

Institut für Hydrologie
Albert-Ludwigs Universität Freiburg i. Br.

Thermodynamic and kinetic
degradation reactions of organic
substances in groundwater modelled
with PHREEQC

Jakob Holch

Supervisors:

Prof. Dr. Christian Leibundgut, Christoph Kuells

Mentor:

D. Christoph Kuells

Co-mentor:

Gunter Adolph

Freiburg i. Br., June 2008

Acknowledgment

I appreciate to Prof. Dr. Christian Leibundgut, Dr. Christoph Kuells and Gunter Adolph for the excellent mentoring of this diploma thesis. Special acknowledgment goes to Dr. Christoph Kuells for motivation and the distinguished attendance in scientific advices and to Gunter Adolph for the competent counseling during the elaboration of this paper. Furthermore I am deeply thankful for my father for the co-funding of the study especially during the diploma period.

Contents

Contents	III
List of Figures	V
List of Tables	VII
Summary	IX
Zusammenfassung	XI
1 Introduction	1
2 Problem statement	3
3 State of the Art	5
4 Theory	19
4.1 Introduction	19
4.2 Equilibrium chemistry	19
4.2.1 The law of mass action	19
4.2.2 Temperature dependency of the mass action constant	20
4.2.3 Concentration and activity	20
4.2.4 Calculation of saturation states	21
4.3 Fundamentals of redox chemistry	23
4.4 Kinetics of geochemical reactions	25
4.5 Degradation of carbon in groundwater environments	27
4.6 Kinetics of biodegradation	31
5 PHREEQC	35
5.1 Redox process modelling with PHREEQC	36
5.2 Rate expressions within PHREEQC	36
5.3 Examples of PHREEQC applications	36
6 Application of PHREEQC	39
6.1 Introduction	39
6.2 The degradation of organic matter modelled with PHREEQC	39
6.2.1 Simulation 1: Reference simulation	40
6.2.2 Temperature dependency	42

6.2.3	Simulation 2: Smaller increments	42
6.2.4	Simulation 3: Different database	44
6.2.5	Simulation 4: Higher nitrate content	45
6.2.6	Simulation 5: Nitrogen species	45
6.2.7	Simulation 6: Reduced partial pressure of oxygen	46
6.3	Kinetic reactions	48
6.3.1	Monod degradation kinetics	48
6.3.2	Monod sensitivity analysis	49
6.3.3	Michaelis-Menten kinetics	51
6.3.4	Sensitivity analysis on Michaelis-Menten kinetics	51
6.4	Discussion	56
7	Conclusion	57
	Bibliography	59
A	List of abbreviations	
B	PHREEQC Code	
B.1	Simulation 1	
B.2	Simulation 8	
B.3	Simulation 13	

List of Figures

1	Preliminary ranking of codes evaluated by EMS for the Alberta Government (ALBERTA RESEARCH GROUP, 2005)	17
2	Rate laws for the reaction A to B (APPELO & POSTMA, 2005, p. 154) .	26
3	Conceptual model of hydrocarbon degradation and its sequential impact on groundwater chemistry. (WIEDEMEIER ET AL., 1999, p. 208) . . .	28
4	The different TEAPs in time and/or space. The source of carbon here is a leaking barrel of NAPLs and LNAPLs. NAPL means Non-Aqueous Phase Liquid, LNAPL means Light Non-Aqueous Phase Liquid) (WIEDEMEIER ET AL., 1999, p. 210)	29
5	Conceptual model of hydrogen and carbon as electron donor, the sequential TEAP and typical hydrogen concentrations (WIEDEMEIER ET AL., 1999)	30
6	Graphical representation of the Monod equation (ALVAREZ & ILLMAN, 2006)	32
7	Moles of organic carbon added to solution	40
8	Simulation 1. Changes of hydrochemistry due to the reduction of organic matter	41
9	Temperature dependency: Straight lines represent 5°C, dashed one 25°C water temperature.	42
10	Temperature dependency: The changes of pH and pe due to different temperatures, range is from 0 to 20°C.	43
11	Simulation 2: Changes of hydrochemistry in small incremental steps of organic carbon added	43
12	Simulation 3: The influence of the different database on simulation 2. Database used is wateq4f.dat	44
13	Simulation 4: Water with higher nitrate concentrations	45
14	Simulation 5: Nitrogen species	46
15	The databases <i>llnl.dat</i> and <i>phreeqc.dat</i> compared running simulation 5	47
16	Simulation 6: Reduced partial pressure of oxygen in the initial solution	47
17	Simulation 7: The degradation of Phenol modelled with PHREEQC using the Monod equation	48
18	Sensitivity of the Monod parameters, as listed in table 4	50
19	Simulation 7: The degradation of Phenol modelled with PHREEQC using the Monod equation	50
20	Simulation 14: Degradation of phenol and biomass growth	52

21	Sensitivity analysis of biodegradation modelled with the Michaelis-Menten approach	52
22	Simulation 19 to 21. The influence of the bacterial death rate on the degradation process	54
23	Simulation 21 - 23. The influence of the half-saturation constant on the degradation process	55
24	Simulation 24 and 25. The influence of the maximum growth rate on the degradation process	55
25	The factor time in kinetic and equilibrium chemistry	57

List of Tables

1	Selected geochemical models	7
2	Selected redox reactions in groundwaters and its pe and ΔG values (STUMM & MORGAN, 1996, taken from p. 474)	27
3	Potential energy yield and steady-state hydrogen concentrations characteristic of different anaerobic oxidation processes (CHAPELLE, 2001, p. 291)	29
4	Values of parameters in the Monod equation	49
5	Values of parameters in the Monod equation	53

Summary

Aim of this diploma thesis is to approach to kinetic modelling of subsurface hydrochemistry with the program code PHREEQC. The reaction considered is the degradation of organic mass and its concomitant reactions. PHREEQC is a program for thermodynamical based equilibrium calculations of geo- and hydrochemistry. Although the degradation of organic matter, and the associated reduction reactions due to the oxidation of organic matter, can be modelled with PHREEQC, it does not account for kinetically controlled reactions, whose characteristic feature is the dependency of time. This study focuses on the state of the art of environmental modelling, the thermodynamical based calculation of the degradation of organic matter and on two mathematical approaches to model bacterial degradation of a contaminant, the Monod equation and the Michaelis-Menten approach. Sensitivity analyses of the respective model runs were done.

As a result one can see, that the redox chemistry of a natural water depends strongly on the abundance of oxygen and nitrate and, as a matter of course, on the abundance of organic matter. Considering bacterial activity within the degradation process, two basic mathematical formulations have been stated. The Monod equation and the Michaelis-Menten formulation were implemented in a BASIC interpreter in PHREEQC. The sensitivity analyses show, that that a accurate determination of the parameters in laboratory of field is essential. The coupling of kinetically controlled reactions and thermodynamical based equilibrium calculations might lead to auspicious hydrochemical modelling capabilities.

Zusammenfassung

Ziel dieser Diplomarbeit ist eine nähere Betrachtung des Abbaus organischer Materie im Grundwasser und dessen Folgen auf die Grundwasserchemie mit Hilfe des Programms PHREEQC. PHREEQC ist Software-Paket, welches chemisches Gleichgewicht numerisch auf der Basis von thermodynamischen Daten der einbezogenen Spezies und Reaktionen berechnet. Der Abbau organischer Materie und die zusammenhängenden Reaktionen wurden mit PHREEQC modelliert. Zeitabhängige kinetisch kontrollierte Reaktionen sind im PHREEQC-Code nicht implementiert, jedoch ist ein BASIC-Interpreter enthalten, mit welchem kinetische Reaktionen gerechnet wurden. Diese Arbeit betrachtet den aktuellen Stand der hydrochemischen Modellierung, die Modellierung des Abbaus organischer Materie auf thermodynamischer Basis und die Implementierung der wichtigsten mathematischen Formulierungen des bakteriellen Abbaus organischer Verbindungen, der Monod- und der Michaelis-Menten-Formel.

Die Redox Verhältnisse natürlicher Waasser hängen sehr stark von dem Gehalt des vorhandenen organischen Kohlenstoffs und der Menge an gelöstem Sauerstoff sowie dem Nitratgehalt ab. Um den bakteriellen Abbau organischer Verbindungen einzubeziehen, wurden in den BASIC-Interpreter die Monod- und die Michaelis-Menten-Formel implementiert. Sensitivitätsanalysen zeigen, dass die genaue Bestimmung der Parameter in Labor- oder Feldmessungen unerlässlich ist.

1. Introduction

Contamination of aquifers is, besides the abundance of water, a major problem for water supply bodies and the population to be supplied with. In many cases the contamination act had happened years to decades before, in times where it even was not illegal to dispose fabrical waste in the nearby soil. Therefore it is essential to develop answers and solutions to the simple question, whether the water quality will be at risk or not, and if so, to estimate as precise as possible quality, quantity, time and space; or in other words, what, how much, where and when.

Geochemical modelling is a useful tool to determine

- a) the movement of potential toxic substances in time and space and
- b) chemical changes and its impacts on the aquifer chemistry regarding toxical substance mobility.

The presence of hydrocarbons in aquifers is a particular issue, because its degradation and natural attenuation changes the redox chemistry of the aquifer. These changes yield to other changes of the overall geochemistry, which change the conditions for degradation, which in turn change the geochemistry. This interdependence of geochemical reactions characterizes the system as a highly complex one. Complex problems in complex systems can solely be modelled with an iterative procedure. Software systems, which converge to a solution numerically, including equilibrium chemistry and thermodynamical data, may act as a suitable tool for this kind of problem.

2. Problem statement

Since the year 2006, the Institute of Hydrology in Freiburg (IHF) is in charge of the project *ERGO* (Effektive Risikoabschaetzung zur Gefaehrdung des Trinkwassers durch Altlasten im Oberrheingraben \approx Effective assessment of risk for drinking water supplies from contaminated sites in the Upper Rhine valley), under the commission of the *Arbeitsgemeinschaft Wasserwerke Bodensee-Rhein* (Joint-venture of water suppliers Lake Constance-Rhine) AWBR. The aim is to assess the risk of contamination sites to water quality in the aquifer, regarding its use as a source of drinking water. Further to give technical instructions to the water supply bodies how to avoid the uptake of contaminated water, e.g. by displaying zones of different risk. The judicial scope is given by the *Bundes-Bodenschutz- und Altlastenverordnung* (BBodSchV) (German Federal Soil Protection Act and Ordinance) and the *Europaeische Wasserrahmenrichtlinie* (EU WATER FRAMEWORK DIRECTIVE - GROUNDWATER, 2006), with special consideration of its list of priority substances.

Objective of this work is to exemplify and to evaluate the use of PHREEQC for the modelling of bacterial and/or kinetically driven degradation of carbon species in groundwater environments and its effects on the groundwater chemistry.

3. State of the Art

Natural waters are generally not at internal redox state equilibrium (LINDBERG & RUNNELS, 1984). Measuring the redox state with a standard platin electrode for 611 samples and computing corresponding Eh values with WATEQFC (RUNNELLS & LINDBERG, 1981), the difference between the values was spanning around 1000 millivolts. "Redox potentials in natural observed in waters are usually mixed potentials, which are impossible to relate to a single dominant redox species. The use of any measured Eh value as input to equilibrium hydrogeochemical computer models will generally yield misleading results for normal ground waters" (LINDBERG & RUNNELS, 1984, p. 925). So not only adequate measurements of redox couples are required, but also the modeling of kinetically controlled redox reactions in ground waters may be necessary. The degradation of organic compounds in groundwaters have been reported as abiological mechanisms until the mid-eighties (LOVLEY ET AL., 1994). The investigation of a contamination of crude oil at the Bemidji site in Minnesota, USA, revealed, that bacteria control the degradation of hydrocarbons also under anaerobic conditions. Furthermore, these bacteria rely upon electron accepting elements, such as Fe(III) (LOVLEY ET AL., 1989). FROELICH ET AL. (1979) measured concentrations of electron accepting elements in pelagic sediments as a function of depth, revealing that there is a thermodynamic controlled sequence in the reduction of those elements (see section 4.5 on page 28). Increasing the bioavailability of Iron by adding NTA (Nitrilotriacetic acid, $C_6H_9NO_6$), "that bind to Fe(III) dramatically" (LOVLEY ET AL., 1994, p.370), the bacteria reduced the organic pollutants much faster (LOVLEY ET AL., 1994). So the "quantitative aspect" (MONOD, 1949, p. 371) describing "the growth of bacterial cultures" by Jaques Monod in 1949 became an important subject in groundwater chemistry. This "hyperbolic saturation function" presented by Monod is commonly "referred to as Monod or Michaelis-Menten kinetics" (WIEDEMEIER ET AL., 1999, see p. 183). The latter "is similar to the Langmuir isotherm" (APPELO & POSTMA, 2005, p. 521). MOLZ ET AL. developed in 1986 a model for microbial growth dynamics coupled with transport based on modified Monod kinetics. According to (REGNIER ET AL., 2005, p.107) "Comprehensive modelling of reactive transport in subsurface environments therefore requires mathematical expressions that predict the rates at which microorganisms consume and produce chemical constituents". For examples of the use of modified Monod kinetics see (ESSAID ET AL., 1995; HUNTER ET AL., 1998; VAN CAPELLEN & WANG, 1996).

A very comprehensive reaction-transport modelling framework based on the Michaelis-Menten approach is documented in (BARRY ET AL., 2002). The authors consider also concomitant secondary reactions due to the changes in the redox state, and compare there results with measurements in the Vejen landfill in Denmark, a highly investigated research site; see (PERSSON ET AL., 2006; BAUN ET AL., 2003; RICHNOW ET AL., 2003; BARRY ET AL., 2002; BRUN & ENGESGAARD, 2002; BRUN ET AL., 2002; CHRISTENSEN

ET AL., 1996; KJELDSSEN, 1993; LYNGKILDE & CHRISTENSEN, 1992b,a).

A standard book for geochemistry is "Geochemistry, groundwater and pollution" (APPELO & POSTMA, 2005). More about conceptual models for reactive transport in soil and groundwater can be found in (SCHULZ & TEUTSCH, 2002) and (NÜTZMANN ET AL., 2005). An overview of different point of views about natural attenuation in groundwater, implying community concerns, scientific basis, protocol standards and common techniques is published by the NATIONAL RESEARCH COUNCIL (2000). For students and researchers WIEDEMEIER ET AL. (1999) published an excellent lecture dealing with chemical and physical processes of natural attenuation, its applications, case studies and the referring physical and geochemical data . A focus on process fundamentals and mathematical models is presented by (ALVAREZ & ILLMAN, 2006). Microbiology, Biochemistry and its interactions with groundwater geochemistry is the topic of (CHAPELLE, 2001) and (BUFFLE & DE VITRE, 1994). A step forward to environmental modeling in higher resolution is the article of Jin and Bethke. A mathematical description of "rate expression, that predicts electron flux [through the respiratory chain] under arbitrary chemical conditions and varying thermodynamic drive and proton force" (JIN & BETHKE, 2002, p. 1807). Deeper insight in environmental chemistry can be found in (MANAHAN, 2000) and (STUMM & MORGAN, 1996). A very copious view in the materia of environmental organic chemistry is printed on 1313 pages by SCHWARZENBACH ET AL. (2003). Despite the numerous excellent publications dealing with groundwater pollution, joining geochemistry and biochemistry, one may think that geochemical modelling is in an advanced state. It is, but the complexity of the subsurface interactions increases the intricacy almost to infinity. Although, some models will be charted here.

Table 1.: Selected geochemical models

Model name	Applicability	Distributor Reference
AQUA	2D transient groundwater flow and transport. Aquifer may be heterogeneous and anisotropic. Can simulate advection, dispersion, linear sorption and decay. A proprietary code with interactive/graphical interface. ⁽¹⁾	Scientific Software Group ⁽⁶⁾
ASM	Aquifer simulation model for two-dimensional modeling of groundwater flow and solute transport. Uses random-walk method for solute transport, and can simulate advection, dispersion, linear sorption, and decay. Aquifer can be heterogeneous and anisotropic. Menu-driven, graphical interface. A proprietary program prepared by W. KINZELBACH (University of Heidelberg) and R. RAUSCH (University of Stuttgart)(1995) ⁽¹⁾ .	
BIO1D	1D model for aerobic and anaerobic biodegradation and sorption of hydrocarbons ⁽²⁾ . Transport of substrates and electron acceptors is considered, assuming an uniform flow field. Several reaction options are available for biodegradation and sorption. Has a pre-processor and display graphics. A proprietary code developed at GeoTrans, Inc. ⁽¹⁾	GeoTrans ⁽⁸⁾ .
BIOF & T 3-D	2D or 3D model for flow and transport in saturated/unsaturated zone. Includes convection, dispersion, diffusion, desorption, first order or Monod biodegradation, sequential biodegradation. ⁽²⁾	Scientific Software Group ⁽⁶⁾
BIOREDOX	3D model for chlorinated solvents and petroleum hydrocarbons. Couples biodegradation and reduction of oxygen, nitrate, sulphate and carbon dioxide. ⁽²⁾	(CAREY ET AL., 1999)
BIOPLUME II	2D model for simulating transport of a single dissolved hydrocarbon species under the influence of oxygen-limited biodegradation, first-order decay, linear sorption and advection and dispersion. Aquifer may be heterogeneous and anisotropic. Based on the USGS two-dimensional MOC model (including a finite-difference flow model) by (KONIKOW & BREDEHOEFT, 1978). Oxygen-limited biodegradation is a reactive transport process. A public-domain code with a menu-driven preprocessor and limited post-processing abilities. Developed by (RIFAI ET AL., 1988) at Rice University. ⁽¹⁾	IGWMC ⁽⁴⁾ (RIFAI ET AL., 1988)
BIOPLUME III	Successor to BIOPLUME II. Two-dimensional model for reactive transport of multiple hydrocarbons under the influence of advection, dispersion, sorption, first-order decay, and reactant-limited biodegradation. Development by AFCEE. Has interactive, graphical pre- and postprocessing capabilities. ⁽¹⁾	Development commissioned by AFCEE; EPA ⁽³⁾
BIOSLURP	Finite element 2D model for vapor transport of LNAPLs in the groundwater in the vadose zone. Includes convection, dispersion, diffusion, adsorption, first-order biodegradation kinetics. ⁽²⁾	Scientific Software Group ⁽⁶⁾
BioTracker	1D Natural attenuation screening model with visualization tools for groundwater. Multispecies transport and transformation. Used with Sequence and BioTrends. Based on Bioredox. ⁽²⁾	Scientific Software Group ⁽⁶⁾

Model name	Applicability	Distributor Reference
BioTrans	Proprietary two-dimensional finite-element transport code requiring flow velocity data from another code (e.g. MODFLOW). Models transport of multiple species and influence of advection, dispersion, sorption, first-order decay and oxygen-limited biodegradation. Allows internal computation of source terms due to dissolution of NAPL. Graphical, interactive user interface with pre- and postprocessing capabilities. Prepared by Environmental Systems and Technologies, Inc. ⁽¹⁾	Environmental Systems and Technologies, Inc ⁽⁹⁾
CHEMFLO-2000	CHEMFLO-2000 enables users to simulate water movement and chemical fate and transport in vadose zones. The software could be used to assist regulators, environmental managers, consultants, scientists, and students in understanding unsaturated flow and transport processes. Water movement and chemical transport are modeled using the Richards and the convection-dispersion equations, respectively. The equations are solved numerically using the finite differences approach. CHEMFLO-2000 is an upgraded version of CHEMFLO V1.3 that was released in 1989. In addition to the functions in the previous version, a number of new functions and features were added in CHEMFLO-2000 such as graphic sensitivity analyses and a Java interactive interface to facilitate the simulations of water flow and chemical transport. (EPA, 2003)	EPA ⁽³⁾
3DFATMIC	3D model to simulate subsurface flow, transport, and fate of contaminants which are undergoing chemical and/or biological transformations for both saturated and unsaturated zones. ⁽²⁾	EPA ⁽³⁾
3DFEMFAT	3DFEMFAT is a 3-Dimensional Finite-Element Model of Flow And Transport through saturated-unsaturated media. Typical applications are infiltration, wellhead protection, agriculture pesticides, sanitary landfill, radionuclide disposal sites, hazardous waste disposal sites, density-induced flow and transport, salt-water intrusion, etc. 3DFEMFAT can do simulations of flow only, transport only, combined sequential flow and transport, or coupled density-dependent flow and transport. Based on a hybrid Lagrangian-Eulerian finite-element approach, 3DFEMFAT can use very large time steps and is recommended [by the author] for applications to large field problems. (SCIENTIFIC SOFTWARE GROUP, 1998, taken from model overview page)	Scientific Software Group ⁽⁶⁾ ; (SCIENTIFIC SOFTWARE GROUP, 1998)
FEMSEEP	Set of programs for solving steady-state and transient groundwater flow and solute transport problems in simplified two- and three-dimensional systems. Transport under influence of advection, dispersion, linear sorption, and first-order decay may be simulated using finite element methods. A proprietary program with graphical and menu-driven interfaces and pre- and postprocessing capabilities. Prepared by D. Meiri of FEMSEEP Software, Inc. (MEIRI, 1990)	FEMSEEP Software, Inc.; IGWMC ⁽⁴⁾

Model name	Applicability	Distributor Reference
FEMWATER, FEMWASTE	Finite-element flow (FEMWATER) and transport (FEMWASTE) models. FEMWATER and FEMWASTE can simulate variably saturated conditions in two and three dimensions. FEMWASTE can simulate transport in one, two and three dimensions. The system may be heterogeneous and anisotropic, and the code can account for dispersion, linear sorption, first-order decay and three types of sorption. Public-domain codes developed by researchers at Oak Ridge National Laboratories. Some proprietary versions of FEMWATER are available; they are based on the Department of Defense's Groundwater Modeling Systems (GMS) and data management package.	Oak Ridge National Laboratories; NTIOS, distributors of proprietary GMS programs (ENVIRONMENTAL MODELING SYSTEMS, 1993)
FLONET® FLO- TRANS	Two-dimensional steady-state groundwater flow (FLONET) and transient solute transport (FLOTTRANS) models for cross-sectional problems. FLOTTRANS is an extension of FLONET that can simulate transport under the influence of advection, dispersion, linear sorption and first-order decay. A proprietary program with an interactive graphical user interface and extensive pre- and postprocessing capabilities. Developed by Waterloo Hydrogeologic Software, Inc. (WATERLOO HYDROGEOLOGIC SOFTWARE, 1998)	Waterloo Hydrogeologic Software, Inc. now Schlumberger Water Services ⁽⁷⁾ ; IGWMC ⁽⁴⁾
FTWORK	Block-centered finite-difference model for one-, two, and three-dimensional flow and transport. The transport model advection, dispersion, first-order decay and two types of sorption (linear and non-linear equilibrium). A public-domain code that may be acquired with a proprietary (IGWMC) textual and menu-driven preprocessor and postprocessor. Originally developed by (FAUST ET AL., 1989) at GeoTrans, Inc. ⁽¹⁾	GeoTrans ⁽⁸⁾ ; IGWMC ⁽⁴⁾
HST3D	Program for simulating groundwater flow and associated heat and solute transport in three dimensions. Solute transport is for a single solute with advection, dispersion, linear sorption and first-order decay. A public-domain code with no pre- and postprocessors. Prepared by K.L. Kipp of the USGS. ⁽¹⁾ and (KIPP, 1987, 1997)	(KIPP, 2007, manual); USGS ⁽⁵⁾ ; IGWMC ⁽⁴⁾

