Investigation of contaminant mass fluxes and reactive transport modelling of heterocyclic hydrocarbons at former gasworks sites

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Abstract

The presented thesis deals with the investigation of contaminant mass fluxes, offers an improved analysis of integral pumping tests and presents a reactive transport model based on those contaminant mass fluxes to improve our knowledge about the biogeochemical processes acting in a heterogeneous aquifer undergoing remediation.

The inherent heterogeneity of groundwater bodies poses a problem for their investigation and remediation. Accessibility is usually limited at contaminated sites leaving often only few groundwater wells for observation. It is common practice to interpolate those values for analysis, however, as presented here, if the contaminant plume is distributed heterogeneously in the subsurface this might lead to over- or underestimation of contaminant mass fluxes. This can be counteracted if Integral Pumping Tests (IPTs) are employed. Here, the results of the interpolation of concentration point measurements were compared to the results of the analysis of IPTs along the same control plane at a former gasworks site in Southern Germany which is contaminated mainly by polycyclic aromatic hydrocarbons and heterocyclic aromatic hydrocarbons.

The correct planning and implementation of IPTs provides reliable results of contaminant mass flow rates, however, the determination of the exact plume extent is somewhat hampered as only three scenarios can be analysed: the plume is situated to the right or left of the pumping well or is distributed symmetrically around the pumping well. As presented here, this analysis can be improved when concentration point measurements are used to condition the inversion solution. This approach helped to narrow down the plume position which is especially valuable for the planning and implementation of remediation measures as well as when employing backtracking techniques for source delimiting.

Reactive transport models have been used since a couple of years to improve our knowledge about degradation of contaminants and to study possible remediation measures as well as the effectiveness of already implemented ones. Such a model has been devised for the site under investigation using the contaminant mass fluxes previously determined. The site has been subjected to remediation using a groundwater circulation well injecting H_2O_2 and the reactive transport model was used to study the situation prior and during the remediation. The model was able to confirm the proposed degradation pathways, however, due to the hydrochemical heterogeneity of the site certain phenomena could not be sufficiently explained. The model was then used to explore different remediation scenarios and their effectiveness as well as the possibility of an additional compound consuming oxidation capacity and the resulting uncertainty in remediation effectiveness.

Zusammenfassung

Die vorliegende Dissertation beschäftigt sich mit der Untersuchung von Schadstoffmassenflüssen und stellt eine verbesserte Auswertung von Immissionspumpversuchen (IPV) vor. Des Weiteren wird ein reaktives Strömungs- und Transportmodell beschrieben, welches auf den untersuchten Schadstoffmassenflüssen basiert und dem besseren Verständnis der biogeochemischen Prozesse in einem heterogenen Grundwasserleiter dient, welcher einer Schadstoffsanierung ausgesetzt ist.

Die Heterogenität von Grundwasserkörpern stellt ein Problem für deren Untersuchung und Sanierung dar. Häufig ist der Zugang zu kontaminierten Standorten begrenzt und nur wenige Grundwassermessstellen können u. A. zur Probenahme genutzt werden. Üblicherweise werden diese Messwerte interpoliert, allerdings kann die Heterogenität der Schadstoffverteilung dazu führen, den Schadstoffmassenfluss auf diese Weise falsch einzuschätzen. Diesem Problem kann man durch Anwendung von IPVs begegnen. Die vorliegende Arbeit beschreibt den Vergleich von interpolierten Konzentrationspunktmessungen mit den Resultaten von IPV-Auswertungen. Beide Methoden wurden entlang derselben Kontrollebene am Standort eines ehemaligen Gaswerks in Süddeutschland durchgeführt, wo der Grundwasserleiter durch polyzyklische und heterozyklische aromatische Kohlenwasserstoffe kontaminiert ist.

Durch korrekte Planung und Durchführung von IPVs können zuverlässige Aussagen über den Schadstoffmassenfluss getroffen werden, allerdings können die Ausmaße der Schadstofffahne nicht exakt bestimmt werden, da die Auswertung der IPVs auf drei Szenarien begrenzt ist: die Fahne befindet sich rechts oder links vom Pumpbrunnen oder ist symmetrisch um ihn verteilt. Der zweite Teil dieser Arbeit beschäftigt sich mit der Verwendung von Punktkonzentrationsmessungen bei der IPV-Auswertung, um die Inversionslösung zu konditionieren. Dieser Ansatz unterstützt die Eingrenzung der Fahnenposition, was wiederum zu größerer Planungssicherheit bei der Implementierung von Sanierungsmaßnahmen führt. Des Weiteren können damit Backtracking-Verfahren unterstützt werden, die versuchen, die Schadensherdposition einzugrenzen.

