual model and the level of effort required. Some of the available biogeochemical numerical codes are catalogued, and one is applied in an example problem as a demonstration of model capabilities. The example concerns the natural attenuation (biodegradation) of a dissolved petroleum hydrocarbon plume in groundwater, accounting for coupling of transport, geochemistry, NAPL dissolution and microbial growth and decay.

1   INTRODUCTION

Over the last two decades, mathematical modelling has become an increasingly important tool to assist in analysing and understanding complex environmental systems. Wherever a multitude of processes, either of a physical, chemical or biological nature interact with each other, mathematical modelling has been shown to provide a rational framework to formulate and integrate knowledge that has otherwise been derived from (i) theoretical work, (ii) fundamental (e.g., laboratory) investigations and/or (iii) from site-specific experimental investigations. In the case of subsurface systems, data acquisition is typically very expensive, especially in the field, and so data sets are usually sparse. Thus, validation of complex models can be difficult. At the same time, it is also the lack of spatially and temporally dense information and the need to fill the gaps between measured data that provides an important driving force for modelling. The application of existing numerical models and their further development are motivated by questions such as:

- To what extent will environmentally important receptors downgradient of the source zone be impacted by a contaminant?
- What are the expected average and maximum concentration levels?

- What are the time-scales for cleanup to below given limits for different remediation schemes?
- What is the *optimal* design (in a multi-objective environment) of a particular (active/passive) remediation scheme?
- What is the sensitivity of, say, the duration of the remediation process to changes in physical or biogeochemical conditions?
- To what extent do remediation strategies impact the risk of pollution at a given location over a specified time frame?

Modelling can play an important role in answering such questions by making use of possibly its most important features: its integrative and predictive capability. Of course predictions bear, to a variable degree, uncertainty that originates from:
- Incomplete hydrogeological and hydrogeochemical site characterization,
- Incomplete process understanding, and
- Parameter ambiguity due to spatial and/or temporal scaling issues.

Modelling provides the best tool to incorporate observed data or, where data are lacking, investigate quickly a suite of scenarios to assist in gaining a better understanding of, as already suggested above, factors dominating the duration of site clean-up. The purpose of this paper is to discuss the main physical and chemical processes affecting the fate of dissolved petroleum hydrocarbons in groundwater and to demonstrate their incorporation into numerical models. For the latter part we provide an overview of some of the common mathematical descriptions and modelling approaches involved in the simulation of the fate of petroleum hydrocarbons. Reactive transport simulators are also discussed, and an example is given to illustrate the capability of these codes in elucidating the complex coupling between processes where petroleum hydrocarbons are transported, sorb and biodegrade in groundwater.

2 PHYSICAL AND BIOGEOCHEMICAL, REACTIVE PROCESSES GOVERNING THE FATE OF HYDROCARBONS

2.1 OVERVIEW

Spreading of petroleum hydrocarbons that have reached, as a separate NAPL (Non Aqueous Phase Liquid) phase, the saturated groundwater zone and thus might provide an increased health risk, is governed by a range of physical, chemical and biological processes. The most important processes affecting the fate of the organic compounds in groundwater are (Barry *et al.*, 2002):
- Dissolution from the NAPL phase into the (passing) groundwater
- Advective transport
- Dispersive transport in longitudinal and transversal direction
- Sorption to the aquifer material
- Biologically mediated degradation, i.e., transformation and/or mineralisation

The relative importance and dominance of these processes varies strongly from the beginning of groundwater contamination to complete contaminant disappearance. The following (major) stages (see Figure 1) are typical if no (active) remediation of groundwater takes place:
- *Stage 1: Emerging groundwater contamination* – NAPL is in contact with groundwater and, with ongoing dissolution, advective-dispersive transport leads to

growing plumes of dissolved hydrocarbon constituents. The total mass of dissolved hydrocarbons steadily increases as the rate of mass dissolving from the NAPL source exceeds the rate at which it is removed by sorption and biodegradation. For large longitudinal dispersivities plume fronts might travel significantly faster than the average groundwater flow velocities.

- *Stage 2: Steady state or slowly changing plumes of organic constituents* – The overall rate at which the various organic constituents are biodegrading equals the rate at which they dissolve from the NAPL source. Furthermore, in this (quasi) steady state sorption and desorption to and from the aquifer material occur at the same rate and thus do not affect the contaminant distribution. Both aqueous electron acceptors (O_2, NO_3^-, SO_4^{2-}, CO_2) and solid, mineral-form electron acceptors (e.g., iron-oxides such as ferrihydrite or goethite) provide the oxidation capacity needed for the oxidation/mineralisation of the organic compounds. Important processes that affect the length of plumes are (i) the total (i.e., spatially integrated) contaminant mass that emanates from the NAPL source zone, (ii) the transversal dispersion of the aquifer which mixes aqueous phase oxidation capacity into the contaminant plume and (iii) the dissolution rates of mineral-form electron acceptors. This final stage occurs only if solid-phase electron acceptors are available and if thermodynamically more favourable electron acceptors are locally unavailable within the contaminant plume(s).

- *Stage 3: As above, but (immobile) mineral-form electron acceptors are depleted (or mineral dissolution rates have become insignificant)* – The oxidation capacity that is necessary to biodegrade the organic compounds is (fully) provided by aqueous electron acceptors that are (more or less) continuously replenished. As in the previous stage, sorption and desorption rates are similar (the mass of organic compounds sorbed to aquifer material remains constant) and the length of individual plumes is insensitive to the longitudinal dispersivity of the aquifer.

- *Stage 4: Depletion of the NAPL source* – The total mass of dissolved organic substances within the groundwater decreases. The time taken for source depletion differs for each organic compound, depending on the initial mass, the compound's solubility and on its (mole) fraction within the NAPL source. Source depletion occurs successively for individual compounds (Imhoff *et al*., 1993). The size of individual plumes might shrink as a result of increased electron acceptor availability.

Hydrocarbon concentrations Aqueous-phase electron acceptors   Mineral-phase electron acceptors
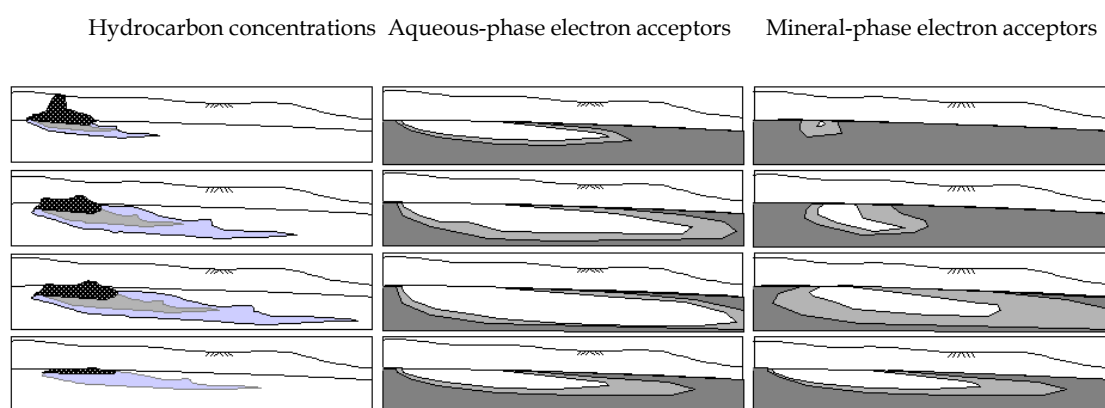
Figure 1. Stages 1 to 4 (from top to bottom) in the development and depletion of a petroleum hydrocarbon plume in groundwater from the beginning of groundwater contamination to significant contamination disappearance (darker shades indicate higher concentrations).

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Mathematically the combination of the above processes can be collectively expressed by the governing equation for a single organic compound subject to physical transport and chemical reactions (indical notation):

$$\theta_m \frac{\partial C_{org}}{\partial t} = \theta_m \frac{\partial}{\partial x_i}(D_{ij} \frac{\partial C_{org}}{\partial x_j}) - \theta_m \frac{\partial}{\partial x_i}(v_i C_{org}) + q_s C_{org,q} + \theta_m R_{org,dis} + \theta_m R_{org,deg} + \theta_m R_{org,sorb},$$ (1)

where t is time, C_{org} [ML^{-3}] is the aqueous concentration of the chemical species (here the petroleum hydrocarbon(s) of interest), v_i [LT^{-1}] is the pore water velocity in direction x_i [L], D_{ij} [L^{2}T^{-1}] is the hydrodynamic dispersion coefficient tensor, θ_m is the porosity of the aquifer material, q_s [L^{3}L^{-3}T^{-1}] is the volumetric flux rate of water per unit volume of water representing external sources and sinks, and $C_{org,q}$ [ML^{-3}] is the concentration of the organic species within this flux if q_s is positive (injection), otherwise $C_{org,q} = C_{org}$. The three reaction terms $R_{org,dis}$, $R_{org,deg}$ and $R_{org,sorb}$ represent, in a general way, the appropriate reactive processes of dissolution, (bio)degradation and sorption. Each term might be a function of other aqueous species, NAPL or mineral concentrations. Below we discuss the individual physical and chemical processes in more detail.