Model name	Applicability	Distributor Reference
HYDRUS	A software package for simulating water, heat, and solute movement in two- and three- dimensional variably saturated media. The software package consists of the computational computer program, and the interactive graphics-based user interface. The HYDRUS program numerically solves the Richards equation for variably saturated water flow and advection-dispersion equations for both heat and solute transport. The flow equation incorporates a sink term to account for water uptake by plant roots. The heat transport equation considers transport due to conduction and convection with flowing water. The solute transport equations consider advective-dispersive transport in the liquid phase, as well as diffusion in the gaseous phase. The transport equations also include provisions for nonlinear nonequilibrium reactions between the solid and liquid phases, linear equilibrium reactions between the liquid and gaseous phases, zero-order production, and two first-order degradation reactions. In addition, physical nonequilibrium solute transport can be accounted for by assuming a two-region, dual-porosity type formulation which partitions the liquid phase into mobile and immobile regions. Attachment/detachment theory, including filtration theory, is additionally included to enable simulations of the transport of viruses, colloids, and/or bacteria. (ŠIMŮNEK ET AL., 1998)	IGWMC ⁽⁴⁾
MINTEQA2	MINTEQA2 is an equilibrium speciation model that can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. The model is useful for calculating the equilibrium mass distribution among dissolved species, adsorbed species, and multiple solid phases under a variety of conditions including a gas phase with constant partial pressures. A comprehensive data base is included that is adequate for solving a broad range of problems without need for additional user-supplied equilibrium constants. The model employs a pre-defined set of components that includes free ions such as Na ⁺ and neutral and charged complexes (e.g., $H_4SiO_4^0$, $Cr(OH)^{2+}$). The data base of reactions is written in terms of these components as reactants. An ancillary program, PRODEFQA2, serves as an interactive pre-processor to help produce the required MINTEQA2 input files. (ALLISON, 1999)	(ALLISON ET AL., 1991; ALLISON, 1991)
MOC, USGS2D- MOC	Two-dimensional model for simulation of groundwater flow and non-conservative solute transport. Derived from the original model developed by (KONIKOW & BREDEHOEFT, 1978). The latest version (March 1995) simulates transport under the influence of advection, dispersion, first-order decay, reversible equilibrium-controlled sorption, and reversible equilibrium-controlled ion exchange. The flow model is a finite-difference model, while transport is simulated using MOC methods. A public-domain code with an interactive processor. ⁽¹⁾	USGS ⁽⁵⁾ ; IGWMC ⁽⁴⁾

Model name	Applicability	Distributor Reference
MODFLOW	3D finite difference model for estimating the vertical migration of dissolved organic solutes through the vadose zone to groundwater and is a closed-form analytical solution of the advective - dispersive - reactive transport equation. Evapotranspiration and drainage included.	(MCDONALD & HARBAUGH, 1988); USGS ⁽⁵⁾
MT3D, MT3DMS	For simulation of unsaturated zone flow and transport of oily wastes by finite difference. Advection, dispersion, partitioning of pollutant between the liquid, soil, vapor, and oil phases by linear equilibrium isotherms. Degradation of pollutant and oil is described as first-order process. ⁽²⁾	S.S. Papadopoulos and Associates; EPA ⁽³⁾
PESTAN	Finite difference model for transient and steady state groundwater flow. Used with transport models MT3D, Biotrans, RAND3D. ⁽²⁾	EPA ⁽³⁾
PHAST	The computer program PHAST simulates multi-component, reactive solute transport in three-dimensional saturated groundwater flow systems. PHAST is a versatile ground-water flow and solute-transport simulator with capabilities to model a wide range of equilibrium and kinetic geochemical reactions. The flow and transport calculations are based on a modified version of HST3D that is restricted to constant fluid density and constant temperature. The geochemical reactions are simulated with the geochemical model PHREEQC, which is embedded in PHAST.(PARKHURST ET AL., 2004, p. 1)	USGS ⁽⁵⁾ ; (PARKHURST ET AL., 2004)
PHREEQC	PHREEQC version 2 is a computer program written in the C programming language that is designed to perform a wide variety of low-temperature aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has capabilities for (1) speciation and saturation-index calculations; (2) batch-reaction and one-dimensional (1D) transport calculations involving reversible reactions, which include aqueous, mineral, gas, solid-solution, surface-complexation, and ion-exchange equilibria, and irreversible reactions, which include specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and temperature changes; and (3) inverse modeling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters, within specified compositional uncertainty limits. Since the version 2.7 the calculation of isotope equilibria of certain species is included. (more detailed information see chapter 5 of this thesis) (PARKHURST & APPELO, 1999, p. 1)	USGS ⁽⁵⁾ ; (PARKHURST & APPELO, 1999)
PHTRAN	1-D multi-component model accounting for hydrological transport, in organic equilibrium chemistry and microbial activity during kinetically controlled biodegradation in groundwater of compounds such as benzene, toluene, ethylbenzene and xylene (BTEX). The problem is solved numerically using an operator-splitting method to couple advective-dispersive transport of organic and inorganic solutes with a geochemical equilibrium package PHREEQC and a biodegradation module (PROMMER ET AL., 1999, p. 1)	(PROMMER ET AL., 1999)

Model name	Applicability	Distributor Reference
RITZ	3D transport model for advection, linear and non-linear sorption dispersion, first order decay of single species. Coupled with MODFLOW	EPA ⁽³⁾
RAN3D	Three-dimensional version of the random walk algorithm developed by Prickett et al. (1981). RAN3D is designed to be coupled with MODFLOW input files for calculation of velocity files that are used to run the code. May be used for transient simulation of advection, dispersion, linear sorption, and zero order decay, first-order, or variable order decay. Code has some pre- and post-processing capabilities. A proprietary code prepared by D. Koch of Engineering Technologies Associates and T. A. Prickett. ⁽¹⁾	IGWMC ⁽⁴⁾
RT3D	Modification of MT3D. For multispecies transport of chlorinated compounds, by-products and solid-phase species. Instantaneous aerobic degradation, BTEX degradation with multiple electron acceptors, sequential anaerobic degradation of PCE/TCE, and combined aerobic/anaerobic degradation of PCE/TCE. Advection, dispersion, Monod biodegradation, sorption, decay. ⁽²⁾	Washington State University and Pacific Northwest National Laboratory
SEAM3D	Transport of multiple solutes in aquifers. Monod kinetics biodegradation, based on engine of MT3D. Can follow NAPL dissolution. ⁽²⁾	U.S. Military
SESOIL	Transport through vadose zone in water, soil and air phases. Can be combined with MODFLOW. Includes surface runoff and erosion pollution transport, volatilization to soil surface ⁽²⁾	U.S. Salinity Lab
STANMOD	STANMOD (STudio of ANalytical MODEls) is a Windows based computer software package for evaluating solute transport in porous media using analytical solutions of the convection-dispersion solute transport equation. The STANMOD package includes a graphical user interface, a post-processing tool and seven included programs for different issues. CXTFIT can be used to estimate solute transport parameters for the one-dimensional advection-dispersion equation (ADE). CFITM and CFITIM analyzes observed column data using analytical solutions for the one-dimensional equilibrium and non-equilibrium ADE, respectively. Advective-dispersive transport of solutes involved in sequential first-order decay reactions can be analyzed with CHAIN. SCREEN models the fate and transport of soil-applied organic chemicals and the different loss pathways, as long as the required thermodynamical data is available. Evaluating analytical solutions for 2D- and 3D-equilibrium solute transport and 2D- and 3D non equilibrium solute transport in the subsurface 3DADE and N3DADE are given, respectively. (ŠIMŮNEK ET AL., 1999, see manual p. 3-5 and STANMOD web page (Dec. 2003))	IGWMC ⁽⁴⁾ ; (ŠIMŮNEK ET AL., 1999)

Model name	Applicability	Distributor Reference
SUTRA	SUTRA (Saturated-Unsaturated Transport) is a computer program that simulates fluid movement and the transport of either energy or dissolved substances in a subsurface environment. The code employs a two- or three-dimensional finite-element and finite-difference method to approximate the governing equations that describe the two interdependent processes that are simulated: 1) fluid density-dependent saturated or unsaturated ground-water flow; and 2) either (a) transport of a solute in the ground water, in which the solute may be subject to: equilibrium adsorption on the porous matrix, and both first-order and zero-order production or decay; or (b) transport of thermal energy in the ground water and solid matrix of the aquifer. Solute-transport simulation using SUTRA may be employed to model natural or man-induced chemical-species transport including processes of solute sorption, production, and decay. (VOSS & PROVOST, 2002, p. 1) SUTRA comes also with a graphical user interface that supports two-dimensional (2D) and three-dimensional (3D) simulation. SutraGUI is a public-domain computer program designed to run with the proprietary Argus ONE TM package, which provides 2D Geographic Information System (GIS) and meshing support (VOSS & PROVOST, 2004, p. 1)	USGS ⁽⁵⁾ ; (VOSS & PROVOST, 2002)
SWIFT, SWIFT/486	3D finite difference model to simulate contaminant, fluid and heat transport in porous and fractured media. Linear and nonlinear desorption, dispersion, diffusion, dissolution, leaching and decay. Public domain ⁽²⁾	Sandia National Laboratory
SWM SM_2D	3D Modeling transient and steady-state flow and mass transport in the groundwater (saturated) and vadose (unsaturated) zones of aquifers. Physical, chemical and biological processes. Includes multiple organic NAPL phases; the dissolution and/or mobilization of NAPL's by nondilute remedial fluids; chemical and microbiological transformations; and changes in fluid properties. Includes non equilibrium interphase mass transfer; sorption; geochemical reactions; and the temperature dependence of pertinent chemical and physical properties. Model includes inhibition, sequential use of electron acceptors, and cometabolism for a general class of bioremediation processes. ⁽²⁾	U.S. Salinity Lab
TBC	The reactive transport model TBC (transport, biochemistry, and chemistry) numerically solves the equations for reactive transport in three-dimensional saturated groundwater flow. A finite element approximation and a standard Galerkin method are used. Solute transport is coupled to microbially mediated organic carbon degradation. Microbial growth is assumed to follow Monod-type kinetics. Substrate consumption and release of metabolic products is coupled to microbial growth via yield coefficients and stoichiometric relations. Additionally, the effects of microbial activity on selected inorganic chemical species in the aquifer can be considered.(SCHAEFER ET AL., 1998a, p. 1)	(SCHAEFER ET AL., 1998a)

Model name	Applicability	Distributor Reference
TOUGH2	TOUGH2 is a numerical simulator for nonisothermal flows of multicomponent, multiphase fluids in one, two, and three-dimensional porous and fractured media. The chief applications for which TOUGH2 is designed are in geothermal reservoir engineering, nuclear waste disposal, environmental assessment and remediation, and unsaturated and saturated zone hydrology. TOUGH2 was first released to the public in 1991; the 1991 code was updated in 1994 when a set of preconditioned conjugate gradient solvers was added to allow a more efficient solution of large problems. The current Version 2.0 features several new fluid property modules and offers enhanced process modeling capabilities, such as coupled reservoir-wellbore flow, precipitation and dissolution effects, and multiphase diffusion. The T2VOC module for three-phase flows of water, air and a volatile organic chemical (VOC), and the T2DM module for hydrodynamic dispersion in 2-D flow systems have been integrated. (PRUESS ET AL., 1999, p. iii)	Berkeley Lab, Earth Science Division; (PRUESS ET AL., 1999)
UTCHEM	2D model for transport of water and solutes in various saturated media. Linear sorption, zero-order production, first-order decay, dispersion. Public domain ⁽²⁾	EPA ⁽³⁾
VLEACH	1D finite difference model for evaluating effects on ground water from the leaching of volatile, sorbed contaminants through the vadose zone. Includes liquid-phase advection, solid-phase sorption, vapor-phase diffusion, and three-phase equilibration in terms of soil properties, recharge rates, depth of water, or initial conditions. Public domain ⁽²⁾	EPA ⁽³⁾
VS2DT	VS2DT is a finite-difference model that solves Richard's equation for fluid flow, and the advection-dispersion equation for solute transport. The model can analyze problems in one or two dimensions using either cartesian or radial coordinate systems. Relations between pressure head, moisture content, and relative hydraulic conductivity may be represented by functions developed by van Genuchten, Brooks and Corey, Haverkamp and others, or by data points. Initial hydraulic condition can be specified as static equilibrium, specified pressure head, or specified moisture content. Boundary conditions include specified pressure or total head, specified flux, infiltration with ponding, evaporation, plant transpiration, and seepage faces. Solute transport processes include advection, dispersion, first-order decay, adsorption, and ion exchange. (HSIEH ET AL., 2000)	USGS ⁽⁵⁾ ; (HSIEH ET AL., 2000)

Model name	Applicability	Distributor Reference
WATEQ4F	A FORTRAN 77 version of the PL/1 computer program for the geochemical model WATEQ2 has been developed, which computes major and trace element speciation and mineral saturation for natural waters. The code WATEQ4F has been adapted to execute on an IBM PC or compatible microcomputer with or without an 8087, 80287 or 80387 numeric coprocessor and, if recompilation is desired, a full-featured microcomputer FORTRAN compiler. The calculation procedure is identical to WATEQ2, which has been installed on many mainframes and minicomputers. Several data base revisions have been made that include the addition of Se (-II, 0, IV, VI) and U (III, IV, V, VI) species as well as the recently published values of Nordstrom and others (1990) (NORDSTROM ET AL., 1990) (BALL & NORDSTROM, 1998; WELCH & STOLLENWERK, 2002, for thermodynamical data of Cr and As). A new set of redox options has been introduced so that all species that would exist in a disequilibrium system can be independently calculated, or selected species can be coupled, at the desire of the user.	USGS ⁽⁵⁾ , (BALL & NORDSTROM, 1991)

⁽¹⁾ (WIEDEMEIER ET AL., 1999, P 409-412)

⁽²⁾ (MULLIGAN & YONG, 2004, p. 594)

EPA⁽³⁾: List of models, information and download: www.epa.gov/ada/csamos/models.html

IGWMC⁽⁴⁾: International Ground Water Modeling Center: <http://typhoon.mines.edu/>

USGS⁽⁵⁾: Information and download: http://water.usgs.gov/software/lists/ground_water

Scientific Software Group⁽⁶⁾: www.scisoftware.com/environmental_software/index.php?cPath=21

Schlumberger Water Services⁽⁷⁾: www.swstechnology.com

GeoTrans⁽⁸⁾: www.geotransinc.com/

Environmental Systems and Technologies, Inc⁽⁹⁾: www.esnt.com; <http://www.gesonline.com>

As gathered from table 1, one can classify the models in three basic algorithms for the solution of the partial differential transport equation. The method of Finite Differences (FD), Finite Elements (FE) and Random Walk (RW). ASM and RAN3D are using the Random Walk algorithm. As one can guess by the model name, FEMSEEP, 3DFEMFAT, FEMWASTE and FEMWATER operate with the FE method, as well as BIOSLURP and BioTrans. The most famous representative in groundwater modeling implying the Finite Difference method is the MODFLOW family. Going from that, nearly all models are capable of modeling advection, dispersion, linear sorption and first-order decay. SUTRAGui as well provides 2D GIS support. The fate of a single solute is modeled by FTWORK, and of a single hydrocarbon species by BIOPLUME II. The successor, BIOPLUME III, solves the reactive transport problem for multiple hydrocarbon species, yet with oxygen limited biodegradation. Biodegradation coupled with sequential redox reactions is implemented in the models BIOREDOX, BIOTRACKER, 3DFATMIC, MT3D, SWM and TBC. NAPLs and LNAPLs are included in the models BIOSLURP and BioTrans. Modeling the fate of the widespread BTEX compounds (Benzene, Toluene, Ethylbenzene, Xylene) BIOPLUME, RT3D, SWM and PHTRAN are stated. The latter also includes kinetically controlled biodegradation

reactions, whereas BIOF, T3D, SEAM and TBC are using the Monod-type formulation for bacterial attenuation activity. Capable of geochemical equilibrium of multiple components are MINTEQ, PHAST, PHREEQC and WATEQ4F, whereas SWM includes physical non-equilibrium between phase interactions. The phase interactions represented in HYDRUS are such as the non-equilibrium between feldspar and groundwater and the assumed equilibrium between CO₂ and groundwater. And with a trick, physical non-equilibrium solute transport can be applied. 1D, 2D and 3D equilibrium and non-equilibrium solute transport modeling achieved by an analytical solution is implemented in the STANMOD package.

On the website of the IGWMC, a list of common models, classified in purpose, and some reviews of the models is posted (<http://typhoon.mines.edu/software/igwmcsoft/>). All the groundwater models developed by the USGS until 1994, with an update until Aug. 2007, are listed in (APPEL & REILLY, 1994). A disquisition about reactive transport modeling was published by (STEEFEL ET AL., 2005). Modeling the reactions of multiple TEAPS (Terminal Electron Acceptor Processes) and comparing the use of the irreversible Monod rate law and kinetically controlled reactions showed that the Monod rate law approach over estimated the reduction of Fe(II) (CURTIS, 2003). In the same issue of *Computers & Geosciences* ZHU (2003, p.1) illustrates the "shortcomings of the K_d approach" comparing the results with the multicomponent reactive model PHREEQC (ZHU, 2003).

A detailed code testing protocol for groundwater models was established by the IGWMC by order of the US EPA (VAN DER HEIJDE & KANZER, 1997a,b). The federal office for environment and geology of Saxonia, Germany, provides a list of simulation models for groundwater flow and contaminant transport in its online database DASIMA (LFUG, 2004). The government of Alberta, Canada, commissioned an "Evaluation of Computer Models for Predicting the Fate & Transport of Hydrocarbons in Soil and Groundwater" (ALBERTA RESEARCH GROUP, 2005). In this study 130 codes were evaluated, concluding in a preliminary ranking chart. PHREEQC was not included due to the limited flow simulation capabilities. The leading top ten in the ranking chart are listed in figure 1. Not all models charted in figure 1 are listed in table 1, and it would be beyond of scope to dwell on the highly informative model evaluation in detail. For further interest in groundwater models dealing with different salinities, a two-phase "Evaluation of Computer Models for Predicting the Fate & Transport of Salt in Soil and Groundwater" is published, also under comission of the Alberta goverment (SCIENCE AND STANDARDS BRANCH ALBERTA ENVIRONMENT, 2003a,b).

PROGRAM NAME	Ranking Sum	Water Balance	Subsurface Flow Capabilities	Transport Mechanisms	Biodegradation Reactions	Sorption/Volatilization	Dimensionality	Domain Variability	Mesh Flexibility	Data Requirements	Computational Requirements	Code Availability	Source Code Availability	Program Installation	Code Validation	Support Availability	Documentation Quality	Ease of Use	Cost \$ U.S
WEIGHTING FACTOR		1	3	1	3	1	3	2	2	1	1	1	1	1	1	1	1	2	
FEMWATER with GMS	9.4	10	10	10	8	8	10	10	10	10	7	8	10	10	10	8	10	10	*
VS2DTI	9.3	10	10	10	8	8	10	10	10	8	7	10	10	10	10	4	10	10	FREE
TOUGH2v2	9.1	10	10	10	8	10	10	10	10	8	7	8	10	1	10	8	10	10	\$2300
UTCHEM with GMS	9.0	10	10	10	10	8	10	10	10	5	10	8	10	1	8	8	7	10	*
MT3D and MODFLOW with ARGUS	8.9	10	9	10	8	8	10	10	10	8	7	8	10	1	10	8	10	10	**
3DFATMIC with GUI	8.8	10	10	10	10	8	10	10	10	8	3	8	10	1	8	8	6	10	\$2000
HYDRUS-2D	8.8	10	10	10	8	8	7	10	10	10	7	8	10	10	6	8	8	10	\$600
RT3D and MODFLOW with GMS	8.8	10	9	10	10	8	10	10	10	8	7	8	1	1	10	8	10	10	*
3DFEMFAT	8.7	10	10	10	8	8	10	10	10	8	3	8	10	9	9	2	6	10	\$1000
SUTRA with ARGUS	8.7	10	10	10	8	8	7	10	10	8	7	8	10	7	10	8	6	10	**
CTRAN and SEEP/W	8.6	10	10	10	8	8	7	10	10	10	7	8	1	7	10	8	10	10	\$6000
SEVIEW	8.5	10	10	10	8	8	10	10	3	8	10	8	10	7	10	8	3	10	\$1000
FEFLOW	8.5	10	10	10	8	8	10	10	10	8	7	8	1	1	10	7	7	10	\$7000
FEMWATER no GUI	8.5	10	10	10	8	8	10	10	10	8	3	10	10	9	10	3	8	4	FREE
MT3D and MODFLOW no GUI	8.5	10	9	10	8	8	10	10	10	8	3	9	10	10	10	3	10	4	FREE
CHEMFLUX3D with SVFLUX3D	8.4	10	10	10	8	8	10	10	10	8	7	8	1	1	6	8	7	10	\$6000
SUTRA no GUI	8.4	10	10	10	8	8	7	10	10	8	10	10	10	10	10	3	6	4	FREE

Figure 1.: Preliminary ranking of codes evaluated by EMS for the Alberta Government (ALBERTA RESEARCH GROUP, 2005)

The geochemical modeling tool PHREEQC used in this study is placed in the top regions regarding geochemistry. In spite of transport it just can model in one dimension, including diffusion, sorption, advection and dispersion though. For a more detailed description of PHREEQC see chapter 5.

4. Theory

4.1. Introduction

Due to the scope of this master thesis, just the very basics of hydrochemistry will be outlined in this chapter. It might appear inappropriate to leave some out, especially in hydrochemical questions, where everything interacts with almost everything in time, space, quality and quantity. For a deeper insight in the theory of these coherences of overwhelming complexity, other sources will be more auxiliary (see line 3 on page 6 et sqq.).

4.2. Equilibrium chemistry

4.2.1. The law of mass action

Some minerals react faster upon contact with water, such as halite (NaCl) or gypsum (CaSO₄) (APPELO & POSTMA, 2005) than others, like Silicate or feldspar. The water molecules surrounds the salt molecules (e.g. Na⁺ and Cl⁻) by solubilizing them, until the water is saturated with respect to salt. Then equilibrium between the solid and the aqueous phase is obtained. From this moment on, solution and precipitation occur in the same amount equally, so that equilibrium is maintained. The fundamental to any description of equilibria in water is the *law of mass action* (APPELO & POSTMA, 2005). It states for a generalized type in the left row and for fluorite (CaF₂ in the right one) (APPELO & POSTMA, 2005, p. 119):



The quantities of the species at the left and the right side of the reaction, e.g. for the solid fluorite and the fluorite in solution, is given by

$$K_{fluorite} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (3) \qquad K_{fluorite} = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]} \quad (4)$$

The term in the denominator $[CaF_2]$ is left out, since the solubility product for a pure phase equals one by definition (STUMM & MORGAN, 1996). Thus the equation becomes:

$$K_{fluorite} = [Ca^{2+}] [F^-]^2 = 10^{-10.57} \quad (5)$$

Formula 5 can be written in logarithmic form for an easier use of the magnitudes:

$$\log K_{\text{fluorite}} = \log [Ca^{2+}] \log [F^-]^2 = -10.57 \quad (6)$$

If we assume, that groundwater is at equilibrium with fluorite, than a water with high concentration of Ca^{2+} will have lower F^- concentration values, and vice versa, corresponding to equation 6. At saturation for fluorite, an increase of Ca^{2+} will decrease the F^- concentration. A way that might be used for water treatment (APPELO & POSTMA, 2005).

4.2.2. Temperature dependency of the mass action constant

The solubility of a mineral is correlated to the temperature of the aquatic system. The mass action constants in literature are valid for a standard state, pressure of one atm and temperature of 25 °C. Generally, the variations of solubility with pressure can be neglected, so the van't Hoff equation (eq. 7) is used to convert given values to the temperature needed (SIGG & STUMM, 1994).