Reaktive Strömungs- und Transportmodelle werden seit einigen Jahren verwendet, um Schadstoffabbau und mögliche Sanierungsmaßnahmen besser zu verstehen und um die Effektivität von bereits vorhandenen Sanierungsmaßnahmen besser einschätzen zu können. Ein solches Modell wurde unter Verwendung der zuvor bestimmten Schadstoffmassenflüsse im Zuge dieser Arbeit für den untersuchten Standort erstellt. Der Standort wurde mit Hilfe eines Grundwasserzirkulationsbrunnens, welcher H_2O_2 in den Grundwasserleiter injiziert, teilweise saniert und das reaktive Strömungs- und Transportmodell wurde verwendet, um die Situation vor der Sanierung als auch während der Sanierung zu untersuchen. Mit Hilfe des Modells konnten die Abbaupfade

der Schadstoffe bestätigt werden, allerdings konnten aufgrund der hydrochemischen Heterogenität des Standorts manche Beobachtungen nicht ausreichend geklärt werden. Das Modell wurde weiterhin verwendet, um unterschiedliche Sanierungsmaßnahmen und deren Effektivität zu untersuchen, als auch um die Möglichkeit zu erkunden, welchen Einfluss ein weiterer Stoff, welcher Oxidationskapazität verbraucht, auf den Schadstoffmassenfluss hat.

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Chapter 1

Introduction

1.1 Motivation and background

Contaminated sites are a common feature of industrialised areas and differ in their characteristics depending on their origin, history and composition, making each site unique in its properties and responses. Studying, monitoring or remediating such a site therefore calls for a set of methods that enables us to recover the evolution of the site, gain an understanding of on-going processes and make predictions about future developments.

Manufactured gas plants were a common sight in Europe throughout the 19th century and well into the 20th century and produced a variety of by-products, the most prominent and persistent being coal-tar. This viscous, dark liquid contains a mixture of polycyclic aromatic hydrocarbons (PAHs), phenols and heterocyclic aromatic hydrocarbons (HETs). PAHs and HETs pose a particular threat to groundwater quality as they tend to dissolve slowly and form a continuous source in the subsurface. They thereby might cause a deterioration of water supply quality as well as pose a threat to aquatic wildlife.

The investigation of any contaminated site should ensure that no part of the contaminant plume is omitted. This is no trivial task as subsurface heterogeneities lead to dispersed, variably distributed and fingering plumes, which are hard to spot given the often limited financial means for investigation. Integrated Pumping Tests (IPTs) offer the means to ensure the capture of the whole plume while avoiding the necessity of a dense observation well network. A direct comparison of the advantages and disadvantages of IPTs and point measurements and their applicability at field sites is necessary but not easily implemented. In addition, IPTs have had the disadvantage so far of offering only a limited set of scenarios for analysis: either the contaminant plume is located to the right or to the left of the well, or the plume is distributed symmetrically around it. These analyses are accurate regarding the mass flow rate estimation, however, not very realistic concerning the plume position determination. Especially when using data from IPTs for the development of a reactive transport model, the actual plume shape and distribution is decisive.

Reactive transport modelling is a useful tool to gather a greater understanding of subsurface processes and their interactions with anthropogenic influences. However, reactive transport modelling requires a thorough data collection leading to an often quite expansive model, thus making the undertaking usually quite time-consuming. A calibrated reactive transport model can, on the other hand, be used as a prediction tool to support decision-making, e.g. during the design and implementation of a remediation measure.

1.2 Objectives and approaches

This thesis aims to present an improved set of tools for exploring contaminant mass fluxes, beginning with the actual data collection, followed by data analysis and application using a reactive transport model which is then implemented as a prediction tool for possible remediation scenarios.