2.2   NAPL DISSOLUTION (CONTAMINATION SOURCE)

In a typical petroleum hydrocarbon contamination scenario, e.g., a case of a leaking underground storage tank, free product such as gasoline migrates downwards through the unsaturated zone until it reaches the capillary zone (assuming the spill volume is sufficient). There, the mobility of the hydrocarbons decreases as water saturation increases and accumulation takes place above the watertable. Since petroleum hydrocarbons are less dense than water, watertable fluctuations cause a vertical smearing of the NAPL, thus increasing the contact zone between it and groundwater. In this zone, dissolution of NAPL compounds (e.g., Miller *et al.*, 1990) acts as a continuous contamination source for the passing groundwater. The rate at which mass is transferred from the NAPL into the aqueous phase is a function of:
- Interfacial area between the NAPL phase and the aqueous phase
- Extent and morphology of the source (in particular the maximum cross-sectional area perpendicular to the main groundwater flow direction)
- Groundwater flow velocity
- Solubility of individual hydrocarbon compounds
- Composition of the NAPL source (mole fraction)

Notwithstanding the relative importance of each of these factors, the concentration of individual hydrocarbon compounds in the groundwater will, within the contamination source zone, very often reach an equilibrium concentration that is equal or close to the multi-component solubility of the compound (Eberhardt and Grathwohl, 2002). This multicomponent solubility $C_{org,i}{}^{sat,mc}$ is described by *Raoult's law* (Schwarzenbach *et al.*, 1993):

$$C_{org,i}^{sat,mc} = C_{org,i}^{sat} \gamma_{org,i} m_{org,i},$$ (2)

where $C_{org,i}{}^{sat}$ is the single-species aqueous-phase solubility (available from tabulated sources, e.g., Schwarzenbach *et al.*, 1993) of the organic compound in question within a mixture of compounds with different physico-chemical properties, $\gamma_{org,i}$ is the activity coefficient of the ith organic compound (typically assumed to be unity) and $m_{org,i}$ is the mole fraction of the ith organic compound within the NAPL mixture. A high groundwater

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flow velocity, among other factors, might result in the kinetically–limited dissolution of NAPL compounds. The simplest model that describes the concentration change of the ith compound in groundwater is

$$R_{org,dis} = \varpi (C_{org,i}^{sat,mc} - C_{org,i}) \, , \tag{3}$$

where $C_{org,i}$ is the concentration of the ith organic compound in the groundwater and ϖ is a mass-transfer rate coefficient that is a product of a mass transfer coefficient and the specific interfacial area between NAPL phase and water. The combination of (2) and (3) applies to arbitrary dissolution rates. Note that ϖ approaches infinity for equilibrium dissolution. In that case $C_{org,i}$ equals $C_{org,i}^{sat,mc}$.

2.3 ADVECTION AND DISPERSION

Once the hydrocarbon compounds have dissolved into the aqueous phase they are subject to both advective and dispersive transport. In contrast to the unsaturated zone, mass transport in the saturated zone of the aquifer occurs mainly in the horizontal direction, i.e., the typical direction of groundwater flow. Within (1) advection and dispersion terms result from averaging microscopic flow and transport processes occurring at the pore scale within a representative elementary volume (REV), leading to a continuum model at the macroscopic level (Bear, 1972). The advection term describes the transport of a dissolved species transported at the same mean velocity as the groundwater, which is the dominant physical process in most field-scale contamination problems within the water–saturated groundwater zone. The dispersion term represents two processes, mechanical dispersion and effective molecular diffusion. Mechanical dispersion results from the fluctuation of the (microscopic) streamlines in space with respect to the mean flow direction and inhomogeneous conductivities within the REV. Molecular diffusion is caused by the random movement of the molecules in a fluid. It is usually negligible compared to mechanical dispersion (Bear and Verruijt, 1987). The (macroscopic) pore velocity v_i in (1) is derived from Darcy's law (Darcy, 1856)

$$v_i = -\frac{K_{ij}}{\theta} \frac{\partial h}{\partial x_j} \, , \tag{4}$$

and the three-dimensional flow equation for saturated groundwater (Bear, 1972):

$$\frac{\partial}{\partial x_i} \left(K_{ij} \frac{\partial h}{\partial x_j} \right) + q_s = S_s \frac{\partial h}{\partial t} \, , \tag{5}$$

where K_{ij} [LT^{-1}] is the hydraulic conductivity tensor, h [L] is the hydraulic head and S_s [L^{-1}] is the specific storativity. Note that the off-diagonal entries of the hydraulic conductivity tensor become zero if the principal components are aligned with the principal axes of the flow domain.

Analytical solution of the advection-dispersion equation exist only for relatively simple cases. Thus, for solving more complicated and realistic cases, e.g., involving heterogeneous aquifers, transient boundary conditions, etc., numerical techniques such as the Finite Difference and the Finite Element Methods (Pinder and Gray, 1977; Wang and Anderson, 1982; Bear and Verruijt, 1987; Istok, 1989) are required.

2.4 SORPTION

Depending on the soil type, sorption, in particular to carbonaceous material (Miller and Weber, 1986, Grathwohl, 1990; Pedit and Miller, 1994, Allen-King *et al.*, 2002), might influence significantly aqueous concentrations of petroleum hydrocarbons. However, as indicated in Section 2.1, in most cases sorption kinetics mainly influences the time it takes for petroleum hydrocarbon plumes to reach a steady-state length. At this stage, adsorption and desorption occur at the same rate and the sorption capacity of the soil generally does not influence the length of the plume, unless the flow-field is transient (Prommer *et al.*, 2002). For quantification of the sorption process in a reactive transport model the rates at which the sorption reactions proceed dictate whether an equilibrium or kinetic sorption model is needed. An equilibrium model is appropriate if the sorption reactions are fast compared to transport whereas in the case of a high flow-velocity and a slow sorption reaction a kinetic model might be required. In many cases slow sorption and desorption is a result of intra-particle diffusion (Grathwohl *et al.*, 2000; Eberhardt and Grathwohl, 2002). Models commonly used to quantify sorption at the field-scale are the:

- Linear sorption equilibrium model
- Freundlich nonlinear equilibrium model
- Langmuir nonlinear equilibrium model

The linear model is the simplest and of the form (Farell and Reinhard, 1994)

$$C_{org,s} = K_D C_{org} ,$$
(6)

where $C_{org,s}$ is the sorbed concentration and K_D is the partition coefficient, which depends upon solid and solute properties (Karickhoff *et al.*, 1979). The Freundlich model is (Grathwohl, 1998):

$$C_{org,s} = K_F C_{org}^{n_F} ,$$
(7)

where K_F is the Freundlich sorption capacity coefficient, and n_F is the Freundlich sorption energy coefficient (Freundlich, 1931; Weber, 1972). Although the literature reports values of n_F between 0.7 and 1.8, typically it is less than and close to unity (Barry and Bajracharya, 1995). The Langmuir model (Schwarzenbach *et al.*, 1993) is

$$C_{org,s} = \frac{K_L C_{org}}{1 + K_L C_{org}} C_{org,s,max} ,$$
(8)

where K_L is the (Langmuir) sorption monolayer capacity coefficient and $C_{org,s,max}$ is the adsorption capacity. Note, that $C_{org,s}$ and $C_{org,s,max}$ are mass fractions, i.e., are defined as the mass of an organic compound that is sorbed to a specific mass of soil [M M^{-1}]. Of the above models, the linear sorption equilibrium model is the simplest and perhaps most commonly used, especially for relatively low contaminant concentrations. However, its inadequacy as a generally applicable model has been often demonstrated (Miller and Weber, 1984; 1986). The Freundlich model is also frequently used and adequately describes most systems. Its power-law form leads to self-sharpening fronts for the typical case of $n_F < 1$ and to increased complexity in the solution methods needed compared to the linear case. The Langmuir model is applicable to cases in which sorption is limited to a finite capacity represented by, for example, a monolayer of solute coverage on the solid phase.

In practice, i.e., when modelling a hydrocarbon plume at field-scale, it is usually very difficult to identify, from measured data at the contaminated site, which model is appropriate in a particular case and decisions need to be made on the basis of results from laboratory batch or column experiments using soils-solid media from the specific contaminated site.

2.5 BIODEGRADATION

Long-term, biodegradation will be the dominant process that decreases the total dissolved mass within a plume generated by dissolution from NAPL sources. As dissolved chemicals they are subject to both abiotic and biotic reactions. However, microbially-mediated (biotic) transformations are the major mechanism of contaminant removal as reaction rates are often accelerated by several orders of magnitude compared to abiotic reaction rates (Schwarzenbach *et al.*, 1993). The degradation of petroleum hydrocarbons occurs as a redox-reaction in which the hydrocarbons are oxidised at a significant rate if:

- One or more aqueous electron acceptors such as O_2, NO_3^-, SO_4^{2-}, CO_2 or electron acceptors in mineral form are readily available,
- A bacterial population capable of using the appropriate hydrocarbon compound is present (at least at low concentration) or a population that can adapt itself to oxidising the hydrocarbon compound, and
- Basic nutrient requirements for the bacteria such as nitrogen, phosphorus or trace metals are present.