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H}{RT^2} \quad (7)$$

K = mass action constant
 T = Temperature in Kelvin
 ΔH = Reaction enthalpy in kJ/mol
 R = Gas constant 8.3144 J/K mol

Here, the ΔH is the reaction enthalpy, a measure for the heat gained or lost by a chemical system (APPELO & POSTMA, 2005). Since between 5 °C and 35 °C the reaction enthalpy can be seen as independent of temperature (SIGG & STUMM, 1994), the change of K between two temperatures can be calculated as follows:

$$\log K_{T_1} - \log K_{T_2} = \frac{-\Delta H}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (8)$$

see equation 7 for the abbreviations

4.2.3. Concentration and activity

The law of mass action is only valid, when there occur no interactions with other ions in the solution. "In the ideal case of an infinitely dilute solution, where the interactions amongst the ions are close to zero, the activity coefficient is one and the activity equals the concentration" (MERKEL, 2005, p. 8). Ions in aqueous solutions interact with each other, arranging around opposite charged ions, thus the overall charge of the solution is lowered. The temperature and the concentration of ions in the solution also affects the activity, controlling the movement of molecules and the effective size

of the hydrated molecule, respectively. In the range of temperature of groundwater, the derivations of the activity coefficient are small. In thermodynamics, the activity of gases, components in solid solutions and absorbed ions are all expressed as a fraction relative to a standard state (e.g. 25°C) (APPELO & POSTMA, 2005). So the activity coefficient is dimensionless. The activity i is related to the molal concentration m_i by an activity coefficient (γ) (STUMM & MORGAN, 1996), which corrects for non-ideal behavior.

$$i = \frac{\gamma_i \cdot m_i}{m_i^0} \equiv \gamma_i \cdot m_i \quad (9)$$

Activity coefficients for solutes are calculated using the Debye-Hueckel theory. First the *ionic strength* I is defined. Then the ionic strength is related to the temperature and the effective ion size (APPELO & POSTMA, 2005).

$$I = \frac{1}{2} \sum \frac{m_i}{m_i^0 \cdot z_i^2} \quad (10)$$

I = Ionic strength
 m_i = molality of ion i
 m_i^0 = standard state (i.e. 1 mol/kg H_2O)
 z_i^2 = charge number of ion i

$$\log \gamma = -\frac{Az_i^2\sqrt{I}}{1 + B\overset{\circ}{a}_i\sqrt{I}} \quad (11)$$

γ = activity coefficient
 A, B = temperature dependent constants
 $\overset{\circ}{a}_i$ = empirical ion size parameter

This form of the Debye-Hueckel equation is only valid for solutions, where the ionic strength is less than 0.1. For more saline waters, there exist variations of the Debye-Hückel equation, such as (TRUEDELL & JONES, 1973) or (GARREL & CHRIST, 1965), which are not shown here, because such salinities are not to be concerned with in this work.

4.2.4. Calculation of saturation states

Analogue to the law of mass action, one can calculate with the activities, gaining the *Ion Activity Product (IAP)*. Comparing the ion activity product with the equilibrium constant K leads to an expression of the saturation conditions, or the *saturation state* Ω :

$$\Omega = \frac{IAP}{K} \quad (12)$$

So for equilibrium $\Omega = 1$, for supersaturation $\Omega > 1$ and for subsaturation $\Omega < 1$. The logarithmic scale is useful for larger derivations from equilibrium, given by the *saturation index SI* (APPELO & POSTMA, 2005). In PHREEQC the saturation index

can be defined in the input file for selected species, and will also be shown in the output file for the referring species.

$$SI = \log\left(\frac{IAP}{K}\right) \quad (13)$$

SI = 0 reflects equilibrium between the mineral and the solution; SI > 0 supersaturation and SI < 0 subsaturation (APPELO & POSTMA, 2005, p. 131).

The equations presented so far do not include the energy distributions and transfers of reactions. The general reaction presented in formula 1 can also be expressed as:

$$\Delta G = \Delta G_r^0 + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (14)$$

ΔG_r	= change in free Gibbs energy
ΔG_r^0	= standard Gibbs free energy
R	= gas constant ($8.314 \cdot 10^{-3}$ kJ/mol/deg)
T	= absolute temperature in Kelvin

The value of ΔG_r indicates, which direction the reaction will go. If $\Delta G_r = 0$, the reaction is at equilibrium. For $\Delta G_r < 0$ the reaction proceeds to the right, or the products (C and D), for $\Delta G_r > 0$ it proceeds to the left, to the educts (A and B). This formulation has some practical advantages. It allows us to calculate the mass action constant K for any reaction, if data of ΔG_r is available and we see the gain or loss of energy of reactions, which allows us to predict reactions and sequences of certain reactions.

4.3. Fundamentals of redox chemistry

Oxidation and reduction are principle reactions in groundwater chemistry. They control the abundance of oxygen, nitrate, sulfate and other redox sensitive elements and/or molecules due to the oxidation of organic matter or reducible pollutants. The order in which oxidation of some elements and related reduction of others occurs can be predicted from thermodynamic equilibrium data (APPELO & POSTMA, 2005).

Oxidation and reduction can never occur alone. They are always related to another, in the sense that no electron can be appear or disappear. That is why the overall reaction will be referred as a redox reaction. Oxidation of an element is the loss of some of its electrons, whereas reduction means the gain of electrons for an element. The *oxidation number* specifies redoxstate of an element. In its elemental state, the oxidation number of an element is 0, increases with oxidation and decreases with reduction. Usually the oxidation number is written above the element symbols in roman letters, as:



In a general form, as the formula 1 in chapter 4.2.1 redox reactions can be written as:



and in terms of *free energy* (equation: 14):

$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{[C_{ox}]^c [D_{red}]^d}{[A_{red}]^a [B_{ox}]^b} \quad (17)$$

A redox reaction is a transfer of electrons. So we can express redox reactions quantitatively by substituting ΔG by the number of electrons n transferred, the potential E in Volts, a standard potential E^0 and the Faraday constant F (96.42kJ/Volt gram equivalent), which gives us the *Nernst* equation:

$$E = E^0 + \frac{RT}{nF} \ln \frac{[C_{ox}]^c [D_{red}]^d}{[A_{red}]^a [B_{ox}]^b} \quad (18)$$

Though a single oxidation reaction can never occur, their standard potential is measured as a half-reaction, compared to the H_2/H^+ reaction, measured in $pH = 0$ with a Pt-electrode, and which is conventionally set to the value of 0 Volts. All the other half-reactions are listed in databases, to be able to predict reactions and their electron transfer. But the potential of one half-reaction is not useful in geochemical applications, because in natural groundwaters, there is almost no internal redox equilibrium and therefore the measurement the Eh value can lead to biased conclusions (see chapter 3).

To simplify the theoretical treatment of redox reactions, one can write redox half-reactions in terms of the law of mass action, e.g.:



$$K = \frac{[Fe^{3+}][e^-]}{[Fe^{2+}]} = 10^{-13.05} \quad (20)$$

Here, the activity of the electrons is noted in the activity product. For a simpler use we take the logarithm of the activity of electrons:

$$pe = \log[e^-] \quad (21)$$

To reveal the relationship between Eh and pe , we combine formula 21 with formula 18, at 25 °C it is the equal to

$$Eh = 0.059pe(Volt) \quad (22)$$

This is just a basic approach to redox chemistry and can be studied in detail in every book about general-, hydro- or geogeochemistry.

4.4. Kinetics of geochemical reactions

Equilibrium chemistry as shown in formula (14) allows to predict the direction of a chemical reaction, e.g. if precipitation or dissolution will occur. It doesn't show how much time the reaction needs to obtain equilibrium. For some reactions it is not necessary, because the reaction proceeds relatively fast, for example the dissolution of halite (NaCl) in water.

Introducing the factor time in a reaction, where A converts to B in a certain time and at a certain reaction rate. The *reaction rate*, the change of A as function of time, can be calculated with the formula (APPELO & POSTMA, 2005):

$$rate = -\frac{dC_A}{dt} \quad (23)$$

The rate at the time t_1 can be determined from the slope of the tangent at that time. Of course the concentration of A is inversely proportional to the concentration of B. So if there is a decrease in A, the rate is given a negative sign, whereas the rate of B and the corresponding slope of the tangent are positive.

$$rate = -\frac{dC_A}{dt} = \frac{dC_B}{dt} \quad (24)$$

Reactions, where the reaction rate is independent of the concentration of its reactants, are called *zerth order reactions*. Thus the rate is expressed by an integer, and the slope of the tangent is zero. *First order reactions* are represented by radioactive decay reactions, for example. The reaction rate is described by the *rate constant*, or *specific rate*, represented by the latter k in figure 2, multiplied by the concentration of the reactant A.

The overall order of reactions is determined by the sum of the different reaction orders of its reactants. For the reaction



the rate is

$$rate = -\frac{dC_C}{dt} = 3\frac{dC_A}{dt} = 3/2\frac{dC_B}{dt} \quad (26)$$

If its found experimentally that the reaction rate is proportional the the α th order of the concentration of reactant A and the β th power of reactant B, then the rate is:

$$rate = k \cdot C_A^\alpha \cdot C_B^\beta \quad (27)$$

The overall order n of this reaction is:

$$n = \alpha + \beta \quad (28)$$

Since the rate has fixed units, for example (mol/L·s), for an n-order reaction the units of k are $(mol/L)^{1-n/s}$. Rate dependent reactions are dissolution of some minerals such as feldspar or quartz, crystallization like in a jaw of honey, exchange reactions of cations on clay minerals, radioactive decay and degradation reactions, like the degradation of

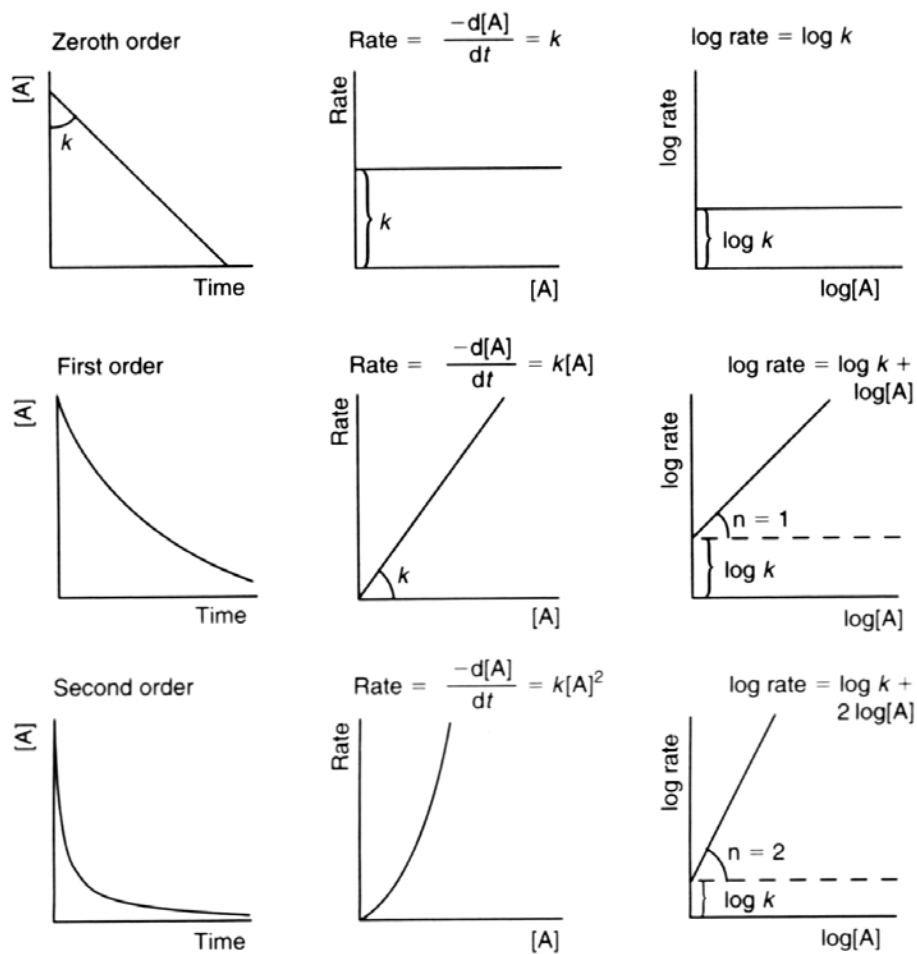
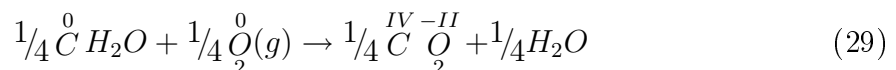


Figure 2.: Rate laws for the reaction A to B (APPELO & POSTMA, 2005, p. 154)

organic matter. The latter depends on the availability of C, bacteria density, electron waste disposal sites for the bacteria (electron acceptors) and the overall energy yield of the reactions. These kinetically controlled reactions are described in section 4.6

4.5. Degradation of carbon in groundwater environments

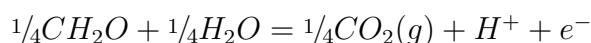
Organic carbon is degraded in groundwater environments. Heterotrophic bacteria use the carbon as an electron donor and the elemental oxygen as an electron acceptor. In this metabolism, using oxygen as an electron acceptor, they gain the most energy, compared to other electron acceptors. The simplified reaction is shown in equation 29, here, for a better comparison, a stoichiometrical balance is chosen that one mole of electrons is transferred (MANAHAN, 2000), the roman numbers above the elements display the oxidation number (see chapter: 4.3):



When the available oxygen is depleted, bacteria use other oxidised elements as electron acceptors. There exist a certain sequence in which bacteria reduce the abundant oxidised elements, due to the energy that yields to the bacteria in the overall process. The energy change in Gibbs free energy (ΔG) for the oxidation of CH_2O and different reduced substances is listed in table 2. The change in the pe gives the value, in which redox states the reactions occur. The decreasing values of ΔG imply that denitrification begins, when oxygen is depleted, otherwise it would be energetically not favorable.

Table 2.: Selected redox reactions in groundwaters and its pe and ΔG values (STUMM & MORGAN, 1996, taken from p. 474)

process	pE	ΔG
Aerobic respiration		
$\frac{1}{4} O_2 + H^+ + e^- = \frac{1}{2} H_2O$	+13.75	-125
Denitrification		
$\frac{1}{5} NO_3^- + \frac{6}{5} H^+ + e^- = \frac{1}{10} N_2(g) + \frac{3}{5} H_2O$	+12.65	-119
Manganese reduction		
$\frac{1}{2} MnO_2(s) + \frac{1}{2} HCO_3^-(10^{-3}) + \frac{3}{2} H^+ + e^- = \frac{1}{2} MnCO_3(s) + H_2O$	-30	+8.9
Nitrate reduction		
$\frac{1}{8} NO_3^- + \frac{5}{4} H^+ + e^- = \frac{1}{8} NH_4^+ + \frac{3}{8} H_2O$	-82	+6.15
Iron reduction		
$FeOOH(s) + HCO_3^-(10^{-3}) + 2H^+ + e^- = FeCO_3(s) + 2H_2O$	-	-0.8
Fermentation		
$\frac{1}{2} CH_2O + H^+ + e^- = \frac{1}{2} CH_3OH$	-	-3.01
Sulfate reduction		
$\frac{1}{8} SO_4^{2-} + \frac{9}{8} H^+ + e^- = \frac{1}{8} HS^- + \frac{1}{2} H_2O$	-25	-3.75
The values of ΔG are coupled with this oxidation reaction:		



The most pristine groundwaters are not depleted in oxygen, due to the lack of electron donors, and therefore aerobic metabolisms dominate the process of degradation of organic matter. But once groundwater is isolated and there is a sufficient pool of

organic carbon, the aquifer is dominated by a succession of terminal electron acceptor processes (CHAPELLE, 2001). The end of the electron transfer processes to an electron acceptors, in other words, the final arrival, is [commonly] referred to as the terminal electron acceptor processes (TEAP) (LOVLEY & CHAPELLE, 1995).

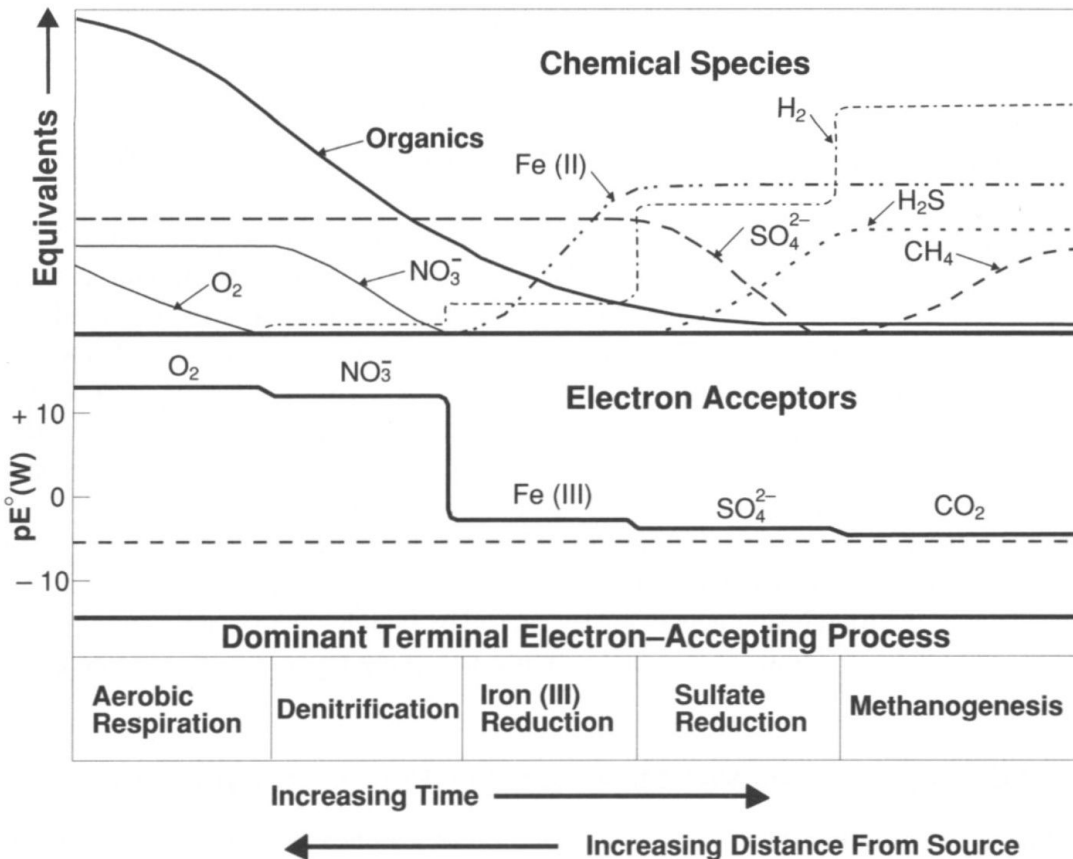


Figure 3.: Conceptual model of hydrocarbon degradation and its sequential impact on groundwater chemistry. (WIEDEMEIER ET AL., 1999, p. 208)

So the redox state of an aquifer depends on the pool of organic carbon or organic matter, and can be seen as a function of time. The older a sediment, the further is its redox state respective to sequence of TEAPs. FROELICH ET AL. (1979) (1979) measured the concentrations of O_2 , NO_3^- , NO_2^- , Mn^{2+} , Fe^{2+} , SO_4^{2-} and S^{2-} in pelagic sediments. In the profile, once oxygen was depleted, nitrate concentrations diminished. When the sediment was anoxic, Mn^{2+} began to appear until the reduction of Fe^{3+} to Fe^{2+} , in the zone where the nitrate was completely consumed .

There is a great variety in the common electron accepting processes that occur and therefore it is "much more challenging identifying electron acceptors" than electron donors (CHAPELLE, 2001, p.289). Furthermore, measuring voltage difference between a standard electrode and the groundwater environment, the measured value of Eh would be inaccurate, because "the concept and its measurement of Eh requires thermodynamic equilibrium in the solution being considered" (CHAPELLE, 2001, p. 286), as LINDBERG AND RUNNELS showed 1986 (see 3). Another way to determine the state of anaerobic

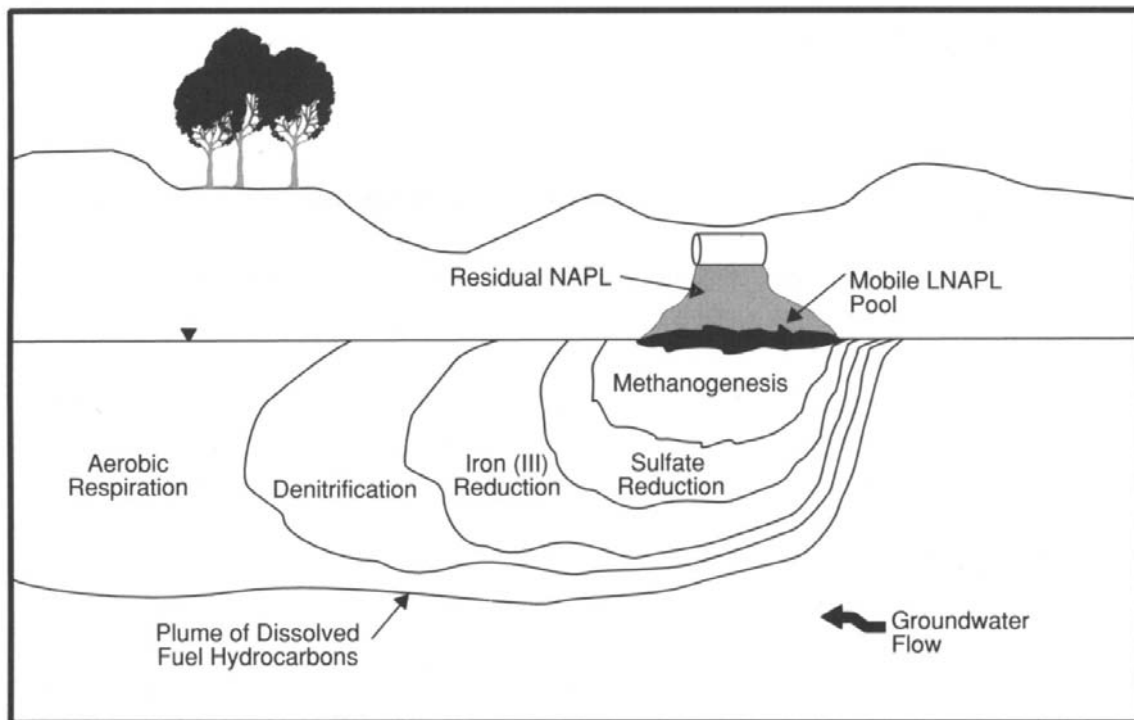


Figure 4.: The different TEAPs in time and/or space. The source of carbon here is a leaking barrel of NAPLs and LNAPLs. NAPL means Non-Aqueous Phase Liquid, LNAPL means Light Non-Aqueous Phase Liquid) (WIEDEMEIER ET AL., 1999, p. 210)

oxidation processes is the concentration of hydrogen. Molecular hydrogen (H_2) is a waste product from fermentative bacteria that initiate the oxidation of organic matter. This hydrogen is then utilized by respiring microorganisms such as nitrate reducers, Fe(III) reducers, sulfate reducers and methanogens (CHAPELLE, 2001). The hydrogen concentration is an indicator, which TEAP dominates. For example, if nitrate is in sufficient abundance, the hydrogen concentration will maintain the range of 0.01-0.05 nM/L, because the concentrations of molecular hydrogen are too low for e.g. Mn^{4+} reducers to effectively respire. The characteristic hydrogen concentrations are shown in table 3

Table 3.: Potential energy yield and steady-state hydrogen concentrations characteristic of different anaerobic oxidation processes (CHAPELLE, 2001, p. 291)

Redox reaction	Potential standard free energy (kJ per H_2)	Characteristic Hydrogen Concentrations (nM/L)
$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6H_2O$	224	0.01-0.05
$MnO_2 + H_2 \rightarrow Mn(OH)_2$	163	0.1-0.3
$Fe(OH)_3 \rightarrow 2Fe(OH)_2 + 2H_2O$	50	0.2-0.8
$SO_4^{2-} + 4H_2 + H^+ \rightarrow HS^- + 4H_2O$	38	1.0-4.0
$HCO_3^- + 4H_2 + H^+ \rightarrow CH_4 + 3H_2O$	34	5.0-15.0

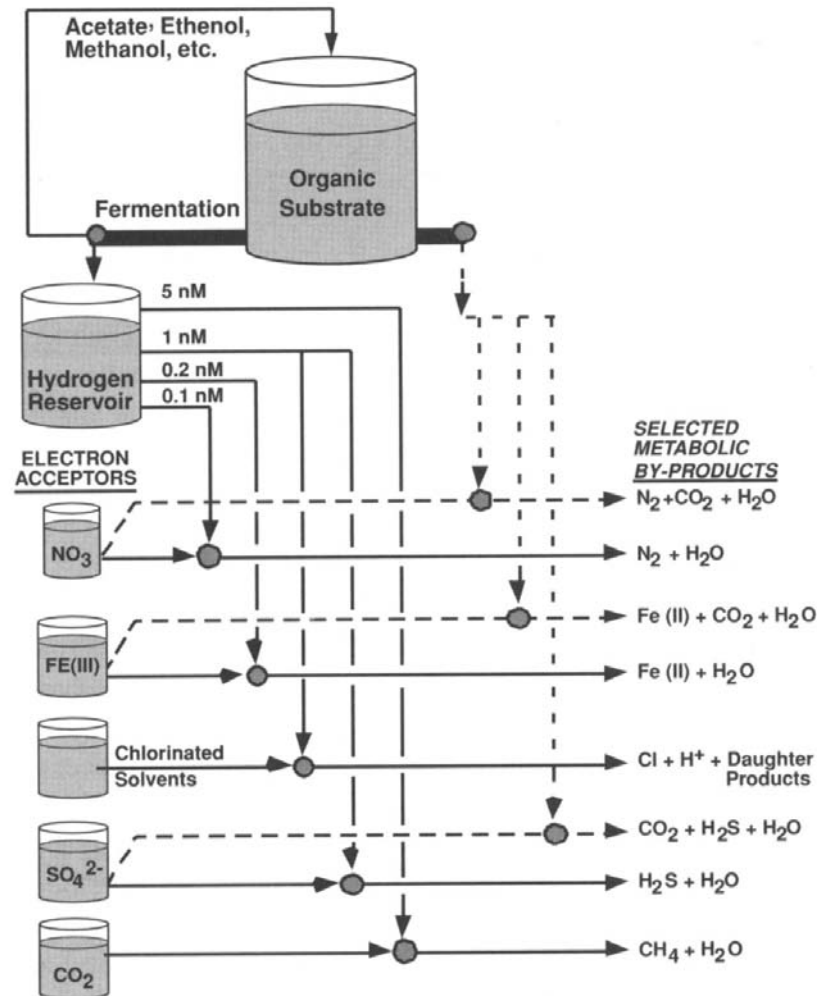


Figure 5.: Conceptual model of hydrogen and carbon as electron donor, the sequential TEAP and typical hydrogen concentrations (WIEDEMEIER ET AL., 1999)

WIEDEMEIER ET AL. (1999) published a flow chart of the concluding processes, involving the sequential use of TEAPs and the characteristic hydrogen concentrations. Chlorinated solvents are included, where the oxidised chlorine also acts as an electron acceptor. In figure 5 the dashed lines represent the reactions, where carbon is the direct electron donor, solid lines represent hydrogen as electron donor. The pipes in the hydrogen reservoir show the correlation between TEA and the corresponding hydrogen concentration in the aquifer, under which the following TEAP cannot function.