Subsurface investigation techniques are only rarely compared with one another as the ‘true solution’ is usually unknown. This holds true for applications as different as conductivity and contaminant flow rate measurements. In addition, it is quite uncommon, due to financial restrictions, to implement more then one technique at one particular site. Though the first objection can almost never be removed, test sites offer the possibility to implement more than one technique. The test site ‘Testfeld Süd’ will be used for such a purpose, comparing the results of three Integral Pumping Tests (IPTs) with interpolated point measurements that are located in their immediate surroundings with a maximum distance of 3 m in between them. The results will give an indication of the applicability of each method and highlight the advantages and disadvantages of each technique.

The analysis of IPTs can be handled analytically or numerically with the help of a flow and transport model where the numerical evaluation takes the subsurface heterogeneities into account. However, the inversion solution is restricted to 3 scenarios: (i) the plume is positioned to the left of the pumping well, (ii) the plume is situated to the right of the well or the (iii) the plume is distributed symmetrically around the well. These restrictions will be overcome by conditioning the numerical solution using point measurements from within the IPT well capture zone. The conditioned solution will enable a more realistic view of the plume while still estimating the contaminant mass flow rates accurately.

Reactive transport models can help in understanding subsurface processes by representing nature as close as possible. The reactive transport processes at the test site ‘Testfeld Süd’ will be modelled with the help of the reactive transport software PHT3D (Prommer et al., 2003). The flow and transport model will cover the whole area while the reactive transport model will consider only the area between two control planes. Using contaminant mass flow rate results from

IPTs conducted at those control planes ensures the validity of the model for the aforementioned reasons. The model aims to reproduce (i) the processes acting on the contaminant plume prior to any remediation, (ii) the processes influencing the plume during the remediation by H_2O_2/O_2 injection and give (iii) an indication of the effectiveness of two different remediation scenarios. The model will also be used to explore the uncertainty resulting from the presence of an additional consumer of oxidation capacity and its effect on the effectiveness of the remediation measure.

1.3 Format of the thesis

Chapter 2 presents a general overview of subsurface investigation methods with a particular emphasis on Integral Pumping Tests (IPTs) and their application. Then, factors influencing contaminant mass fluxes and their quantification will be discussed. Next, a short review of reactive transport modelling is given. The main research work is presented in chapters 3, 4 and 5, which are presented in the form of manuscripts for publication in scientific journals.

Chapter 3 deals with the comparison between two subsurface investigation methods, IPTs and interpolated point measurements, respectively, highlighting their individual applicability.

Chapter 4 presents an approach to condition the results of an Integral Pumping Test (IPT) by integrating point measurements in the numerical analysis, providing a more realistic but still accurate view of the contaminant distribution in the subsurface.

Chapter 5 presents a reactive transport model of the test site including its application as a prediction tool for possible remediation scenarios and to evaluate the uncertainty in remediation success resulting from the presence of pyrite.

Chapter 6 summarises the conclusions with respect to the objectives of this thesis and provides suggestions for further research.

Please note that as a result of the cumulative nature of this thesis a reference list is provided at the end of every chapter.

1.4 References

Prommer, H., Barry, D. A., Zheng C. (2003) MODFLOW/MT3DMS based reactive multi-component transport modelling. Ground Water, 41(2), pp. 247– 257.

Chapter 2

General overview

2.1 Subsurface investigation techniques

The existence of water within the subsurface leads to the formation of a quite unique reaction zone comprised of consolidated and unconsolidated material in addition to liquid water and the occasional gaseous elements. The reactions affecting the conditions in the subsurface are manifold, due to the tremendous variety of structures, materials and textures present, and can be categorized into hydrogeochemical, microbiological and, at greater depths, geothermal components. Those, however, are highly interlinked and should not be seen as separate entities. The water present in the areas closest to the surface comprises approximately 30 % of all freshwater resource on earth, a resource which is quite readily available compared to the majority of freshwater which is stored in icecaps and glaciers. It is therefore vital to gather an in-depth knowledge about quantity as well as quality of groundwater, this being, however, a rather demanding task. The invisibility of groundwater and the subsurface conditions it is surrounded by, requires a combination of engineering, analytical as well as modelling efforts to secure the supply of clean groundwater for future generations.

Subsurface investigations, in a hydrogeological context, aim to characterise the underground to give a clearer picture of the hydrogeological and geological conditions by applying techniques such as drillings, sediment or rock sampling and analysis, pumping tests, sampling of groundwater and measuring the water level in the whole area.