Despite the acceleration of reaction rates by bacteria, in most cases the reactions are kinetically controlled, i.e., reactions do not proceed fast enough to allow the application of equilibrium models. If multiple electron acceptors are involved in the biodegradation of organic compounds, their consumption will typically be in the order of their thermodynamic preference, i.e., in the order of decreasing Gibb's free energy of the reaction, unless the electron accepting step is the rate-limiting step. This might happen indeed in the case of mineral form electron acceptors. If oxygen is present in an aquifer, it will be consumed first, followed by nitrate. Under standard conditions iron-reduction or, occasionally, manganese-reduction might occur next (e.g., Stumm and Morgan, 1995), once nitrate is depleted. However, there are also cases where sulfate-reduction might occur first (Postma and Jakobsen, 1996) because the process is thermodynamically more favourable or as a result of kinetic limitations of the dissolution of iron(III) minerals. During aerobic degradation and nitrate-, sulfate-, iron- and manganese-reduction the carbon within the organic contaminants is converted, i.e., mineralised to inorganic carbon, typically in the form of (aqueous) CO_2, but also to carbonate minerals such as calcite ($CaCO_3$) or siderite ($FeCO_3$), depending on the geochemical conditions. The CO_2 produced finally might serve itself as an electron acceptor whereby the carbon is partially transferred to methane (CH_4).

A range of kinetic reaction models of differing complexity is available and has been applied in the past. The simplest way to mathematically describe the mass removal of organic compounds due to biodegradation (with time) is to neglect any dependency of the transformation rate of the organic substance on the concentration of other chemicals or microbial populations. Given these assumptions the most common kinetic degradation model is the first-order model (Bekins *et al.*, 1998):

$$R_{\deg,org} = -k_1 C_{org} \, , \tag{9}$$

where k_1 is a first-order biodegradation rate. This model assumes that the only factor affecting the biodegradation rate is the concentration of substrate present; this may be the case under some circumstances but very often is not. In particular the above-mentioned dependency of the biodegradation process on the presence of one or more electron acceptors is completely ignored by this model. Note that although the first-order model often fits reasonably well to data observed in the laboratory or in the field, the rate constants (k_1) obtained in the fitting process are generally not applicable for predictions at other sites with different hydrochemistry, organic compound mixtures, source zone geometry, etc.

A simple model that takes into account the availability of one (dominant) electron acceptor was proposed by Borden *et al.* (1986). It assumes that an instantaneous biodegradation reaction occurs where both substrate and electron acceptor are present simultaneously, i.e., that the reaction is limited only through the availability of either of the two reactants. Over a time step, Δt, equations for the reactants on the left-hand side are (Barry *et al.*, 2002)

$$R_{deg,org} = -\frac{C_{org}}{\Delta t} \qquad \text{if } C_{org} \leq \frac{Y_{org}}{Y_{EA}} C_{EA} \text{ ,}$$

$$R_{deg,org} = -\frac{Y_{org}}{Y_{EA}} \frac{C_{EA}}{\Delta t} \qquad \text{if } C_{org} > \frac{Y_{org}}{Y_{EA}} C_{EA} \text{ ,} \qquad (10)$$

where C_{EA} is the electron acceptor concentration and Y_{org} and Y_{EA} are stoichiometric coefficients for the organic compound and the electron acceptor, respectively. The first expression in (10) is for the case when the contaminant concentration limits the reaction rate whereas the second applies when the electron acceptor concentration is limiting. A key aspect of the instantaneous reaction model is that the concentration of at least one of the reacting species is zero for all times everywhere in the domain. In contrast to the first-order model, the instantaneous reaction model requires the simultaneous solution of transport and reactions for the electron acceptor, i.e., the problem becomes a multi-species transport problem. For the instantaneous reaction model, the governing transport equation for the second species, the electron acceptor is:

$$\frac{\partial C_{EA}}{\partial t} = \frac{\partial}{\partial x_i}(D_{ij}\frac{\partial C_{EA}}{\partial x_j}) - \frac{\partial}{\partial x_i}(v_i C_{EA}) + \frac{q_s}{\theta}C_{EA,q} + R_{EA,deg} + R_{EA,sorb} \text{ ,} \qquad (11)$$

where $R_{EA,deg}$ and $R_{EA,sorb}$ are the reaction terms that represent concentration changes due to organic compound degradation and due to sorption, respectively.

The reaction term that results from the electron acceptor consumption during biodegradation is given by:

$$R_{EA,deg} = -\frac{Y_{EA}}{Y_{org}} \frac{C_{org}}{\Delta t} \qquad \text{if } C_{org} \leq \frac{Y_{org}}{Y_{EA}} C_{EA} \text{ ,}$$

$$R_{EA,deg} = -\frac{C_{EA}}{\Delta t} \qquad \text{if } \quad C_{org} > \frac{Y_{org}}{Y_{EA}} C_{EA} \text{ ,} \qquad (12)$$

Lu *et al.* (1999) proposed an alternative simple reaction model that incorporates the rate-dependency on both organic substrate and electron acceptor availability. If only a single

electron acceptor is considered, the first-order model in (9) might be replaced by one that incorporates Michaelis-Menten type kinetics, leading to the degradation reaction term:

$$R_{org,deg} = -k_1 C_{org} \frac{C_{EA}}{K_{EA} + C_{EA}}, \tag{13}$$

where K_{EA} is the half-saturation constants of the electron acceptor. Another commonly applied model for the determination of the biodegradation term incorporates a double Michaelis-Menten term:

$$R_{org,deg} = -k_2 \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{EA}}{K_{EA} + C_{EA}}, \tag{14}$$

where K_{org} is the half-saturation constant of the organic substance and k_2 is a (pseudo second-order) reaction constant. The corresponding reaction term for the electron acceptor differs only by a constant factor that depends on the stoichiometry of the degradation reaction.

$$R_{EA,deg} = \frac{Y_{EA}}{Y_{org}} R_{org,deg}, \tag{15}$$

For example, for the degradation of toluene under sulfate-reducing conditions,

$$C_7 H_8 + 4.5\, SO_4^{2-} + 3\, H_2O + 2\, H^+ \longrightarrow 7\, HCO_3^- + 4.5\, H_2S, \tag{16}$$
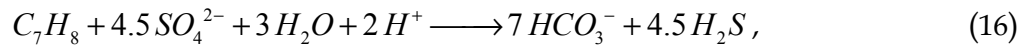
the stoichiometric coefficients Y_{org} and Y_{EA} would be 1 and 4.5, respectively (if molar concentrations are used), thus

$$R_{EA,deg} = 4.5 R_{org,deg}, \tag{17}$$

As mentioned before, the biodegradation of petroleum hydrocarbons might involve multiple electron acceptors that, typically, are used in a sequential manner. Accordingly, the number of transport equations that needs to be solved simultaneously increases further. The appropriate degradation term for the organic compound proposed by Lu *et al.* (1999) then consists of the sum of individual terms for each step included in the (redox-sensitive) degradation process

$$R_{org,deg} = R_{org,O_2} + R_{org,NO_3^-} + R_{org,Fe^{2+}} + R_{org,SO_4^{2-}} + R_{org,CH_4}, \tag{18}$$

where $R_{org,O2}$, $R_{org,NO3-}$, $R_{org,Fe2+}$, $R_{org,SO4-2}$ and $R_{org,CH4}$ represent the contributions from aerobic degradation, denitrification, iron-reduction, sulfate-reduction and methanogenesis, respectively. A common way of modelling the sequential consumption of electron acceptors in multi-species models is to introduce additional terms into (14), such that $R_{EA,deg}$ remains negligible in the presence of thermodynamically more favourable electron acceptors and such that only one of the individual terms on the RHS of (18) differs significantly from 0 at a time. For example, organic compound degradation due to denitrification in the (occasional) presence of oxygen is then modelled as:

$$R_{org,NO_3^-} = -k_{NO_3^-} C_{org} \frac{K_{inh,O_2}}{K_{inh,O_2} + C_{O_2}} \frac{C_{NO_3^-}}{K_{NO_3^-} + C_{NO_3^-}} , \tag{19}$$

where k_{NO3^-} is the rate constant for denitrification and $K_{inh,O2}$ is an inhibition constant for oxygen. For other degradation processes modified forms of (19) exist, as described in more detail by Lu *et al.* (1999).