4.6. Kinetics of biodegradation

In order to describe mathematically natural attenuation together with growth of bacterial cultures, the formulation of MONOD (1949) is still widely used. This empirical hyperbolic function can describe biodegradation rates following zero- to first-order kinetics with respect to the target concentration (ALVAREZ & ILLMAN, 2006). Monod formulated primarily this equation, for "quantitative aspects [...], as a method for the study of bacterial physiology and biochemistry" (MONOD, 1949, p. 371), as follows:

$$\mu = \mu_{\max} \frac{C}{k_{1/2} + C} \quad (30)$$

$$\begin{aligned} \mu &= \text{growth rate (time}^{-1}\text{)} \\ \mu_{\max} &= \text{maximum specific growth rate (time}^{-1}\text{)} \\ C &= \text{concentration of growth-limiting substrate (mg/L)} \\ k_{1/2} &= \text{half-saturation constant} \end{aligned}$$

The *half saturation constant* $k_{1/2}$ is also known as the growth limiting substrate concentration, which is the substrate concentration corresponding to a specific growth rate equal to half the maximum concentration (ALVAREZ & ILLMAN, 2006). As said before, the rate equation describing μ as a function of C contains zero-order, mixed-order and first-order regions. Is $C \gg k_{1/2}$, $k_{1/2}$ and C is almost equal to C , μ_{\max} becomes the limiting maximum reaction rate and the reaction becomes zero-order with:

$$\mu = \mu_{\max} \quad (31)$$

When $C \ll k_{1/2}$, equation 30 reduces to:

$$\mu = \frac{\mu_{\max}}{k_{1/2}} C \quad (32)$$

and $\mu_{\max}/k_{1/2}$ is equal to the first-order rate constant (WIEDEMEIER ET AL., 1999). The degradation of the substrate or contaminant (in equation 30 referred to as concentration of growth-limiting substrate) is related to the growth of microorganisms. This relation is described by the *yield coefficient* Y . It is a measure of the organisms formed per substrate utilized. So the change in substrate concentration can be expressed as follows:

$$\frac{dC}{dt} = \frac{\mu_{\max} M \cdot C}{Y(k_{1/2} + C)} - bM \quad (33)$$

$$\begin{aligned} \mu &= \text{growth rate (time}^{-1}\text{)} \\ \mu_{\max} &= \text{maximum specific growth rate (time}^{-1}\text{)} \\ C &= \text{Concentration of growth-limiting substrate (mg/L)} \\ k_{1/2} &= \text{half-saturation constant} \\ M &= \text{Microbial mass in mg/L} \\ Y &= \text{yield coefficient moles biomass-C/ moles C} \\ b &= \text{first-order decay coefficient for cell death} \end{aligned}$$

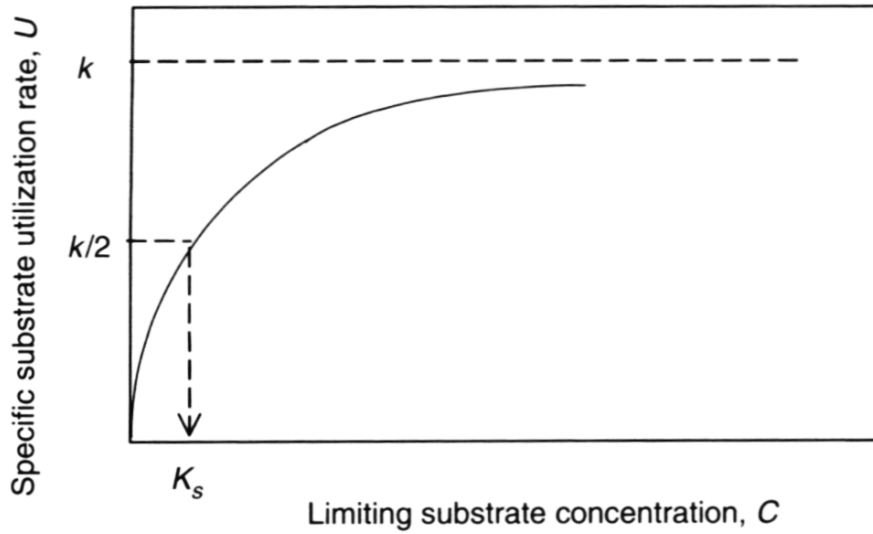


Figure 6.: Graphical representation of the Monod equation (ALVAREZ & ILLMAN, 2006)

In scientific literature, the nomenclature of the formulas 30 and 33 is not exactly defined, but it can be noticed, that formula 30 is commonly referred to as the Monod equation and formula 33 as the Michaelis-Menten equation.

A special case in groundwater redox chemistry is, that in case of pollution by hydrocarbons, after a lag time due to bacterial growth, attenuation depends more on the availability of TEAPs than on the activity of bacteria (LOVLEY & CHAPELLE, 1995; BARRY ET AL., 2002). This decay inhibiting process can be described with the extension, similar to that of electron donors: Here, the term of growth of the limiting substance is referred to as TEA (terminal electron acceptors):

$$\frac{dC}{dt} = - \left(\frac{\mu_{\max} \cdot C}{k_{1/2}} \right) \left(\frac{\mu_{\max TEA} \cdot C_{TEA}}{k_{1/2 TEA} + C_{TEA}} \right) \quad (34)$$

$\mu_{\max TEA}$ = maximal rate multiplier for the TEA
 $k_{1/2}$ = half-saturation constant for a TEA (mol/L)
 C_{TEA} = concentration of the TEA (mol/L)
 (APPELO & POSTMA, 2005, p. 525)

Based on empirically determined degradation rates, APPELO & POSTMA (2005) developed an expression for the oxidant multiplier showed in equation 34:

$$r_{oxidants} = \left(\frac{C_{O_2}}{2.94 \times 10^{-4} + C_{O_2}} + \frac{C_{NO_3^-}}{1.55 \times 10^{-4} + C_{NO_3^-}} + \frac{C_{SO_4^{2-}}}{1 \times 10^{-4} + C_{SO_4^{2-}}} \right) \quad (35)$$

So the overall degradation of organic carbon is:

$$\frac{dS_{OC}}{dt} = -k_l \cdot S_{OC} \cdot r_{oxidants} \quad (36)$$

S_{OC} = organic carbon content
 C_i = is in molalities (moles/kgw)
 k_l = first-order decay constant
(APPELO & POSTMA, 2005; APPELO & PARKHURST, 1998)

The values for the parameters in the Monod equation just can be found out experimentally in column studies or via field measurements. The maximum specific growth rate μ_{max} ranges from 0.04 to 10 (1/day) (PROMMER ET AL., 1999; BARRY ET AL., 2002; OSTENDORF ET AL., 2007, e.g.), whereas the value of the half-saturation constant ($k_{1/2}$) in the most studies is 1×10^{-5} (PROMMER ET AL., 1999; BARRY ET AL., 2002; APPELO & POSTMA, 2005). The yield coefficient ranges from 0.3 to 0.5 (ESSAID ET AL., 1995; PROMMER ET AL., 1999; OSTENDORF ET AL., 2007).

5. PHREEQC

PHREEQC is a computer program for modeling chemical reactions and transport processes in groundwater environments. As seen in chapter 3 on page 5, there are many programs modeling reactive transport. PHREEQC's advantage is the numerical solution algorithm and the implementation of various coherent databases comprising thermodynamical data of elements, compounds and reactions, enabling PHREEQC to calculate:

- speciation and saturation-index based reactions
- isotope mole balances
- inverse modeling
- batch reactions and 1D transport
- reversible reactions, including
 - aqueous equilibria
 - mineral equilibria
 - gas equilibria
 - solid-solution equilibria
 - surface complexation equilibria and
 - ion-exchange equilibria.

Further

- irreversible reactions, involving
 - specified mole transfer of reactants
 - kinetically controlled reactions
 - mixing of solutions
 - temperature changes. (PARKHURST & APPELO, 1999)

(PARKHURST & APPELO, 1999)

PHREEQC is based on the Fortran code PHREEQE. 15 years later, PARKHURST (1995) published the completely new program PHREEQC 1, written in the C language. The second version (PARKHURST & APPELO, 1999) extends the previous, resuming the capabilities of the program listed above. The orientation "towards system equilibrium rather than just aqueous equilibrium" (PARKHURST & APPELO, 1999, p. 3) is possible due to the implementation of various chemical databases. The database

phreeqc.dat is taken from the PHREEQE version and includes the most important elements and some major heavy metals. One also can use calculate with the database of the WATEQ4F-model (NORDSTROM ET AL., 1990) or the database files of MINTEQA2 (ALLISON ET AL., 1991). The database *lnl.dat* was originally made in geochemist workbench format, and reformatted to fit the PHREEQC code. The major problem concerning the databases is the lack internal consistency. The log K's and the enthalpies have been taken from various literature sources. But *phreeqc.dat* and *wateq4f* are consistent with BALL & NORDSTROM (1991) and NORDSTROM ET AL. (1990) (PARKHURST & APPELO, 1999). In this thesis the PHREEQC version 2.14. is used.

5.1. Redox process modelling with PHREEQC

Redox states and processes (see chapter 4.3) are implemented. Regarding a particular redox state, the user can specify the pe-value, or, as LINDBERG & RUNNELS (1984) proposed, enter the concentrations of a certain redox couple, such as Fe(III)/Fe(II) or As(V)/As(III). PHREEQC calculates the pe-value corresponding to the given redox couple. Without specification of an redox state, PHREEQC begins its calculations with the standard pe-value of 4 (APPELO & POSTMA, 2005).

5.2. Rate expressions within PHREEQC

Rate expressions of geochemical reactions that not reach equilibrium in the modeled time frame can be calculated with the embedded BASIC interpreter in PHREEQC. The different rates are integrated over a time interval using the Runge-Kutta algorithm (APPELO & POSTMA, 2005). The user can specify which tolerance the error estimation of the numerical method should not exceed. There are two data blocks within the user specifies its rate equations. In the data block **RATES**, the mathematical expression of the kinetic reactions is defined. In the **KINETICS** data block, the parameters controlling the reaction rates set in the **RATES** block are defined, further which phase or chemical species reacts, their stoichiometric coefficients and at last parameters controlling the iterations of the Runge-Kutta algorithm (PARKHURST & APPELO, 1999). The user can decide with the keyword "**INCREMENTAL_REACTIONS**", whether every time step starts at time zero and so the results of the previous one does not affect the next run, or that the results of the previous time step are the starting point of the next iteration (PARKHURST & APPELO, 1999).

5.3. Examples of PHREEQC applications

PROMMER ET AL. (1999) used the PHREEQC code to model the transport and the changes of all inorganic components considered. In a study concerning the reactive processes during biodegradation the source or sink term of chemical inorganic species due to precipitation or solution was modeled with PHREEQC (PROMMER ET AL., 2002). BRUN & ENGESGAARD (2002) cite in their review several approaches modeling the geochemical reactions in pollution plumes using a *partial equilibrium approach*. These

studies published in the late nineties "either use the PHREEQE or the PHREEQC code as the geochemical equilibrators" (BRUN & ENGESGAARD, 2002, p. 215). As a simplification of the degradation of organic matter, the cited studies add carbon in the valence state of zero to the solution (BRUN & ENGESGAARD, 2002). AAGAARD ET AL. (2002, A5) wrote in an abstract for the Goldschmidt Conference, that "PHREEQC reactive flow simulations with dual Monod kinetics included, represent an attractive approach to evaluate the degradation potential for contaminated aquifers." Unfortunately it was not possible to obtain this publication in the thesis' time frame.

6. Application of PHREEQC

6.1. Introduction

As shown in chapter 4.5, the microbial consumption of carbon in groundwater environments generates specific sequential chemical reactions, whose characteristics depend on the abundance of degradable carbon and terminal electron acceptors. Furthermore the mathematical description of the bacteria population activity consuming carbon has been elucidated in chapter 4.6. In this chapter, different modelling approaches with PHREEQC will be outlined. First, organic carbon is added incrementally to three different solutions. One gneissic periglacial water, one with higher nitrate concentrations and one partially depleted in oxygen. The organic carbon added reacts to thermodynamical equilibrium instantaneously. The simulations are run with the default database *phreeqc.dat*. For comparison, one simulation is run with the database *watq4f.dat* and one compares the changes of nitrogen equilibrium modelled with two different databases.

6.2. The degradation of organic matter modelled with PHREEQC

The keyword **REACTION** in PHREEQC enables to add or remove elements or compounds to the defined solution. Representing organic matter, the formula $CH_2O(NH_3)_{0.07}$ is added incrementally in $\log \cdot n$ ($n= 1-20$) steps, multiplied by 0.01, as shown in figure 7. The formula for biomass is taken from (PARKHURST & APPELO, 1999, p. 236), where biomass degradation is modelled without the principal ions serving as TEAs.

Three different waters are chosen to determine, how the chemical composition infers the redox changes due to biomass degradation. The values for the hydrochemistry of the initial solution are taken from the official website of the local water supplier *badenova* (BADENOVA, 2007). The first water is taken from a gneissic periglacial area in the west of Freiburg, south-western Germany. The second water derives from the Upper Rhine valley, which has higher values of sulfate and calcite. To see how higher nitrate values affect the redox chemistry of the degradation process, an arbitrary chosen value of 20 mg of $NaNO_3$ was added to the original solution. In simulation 6 the partial pressure of oxygen is set to $\frac{2}{3}$ of the original value, from 20.17 % to 13.85 %.

The partial pressure of the gas composition of the atmosphere has to be defined with the keyword **GAS_PHASE**. Nitrogen has to be defined as a chemically inert gas, represented as `Nzero`. Otherwise nitrogen and oxygen react to equilibrium, which in natural environments hardly happens, due to the thermodynamically inertia of nitro-

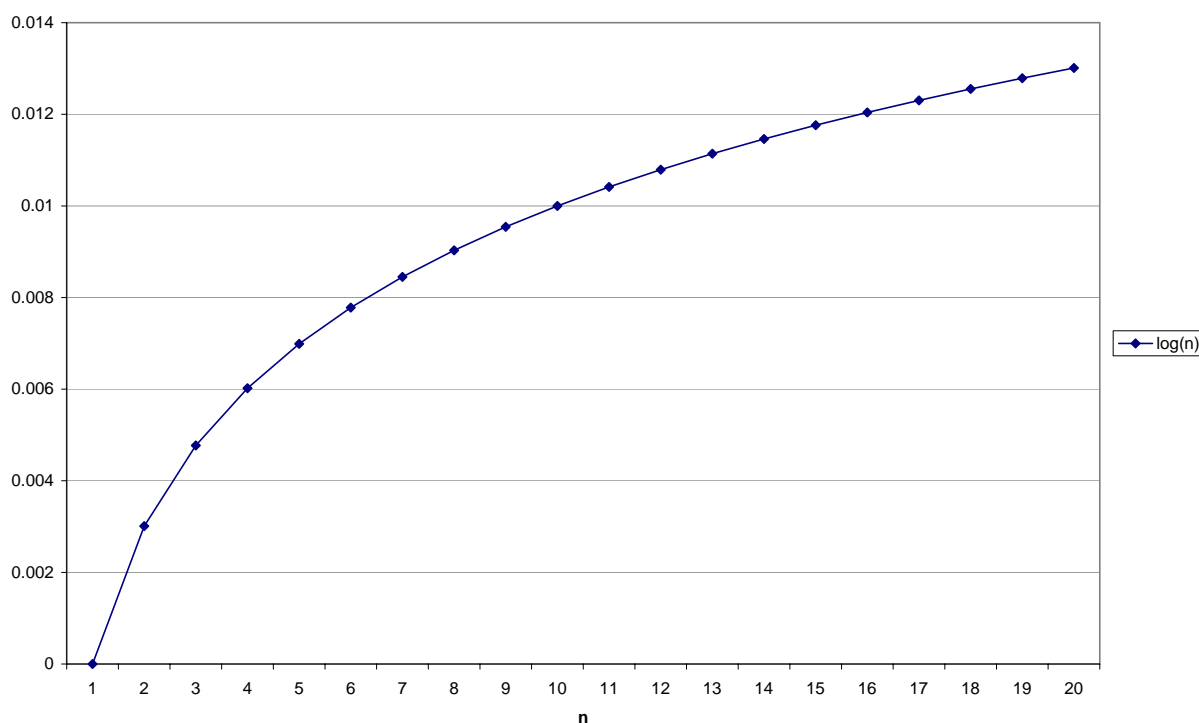


Figure 7.: Moles of organic carbon added to solution

gen. As second step, PHREEQC equilibrates the gases and the solutes given, due to their thermodynamical properties, as defined in the database. Then the addition of the formula given in the **REACTION** block begins, in intervals defined by the user. After each run, PHREEQC calculates chemical equilibrium.

6.2.1. Simulation 1: Reference simulation

In figure 8, the values of organic matter added to the solution are set to the abscissae. The left ordinate represents the concentrations in moles/kg H₂O and the right ordinate the values of the pe and the pH.

Figure 8 shows the changes of pH, pe and the concentrations of principal elements due to the addition and oxidation of organic matter. In the abscissa, the concentrations in moles/kg H₂O of the formula $CH_2O(NH_3)_{0.07}$ added are displayed, which represents organic matter, and it increases in $\log \cdot n \cdot$ ($n=1-20$) steps. In the first step, when 0 moles are added, PHREEQC equilibrates the solution thermodynamically. As long as oxygen is abundant in concentrations above 1×10^{-3} moles/kg H₂O, the pe increases little, from 18.43 to 18.72. Then the depletion of oxygen proceeds rapidly and the pe value decreases to ~ -1.7 . With that change of the redox conditions, the pH value increases from ~ 3.35 to ~ 5.15 . The pe values is strongly correlated to the concentration of oxygen, whose value changes from 1.63 mmoles/kg H₂O, according to the partial pressure of 20.78 %, to 8.19×10^{-4} moles/kgw, and in the further step to 8.81×10^{-08} moles/kgw, and then to zero. The value of nitrate ranges around 1 and

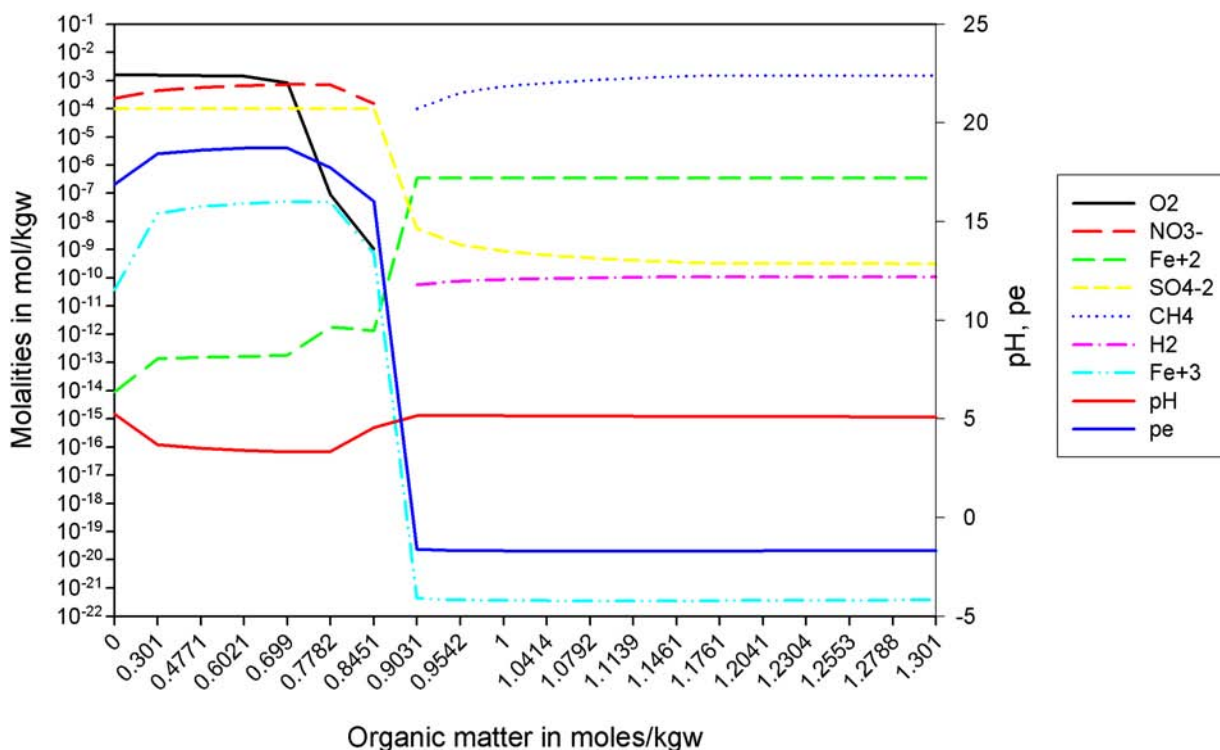


Figure 8.: Simulation 1. Changes of hydrochemistry due to the reduction of organic matter

0.1 mmoles/kgw. The nitrogen species in the degradation process are regarded more specified in figure 14. Iron is increasing in both redox states. Fe+3 goes from zero to 7.15×10^{-10} moles/kgw and back to zero, when oxygen is depleted. The concentration of the reduced state of iron (Fe+2) increases a little from 9.24×10^{-15} moles/kgw to 1.34×10^{-12} moles/kgw. As the pe remains negative, the molality of Fe+2 stays at the value of 3.45×10^{-7} moles/kg H₂O. In oxidising conditions, sulfate varies around 0.1 mmoles/kgw, and decreases fastly corresponding to the change of redox state to $\sim 3.0 \times 10^{-10}$ moles/kgw. Methane increases at step 8 from 9.97×10^{-5} moles/kgw to maximal 1.51×10^{-3} moles/kgw. The concentration of hydrogen varies around 1×10^{-10} moles/kgw.