In recent times, direct-push technology has advanced the speed and precision of subsurface investigations tremendously, including in-situ hydraulic conductivity tests (Butler et al., 2002), electrical conductivity logging (Sellwood et al., 2005) and high resolution geochemical groundwater sampling (Charette and Allen, 2006).

2.2 Integral Pumping Tests

Wood (2000) pointed out that heterogeneity is ‘the great challenge of hydrology’ as physical as well as chemical and biological heterogeneity is mostly unknown and increases the uncertainty regarding issues such as water supply and remediation immensely. Though heterogeneity can be actively studied by investigating the subsurface using a large array of point measurements, such an endeavour is seldom undertaken due to limited financial means. However, a smaller set of point measurements can often not ensure that the heterogeneous distribution of a contaminant is adequately represented (Kübert & Finkel, 2006). Alternatively, Integral Pumping Tests (IPTs, Teutsch et al., 2000; Ptak et al., 2000) can be employed, which consist of a pumping test with simultaneous recording of concentration-time series. These can be employed along control planes situated perpendicular to the main flow direction downstream of a suspected contaminant source. The pumping tests should then draw water from the centre of the contaminant plume as well as from its fringe. This requires adaptation of the position of the wells, their pumping rates and pumping times thereby ensuring that the complete plume is captured. Other factors influencing the dimensioning of the IPTs are the natural groundwater flow, the aquifer thickness and the effective porosity. The concentration-time series can be recorded for a variety of dissolved components, including contaminants as well as electron acceptors. These concentration-time series are then analysed using a transient inversion algorithm and, if available, a numerical flow and transport model of the site, resulting in the mass flow rate and the average concentration along the control plane. At first, the concentration time series can be interpreted analytically (Schwarz, 2000) where it is assumed that conditions are in steady state, the flow is radially symmetrical towards the pumping well, i.e. the natural groundwater flow gradient is neglected, the aquifer is assumed to be homogeneous with regard to hydraulic conductivity, porosity and thickness and the concentration is assumed to be constant within each streamtube. This method aims to quantify the concentration in those parts of the aquifer that are highly conductive and contribute most to the mass flow rate. The analytical solution was then expanded to include the natural groundwater flow in the aquifer (Bayer-Raich et al., 2004) and by integrating the solution into a numerical flow and transport model it became possible to include heterogeneous distributions of hydraulic conductivity. The program CSTREAM (Bayer-Raich et al., 2002; 2003; Bayer-Raich, 2004) implements this algorithm, MODFLOW (McDonald and Harbaugh, 1988) calculates the groundwater flow and MODPATH (Pollock, 1994) uses particle tracking to define the isochrones and streamtubes. This also allows the consideration of the influence of consecutive or simultaneous IPTs and their catchment zones on each other. Generally, it can be assumed that an IPT only increases the transport velocity at a contaminant source minimally and therefore does not cause any mobilisation of contaminants.

2.3 Natural attenuation

Groundwater is characterised by an interplay between the solid aquifer matrix, the dissolved solids and the microorganisms attached to the grain surfaces. Dissolved solids, especially contaminants, can undergo a variety of processes that decrease their concentration in the groundwater. Possibilities are the sorption onto or into the sediment matrix (e.g. Brusseau et al., 1989;

Tratnyek et al., 2001; Broholm et al., 1999a; Bi et al., 2006), ion exchange processes (e.g. Clifford & Liu, 1993; Gingras & Batista, 2002) and microbially mediated biodegradation reactions (e.g. Vroblesky & Chapelle, 1994; Lovley & Coates, 1997; Rooney-Varga et al., 1999). The former two can be reversed whereas the latter process is irreversible.

Biodegradation in the groundwater environment refers to the transformation of an organic compound into other compounds through microbial action. Should this process result in the formation of inorganic species it is referred to as mineralisation. The agents of biodegradation in groundwater are primarily bacteria and fungi that are attached to sediment grains forming biofilms (e.g. Kissel et al., 1984; Bouwer & Wright, 1988; Zhang et al. 1995). Biodegradation was observed and studied in the lab and under field conditions for compounds as diverse as methyl tert-butyl ether (MTBE) (Borden et al., 1997), BTEX compounds (Edwards et al., 1992; Nielsen and Christensen, 1994; Borden et al., 1997; Davis et al., 1999; Gieg et al., 1999; Griebler et al., 2004), creosote compounds (Broholm et al., 1999b; King et al., 1999), polycyclic aromatic hydrocarbons (Yuan and Chang, 2007), heterocyclic aromatic hydrocarbons (Jensen et al., 1988; Grosser et al., 1995; Licht et al., 1996; Kaiser et al., 1996; Dyreborg et al. 1996; 1997) and chlorinated hydrocarbons (Nielsen et al., 1995; Hunkeler et al., 1999). Arcangeli and Arvin (1995) observed in addition to the adaptation of microorganisms to a variety of contaminant electron donors that the presence of certain compounds (heterocyclic aromatic hydrocarbons) can inhibit the degradation of other aromatic hydrocarbons.