While the activity of microbes in most cases is directly responsible for the occurrence of significant contaminant mass removal (in contrast to mass removal by abiotic reactions), the rate expressions in (19) and all other previously mentioned models do not explicitly incorporate a rate-dependency on microbial concentrations. Thus, these approaches are not suitable to simulate subsurface systems where temporal changes of bacterial concentrations play an important role. The equations that govern the microbial dynamics are typically based on the assumption that a specific fraction of the degrading organic carbon (within the contaminant) is converted to cell material whereas the remaining fraction is converted to CO_2, i.e., inorganic carbon. The composition of the cell-material is in most cases approximated as $C_5H_7O_2N$. The mass balance equation for the microbial mass, X, describing the change of microbial concentration as a function of time, consists of a growth and a decay term:

$$\frac{\partial X}{\partial t} = \frac{\partial X_{growth}}{\partial t} + \frac{\partial X_{decay}}{\partial t} , \tag{20}$$

whereby microbial growth, i.e., the conversion to cell-material is usually described as (Celia *et al.*, 1989; Kindred and Celia, 1989; Lensing *et al.*, 1994; Essaid *et al.*, 1995; Schäfer *et al.*, 1998; Prommer *et al.*, 1999a; 1999b):

$$\frac{\partial X_{growth}}{\partial t} = v_{max} Y_x \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{EA}}{K_{EA} + C_{EA}} X , \tag{21}$$

and the decay term as

$$\frac{\partial X_{decay}}{\partial t} = -v_{dec} X , \tag{22}$$

where v_{max} is the maximum bacterial uptake rate, v_{dec} is a decay rate constant, Y_x is a stoichiometric factor. Note, that the concentrations are here, for simplicity, defined as mass per volume of (ground)water. The removal rate of the organic compound is proportional to the microbial growth rate. Thus the reaction term $R_{org,deg}$ in (1) can be obtained from:

$$R_{org,deg} = v_{max} \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{EA}}{K_{EA} + C_{EA}} X , \tag{23}$$
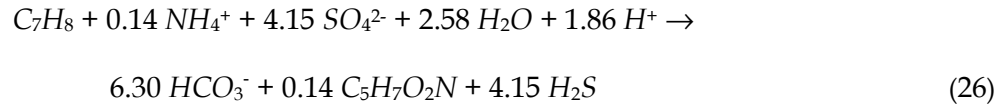
and similarly the consumption of the electron acceptor during microbial growth is:

$$R_{EA,deg} = v_{max} Y_{EA} \frac{C_{org}}{K_{org} + C_{org}} \frac{C_{EA}}{K_{EA} + C_{EA}} X , \tag{24}$$

or

$$R_{EA,deg} = Y_{EA} R_{org,deg} \ . \tag{25}$$

The stoichiometric coefficients have typically been obtained from the reaction stoichiometry such as given by (16). However, Prommer *et al.* (2002) and Barry *et al.* (2002) note that it would be more appropriate to base the stoichiometry on the degradation reactions that explicitly include microbial growth. In the case described by (16), i.e., toluene degradation under sulfate-reducing conditions this would be

$$C_7H_8 + 0.14 \ NH_4^+ + 4.15 \ SO_4^{2-} + 2.58 \ H_2O + 1.86 \ H^+ \rightarrow$$

$$6.30 \ HCO_3^- + 0.14 \ C_5H_7O_2N + 4.15 \ H_2S \tag{26}$$

assuming that 10% of the toluene degraded is diverted to cell material.

It can be seen that (14), which describes the biodegradation reaction term in the case where microbial dynamics are neglected, is very similar to (23). Indeed, the former can be seen as a special case of the latter where

$$k_2 = v_{\max} X \ , \tag{27}$$

i.e., the case where the microbial mass is assumed constant in time (and space). The above formulations for microbial growth apply only to the uptake of a single substrate. In reality, contamination consists rarely of a single organic compound or of a mixture of compounds with identical physico-chemical properties. Thus, several types of models have been proposed to account for the simultaneous uptake of multiple substrates, e.g., benzene, toluene, ethylbenzene and xylene (*BTEX*), by the same bacterial group. The model of Kindred and Celia (1989), for example, that was also, in principle, used, e.g., by Essaid *et al.* (1995), Schäfer *et al.* (1998) and Prommer *et al.* (1999a), suggests for the mass balance of a microbial population:

$$\frac{\partial X_{growth}}{\partial t} = \sum_{n=1,n_{org}} \frac{\partial X_{growth,n}}{\partial t} \ , \tag{28}$$

where, in analogy to (21), each of the growth terms $\partial X_{growth,n}/\partial t$ can be derived from:

$$\frac{\partial X_{growth,n}}{\partial t} = v_{max}^n Y_X^n \frac{C_{org,n}}{K_{org,n} + C_{org,n}} \frac{C_{EA}}{K_{EA} + C_{EA}} \ . \tag{29}$$

The maximum uptake rates v_{max}^n and the stoichiometric factor Y_X^n can differ between different substrates. In this way, it is possible to model degradation of different electron donors at different rates, e.g., when benzene degrades more slowly than toluene.

The above models are based on a conceptual model that assumes that hydrogeochemical changes resulting from hydrocarbon pollution can be approximated sufficiently accurately by modelling solely the *primary* biodegradation reactions, i.e., the oxidation of hydrocarbons coupled to the reduction of one or more electron acceptors. Alternative, more complex model formulations are required where:
• Additional information about the fate of the reaction end products is desired

- The primary reactants are simultaneously involved in other reactions that proceed independently (but at a comparable time-scale) or in response to the biodegradation reactions.

The former point is of particular interest for applying natural attenuation as a remediation scheme. There, the geochemical changes resulting from the biodegradation reactions are used to demonstrate the occurrence of attenuation processes (Wiedemeier *et al.*, 1995). Where the contaminants (e.g., BTEX) are oxidised, this typically includes changes in alkalinity, total inorganic carbon (TIC) and of reduced forms of electron acceptors such as sulfide or ferrous iron. These and other species might undergo further reactions, e.g., they can form mineral precipitates such as siderite ($FeCO_3$), iron sulfide (FeS) or pyrite (FeS_2). The question whether these (secondary) reactions proceed and, if so, at what rate, is more difficult to solve than the more simple cases presented above. The occurrence and rate of these reactions depend, for example, on the pH of the groundwater, which itself changes during biodegradation of organic contaminants. In such cases, the reaction terms within (1) are functions of a large number of chemicals (aqueous species, minerals, etc) and geochemical models that are based on thermodynamic principles are typically used to compute those terms. Among the biodegradation models that include geochemical reactive processes, two different approaches are commonly used to formulate the biodegradation reactions. Brun *et al.* (2002) classified biogeochemical models into:

- Single-step process models, where the oxidation of the organic compound and the electron-accepting step proceed as a single redox reaction at a specific rate, or
- Two-step process models in which it is assumed that the oxidation step is the rate-limiting step and where the electron-accepting step can (but does not have to) be modelled as an equilibrium reaction. The electron-acceptor(s) used during degradation of one or more organic compounds are not defined a priori, but consumed according to their thermodynamic favourability.

Both types of the above biogeochemical transport models are, at present, not applied routinely for the simulation of hydrocarbon pollution problems. However, they are increasingly applied in research projects that aim at an improved understanding of natural and enhanced remediation processes (e.g., Schäfer *et al.*, 2002; Brun *et al.*, 2002; Prommer *et al.*, 2002). Further details on the fundamentals of the (underlying) theory of multicomponent reactive transport can be found for example in Yeh and Triphati (1989) and Steefel and MacQuarrie (1996).

3   NUMERICAL MODELLING

The above mathematical descriptions of physical, chemical and biological processes need for all but the most trivial cases to be incorporated into and solved by numerical models. Below we discuss the steps that are most-often involved in numerical modelling of petroleum hydrocarbon contaminated sites and mention some of the most commonly used modelling tools. An example case is also presented. In tandem with modelling is a process of data gathering, starting with basic background site data, to characterisation data on contaminant distributions, to more detailed measurements depending on the intent of the modelling. This procedure is evident, for example, in Davis *et al.* (1993) and Davis *et al.* (1999).

The application of numerical models of subsurface flow such as MODFLOW (McDonald and Harbaugh, 1988), HST3D (Kipp, 1986), FEMWATER (Yeh *et al.*, 1992) or FEFLOW

(Diersch, 1997) which incorporate information on the hydrological and hydrogeological properties and which can simulate the groundwater flow at a site will typically form the basis for subsequent contaminant transport simulations. It is also the most important step, as any discrepancy between the flow model and reality will be propagated to the transport model. In many cases, a proper groundwater flow model itself can already provide useful information. The flow modelling step provides a process-based interpretation and interpolation of the hydraulic heads recorded at observation wells. It might be used for the delineation of (sub-) catchments, capture zones (e.g., of extraction wells) and for the development of a model-based design of purely hydraulic remediation measures (e.g., *pump and treat* designs). Add-on packages of flow models that simulate purely advective transport might be used for the prediction of the flow path of a plume centre and to estimate how fast the leading edge of a contamination would migrate in a *non-reactive* case, i.e., if no biodegradation or sorption occurred. The latter point, however, concerns only the early stages of a pollution problem (Stage 1). Modelling packages such as PMPATH (Chiang and Kinzelbach, 2000) or MODPATH (Pollock, 1994) allow predictions of the contaminant flow path and travel times of *non-reactive* contaminants using particle-tracking algorithms.

The first step in building a site-specific groundwater flow model is, based on a preliminary site characterisation, the development of a *conceptual* hydrological and hydrogeological model. At this stage, all available geologic and hydrographic information is collated and analysed. The conceptual model formulates qualitatively:

- The general groundwater flow direction;
- Boundaries that might be used as boundaries in the numerical model, such as (subsurface) catchment boundaries and (dividing) streamlines;
- Which stratigraphic layer(s) are more and which ones are less or much less permeable, which layer(s) are suitable to form a boundary in the numerical model; and
- The fluxes into and out of a chosen (model) domain and how to determine/estimate these fluxes quantitatively.

The conceptual model needs then to be translated into a numerical model by:

- Spatially discretising the model domain;
- Allocating measured or estimated hydrogeological aquifer parameters such as conductivity or porosity;
- Allocating/defining initial, starting values, e.g., hydraulic heads;
- Allocating/defining static or time-dependent boundary conditions, e.g., recharge; and
- Model calibration using observed/monitored data (e.g., hydraulic heads) by variation of parameters for values that are not well known.