One can see, that the reduction of oxygen mainly affects the pe and the related redox processes. Once oxygen is depleted, the reduction of other electron acceptors, such as nitrate, sulfate and iron, occurs rapidly. The raising of the value of Fe+3 in the range of zero to 4.77×10^{-1} moles/kgw organic matter may be influenced by the change of the pH of the solution. In the following increments, iron is reduced from Fe+3 to Fe+2. The high value of methane bases on the high concentrations of carbon added and the lack of other electron acceptors. The concentration of hydrogen are almost stable around 0.95 to 1.07 nM/kgw. According to WIEDEMEIER ET AL. (1999), (figure 5 on page 30), this redox state is characterized by a hydrogen concentration of 5 nM/kgw H₂, due to bacterial activity, which PHREEQC does not account for.

6.2.2. Temperature dependency

PHREEQC also accounts for temperature effects. Simulation 8 was run with a temperature given for water and air of 5°C, represented by the straight lines, and 25°C, represented by the dashed lines in figure 9. The solubility of gases in water is highly dependent of the temperature. Thus in colder environments, water has a higher oxygen abundance.

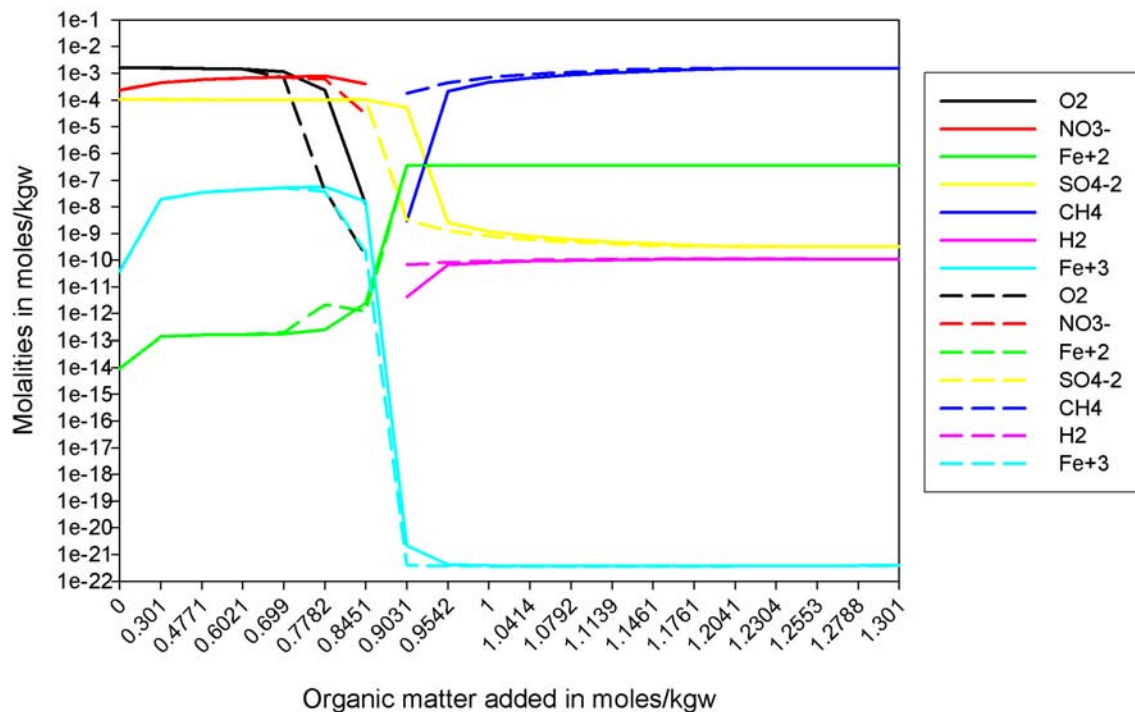


Figure 9.: Temperature dependency: Straight lines represent 5°C, dashed one 25°C water temperature.

The dependency of oxygen abundance with temperature is shown in figure 9. The warmer water depletes in oxygen more rapidly. The other redox reactions are affected by the earlier depletion of oxygen. Such as nitrate, which lasts longer in water with colder temperatures, because oxygen is more abundant and is the first chosen electron acceptor. Figure 10 shows the pe and pH values of temperature increments from 0°C to 20°C. A significant bias toward more biomass is in the simulation with 0°C. With a water and air temperature of 15°C, pH and pe begin to change with less biomass added. With temperature of 20°C, the pe values is higher in oxidising conditions, a change that might be due to program errors.

6.2.3. Simulation 2: Smaller increments

To evaluate the influence of the oxygen concentration on the redox state, smaller increments of the organic matter added were chosen. By starting at the concentration of 8.25 moles/kgw and adding further increments of 0.05 moles $CH_2O(NH_3)_{0.07}$ per kgw in each step, a higher resolution of the redox procedures is obtained.

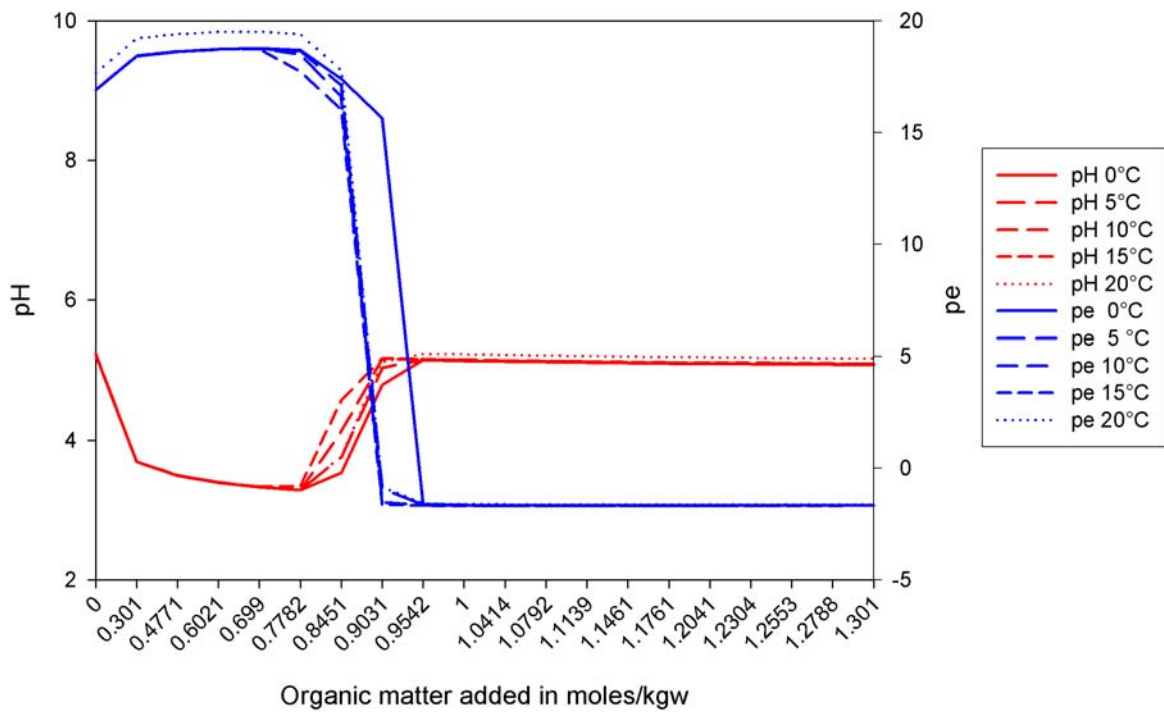


Figure 10.: Temperature dependency: The changes of pH and pe due to different temperatures, range is from 0 to 20°C.

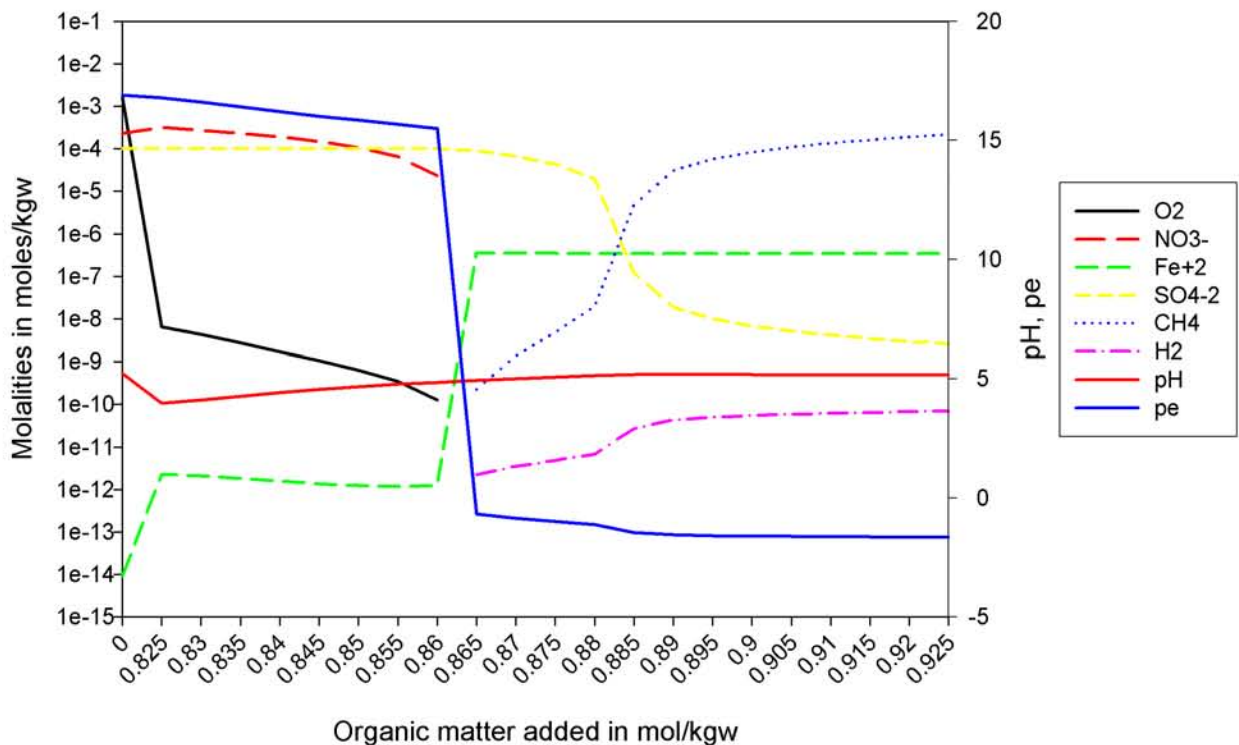


Figure 11.: Simulation 2: Changes of hydrochemistry in small incremental steps of organic carbon added

In figure 11, the results of simulation 2 are displayed. The initial conditions of the water used are the same as in simulation 1 (figure 8). The keyword `INCREMENTAL_REACTIONS` is set to `-true`, resulting in an addition of the increments of organic matter added, as shown in the abscissae in figure 11. In consequence of the smaller increments of the carbon added, the modification of the concentrations is less steep. In comparison to figure 8, oxygen depletes after a lower concentration (1.28×10^{-10} moles/kgw). Fe+2 arrives at the same concentration, whereas the reduction of sulfate and the formation of hydrogen and methane occurs in lower increments. The final concentrations of sulfate, methane and hydrogen are higher, respectively lower, due to the lower total quantity of organic matter added.

6.2.4. Simulation 3: Different database

In figure 12, the influence of the use of a different database is exemplified. In this simulation, the database *wateq4f.dat* was used with the same input parameters as in simulation 2, shown in figure 11.

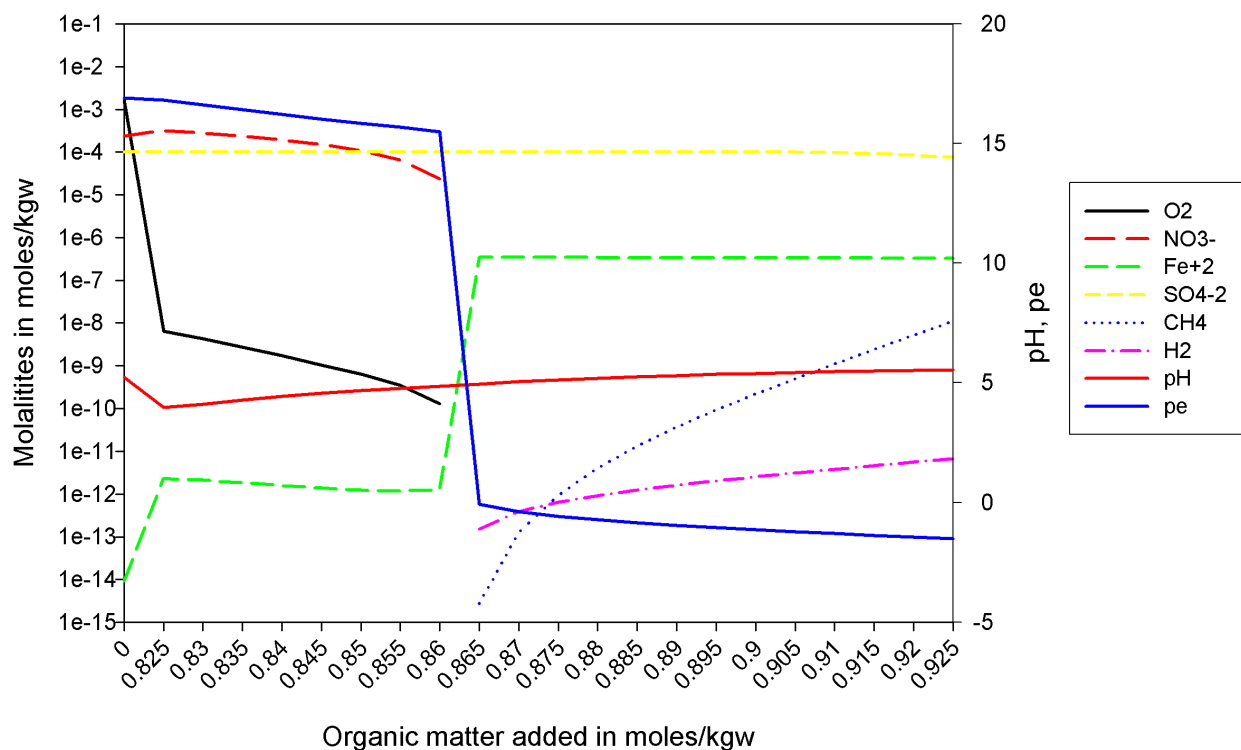


Figure 12.: Simulation 3: The influence of the different database on simulation 2. Database used is *wateq4f.dat*

The progression of oxygen, nitrate, iron(II), pe and pH are the same as in simulation 2. However, reduction of sulfate differs over almost 5 magnitudes. Also the formation of hydrogen and methane does not reach concentrations as high as in simulation 2. To maintain comparability, the following simulations are run with *phreeqc.dat* as the reference simulation (sim. 1).

6.2.5. Simulation 4: Higher nitrate content

A water from the Upper Rhine valley with higher calcite, sulfate and nitrate contents was chosen to evaluate a different response on the sequential addition of organic matter. Principal issue was to determine the influence of higher nitrate concentrations. An influence has been detected clearly with the original composition, but not be seen with a resolution which fits to a page. So the concentration of nitrate has been augmented arbitrarily by adding 20 mg of NaNO_3 . The results are shown in figure 13.

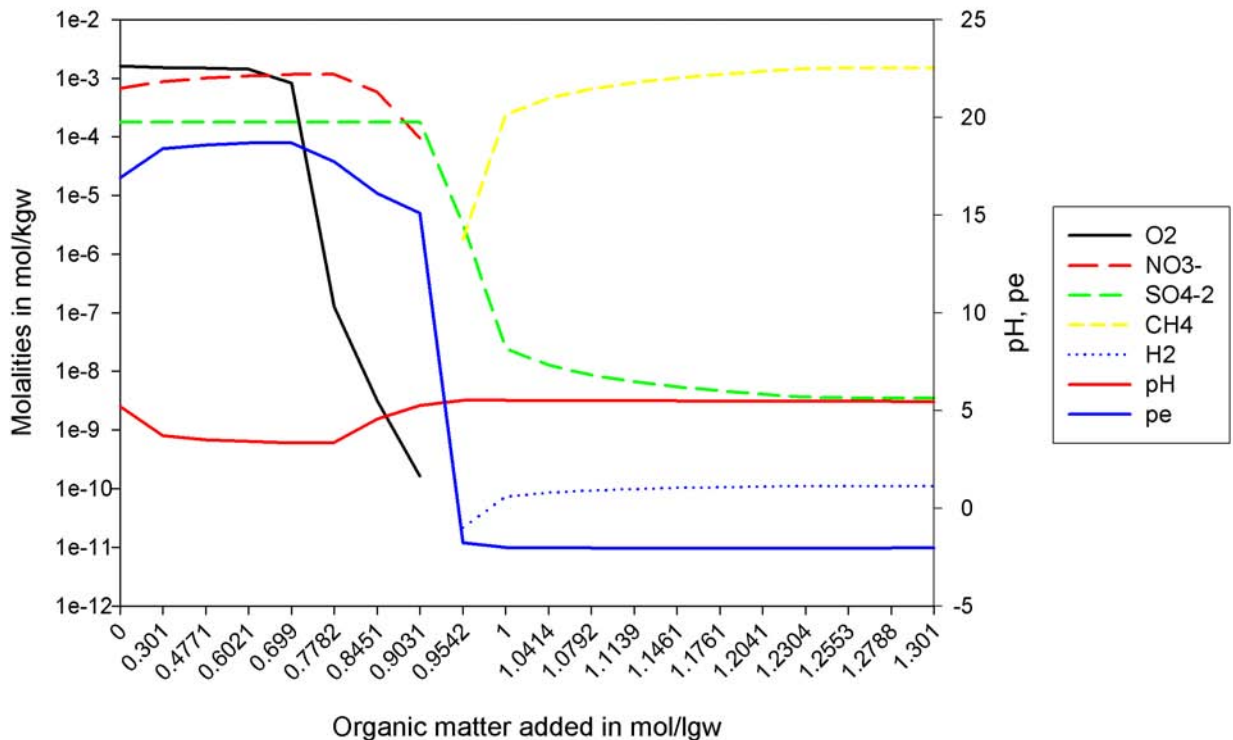


Figure 13.: Simulation 4: Water with higher nitrate concentrations

Some differences between simulation 1 (figure 8) and simulation 4 (figure 13) can be stated. Iron is not abundant in the analyzed water. Even though the concentration of calcium is more than double, the denoted pH value is lower than in simulation 1. The high concentration of nitrate (41.4 mg/L) yields to a capability of the aquatic system, to oxidise more biomass in conditions characterized by a positive pe value. The critical concentration of the biomass added, when the pe value changes from positive to negative values, is one reaction step later than in simulation 1. Quantitatively, the system bears 0.052 moles of $\text{CH}_2\text{O}(\text{NH}_3)_{0.07}$ more than the one in simulation 1, before tilting to reducing conditions (at 0.954 moles $\text{CH}_2\text{O}(\text{NH}_3)_{0.07}$ per kgw added).

6.2.6. Simulation 5: Nitrogen species

To obtain a clearer view of the composition of nitrogen species, the input parameters of simulation 4 were used, but only concentrations of nitrogen species are displayed. The default database *phreeqc.dat* only accounts for the nitrogen species N_2 , NO_2^- and

NO_3^- , therefore the database *llnl.dat* was chosen for simulation 5. And in figure 15, the concentrations of nitrogen species *phreeqc.dat* does account for are compared with the results the simulation with *llnl.dat* gives.

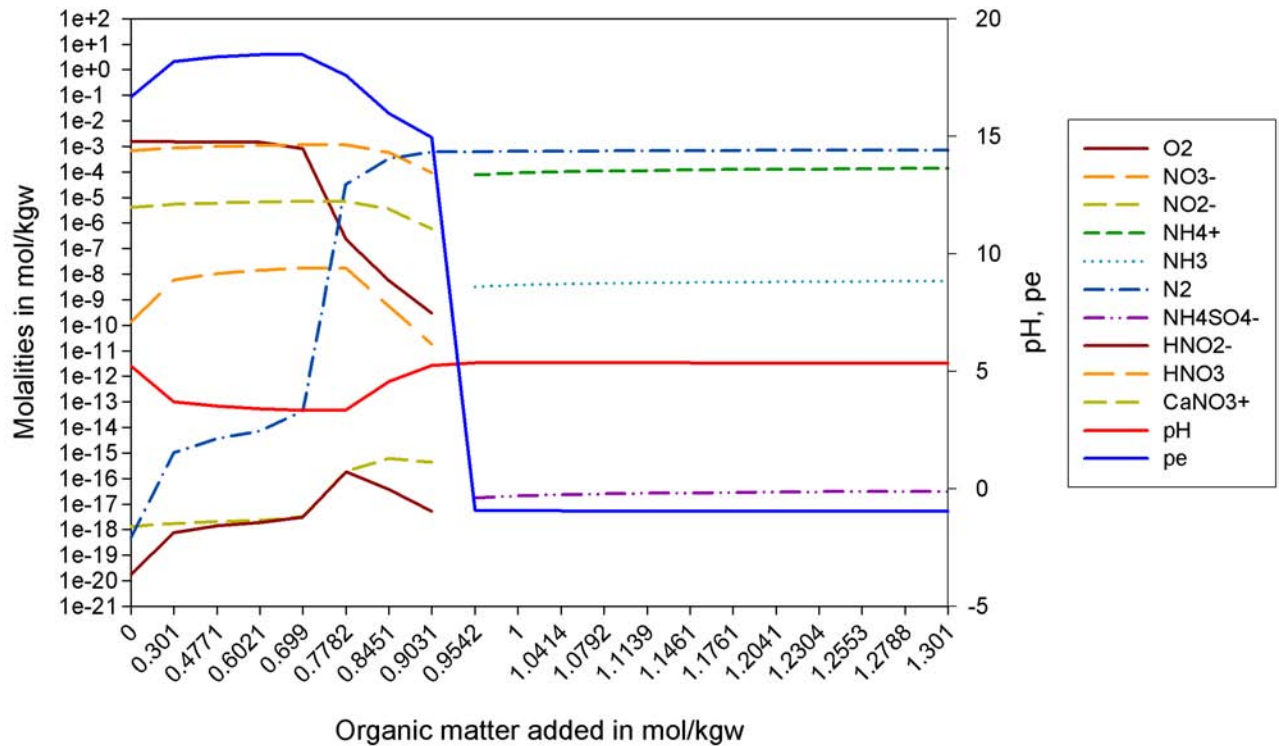


Figure 14.: Simulation 5: Nitrogen species

The pH and the concentrations of O₂ and NO₃⁻ are almost congruent with each other. The pe value in reductive conditions is calculated by *llnl.dat* at -0.95 and by *phreeqc.dat* at -2.05. The database *phreeqc.dat* calculates one magnitude more NO₂⁻ than *llnl.dat* as in the first four steps with N₂.

6.2.7. Simulation 6: Reduced partial pressure of oxygen

In this simulation, the same input parameters as in simulation 1 were used, but the partial pressure of oxygen was set to $\frac{2}{3}$ of the original value, from 20.78 % to 13.85 %.

The results of simulation 6 are displayed in figure 16 show, that the lower abundance of oxygen influences the redox situation strongly. Though the mechanisms are equal to simulation 1 (figure 8), there is a bias of the system toward lower concentration of biomass.

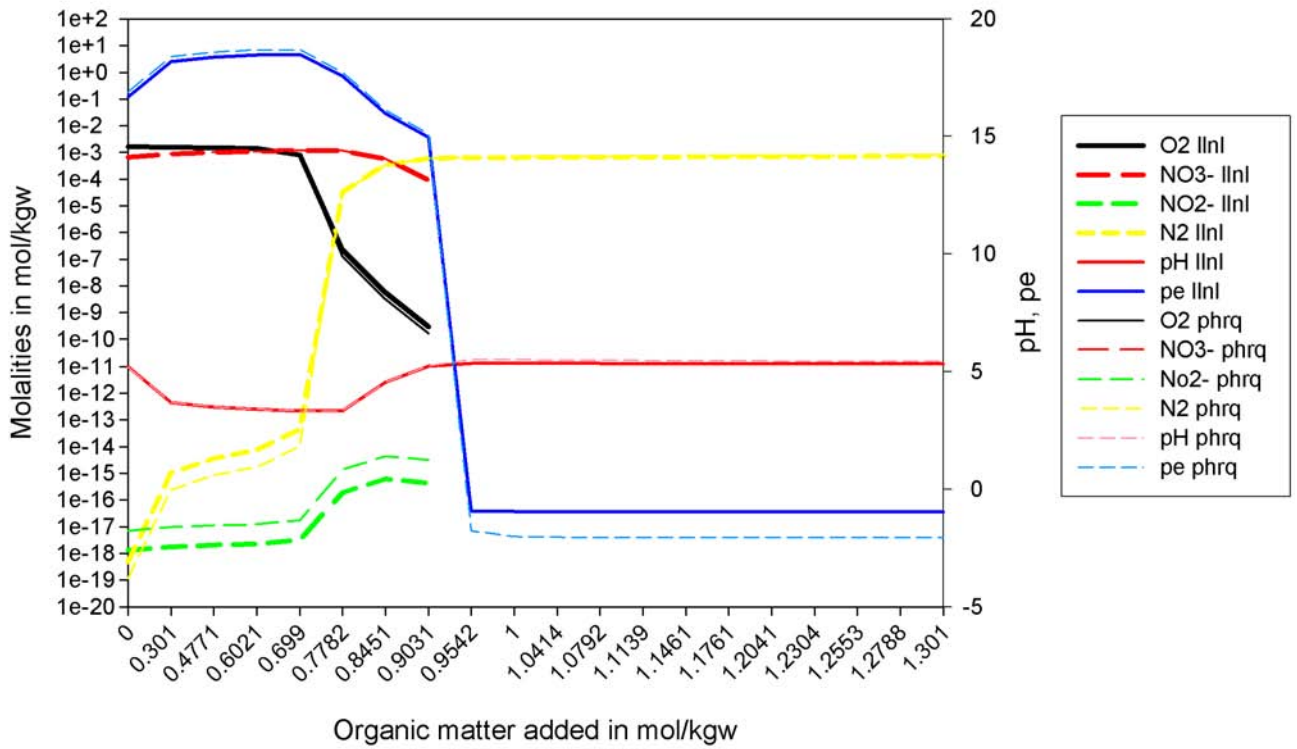


Figure 15.: The databases *llnl.dat* and *phreeqc.dat* compared running simulation 5

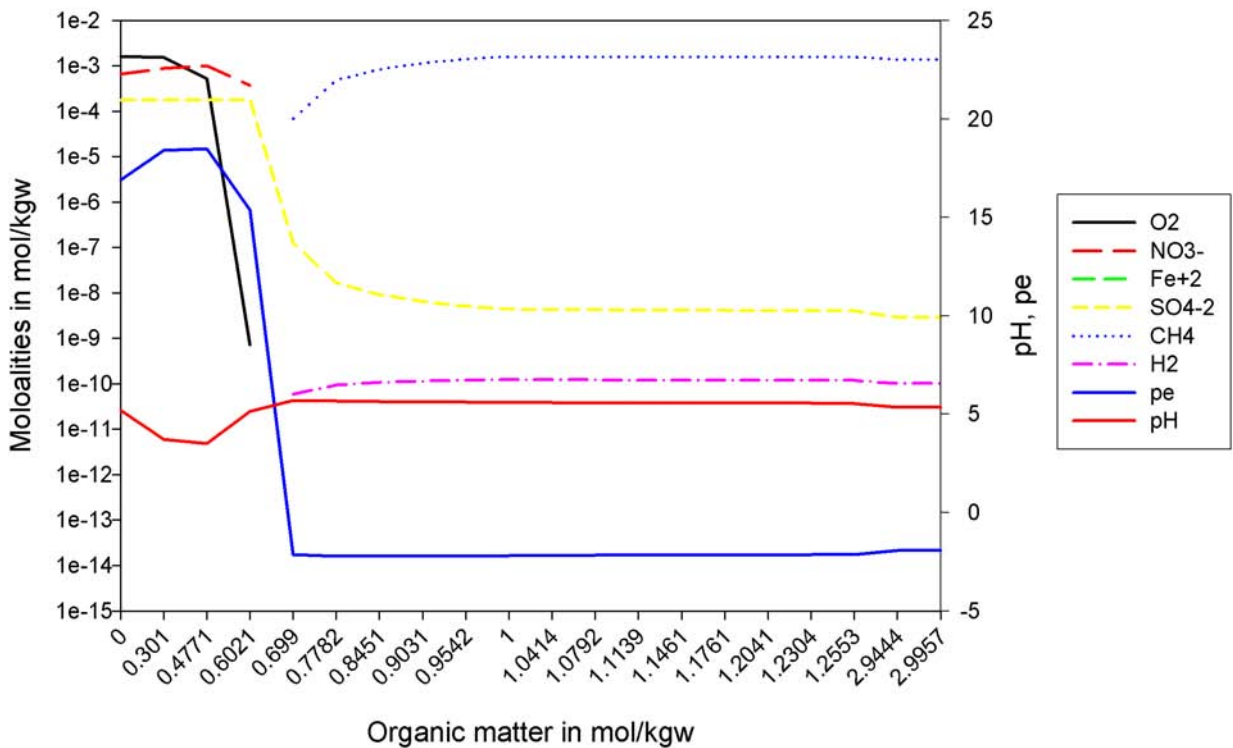


Figure 16.: Simulation 6: Reduced partial pressure of oxygen in the initial solution

6.3. Kinetic reactions

6.3.1. Monod degradation kinetics

In this section, the basic concepts of bacterial degradation of organic compounds will be implemented in PHREEQC. The assumed scenario is an arbitrary contamination of 4 kg phenol, and 2 kg phenol per cubic meter water, resulting in a concentration of 4 g phenol per liter and 2 g/L, equals 4.25×10^{-3} and 2.125×10^{-2} moles/kgw, respectively. The formula used to model the degradation is the Monod equation (formula 30 on page 31). The values of the parameters for the Monod equation were taken from APPELO (2008) (Example 10_7). For that, the formula and its parameters are defined in PHREEQC under the keyword `RATES` as `parm(n)`, the values of the corresponding parameters are set under the keyword `KINETICS` in line `"-parms"`. The values of the parameters used are tabulated in table 4.

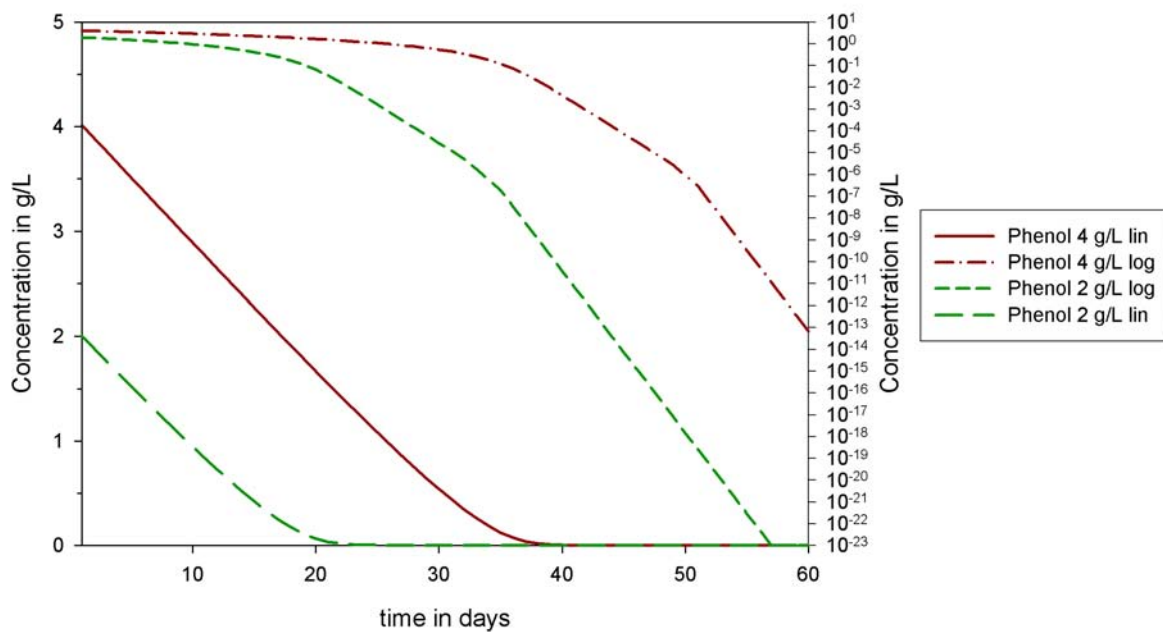


Figure 17.: Simulation 7: The degradation of Phenol modelled with PHREEQC using the Monod equation

The results of the calculation are displayed in figure 17. The left ordinate is set in linear steps, whereas the right ordinate is set in common logarithm steps. The green line (long and short dash) represents the scenario of 2 g/L degraded. After 27 days, the concentration of phenol undercuts half the starting concentration and after 54 days, as can be seen in the logarithmic scale, the concentration of phenol goes below the range of ng/L, a concentration, where the contaminant might be neglected. Starting with 2 g/L phenol, after 11 days, the concentration of phenol is halved, and after 40 days it undercuts the magnitude of 10^{-9} g/L.

Table 4.: Values of parameters in the Monod equation

Sim. Nr	C at t_0 moles/L	μ_{max}	$k_{1/2}$	days to $C_{1/2}$	days to C < ng/L
7	4	1.610×10^{-8}	1.700×10^{-3}	27	54
8	2	1.610×10^{-8}	1.700×10^{-3}	11	40
9	2	3.220×10^{-8}	1.700×10^{-3}	7	23
10	2	0.805×10^{-8}	1.700×10^{-3}	20	85
11	2	1.610×10^{-8}	3.220×10^{-3}	11	67
12	2	1.610×10^{-8}	0.855×10^{-3}	11	31
13	2	1.610×10^{-8}	1.610×10^{-8}	10	18

6.3.2. Monod sensitivity analysis

For a sensitivity analysis of the Monod parameter, the values of the *maximum growth rate* μ_{max} and the *half-saturation constant* $k_{1/2}$ were set to the double and the half of the original value. Simulation 8 represents the reference simulation. A list with the number of the simulation, the initial concentration, the corresponding values, the days within the phenol concentration is halved and the number of days when the concentration undercuts 10^{-9} g/L is tabbed in table 4.

The results are presented in table 4, in figure 18 in a linear scale and in figure 19 in common logarithmic scale. The most sensitive parameter is the *maximum growth rate* μ_{max} . The double of the original value is represented by the red line and the half by the orange one. The time, in which half the contaminant is degraded ($C_{1/2}$), is in the reference simulation (Sim 8) 11 days with the value of μ_{max} of 1.61×10^{-8} . Doubling this value to 3.22×10^{-8} yields to a time of $C_{1/2}$ of 7 days. After 23 days the concentration is below 10^{-9} g/L ($\hat{=}$ ng/L). Taking the half of the initial value for μ_{max} , 0.805×10^{-8} , $C_{1/2}$ is reached after 20 days, and the concentration of ng/L is undercut after 85 days.

Less sensitive than μ_{max} is the *half-saturation constant* $k_{1/2}$. The time to $C_{1/2}$ does not vary, but the concentration < ng/L does vary about $40+27 = 67$ and $40-9 = 31$ days for the double and the half of the reference value, respectively (Sim. 11 and Sim. 12).

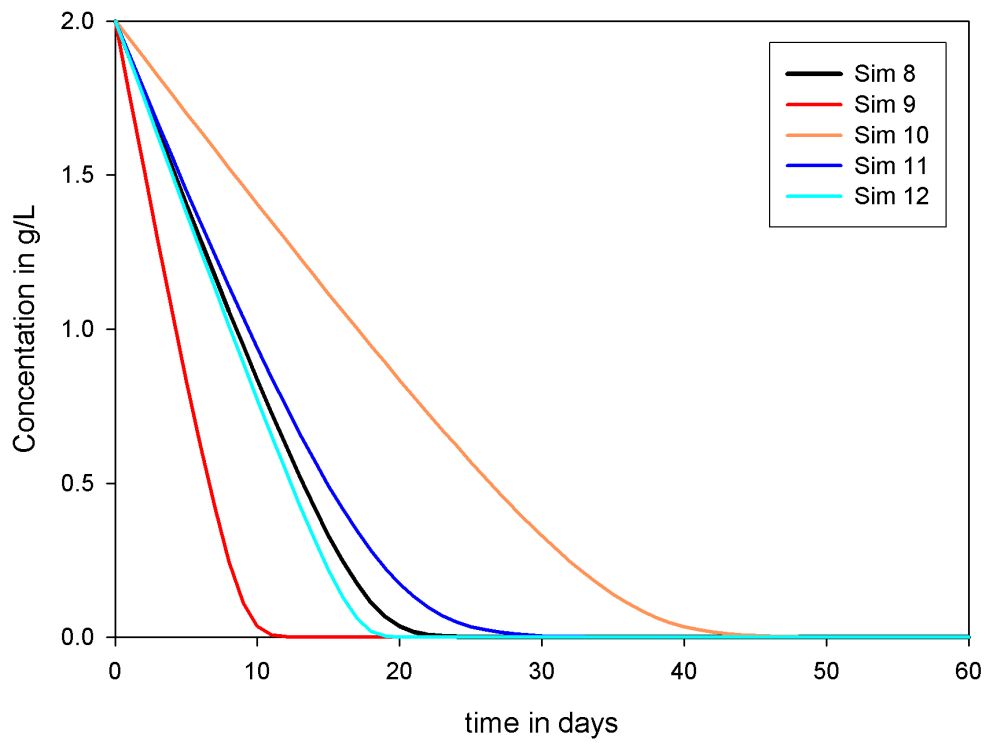


Figure 18.: Sensitivity of the Monod parameters, as listed in table 4

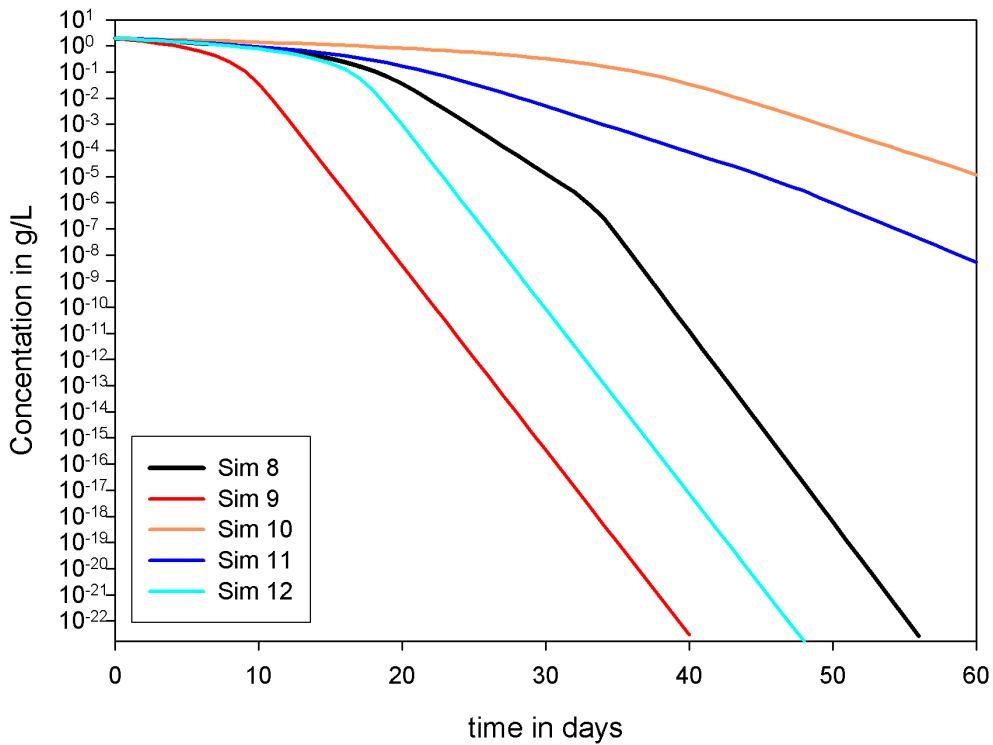


Figure 19.: Simulation 7: The degradation of Phenol modelled with PHREEQC using the Monod equation

6.3.3. Michaelis-Menten kinetics

As microorganisms degrade organic matter and contaminants, their growth and death rate is a controlling factor. This dependency is expressed by the *yield factor* Y (see formula 33 on page 31). The mathematical expression is referred to as the Michaelis-Menten approach. In APPELO & POSTMA (2005) on page 522, the results of a batch experiment determining xylene breakdown in pristine aquifer sediment are implemented in PHREEQC. The degradation of the contaminant is related to the growth of bacteria. Due to better comprehension, the formulation of APPELO was used. The chemical formula was changed to phenol and calibrated to fit the results of the Monod-degradation modelling. The retardation is not included in the sensitivity analyses, because it has to be determined before modelling as a input parameter. The dependency of degradation and biomass growth as APPELO & POSTMA (2005) proposed is implemented in PHREEQC under the keywords [RATES](#) and [KINETICS](#), as follows :

Degradation of C

$$\frac{dC}{dt} = -\mu_{\max} \frac{M}{Y \cdot 8} \frac{C}{k_{1/2}} \frac{1}{1 + R} \quad (37)$$

Biomass M

$$\frac{dM}{dt} = Y \cdot 8 \frac{dC}{dt} R - k_{Md} M \quad (38)$$

C	= Concentration of contaminant moles/L
μ_{\max}	= maximum growth rate 1/s
Y	= Yield coefficient moles Biomass C/moles C
$k_{1/2}$	= half saturation constant moles/L
R	= Retardation factor
M	= Biomass moles C/L
k_{Md}	= Biomass death rate coefficient 1/s

6.3.4. Sensitivity analysis on Michaelis-Menten kinetics

The biomass growth and the degradation are related via the mass of the biomass B. The parameters were calibrated that half of the mass of phenol is degraded after 11 days, in order to compare the simulations of the breakdown of phenol with, and without biomass growth. Time intervals are 12 hours in 30 days. The values of the parameters are listed in table 5. Though after 11 days, the concentration is halved, comparing the results of simulation 7 (figure 17), the way of degradation is completely different. The chemical formula of the bacteria is defined to be $CH_{1.4}O_{0.4}N_{0.2}$ with 22.6 g/moles molesar mass (after (APPELO & POSTMA, 2005, p. 523)). The bacteria start with the mass of 1.68×10^{-6} g/L and grow due to consumption of phenol. Approximately after 7 days, when the concentration of the biomass succeeds 5 mg/L, phenol starts to be degraded rapidly. The lack of a tailing is the most peculiar difference. After 12 days, the concentration of phenol is zero. The concentration of the bacteria diminishes due to the value of the *bacterial death rate* K_{Bd} .

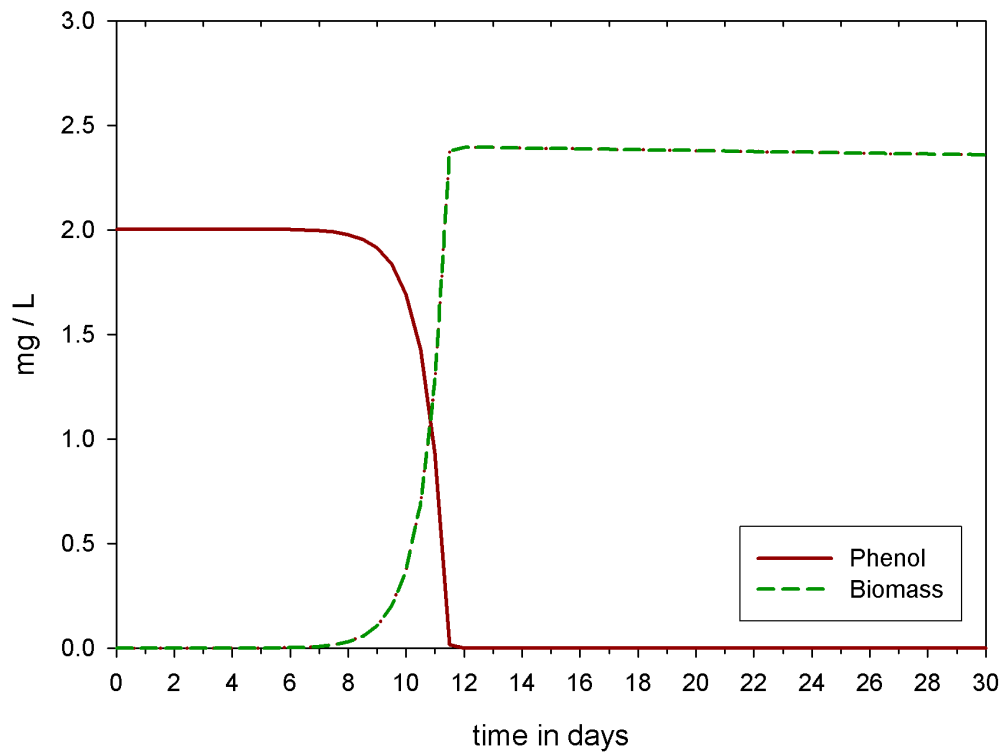


Figure 20.: Simulation 14: Degradation of phenol and biomass growth

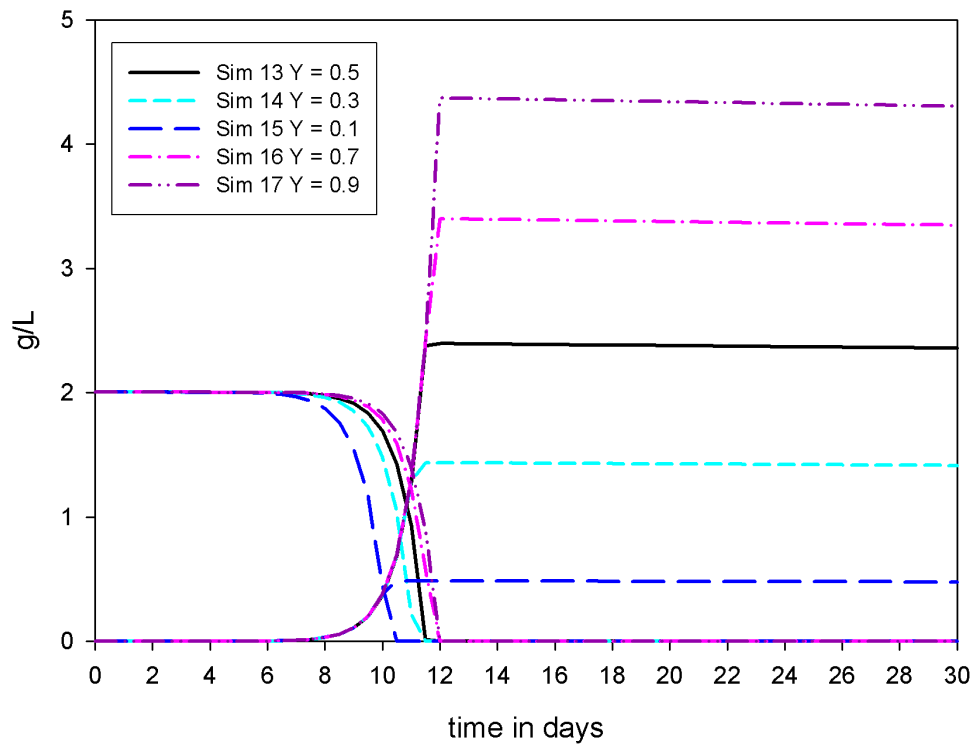


Figure 21.: Sensitivity analysis of biodegradation modelled with the Michaelis-Menten approach

Table 5.: Values of parameters in the Monod equation

Sim. Nr	C at t_0 moles/L	μ_{max}	$k_{1/2}$	Y	K_{Bd}	days to $C_{1/2}$
13	2	1.910×10^{-5}	1×10^{-8}	0.5	1×10^{-8}	11
14	2	1.910×10^{-5}	1×10^{-8}	0.3	1×10^{-8}	11
15	2	1.910×10^{-5}	1×10^{-8}	0.1	1×10^{-8}	10
16	2	1.910×10^{-5}	1×10^{-8}	0.7	1×10^{-8}	11.5
17	2	1.910×10^{-5}	1×10^{-8}	0.9	1×10^{-8}	11.5
18	2	1.910×10^{-5}	1×10^{-8}	0.5	1×10^{-6}	12
19	2	1.910×10^{-5}	1×10^{-8}	0.5	5×10^{-6}	16.5
20	2	1.910×10^{-5}	1×10^{-8}	0.5	8×10^{-6}	23.5
21	2	1.910×10^{-5}	1×10^{-6}	0.5	1×10^{-8}	11
22	2	1.910×10^{-5}	1×10^{-3}	0.5	1×10^{-8}	12
23	2	1.910×10^{-5}	5×10^{-3}	0.5	1×10^{-8}	14
24	2	1.910×10^{-5}	1×10^{-2}	0.5	1×10^{-8}	17
25	2	0.955×10^{-5}	1×10^{-8}	0.5	1×10^{-8}	22
26	2	3.82×10^{-5}	1×10^{-8}	0.5	1×10^{-8}	5.5

In a sensitivity analysis, the *yield coefficient*, the *bacterial death rate*, and the parameters of the Michaelis-Menten equation were modified, as shown in table 5. The results are shown in figure 21. The reference simulation is number 13. In simulation 14 the yield coefficient Y is set to the value of 0.3. In the following simulations, the value of 0.5 was chosen, as proposed by many literature sources (see section 4.6 on page 33). Then, the death rate of the bacteria is set to a higher value of about two orders of magnitude. At last the *half-saturation constant* and the *maximum growth rate* are set to other values, to determine their sensitivity. The input values and the their influence are tabulated in table 5 and graphical demonstrations of the simulations are shown in figures 21 to 24.