Details of this procedure can be found in many groundwater hydrology specific textbooks such as by Freeze and Cherry (1979) or Fetter (1999) or, more modelling specific texts such as that by Anderson and Woessner (1992) and Chiang and Kinzelbach (2000).

3.1   NON-REACTIVE TRANSPORT MODELLING

Based on a (calibrated) groundwater flow model, the next step in a sound modelling study is a non-reactive advective-dispersive transport model. In particular, if one or more of the organic compounds are recalcitrant to biodegradation (or apparently degrading at slow rates), monitoring data for this compound can be used to quantify, i.e., estimate or calibrate the transversal dispersivity of the aquifer, a key parameter that has a controlling

influence on the length of a contaminant plume. Other important roles of the non-reactive model might be:

- Identification of errors in the data and parameter preparation/allocation; and
- Identification of the extent dilution might be responsible for a decrease in pollutant concentrations downstream of a contamination source

Note that the conceptual model (for example the dimensionality of the model) might not need to be the same as in the flow model. For example, a cross-sectional transport model might be constructed along a flow path that was determined in the previous (flow/particle tracking) step.

In principle a wide range of different transport models are suitable for this step. However, over a number of years the MODFLOW-based transport simulator MT3D (Zheng, 1990) has evolved as a quasi-standard groundwater transport model. The reason for this being its modular construction, its robustness and its good documentation, including source code availability. Consequently, it is used by several reactive transport simulators that employ the (newer) multi-species version MT3DMS (Zheng and Wang, 1999) as a module for simulating advective-dispersive transport.

3.2   BIODEGRADATION MODELLING

The above-mentioned extension of the original single-species transport code MT3D to the multi-species transport simulator MT3DMS provided the starting point for the development of a number of models that simulate coupled hydrological transport of multiple chemical species and the chemical reactions among these species. For example, RT3D (Clement, 1997) couples the implicit ordinary differential equation (ODE) solver LSODA to solve arbitrary kinetic reaction problems. RT3D provides a number of pre-defined reaction packages, e.g., for biodegradation of oxidisable contaminants consuming one or more electron acceptors. However, most importantly, users can also define their own reaction packages in order to adapt the numerical model to a site-specific conceptual hydrochemical model. This means that "non-standard" kinetic rate formulations for biodegradation reactions, as per some of the model formulations presented in Section 2.5, can be implemented reasonably quickly into the RT3D model. Other MT3D/MT3DMS-based reactive transport models that simulate the fate of specific pollutants, including BTEX, by solving purely kinetic biodegradation reactions, i.e., the primary biodegradation reactions, are listed in Table 1. Of course, non-MT3DMS based biodegradation models do also exist. However, many of them lack integration into a suitable, user-friendly graphical environment, making them less useful for routine applications.

Table 1: Examples of available biodegradation models

Model	Reference
RT3D	Clement (1997)
MT3D99	SSPA (1999), http://www.sspa.com
BIOREDOX	Carey *et al*. (1999)
SEAM3D	Waddill and Widdowson (1998)

Multispecies biodegradation models require the definition of initial and boundary conditions for each species included. In most cases the initial conditions are defined by the concentrations of the unpolluted zone (background concentrations). Modelling of the pollution source can be handled in various ways, for example as:

- A mass transfer (dissolution) process as indicated in Section 2.2;
- A fixed concentration boundary condition, i.e., the contaminant concentration in the source area is fixed; and
- A flux boundary condition where the contaminant is added to the aquifer at a predefined mass per unit time, independent of the actual groundwater flow velocity.

The first option will typically provide the solution that reflects best the processes at a contaminated site. More details on applied reactive transport modelling are given in, e.g., Zheng and Bennett (2002).

3.3 BIOGEOCHEMICAL MODELLING

A range of numerical simulators is available that can simultaneously account for both biodegradation and geochemical reactions. In contrast to the above-mentioned biodegradation models, the transport equation in so-called 'multi-species' models is typically not solved separately for each chemical species but for total aqueous component concentrations (e.g., Yeh and Tripathi, 1989; Steefel and MacQuarrie, 1996). While it is not possible here to discuss the relative merits of each of the simulators, a list of suitable models for these types of applications is given in Table 2.

Table 2: Examples of available biogeochemical transport models

Model	Reference
CRUNCH	Steefel and Yabusaki (1996), Steefel (2001)
PHT3D	Prommer *et al*. (2002, 2003)
PHAST	Parkhurst *et al*. (1995)
MIN3P	Mayer (1999)
TBC	Schäfer *et al*. (1998)
HBGC123D	Salvage (1998), Salvage and Yeh (1998)

3.4 PRE- AND POST-PROCESSING TOOLS

For routine model applications pre- and post-processing of model input and output data might comprise the majority of effort for a modelling exercise. Over the past few years significant advances have been made in incorporating GIS-type features into the most commonly used graphical user interfaces (GUIs), as well as with respect to rapid three-dimensional visualisation. A list of the most popular GUIs is given in Table 3. No attempt was made to rate them, as the suitability of each product depends on a range of factors such as available hardware and whether the GUI supports a specific biodegradation model.

Table 3: Most commonly used GUIs for MODFLOW/MT3D based flow and transport models

| GUI	Reference
PMWIN	http://www.iesinet.com
	Chiang and Kinzelbach (2000)
Visual Modflow	http://www.visual-modflow.com
GMS	http://www.ems-i.com
Groundwater Vistas	http://www.groundwater-vistas.com
Argus ONE	http://www.argusint.com

3.5   PARAMETER ESTIMATION TOOLS

For many modelling exercises the process of model calibration is typically a tedious, time consuming part of the overall project. Thus, the use of parameter estimation tools is becoming increasingly popular, though so far largely confined to applications related to groundwater flow models, i.e., to the estimation of flow model parameters such as the hydraulic conductivity. A list of the most commonly used tools is given in Table 4.

Table 4: Most commonly used parameter estimation tools

Software	Reference
PEST	http://www.sspa.com
UCODE	http://water.usgs.gov/software/ucode.html
MODFLOW2000	http://water.usgs.gov/software/modflow-2000.html

3.6   MODELLING EXAMPLE

As an illustrative example for a biogeochemical transport modelling scenario, the results from the simulation of the first stages (stage 1 and 2 according to the classification in Section 2.1) of a naturally degrading BTEX plume are shown. The MT3DMS-based model PHT3D (see Section 3.3) was used for the simulation. The modelled case includes a BTEX plume that originates from a NAPL source (as per Davis *et al*., 1999) and undergoes natural attenuation in a sequence of different redox conditions (aerobic, nitrate-, iron- and sulfate-reducing conditions). Details can be found in Prommer *et al*. (2000). The groundwater is assumed to be initially uncontaminated and in geochemical equilibrium. The hydraulic system was computed with MODFLOW. Oxygen, nitrate and sulfate are soluble electron acceptors. Additional oxidation capacity is provided by goethite (FeOOH). Other minerals included in the simulations are magnetite (Fe_3O_4) and pyrite (FeS_2), both potential end products of degradation reactions. The recharge water is assumed to have the same chemical composition as the uncontaminated groundwater. The contamination source is, for simplicity, modelled as an immobile NAPL phase located near the water table close to the upstream end of the model domain. The multi-component NAPL consists of six organic compounds including the BTEX compounds. The dissolution of these compounds was modelled according to equ. (3). Bacterial activity was simulated for three different bacterial groups: facultative anaerobes/denitrifying bacteria, iron-reducing and sulfate-reducing bacterial groups were included. The total time simulated was 2000 days. Dispersivities of 0.5 m, 0.05 m and 0.01 m were assumed for the longitudinal, horizontal transversal and vertical transversal directions, respectively.