The lower yield coefficient generates less bacterial growth, because less of the substrate degraded and less of the energy yielded serves for bacterial growth. In simulation 14 and 15, the yield coefficient is 0.3 and 0.1, respectively. Phenol is degraded earlier than in reference simulation no. 13, and less bacterial cells are produced. Simulation 16 and 17 are calculated with higher yield coefficients. More bacteria mass is produced during the degradation, but nevertheless, the degradation process is not explicitly longer, although with the yield coefficient of 0.9, the fast degradation process starts later, but then it proceeds more efficiently.

Simulation 18 to 20 show the effect of the *bacteria death rate* K_{Bd} . The value is set from 1×10^{-8} to 1×10^{-6} , to 5×10^{-6} and to 8×10^{-6} . The higher the bacterial death rate, the slower phenol is degraded and the faster the bacteria die after the degradation (figure 22). But once bacteria concentration overpasses a certain limit, the degradation process is very likely in time in simulation 13 and 19 to 21.

The influence of the *half-saturation constant* is weaker then in Monod kinetics. A increase of the *half-saturation constant* about 3 magnitudes does not affect the degradation, getting to higher values, a critical point is reached and the parameter gets sensitive in order to slow the degradation process, as simulation 21 to 23 show (see

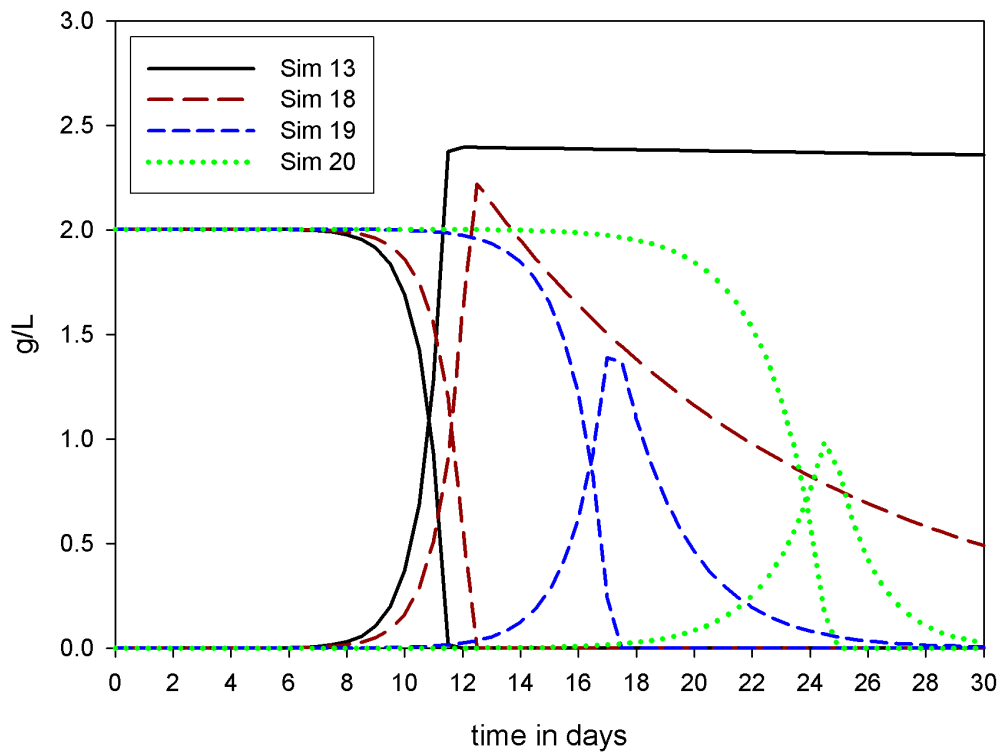


Figure 22.: Simulation 19 to 21. The influence of the bacterial death rate on the degradation process

figure 23.

As in the Monod kinetics, the maximum growth rate is a highly sensitive parameter. Multiplying and dividing it by 2, the degradation time differs about days. The multiplication by 2 shortens the half concentration time to 5.5 days and the division by two extends it to 22 days. This sensitivity analysis shows that measurement of trigger elements, trigger concentrations and/or compositions is an indispensable precondition to determine the corresponding values of the degradation kinetics in a manner, sighting responsible error margins in time, space, quality and quantity.

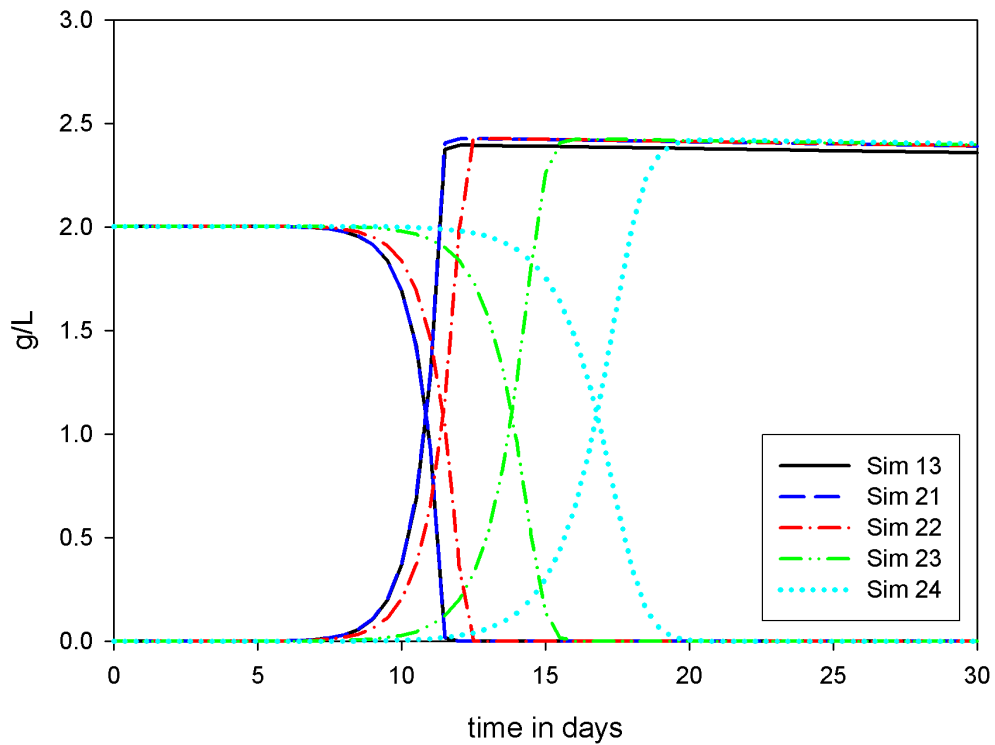


Figure 23.: Simulation 21 - 23. The influence of the half-saturation constant on the degradation process

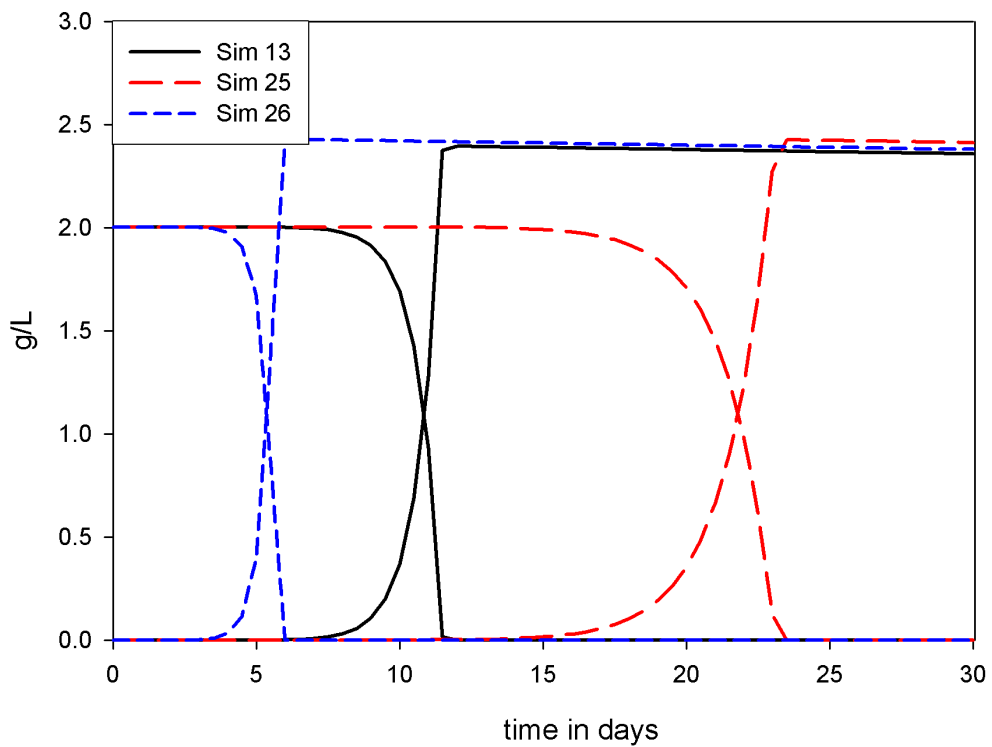


Figure 24.: Simulation 24 and 25. The influence of the maximum growth rate on the degradation process

6.4. Discussion

The modelling of biological degradation of carbon with PHREEQC is a promising attempt to combine thermodynamical equilibrium with kinetically controlled reactions. The possibility of including a self-written script into the PHREEQC-code raises the chance of forecasting the overall chemical processes included within its consequences. The ability of PHREEQC to add elements to the solution via the keyword **REACTION** enables, to simulate on a thermodynamical basis the oxidation of organic matter (See simulation 1 - 6 in section 6). The results show the expected results, the sequence of reduction of the TEAs in consequence of the oxidation of organic matter. The reduction of the given TEAs (oxygen, nitrate, iron, sulfate and carbon) proceeds fast, as once a critical concentration of organic matter is reached (figure 8 and 11). The critical concentration depends on the abundance of oxygen and nitrate. Once more nitrate is abundant, the solution bears one step more organic matter (0.052 moles), before it tilts to reductive conditions, characterized by the negative p_e (see figure 13). Proportional to this scheme, once less oxygen is abundant, the solution bears 1.4472 moles/kgw less organic matter, then in simulation 1 (cp. figure 16 and 8), before tilting to reductive conditions. Though, the results show some deviations compared to the sequences of TEAs shown in literature sources (see chapter 4.5 on page 27). The abrupt turnover to reductive conditions is the main difference. Many tests were run to determine, whether this tilting is produced by steps in which organic matter is added, or composition of master electron acceptors. The conclusion was yields to simulation 1 to 6. Neither the abundance compounds to be reduced affected the character of the redox sequence, nor the incremental steps the biomass was added to the solution. The simulations and the values pre-defined were chosen after the criteria to visualize the critical changes in the hydrochemistry adequately and to simulate natural scenarios. The coinstantaneous reduction of iron, sulfate and carbon could well be due to bacterial growth, death and consumption kinetics, which PHREEQC does not account for. The comparison of different databases used (figure 12 and 15) show the dependency of the source of the thermodynamical data. As the databases chosen result from one source respectively in order to maintain consistency (see chapter 5), it would be overbearing to state which database provides the more accurate results.

Section 6.3 shows the ability of PHREEQC to implement independent reactions in the input code of PHREEQC. The simulations run represent the basic formulas of bacterial kinetics. The modelling of degradation controlled by bacteria population dynamics is a step toward the overall modelling of degradation kinetics. As different parameters in the mathematical description control the degradation, sensitivity analyses were run. The most sensitive parameter is the *maximum growth rate* μ_{max} . While other parameters could be changed in orders of magnitude, comparatively small abbreviations yield to ample differences in the time of degradation. This underlines the importance of an accurate determination of the *maximum growth rate*.

7. Conclusion

As equilibrium chemistry is a useful tool to describe chemical reactions, the kinetically controlled reactions represent the "real world" in environmental chemistry. Equilibrium chemistry works with the final state of a chemical system, represented as c_{eq} in figure 25, whereas kinetics work with the time span between the beginning and the final state. The beginning, expressed as a steep curve before time t_c , can be neglected in the most problems hydrological sciences deal with. Dependent on the residence time of water and the chemical interactions focused on, the critical time t_c shifts on the time axis.

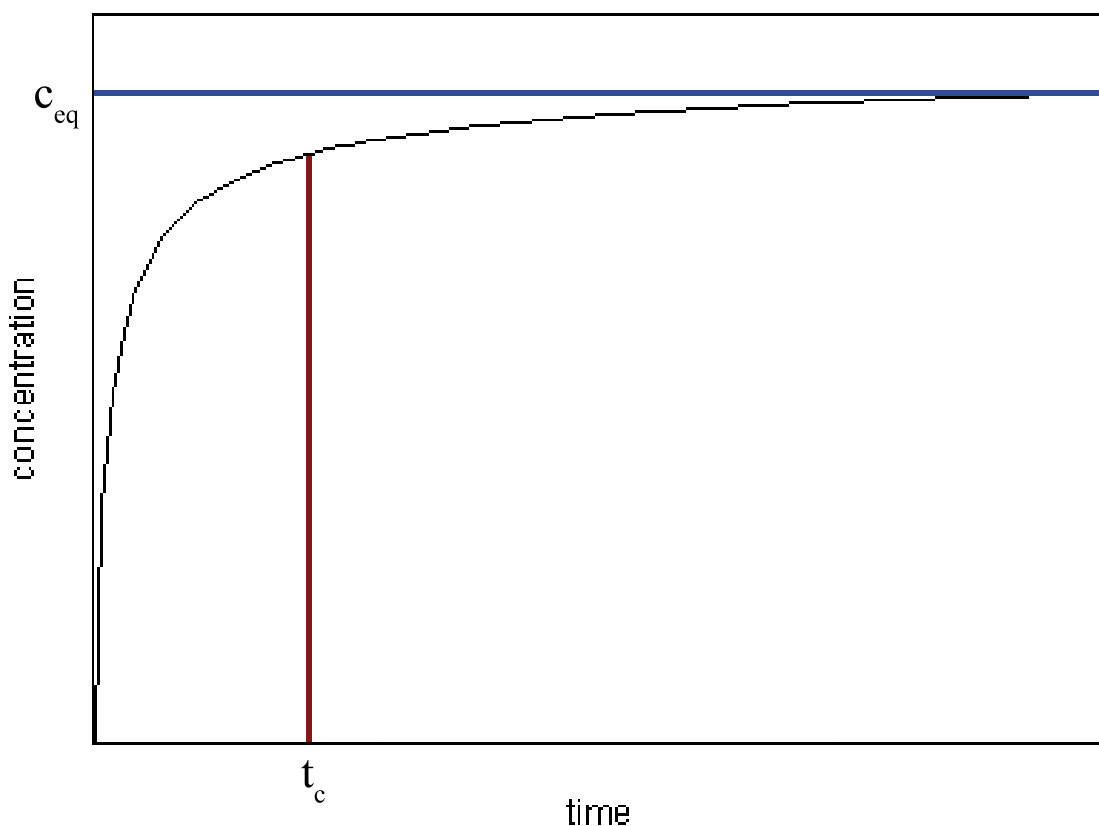


Figure 25.: The factor time in kinetic and equilibrium chemistry

To be able to model this time span of reaction with the concomitant processes bears great opportunities to environmental water sciences. Determination of age, residence time, reaction, future concentration and consequences of contaminants are the possibilities among many which lie upon the horizon of environmental modelling. Regarding contamination geochemistry, the state of the art of current research approaches to these

goals. Models which include degradation kinetics of contaminants with thermodynamical geochemistry have been applied recently and field measurements have been taken to verify the results. Also the research of trigger concentrations and/or elements to understand the state of a system without long-term measurements have been published. Combining the above mentioned techniques may yield to the ability to understand the state of a system in time and/or space. So that the groundwater chemistry gives an image about the recharge conditions in terms of TEA- and DOC-concentration, climate and vegetation or that organic carbon content and the abundance of TEAs gives conclusion which state a groundwater system yields to. PHREEQC is based on thermodynamic data and includes the possibility of implementing self-written scripts. However, other models have been developed to combine equilibrium chemistry and degradation kinetics, such as TBC (SCHAEFER ET AL., 1998a,b), PHTRAN (PROMMER ET AL., 1999) or others presented in table 1 on page 7, which may suite better for contamination modelling. Summing up, hope can be raised that failures by dealing with humanities most important natural resource can be remediated and that groundwater exploitation in present and future might be made in a reasonable way.

Bibliography

- AAGAARD, P., ZHENG, Z., BREEDVELD, G. (2002): Modeling natural attenuation of petroleum contaminants in aquifers: Conceptual model and simulations. IN: Goldschmidt Conference Abstracts.
- ALBERTA RESEARCH GROUP (2005): Evaluation of Computer Models for Predicting the Fate & Transport of Hydrocarbons in Soil and Groundwater. Ed.: MDH Engineered Solutions Corporation, Pub. No: 808. The Water Research Users Group, Alberta Environment, 61 p.
URL <http://environment.gov.ab.ca/info/library/6682.pdf>
- ALLISON, J.D. (1991): MINTEQA2. EPA, abstract, manual and download.
URL <http://www.epa.gov/ceampubl/mmedia/minteq/USERMANU.PDF>
- ALLISON, J.D. (1999): MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0. EPA, abstract.
URL <http://www.epa.gov/ceampubl/mmedia/minteq/SUPPLE1.PDF>
- ALLISON, J.D., BROWN, D.S., NOVO-GRADAC, K.J. (1991): MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems (US EPA/600/3-91/021). EPA - US Environmental Protection Agency, Athens, GA, USA.
URL <http://www.epa.gov/ceampubl/mmedia/minteq/>
- ALVAREZ, P.J.J., ILLMAN, W.A. (2006): Bioremediation and Natural Attenuation. Wiley Interscience, 609 p.
- APPEL, C., REILLY, T. (1994): Summary of selected computer programs produced by the U.S. Geological Survey for simulation of ground-water flow and quality - 1994. U.S. Geological Survey Circular, Vol. 1104.
URL <http://water.usgs.gov/ogw/pubs/Circ1104/index.html>
- APPELO, C. (2008): Phreeqc application examples. Website.
URL <http://www.xs4all.nl/~appt/exmpls/index.html>
- APPELO, C., PARKHURST, D.L. (1998): Enhancements to the geochemical model PHREEQC -1D transport and reaction kinetics. IN: G. Aehart, J. Hulston (Eds.), Water-rock interaction: proceedings of the 9th International Symposium on Water-Rock Interaction, Balkema, Rotterdam, p. 873–876.
- APPELO, C., POSTMA, D. (2005): Geochemistry, groundwater and pollution, Vol. 2. A.A. Balkema Publishers, 649 p.

- BADENOVA (2007): water analysis report. internet.
URL https://www.badenova.de/web/media/dokumente/produkte/wasser_abwasser/qualitaet/.pdf
- BALL, J., NORDSTROM, D. (1991): User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. USGS, open-file report 91-183 Vol., 189 p.
- BALL, J., NORDSTROM, D. (1998): Critical evaluation and selection of standard state thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides, and hydroxides. *Journal of Chemical and Engineering Data*, Vol. 43, p. 895–918.
- BARRY, D., PROMMER, H., MILLER, C., ENGESGAARD, P. BRUN A.AND ZHENG, C. (2002): Modelling the fate of oxidisable organic contaminants in groundwater. *Advances in Water Resources*, Vol. 25, p. 945–983.
- BAUN, A., REITZEL, L., LEDIN, A., T.H., C., BJERG, P. (2003): Natural attenuation of xenobiotic organic compounds in a landfill leachate plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, Vol. 265, p. 269–291.
- BRUN, A., ENGESGAARD, P. (2002): Modelling of transport and biogeochemical processes in pollution plumes: literature review and model development. *Journal of Hydrology*, Vol. 256 (3-4), p. 211–227.
- BRUN, A., ENGESGAARD, P., CHRISTENSEN, T., ROSBJERG, D. (2002): Modelling of transport and biogeochemical processes in pollution plumes: Vejen landfill Denmark. *Journal of Hydrology*, Vol. 256, p. 228–247.
- BUFFLE, J., DE VITRE, R.R. (Eds.) (1994): *Chemical and Biological Regulation of Aquatic Systems*. Lewis Publishers.
- CAREY, G., VAN GEEL, P., , MURPHY, J. (1999): *BioRedox-MT3DMS V2.0: A Coupled Biodegradation-Redox Model for Simulating Natural and Enhanced Bioremediation of Organic Pollutants - User's Guide*. Conestoga-Rovers and Associates, Waterloo, Ontario, Canada.
- CARSTENS, D. (2008): *Modellierung von Adsorption und Transport von Schwermetallen in der gesaettigten Zone mit PHREEQC*. Diploma thesis, Institute of Hydrology, University Freiburg.
URL www.hydrology.uni-freiburg.de
- CHAPELLE, F.H. (2001): *Ground-water Microbiology and Geochemistry*. John Wiley & Sons Inc., 477 p., ISBN 0-471-34825-X.
- CHRISTENSEN, J., D.L., J., CHRISTENSEN, T. (1996): Effect of dissolved organic carbon on the mobility of cadmium, nickel and zinc in leachate polluted groundwater. *Water Resources Research*, Vol. 30 (12), p. 3037–3049.