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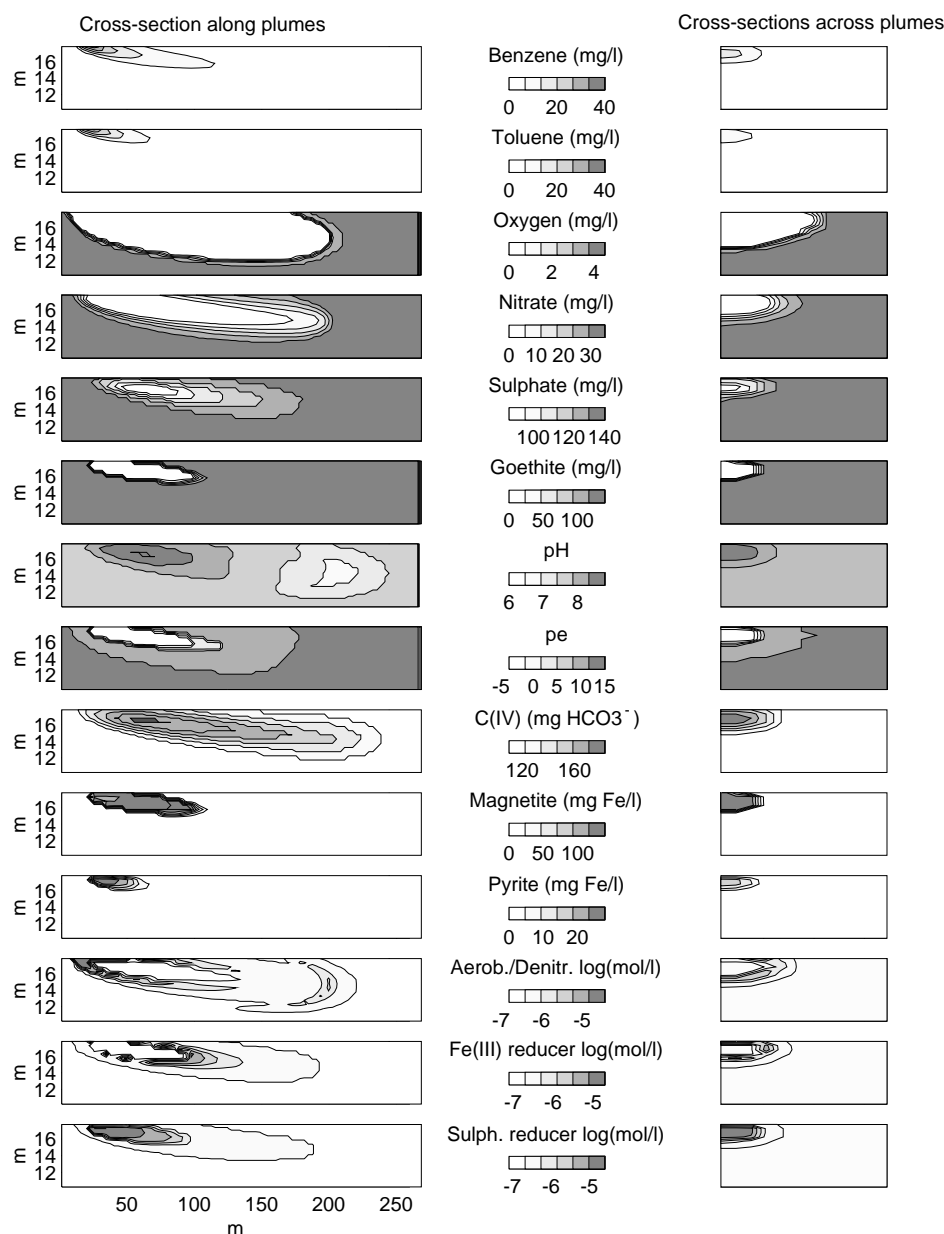
Figure 2. Concentrations of hydrocarbon compounds (e.g., benzene, toluene), electron acceptors (e.g., oxygen, sulfate), mineral phases (e.g., geothite), and bacterial groups (e.g., aerobic/denitrifiers) after a simulation time of 800 days. Cross sections along the plumes are for the plume centreline; half cross sections across the plumes are shown for x = 52.5 m, which is 33 m downgradient of the NAPL source.

Figure 2 summarises some of the output from the simulation. Once dissolved from the NAPL source, the organic compounds migrate downstream while being either partly or completely degraded by a series of biogeochemical reactions. Due to their higher (multi-component) solubility, only the BTEX compounds reach significant concentrations in the dissolved phase (see benzene and toluene plot in Figure 2, other compounds are not shown). Driven by aquifer recharge, the plume centre moves downward toward the base of the aquifer with increasing distance. After 2 years, the mass of dissolved toluene peaks

as dissolution from the NAPL phase and degradation of dissolved toluene reach equilibrium (see Figure 3). No such equilibrium is reached for benzene within the model domain as benzene was assumed to degrade only under aerobic conditions and not enough oxygen was available. This can be seen in Figure 3 where the simulated total masses of dissolved toluene and benzene in the aquifer are plotted. Results are shown for two 3D cases with two different NAPL source widths, *sw* (1.5 m and 4.5 m) and a 2D case (width 1.5 m). For comparison, the appropriate "non-reactive" cases where the biodegradation and geochemical equilibrium modules but not the NAPL dissolution module were switched off are also plotted. The difference between the 2D and 3D plots demonstrate the influence of transversal hydrodynamic mixing on the total (dissolved) contaminant mass. In the toluene case with a source width of 1.5 m, the total mass is only approximately 65% of the mass of the comparable 2D simulation. The benzene plots of the integrated masses from the "nonreactive cases" show a slow decrease of total mass after the maximum has been reached. This indicates that the benzene dissolution rate is decreasing due to a change of the mole fraction of benzene within the NAPL mix.
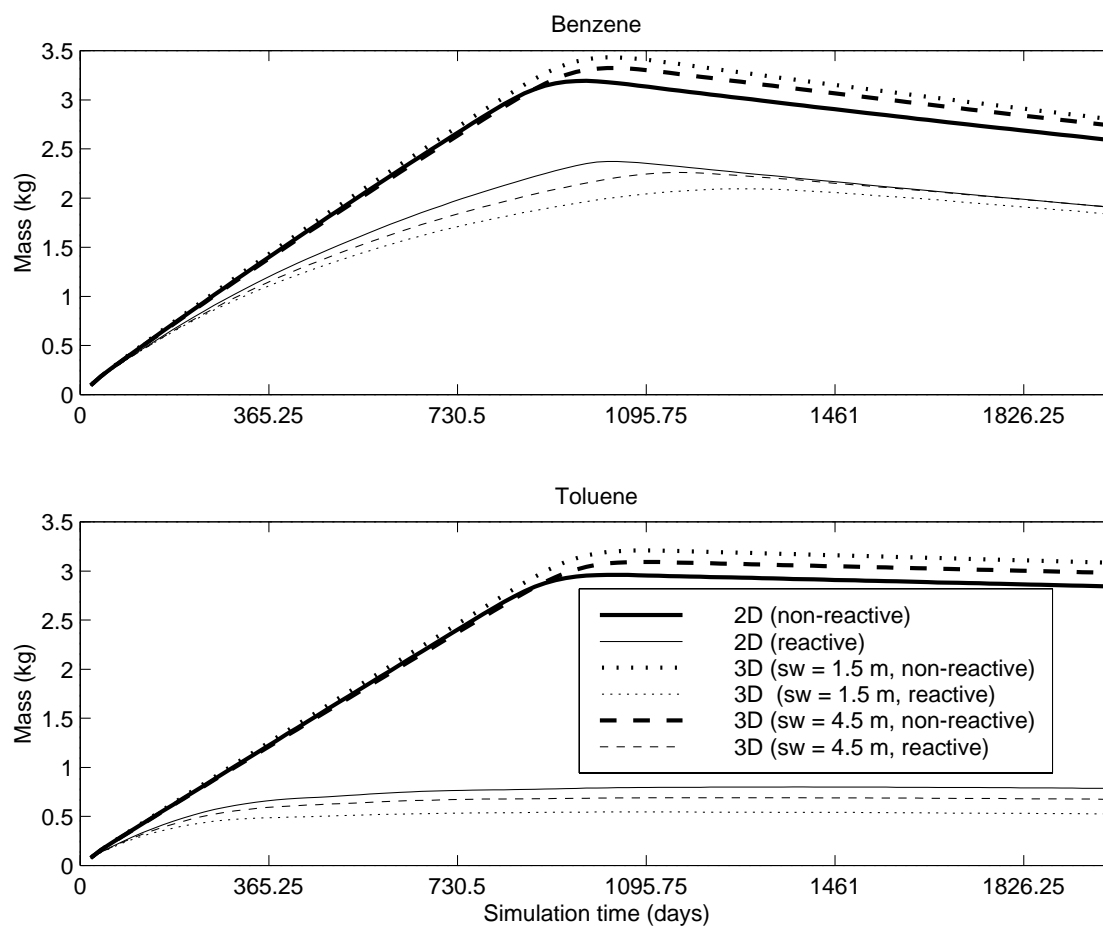

Figure 3. Integrated total dissolved contaminant mass in the plume; sw = width of source; results of cases with sw = 4.5 were scaled by the factor 1.5m/4.5m.

The mineralisation of the organic compounds leads to a zone (i.e., a plume) enriched in inorganic carbon (see C(IV)-plot in Figure 2) and a reduced geochemical milieu (see pe plot in Figure 2). Electron acceptors are used sequentially, leading locally to complete depletion of oxygen, nitrate and goethite (see Figure 2) and partial depletion of sulfate. The zone depleted in oxygen has the largest extent (both along the plume direction and laterally), followed by nitrate and goethite (Figure 2). However, as a consequence of aquifer recharge, i.e., also recharge of oxygen, the frontal end of the zone depleted in

oxygen does not travel as fast as the zone enriched in inorganic carbon. Aerobic degradation and reduction of nitrate cause a decrease in pH whereas pH increases under iron- and sulfate-reducing conditions. In the model scenario presented, a low pH zone is created only at the front of the "reactive zone" (Figure 2), whereas in the rest of the "reactive zone" an increased pH is found. In the model scenario presented, magnetite is the dominant iron species where goethite has been reduced, however, some reduced iron reacts with the sulfide produced in the sulfate-reducing zone and precipitates as pyrite (Figure 2).

The plots for the simulated bacterial concentrations indicate the locations of ongoing degradation and the appropriate dominant reduction reactions. As can be seen in the appropriate plots for aerobes/denitrifying and for iron-reducing bacteria (Figure 2), the bacterial activity related to locally completely depleted components/minerals is confined to the fringes of these zones. However, as oxygen and nitrate are replenished from upstream, the contamination source zone is the most active zone while the iron-reducing zone travels downstream. Sulfate-reducing bacteria dominate within the inner plume core where all other electron acceptors except sulfate have been depleted.

4   SUMMARY AND PRACTICAL IMPLICATIONS

Modelling the fate of petroleum hydrocarbons in groundwater consists of a series of sequential steps. Of course, each site has its own characteristics with respect to the:

* contaminant composition/mixture;
* contamination history and available details of this history;
* availability of hard and soft data;
* hydrogeology; and
* hydrochemistry and mineralogy.

and thus the modelling methodology will need to be adapted to individual, site-specific requirements.

However, the steps listed in Table 5 might serve as a general guideline/checklist that provides a basis for a site-specific schedule of a modelling study.

The importance of a correct conceptual model of flow characteristics and biogeochemical interactions must be highlighted again. Ideally, each of the modelling steps needs testing and validation against data from the site. On the other hand, if modelling is carried out at an early stage during the assessment of a contaminated site its main role might be the identification of gaps in available data (or knowledge in general) for a site or the behaviour of a specific contaminant.

Note, that not all the steps outlined in Table 5 may be required and/or feasible in all modelling studies. However, consideration of each step is recommended where full biogeochemical modelling assessments are to be carried out. As the basis for all subsequent steps, a sound conceptual understanding and model for a site is fundamental, as is adequate site data to translate such a conceptual model into a formalised modelling framework as outlined here.

Table 5: Checklist of major steps in a reactive transport modelling study

Step	Activity
1	Initial assessment of the existing data/situation to be modelled – initial identification of potential physical and chemical interactions including initial 'hand' calculations of flow rates and initial 'electron balance', where possible.
2	Compilation of a first conceptual model for the contaminated site.
	In particular, detailed depth profile data (from multi-level sampling devices) can help formulate the conceptual model for a site. Care is needed as to the source conditions for the plume source – NAPL concentrations, source dimensions. They will strongly influence plume characteristics and the longevity of the contamination source.
3	Formulation of a modelling strategy (dimensionality, spatial and temporal resolution, process-detail of modelled physical and chemical processes) and formulation of the questions that the model(s) will need to answer.
	When deciding upon the process detail of the chemical processes, i.e., the reaction model, remember that:
	Components of petrol products, including benzene, toluene, ethylbenzene, naphthalene, etc do not degrade at similar rates or under similar geochemical conditions – for example, often toluene will degrade more readily than benzene; and
	Zero-, first-order or any non-specific third-party reaction rate should only be used where groundwater and aquifer mineral geochemical signatures are similar.
4	Selection of appropriate modelling tools, depending on available data, questions to be answered and available time.
5	Setup of a flow model, including spatial discretisation of the model domain into grid cells, definition of boundary conditions, temporal discretisation of the simulation period, e.g., to account for seasonal recharge dynamics, time stepping, data input.
6	Data preparation of observation data to allow for comparison with simulation results during flow model calibration.
7	Calibration of steady state or transient flow model using existing observations of hydraulic heads. Model calibration might be carried out by hand (trial-and-error) or using parameter estimation tools.
8	Testing of the plausibility of simulated flow velocities, flow path and water budgets.
9	Ideally (though in most cases not feasible) application/testing of the model for data that have not been used during model calibration.
10	Identification of data gaps which hamper the reliability of the calibrated model. Preparation of plans for acquisition of additional data, where feasible.
11	Setup of a transport model for advective/dispersive non-reactive transport of a single species.
	Note, that the model domain of the transport model might be a sub-domain of the flow model and that the model might have a different dimensionality.
12	Initial model runs of the above single-species model to assess and fix numerical problems that result from pure physical transport (e.g., convergence problems, oscillations, numerical dispersion).
13	Crude adjustment of (longitudinal and transversal) dispersivity values to govern major plume characteristics.
14	Use of initial transport modelling results as a (further) plausibility control for the flow model.
	For example, a conservative, i.e., non-reactive species (tracer) in the model should

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Step	Activity
	travel approximately at the conceptual groundwater flow velocity. Where necessary, adjustments of the conceptual and numerical flow model.
15	If existing reaction modules appear unsuitable – preparation of a site-specific reaction module, testing of the reaction module/package for simplistic, non site-specific flow configurations.
16	Data preparation of observation data to allow for comparison with simulation results during transport model calibration.
17	If a multi-component reactive transport model is employed –- Batch-type geochemical equilibrium modelling of background water chemistry to assess aqueous phase – mineral equilibria of the uncontaminated aquifer. Batch-type reaction simulations to assess geochemical changes in response to the mineralisation of hydrocarbons.
18	Setup of multi-species, multi-component transport model, including first estimate of reaction parameters (from literature), where necessary.
19	Biogeochemical transport modelling simulations. Adjustment of reaction parameters to match observed plume patterns – Plume length/concentrations of hydrocarbons, redox zonation/concentrations of dissolved electron acceptors, occurrence of reaction products.
20	Sensitivity analysis of calibrated model.
21	Computation of detailed mass budgets for dissolved species/components.
22	Predictive model runs to (i) estimate the long-term contaminant plume evolution and the associated risk for receptors (ii) answer 'what if' – type questions. Estimates of future stresses are needed to perform a predictive simulation Care is needed when deciding on 'future' source conditions for predictive runs – the distribution and composition of NAPL may be highly variable depending on its weathered status and the location of the water table in the subsurface. Note – assuming a large lateral dispersivity can lead to predictions of short plumes due to unrealistic (over-predicted) mixing/dilution of reactants (hydrocarbons and electron acceptors) and inducement of biodegradation in those zones.
23	Reporting and documenting the modelling study

5   ACKNOWLEDGEMENT

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REFERENCES

Alexander M (1994) Biodegradation and bioremediation, p. 71-98. Academic Press, A division of Harcourt Brace & Company, New York.

Allen-King RM, Grathwohl P, Ball WP (2002) New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments and rocks. *Adv. Wat. Resour.* 25, 985-1016.

Anderson MP, Woessner WW (1992) *Applied Groundwater Modeling Simulation of Flow and Advective Transport.* Academic Press.

Barry DA, Bajracharya K (1995) Muskingum-Cunge solution method for solute transport with equilibrium Freundlich reactions. *J. Contam. Hydrol.* 18, 221-238.

Barry DA, Prommer H, Miller CT, Engesgaard P, Brun A, Zheng C (2002) Modelling the fate of oxidisable organic contaminants in groundwater. *Adv. Water. Resour.* 25, 899-937.

Bear J (1972) *Dynamics of Fluids in Porous Media.* Dover Publications Inc., New York.

Bear J, Verruijt A (1987) *Modeling Groundwater Flow and Pollution.* D. Reidel Publishing Co.

Bekins BA, Warren E, Godsy EM (1998) A Comparison of zero-order, first-order, and Monod biotransformation models, *Ground Water* 36, 261-268

Borden RC, Bedient PB, Lee MD, Ward CH, and Wilson JT (1986) Transport of dissolved hydrocarbons influenced by oxygen-limited biodegradation, 2. field application. *Water Resour. Res.* 22, 1973-1982.

Brun A, Engesgaard P, Christensen TH, Rosbjerg D (2002) Modelling of transport and biogeochemical processes in pollution plumes: Vejen landfill, Denmark. *J. Hydrol.* 256, 228-247.

Carey GR, Van Geel PJ, Murphy JR (1999) BIOREDOX-MT3DMS: A coupled biodegradation-redox model for simulating natural and enhanced bioremediation of organic pollutants. Version 2.0 User's guide. Conestoga-Rovers & Associates, Waterloo Canada.

Celia MA, Kindred JS, Herrera I (1989) Contaminant transport and biodegradation: 1. a numerical model for reactive transport in porous media. *Water Resour. Res.* 25, 1141-1148.

Chiang W-H, Kinzelbach W (2000) *3D-Groundwater modeling with PMWIN: A Simulation System for Modeling Groundwater Flow and Pollution.* Springer-Verlag.

Clement TP (1997) *RT3D - A Modular Computer Code for Simulating Reactive Multi-species Transport in 3-Dimensional Groundwater Aquifers.* Battelle Pacific Northwest National Laboratory Research Report, PNNL-SA-28967.

Darcy, H (1856) Les Fontaines Publiques de la Ville de Dijon. Dalmont, Paris.

Davis GB, Barber C, Power TR, Thierrin J, Patterson BM, Rayner, JL, Wu Q (1999) The variability and intrinsic remediation of a BTEX plume in anaerobic sulfate-rich groundwater. *J. Contam. Hydrol.* 36, 265-290.

Davis GB, Johnston CD, Thierrin J, Power TR, Patterson BM (1993) Characterising the distribution of dissolved and residual NAPL petroleum hydrocarbons in unconfined aquifers to effect remediation. *AGSO Journal of Australian Geology & Geophysics* 14, 243-248.

Diersch H-JG (1997) *Interactive, Graphics-based Finite-Element Simulation System FEFLOW for Modelling Groundwater Flow. Contaminant Mass and Heat Transport Processes. User's Manual Version 4.6. WASY.* Institute for Water Resources Planning and System Research Ltd., Berlin.

Eberhardt C, Grathwohl, P (2002) Time scales of organic contaminant dissolution from complex source zones: coal tar pools vs. blobs. *J Contam. Hydrol.* 59, 45-66.