- CURTIS, G.P. (2003): Comparison of approaches for simulating reactive solute transport involving organic degradation reactions by multiple terminal electron acceptors. *Computers & Geosciences*, Vol. 29 (3), p. 319–329.
URL <http://www.sciencedirect.com/science/article/B6V7D-484SFTB-1/2/45295ffbfcb3723eb5aaf4fd9b16ad3a>
- ENVIRONMENTAL MODELING SYSTEMS (1993): FEMWATER, FEMWASTE. South Jordan, Utah, USA.
URL http://www.ems-i.com/GMS/GMS_Overview/gms_overview.html
- EPA (2003): CHEMFLO-2000. EPA.
URL <http://www.epa.gov/ada/csos/models/chemflo2000.html>
- ESSAID, H., BEKINS, B., GODSY, E., WARREN, E. (1995): Simulation of aerobic and anaerobic biodegradation processes at a crude oil spill site. *Water Resources Research*, Vol. 31 (12), p. 3309–3327.
- EU WATER FRAMEWORK DIRECTIVE - GROUNDWATER (2006): EU Water Framework Directive.
URL http://ec.europa.eu/environment/water/water-framework/groundwater/policy/current_framework/new_directive_en.htm
- FAUST, C., GUSWA, J., MERCER, J. (1989): Simulation of Three-Dimensional Flow of Immiscible Fluids Within and Below the Unsaturated Zone, *Water Resour. Res.*, 25(12), 2449–2464. *Water Resources Research*, Vol. 25 (12), p. 2449–2464.
- FROELICH, P.N., KLINKHAMMER, G.P., BENDER, M.L., LUEDTKE, N.A., HEATH, G.R., CULLEN, D., DAUPHIN, P., HAMMOND, D., HARTMAN, B., MAYNARD, V. (1979): Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. *Geochimica et Cosmochimica Acta*, Vol. 43 (7), p. 1075–1090.
URL <http://www.sciencedirect.com/science/article/B6V66-4887NC1-C/2/d7450194052b114495f142ec76e42fd2>
- GARREL, R., CHRIST, C. (1965): *Solutions, minerals and equilibria*, Harper and Row, New York.
- GRIFFIOEN, J. (1999): Comment on "Kinetic modelling of microbially-driven redox chemistry of subsurface environments: Coupling transport, microbial metabolism and geochemistry" by K.S. Hunter, Y. Wang and P. van Cappellen. *Journal of Hydrology*, Vol. 226, p. 121–124.
- HSIEH, P., WINGLE, W., HEALY, R. (2000): VS2DI A Graphical Software Package for Simulation of Fluid Flow and Solute or Energy Transport Through Variably Saturated Porous Media. *Water Investigations Report*, Vol. 99-4130, p. 20.
URL http://wwwbrr.cr.usgs.gov/projects/GW_Unsat/vs2di1.2/
- HUNTER, K., VAN CAPELLEN, P. (1999): Reply to Comment on kinetic modeling of microbially-driven redox chemistry of subsurface environments: coupling transport,

- microbial metabolism and geochemistry by J. Griffioen. *Journal of Hydrology*, Vol. 227, p. 292–294.
- HUNTER, K., WANG, Y., VAN CAPELLEN, P. (1998): Kinetic modeling of microbially-driven redox chemistry of subsurface environments: coupling transport, microbial metabolism and geochemistry. *Journal of Hydrology*, Vol. 209, p. 53–80.
- JIN, Q., BETHKE, C.M. (2002): Electron Transfer through the respiratory chain. *Biophysical Journal*, Vol. 83, p. 1797–1808.
- KINZELBACH, W., RAUSCH, R. (1995): Grundwassermodellierung - Eine Einführung mit Übungen. Gebrueder Borntraeger, 8. Vol., 284 p., ISBN 3-443-01032-6.
- KIPP, K.L. (1987): HST3D: A Computer Code for Simulation of Heat and Solute Transport in Three-Dimensional Ground-Water Flow Systems. USGS Water-Resources Investigations Report, Vol. 86-4095, p. 517p.
URL <http://pubs.usgs.gov/wri/>
- KIPP, K.L. (1997): Guide to the Revised Heat and Solute Transport Simulator: HST3D – Version 2. USGS Water-Resources Investigations Report, Vol. 97-4157, p. 149p.
URL <http://pubs.usgs.gov/wri/>
- KIPP, K.L. (2007): A Computer Code for Simulation of Heat and Solute Transport in Three-Dimensional Ground-Water Flow Systems. USGS.
- KJELDSSEN, P. (1993): Groundwater pollution source characterization of an old landfill. *Journal of Hydrology*, Vol. 142, p. 349–371.
- KONIKOW, L.F., BREDEHOEFT, J.D. (1978): Computer model of two - dimensional solute transport and dispersion in ground water, Vol. U.S. Geological Survey Techniques of Water-Resources Investigations. USGS, 90 p., book 7, chap. C2.
- LFUG (2004): DASIMA - Simulationsprogramme zur Stroemungs- und Schadstofftransportmodellierung. online, lfUG - Saechsisches Landesamt für Umwelt und Geologie.
URL <http://www.umwelt.sachsen.de/de/wu/umwelt/lfug/lfug-internet/857.asp?url=/de/wu/umwelt/lfug/lfug-internet/infosysteme/irsa/jsp/anonym/dasima/index.jsp>
- LINDBERG, R., RUNNELS, D. (1984): Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling. *Science*, Vol. 225 (4665), p. 925–927.
- LOVLEY, D., BAEDECKER, M., LONERGAN, D., COZZARELLI, I., PHILLIPS, E., SIEGEL, D. (1989): Oxidation of aromatic contaminants coupled to microbial iron reduction. *Nature*, Vol. 339, p. 298–300.
- LOVLEY, D., CHAPELLE, F.H. (1995): Deep Surface Microbial Processes. *Reviews of Geophysics*, Vol. 33 (3), p. 365–381.

- LOVLEY, D., WOODWARD, J., CHAPPELLE, F. (1994): Stimulated anoxic biodegradation of aromatic hydrocarbons using Fe(III) ligands. *Nature*, Vol. 370, p. 128–131.
- LYNGKILDE, J., CHRISTENSEN, T. (1992a): Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, Vol. 10, p. 291–307.
- LYNGKILDE, J., CHRISTENSEN, T. (1992b): Redox zones of a landfill leachate pollution plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, Vol. 10, p. 273–289.
- MANAHAN, S.E. (2000): *Environmental Chemistry*. Lewis Publishers, 7. Vol., 898 p.
- MCDONALD, M.G., HARBAUGH, A.W. (1988): A modular three-dimensional finite-difference ground-water flow model. USGS.
- MEIRI, D. (1990): FEMSEEP Finite Element Groundwater Flow and Transport Mode, I. Flow Model, Users Manual. Ebasco Services Incorporated.
- MERKEL, B. (2005): *Groundwater Chemistry*. Springer, 199 p.
- MERKEL, B.J., PLANER-FRIEDRICH, B. (2005): *Groundwater Chemistry*. Springer, 199 p.
- MOLZ, F., WIDDOWSON, M., BENEFIELD, L. (1986): Simulation of Microbial Growth Dynamics Coupled to Nutrient and Oxygen Transport in Porous Media. *Water Resources Research*, Vol. 22 (8), p. 1207–1216.
- MONOD, J. (1949): The growth of bacterial cultures. *Annual Review of Microbiology*, Vol. 3, p. 371–394.
- MULLIGAN, C., YONG, R.N. (2004): Natural attenuation of contaminated soils. *Environmental International*, Vol. 30, p. 587–601.
- NATIONAL RESEARCH COUNCIL (2000): *Natural Attenuation for Groundwater Remediation*. Committee on Intrinsic Remediation and Water Science and Technology Board and Board on Radioactive Waste Management and Commission on Geosciences, Environment and Resources.
- NORDSTROM, D., PLUMMER, L., LANGMUIR, ., DONALD, ., BUSENBERG, ., EURYBIADES, ., MAY, H., JONES, B., PARKHURST, D. (1990): Chemical modeling in aqueous systems II. Ed.: Melchior, D.C. and Bassett, R.L., *American Chemical Society Symposium Series*, Vol. 416, Chap. Revised chemical equilibrium data for major water-mineral reactions and their limitations, American Chemical Society, Washington D.C., USA. p. 398–413.
- NÜTZMANN, G., VIOTTI, P., AARGARD, P. (Eds.) (2005): *Reactive Transport in Soil and Groundwater - Processes and Models*. Springer, 295 p.

- OSTENDORF, D., SCHOENBERG, T., HINLEIN, E., LONG, S. (2007): Monod Kinetics for Aerobic Biodegradation of Petroleum Hydrocarbons in Unsaturated Soil Microcosms. *Environmental Science & Technology*, Vol. 41, p. 2343–2349.
- PARKHURST, D. (1995): Users guide to PHREEQC—A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. USGS Water-Resources Investigations Report, Vol. 95-4227, p. 143.
- PARKHURST, D.L., APPELO, C. (1999): User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. USGS, Denver, Colorado, USA, water-Resources Investigations Report 99-4259.
URL http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/; <ftp://brrftp.cr.usgs.gov/geochem/unix/phreeqc/manual.pdf>
- PARKHURST, D.L., KIPP, K.L., ENGESGAARD, P., CHARLTON, S.R. (2004): PHAST - A Program for Simulating Ground-Water Flow, Solute Transport, and Multicomponent Geochemical Reactions. USGS, USGS, Denver, Colorado, USA.
URL <http://pubs.usgs.gov/tm/2005/tm6A8/>
- PERSSON, L., ALSBERG, T., LEDIN, A., ODHAM, G. (2006): Transformations of dissolved organic matter in a landfill leachate - A size exclusion chromatography/mass spectrometric approach. *Chemosphere*, Vol. 64, p. 1093–1099.
- PROMMER, H., BARRY, D., DAVIS, G. (1999): A one-dimensional reactive multi-component transport model for biodegradation of petroleum hydrocarbons in groundwater. *Environmental Modelling and Software*, Vol. 14, p. 213–223.
- PROMMER, H., BARRY, D., DAVIS, G. (2002): Modelling of physical and reactive processes during biodegradation of a hydrocarbon plume under transient groundwater flow conditions. *Journal of Contaminant Hydrology*, Vol. 59, p. 113–131.
- PRUESS, K., OLDENBURG, C., MORIDIS, G. (1999): TOUGH2 USER'S GUIDE, VERSION 2.0. Lawrence Berkeley National Laboratory, Earth Sciences Division, University of California, Berkeley, California 94720.
URL <http://www-esd.lbl.gov/TOUGH2/tough2v2.html>
- REGNIER, P., DALE, A., PALLUD, C., VAN LITH, Y., BONNEVILLE, S., HYACINTHE, C., THULLNER, M., LAVERMAN, A., VAN CAPPELLEN, P. (2005): Incorporating geomicrobial processes in reactive transport models of subsurface environments . Ed: Nuetzmann, G. and Viotti, P. and Aargard, P., Chap. 2, Springer. p. 107–125.
- RICHNOW, H., MECKENSTOCK, R., REITZEL, L., BAUN, A., LEDIN, A., CHRISTENSEN, T. (2003): In situ biodegradation determined by carbon isotope fractionation of aromatic hydrocarbons in an anaerobic landfill leachate plume (Vejen, Denmark). *Journal of Contaminant Hydrology*, Vol. 64, p. 59–72.
- RIFAI, H.S., BEDIENT, P., WILSON, J.T., MILLER, K.M., ARMSTRONG, J. (1988): Biodegradation Modeling at Aviation Fuel Spill Site. *SCE Journal of Environmental Engineering*, Vol. 114 (5), p. 1007–1029.

- RUNNELLS, D.D., LINDBERG, R.D. (1981): Hydrogeochemical exploration for uranium ore deposits: Use of the computer model wateqfc. *Journal of Geochemical Exploration*, Vol. 15 (1-3), p. 37–50.
URL <http://www.sciencedirect.com/science/article/B6VCP-489YNK9-2N/2/6adc437ad1bb74907788104fef9aa859>
- SCHAEFER, D., SCHAEFER, W., KINZELBACH, W. (1998a): Simulation of reactive processes related to biodegradation in aquifers 1. Structure of the three-dimensional reactive transport model. *Journal of Contaminant Hydrology*, Vol. 31, p. 169–186.
- SCHAEFER, D., SCHAEFER, W., KINZELBACH, W. (1998b): Simulation of reactive processes related to biodegradation in aquifers 2. Model application to a column study on organic carbon degradation. *Journal of Contaminant Hydrology*, Vol. 31, p. 187–209.
- SCHULZ, H.D., TEUTSCH, G. (Eds.) (2002): *Conceptual Models for Reactive Transport in Soil and Groundwater*. Deutsche Forschungsgemeinschaft - Wiley-VCH, 278 p., ISBN 3-527-27764-1.
- SCHWARZENBACH, R.P., GSCHWEND, P.M., IMBODEN, D.M. (2003): *Environmental Organic Chemistry*. Wiley Interscience, 2. Vol., 1313 p., ISBN 0-471-35053-2.
- SCIENCE AND STANDARDS BRANCH ALBERTA ENVIRONMENT (2003a): Evaluation of Computer Models for Predicting the Fate & Transport of Salt in Soil and Groundwater: Phase 1 Report. Ed.: MDH Engineered Solutions Corporation, Pub. No.: T/403. Science and Standards Branch Alberta Environment, 56 p., ISBN No. 0-7785-2493-0 (Printed Edition) ISBN No. 0-7785-2494-9 (On-line Edition).
URL <http://environment.gov.ab.ca/info/library/6806.pdf>
- SCIENCE AND STANDARDS BRANCH ALBERTA ENVIRONMENT (2003b): Evaluation of Computer Models for Predicting the Fate & Transport of Salt in Soil and Groundwater: Phase 2 Report. Ed.: MDH Engineered Solutions Corporation, Pub. No.: T/404. Science and Standards Branch Alberta Environment, 101 p.
URL <http://environment.gov.ab.ca/info/library/6809.pdf>
- SCIENTIFIC SOFTWARE GROUP (1998): *3DFEMFAT Overview*. Scientific Software Group, Sandy, Utah, USA.
URL http://www.scisoftware.com/products/3dfemfat_overview/3dfemfat_overview.html
- SIGG, L., STUMM, W. (1994): *Aquatische Chemie*. VdF Zuerich, Teubner Stuttgart.
- STEEFEL, C.I., DEPAOLO, D.J., LICHTNER, P.C. (2005): Reactive transport modeling: An essential tool and a new research approach for the Earth sciences. *Earth and Planetary Science Letters*, Vol. 240 (3-4), p. 539–558.
URL <http://www.sciencedirect.com/science/article/B6V61-4HHWWC6-1/2/03b67eb8454fbd1ee3fe4939b7540bbe>

- STUMM, W., MORGAN, J.J. (1996): Aquatic Chemistry. Wiley, 3. Vol., iISBN 0-471-51184-6.
- TRUESDELL, A., JONES, B. (1973): Wateq, a computer program for calculating chemical equilibria of natural waters, USGS NTIS PB-220 464. p. 73.
- VAN CAPELLEN, P., WANG, Y. (1996): Cycling of iron and manganese in surface sediments: A general theory for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur iron and manganese. American Journal of Science, Vol. 296, p. 197–243.
- VAN DER HEIJDE, P., KANZER, D. (1997a): Ground-Water Model Testing: Systematic Evaluation and Testing of Code Functionality and Performance. Tech. Ber. EPA/600/R-97/007, US EPA.
URL www.epa.gov/ada/download/reports/gwtest.pdf
- VAN DER HEIJDE, P., KANZER, D. (1997b): Project Summary - Ground-Water Model Testing: Systematic Evaluation and Testing of Code Functionality and Performance. Tech. Ber. EPA/600/SR-97/007, US EPA.
URL www.epa.gov/ada/download/project/gwtestng.pdf
- VAN DER PERK, M. (2006): Soil and Water Contamination. Taylor&Francis, 389 p.
- VOSS, C., PROVOST, A. (2002): SUTRA - A Model for Saturated-Unsaturated, Variable-Density Ground-Water Flow with Solute or Energy Transport. USGS Water Investigations Report, Vol. 84-4369.
URL <http://water.usgs.gov/nrp/gwsoftware/sutra.html>
- VOSS, C., PROVOST, A. (2004): SutraGUI - A Graphical User Interface for SUTRA, A Model for Ground-Water Flow with Solute or Energy Transport. USGS Open-File Report, Vol. 03-285, p. 126.
URL <http://water.usgs.gov/nrp/gwsoftware/sutra-gui/sutra-gui.html>
- ŠIMŮNEK, J., ŠEJNA, M., VAN GENUCHTEN, M.T. (1998): The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably saturated media, Version 2.0. IGWMC - TPS - 70s. IGWMC International Ground Water Modeling Center, Colorado School of Mine, Golden, Colorado, USA, 162p p.
- ŠIMŮNEK J., M., VAN GENUCHTEN, T., ŠEJNA, M., TORIDE, N., LEIJ, F. (1999): The STANMOD computer software for evaluating solute transport in porous media using analytical solutions of convection-dispersion equation. Versions 1.0 and 2.0, Vol. IGWMC TPS-71. IGWMC International Ground Water Modeling Center, Colorado School of Mine, 32 p.
URL http://www.pc-progress.cz/Fr_STANMOD.htm(Dec.2003);
<http://typhoon.mines.edu/software/igwmcsoft/STANMOD.PDF>
- WATERLOO HYDROGEOLOGIC SOFTWARE (1998): FLONET, FLOTRANS. now: Schlumberger Waterservices, <http://www.swstechnology.com/>.

URL http://www.scisoftware.com/products/flonet_details/flonet_details.html

WATSON, I., OSWALD, S., BANWART, S. (2002): Modelling natural attenuation of phenol degradation in groundwater. IN: XIVth International Conference on Computational Methods in Water Resources, No.. 47 Vol. 1 IN Developments in Water Science Series, Elsevier Science, p. 827–834.

WELCH, A., STOLLENWERK, K. (2002): Arsenic in Ground Water, Chap. 1: Arsenic thermodynamic data and environmental chemistry, Kluwer Publishers. p. 1–26.

WIEDEMEIER, T., RIFAI, H., NEWELL, C., WILSON, J. (1999): Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface. John Wiley & Sons Inc., 617 p.

ZHU, C. (2003): A case against Kd-based transport models: natural attenuation at a mill tailings site. Computers & Geosciences, Vol. 29 (3), p. 351–359.

URL <http://www.sciencedirect.com/science/article/B6V7D-481MSRS-3/2/bedd8bc64fcee0949833e512073dd3c>

A. List of abbreviations

$\overset{\circ}{a}_i$	empirical ion size parameter	/
b	First-order decay coefficient for cell death	/
C	Concentration	g/L or moles/L
ΔH	Reaction enthalpy	kJ/mol
E^0	Standard potential	/
Eh	Redox potential	/
ΔG_r	Change in free Gibbs energy	kJ/mol
ΔG_r^0	Standard Gibbs free energy	kJ/mol
γ_i	Activity coefficient of ion i	/
i	Activity of ion i	/
IAP	Ion activity product	/
$K_{Element}$	Solubility constant	/
$k_{1/2}$	Half-saturation constant	/
k_{Md}	Biomass death rate coefficient in Michaelis-Menten kin.	time ⁻¹
M	Microbial Mass	mg/L
m_i	Molality of ion i	mol/kg H ₂ O
moles/kgw	Molality	moles / kg H ₂ O
Ω	Saturation state	/
pe	Activity of electrons	/
pH	Activity of H ⁺ ions	10 ^x
R	Gas constant	8.3144 J/K mol
SI	log Ω	/
T	Temperature	Kelvin
TEA	Terminal Electron Acceptor	
TEAP	Terminal Electron Acceptor Process	
μ_{max}	Maximum growth rate	time ⁻¹
μ	Growth rate	time ⁻¹
Y	Yield coefficient	moles biomass / moles C
z_i	charge number of ion i	/

B. PHREEQC Code

B.1. Simulation 1

TITLE Degradation of organic carbon in equilibrium,
gneissic water, Freiburg-Ebnet

SOLUTION_MASTER_SPECIES

Nzero Nzero2 0.0 Nzero 14.006

SOLUTION_SPECIES #NITROGEN

Nzero2 = Nzero2

log_k = 0

delta_h 0 kcal

PHASES

Nzero2(g)

Nzero2 = Nzero2

log_k 0

GAS_PHASE 1

-pressure 1.0

-temp 10.0

CO2(g) 0.0032

Nzero2(g) 0.78

O2(g) 0.2078

H2O(g) 0.0

CH4(g) 0.0

SOLUTION 1 #Values from Freiburg Ebnet, 2007

units mg/l

temp 10.0

pH 8.22

Ca 33.3

Mg 3.5

K 1.5

Na 7.5

S(6) 10.8 as S04-2

```
C1                11.8
N(5)             14.5      as NO3-
Fe               0.02
```

REACTION 1

```
CH2O(NH3)0.07 0.01 # 0.1 mol CH2O, 0.007 mol NH3;
# steps are 0, log(1-20)
0
0.301029996      0.477121255      0.602059991
0.698970004      0.778151250      0.845098040
0.903089987      0.954242509      1
1.041392685      1.079181246      1.113943352
1.146128036      1.176091259      1.204119983
1.230448921      1.255272505      1.278753601
1.301029996 moles
```

```
INCREMENTAL_REACTIONS false
```

SELECTED_OUTPUT

```
-file Biomass_Ebnet.csv
-reaction true
-molalities O2 NO3- Fe+2 Mn+2 SO4-2 CH4 H2 Fe+3
END
```

B.2. Simulation 8

```
TITLE Monod degradation with Phenol; Simulation 8 (Reference)
```

SOLUTION_MASTER_SPECIES;

```
Phenol Phenol 0 94.11 94.11 # C6H6O
```

SOLUTION_SPECIES;

```
Phenol = Phenol; -log_k 0
```

SOLUTION 1

```
-units g/L
Phenol 2
```

RATES

```
Phenol
```

B.3. Simulation 13

```
-start
1 mu_max = parm(1);
2 k_half = parm(2)
3 S = tot("Phenol")
10 rate = (-mu_max )* S/ (k_half + S)
50 dS = rate * time
90 print M m0 S mu_max k_half rate time
100 save dS
-end

KINETICS
Phenol

-formula Phenol 1
-m0 0
-params 1.61e-8 1.7e-3 #mu_max k_half
-steps 5184000 in 60 #60 days

INCREMENTAL_REACTIONS true

SELECTED_OUTPUT -reset false
-file Monod_Phenol_Sensi_2x_mumax.xls
-totals Phenol
-kinetic_reactants Phenol
-time

END
```

B.3. Simulation 13

```
SOLUTION_MASTER_SPECIES
Phenol Phenol 0 94.11 94.11 # C6H6O
SOLUTION_SPECIES
Phenol = Phenol
-log_k 0

RATES
S_degradation
-start
1 mu_max = parm(1)
2 k_half = parm(2)
3 Y = parm(3)
4 R = 1 + parm(4)
10 S = tot("Phenol")
```

```
20 B = kin("Biomass")
30 rate = -mu_max * (B / (Y * 6)) * (S / (k_half + S)) / R
40 dS = rate * time
50 save dS
60 put(rate, 1)          # Store dS/dt for use in Biomass rate
-end

Biomass
  -start
  1 Y = parm(1)
  2 R = 1 + parm(2)
  3 k_Bd = parm(3)
  10 rate_S = get(1) *   # Get degradation rate, multiply by Retardation
  20 B = m
  30 rate = -Y * 6 * rate_S - k_Bd * B
  40 dB = rate * time
  50 save -dB
  -end

SOLUTION 1;
  -units g/L
  Phenol 2

KINETICS 1

S_degradation
  -formula Phenol 1;
  -m0 0
  -parms 1.91e-5 1e-8 0.5 0.86          # mu_max, k_half, Y, K_d
Biomass
  -formula C 0;
  -m0 0.75e-7
  -parms 0.5 0.86 1e-8          # Y, K_d, k_Bd
  -steps 2592000 in 60          #30 days

INCREMENTAL_REACTIONS true

SELECTED_OUTPUT
  -file MM_sensi.csv
  -reset true
  -molalities Phenol
  -kinetic_reactants Biomass S_degradation

END
```

Affirmation

I hereby affirm that this diploma thesis was accomplished solely by my own and with the resources cited.

Freiburg, 6. June 2008

Jakob Holch