Essaid HI, Bekins BA, Godsy EM, Warren E, Baedecker MJ, Cozarelli IM (1995). Simulation of aerobic and anaerobic biodegradation processes at a crude-oil spill site. *Water Resour. Res.* 31, 3309-3327.

Farrell J, Reinhard M (1994) Desorption of halogenated organics from model solids, sediments, and soil under unsaturated conditions. 1. Isotherms. *Environ. Sci. Technol.* 28, 53-62.

Fetter CW (1999) *Contaminant Hydrogeology,* 2nd ed. Prentice Hall Publishers.

Freeze RA, Cherry JA (1979) *Groundwater.* Prentice-Hall, N.J.

Freundlich H (1931) Of the adsorption of gases. section II. kinetics and energetics of gas adsorption. *J. American Chemi. Soc.* 195-201.

Grathwohl P (1990). Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: implications of K_{oc} correlations. *Environ. Sci. Technol.* 24, 1687-1693.

Grathwohl P (1998) *Diffusion in Natural Porous Media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics.* Topics in Environmental Fluid Mechanics. Kluwer, Boston.

Grathwohl P, Klenk ID, Eberhardt C, Maier U (2000) Steady state plumes: mechanisms of transverse mixing in aquifers. In: *Contaminated Site Remediation: From Source Zones to Ecosystems* (ed. by C.D. Johnston), Proc. 2000 Contaminated Site Remediation Conference, Melbourne, 4-8 December 2000, 459-466.

Imhoff PT, Jaffé PR, Pinder GF (1993) An experimental study of the complete dissolution of a nonaqueous phase liquid in saturated porous media. *Water Resour. Res.* 30, 307-320.

Istok JD (1989) *Groundwater Modeling by the Finite Element Method.* American Geophysical Union, *Water Resources Monograph*; 13.

Karickhoff SW, Brown DS, Scott TA (1979) Sorption of hydrophobic pollutants on natural sediments. *Water. Res.* 13, 241-248.

Kipp KL, Jr (1986) *HST3D-A Computer Code for Simulation of Heat and Solute Transport in 3D Ground-Water Flow Systems.* U.S. Geological Survey Water-Resources Investigations Report 86-4095.

Kindred JS, Celia MA (1989) Contaminant transport and biodegradation: II. Conceptual model and test simulations. *Water Resour. Res.* 25, 1149-1160.

Lensing HJ, Vogt M, Herrling B (1994) Modeling of biologically mediated redox processes in the subsurface. *J. Hydrol.* 159, 125-143.

Lu G, Clement TP, Zheng C, Wiedemeier TH (1999) Natural attenuation of BTEX compounds, model development and field-scale application. *Ground Water* 37, 707-717.

Mayer KU (1999) A numerical model for multicomponent reactive transport in variably saturated porous media. PhD Thesis, Department of Earth Sciences, University of Waterloo.

McDonald JM, Harbaugh AW (1988) *A Modular 3D Finite Difference Ground-Water Flow Model.* Technical report, U.S. Geological Survey techniques of Water-Resources Investigations.

Miller CT, Poirier-McNeill MM and Mayer AS (1990) Dissolution of trapped nonaqueous phase liquids: Mass transfer characteristics. *Water Resour. Res.* 26, 2783-2796.

Miller CT, Weber Jr WJ (1984) Modeling organic contaminant partitioning in ground water systems. *Ground Water* 22, 584-592.

Miller CT, Weber Jr WJ (1986) Sorption of hydrophobic organic pollutants in saturated soil systems. *J. Contam. Hydrol*. 1, 243-261.

Parkhurst DL, Engesgaard P, Kipp KL (1995) Coupling the geochemical model PHREEQC with a 3D multi-component solute transport model. In *Fifth Annual V.M. Goldschmidt Conference*, Penn State University, University Park Pennsylvania, USA, May 1995.

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC – A computer program for speciation, reaction-path, 1D-transport, and inverse geochemical calculations: Technical Report 99-4259, US Geol. Survey Water-Resources Investigations Report.

Pedit, JA, Miller CT. (1994) Heterogeneous sorption processes in subsurface systems, 1. Model formulations and applications. *Env. Sci. Technol*. 28, 2094-2104.

Pinder GF, Gray WG (1977) *Finite Element Simulation in Surface and Subsurface Hydrology*. Academic Press, London, 295 pp.

Pollock DW (1994) *User's Guide for MODPATH/MODPATH-PLOT, Version 3: A Particle Tracking Post-processing Package for MODFLOW, the U.S. Geological Survey Finite-difference Ground-water Flow Model*. U.S. Geological Survey Open-File Report 94-464, 234 p.

Postma D, Jakobsen R (1996) Redox zonation: equilibrium constraints on the $Fe(III)/SO_4$-reduction interface. *Geochim. Cosmochim. Acta*, 60, 3169-3175.

Prommer H (2002a) *PHT3D – A Reactive Multicomponent Transport Model for Saturated Porous Media. User's Manual Version 1.0.* Technical report of Contaminated Land Assessment and Remediation Research Centre, The University of Edinburgh, Edinburgh, UK.

Prommer H, Barry DA, Davis GB (1999b) A one-dimensional reactive multi-component transport model for biodegradation of petroleum hydrocarbons. *Env. Modelling Softw*. 14, 213-223.

Prommer, H, Barry DA, Davis GB (2002) Influence of transient groundwater flow on physical and reactive processes during biodegradation of a hydrocarbon plume. J. Contam. Hydrol. 59, 113-131.

Prommer H, Barry DA, Zheng C (2003) MODFLOW/MT3DMS based reactive multi-component transport model. *Ground Water* 42(2), 247-257.

Prommer H, Davis GB, Barry DA (1999a) Geochemical changes during biodegradation of petroleum hydrocarbons: field investigation and modelling. *Org. Geochem.* 30, 423-435.

Prommer H, Davis GB, Barry DA (2000) Biogeochemical transport modelling of natural and enhanced remediation processes in aquifers. *Land Contamination & Reclamation* 8, 217-223.

Salvage KM (1998) Reactive contaminant transport in variably saturated porous media. Biogeochemical model development, verification and application. PhD thesis, Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, PA 16802.

Salvage KM, Yeh GT (1998) Development and application of a numerical model of kinetic and equilibrium microbiological and geochemical reactions (BIOKEMOD). *J. Hydrol.* 209, 27-52.

Schäfer D, Schäfer W, Kinzelbach W (1998) Simulation of processes related to biodegradation of aquifers 1. structure of the 3D transport model. *J. Contam. Hydrol.* 31,167-186.

Schwarzenbach RP, Gschwend PM, Imboden DM (1993) Environmental Organic Chemistry, John Wiley & Sons, Inc. New York, 681p.

SSPA (SS Papadopulos and Associates, Inc.) (1999) MT3D99. /www.sspa.com/products/Mt3d99.htm.

Steefel CI (2001) *GIMRT, Version 1.2: Software for Modeling Multicomponent, Multidimensional Reactive Transport. Users Guide.* Technical Report UCRL-MA-143182, Lawrence Livermore National Laboratory, Livermore, California, 2001.

Steefel CI, MacQuarrie KTB (1996) Approaches to modeling of reactive transport in porous media. In: Reactive Transport in Porous Media (PC Lichtner, CI Steefel, and EH Oelkers, eds.) Min. Soc. of America.

Steefel CI, Yabusaki SB (1996) *OS3D/GIMRT, Software for Multicomponent-Multidimensional Reactive Transport, User Manual and Programmers Guide.* PNL-11166. Technical report, Pacific Northwest National Laboratory.

Stumm W, Morgan JJ (1995) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. 3rd Ed.*, John Wiley & Sons.

Waddill DW, Widdowson MA (1998) Three-dimensional model for sub-surface transport and biodegradation. *ASCE J. Environ. Eng.* 124, 336-344.

Wang H, Anderson M (1982) *Introduction to Groundwater Modeling: Finite Difference and Finite Element Methods*. Freeman.

Weber Jr WJ (1972) *Physicochemical Processes for Water Quality Control.* John Wiley and Sons, New York.

Wiedemeier TH, Wilson JT, Kampbell DH, Miller RN, Hansen JE (1995) *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contaminant Dissolved in Groundwater.* Air Force Center for Technical Excellence, Technology Transfer Division 1 & 2. Brooks A.F.B., TX.

Yeh GT, Sharp-Hansen S, Lester B, Strobl R, Scarbrough J (1992) *3DFEMWATER/3DLEWASTE: Numerical Codes for Delineating Wellhead Protection Areas in Agricultural Regions Based on the Assimilative Capacity.* Environmental Protection Agency, GA.

Yeh G-T, Tripathi VS (1989) A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resour. Res.* 25, 93-108.

Zheng C (1990) *MT3D, A Modular Three-Dimensional Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems.* Report to the Kerr Environmental Research Laboratory, US Environmental Protection Agency, Ada, OK.

Zheng C, Bennett GD (2002) *Applied Contaminant Transport Modeling, 2nd Edition*. Wiley, 621 pp.

Zheng C, Wang PP (1999) *MT3DMS: A Modular Three-Dimensional Multispecies Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems. Documentation and User's Guide.* Contract Report SERDP-99-1, U.S. Army Engineer Research and Development Center, Vicksburg, MS.