Microorganisms obtain energy for activity and growth by physiologically coupling oxidation and reduction reactions. This process involves the transfer of electrons from electron donors to electron acceptors. This energy-releasing process results in the oxidation of the electron donor and the reduction of the electron acceptor. Electron donors are usually organic compounds (organic matter, petroleum hydrocarbons) that occur in a relatively reduced state. On the other hand, electron acceptors are compounds such as oxygen, nitrate, sulphate and ferric iron and occur in relatively oxidised states (Chapelle et al., 1995). Aerobic oxidation is usually carried out by aerobic bacteria that use electron acceptors such as oxygen and nitrate and is considered to be the most effective removal mechanism for petroleum hydrocarbons (Borden, 1994). Anaerobic degradation usually occurs in oxygen-free environments, e.g. within contaminant plumes, where usually the only electron acceptors present are sulphate and ferric iron (Chapelle and Lovley, 1992). Chapelle et al. (2009) observed that the ratio between dissolved ferrous iron and sulfide might give an indication of the occurrence and distribution of iron and sulphate reduction in aquifers. All of these terminal electron acceptors (TEAs) are consumed in a sequential order depending on their redox potential (Stumm and Morgan, 1996; Postma and Jakobsen, 1996; Christensen et al., 2000; McMahon and Chapelle, 2008). Most contaminated aquifers therefore display a distinct redox zonation along the flow direction (Bjerg et al., 1995; Christensen et al., 2000). Using oxygen as an electron acceptor supplies the organism with large amounts of energy when electrons are transferred to oxygen, however, there is only very little mixing of water within the subsurface. This leaves contaminant plumes with anaerobic conditions once the oxygen is used up within the plume as oxygen is only replenished at the fringe zone (Prommer et al., 2006). The decisive factor for any redox reaction is the abundant supply of electron donors and electron acceptors at the same place, as microorganisms can react very sensitively to limitations of either (Bae and Rittmann, 1996).

2.4 Enhanced Natural Attenuation

Enhanced Natural Attenuation (ENA) describes a variety of technologies that encompass the addition of electron acceptors, electron donors or nutrients to stimulate naturally occurring microbial populations (Scow and Hicks, 2005). Another possibility is the introduction of specific microorganisms aimed at enhancing the biodegradation of the target compound. This includes the ex situ stimulation of naturally occurring microbial populations which are then reinjected, as well as the addition of cultures not native to the site that are capable of co-metabolizing or biodegrading the target compound (Gentry et al., 2004).

ENA techniques were first investigated at the lab-scale (Odencrantz et al., 1990) and became more widespread in field scale operations in recent years (Eckert and Appelo 2002; Yabusaki et al. 2007). A study conducted by Hunkeler et al. (2002) showed that the active remediation of a diesel-fuel contaminated aquifer by injection of oxygen and nutrients affected the removal of the petroleum hydrocarbons after biostimulation had ceased as natural attenuation processes continued to remove the contaminants. Devlin et al. (2004) studied the performance of a sequential anaerobic and aerobic in-situ treatment system of an emplaced source of chlorinated solvents and found this system to be more effective than natural attenuation alone. Davis et al. (2009) found that estimated aerobic degradation rates in the field were greater than those observed during laboratory-based studies when they injected oxygen into an anaerobic aquifer contaminated with chlorinated hydrocarbons. A different approach was used by Semprini et al. (2009) who bioaugmented an aquifer with an enrichment culture and injected butane as well as dissolved oxygen or hydrogen peroxide to aid in-situ aerobic cometabolism of chlorinated hydrocarbons.

2.5 Effects of aquifer solids

The dissolution and precipitation of minerals in the subsurface is affected by the groundwater redox conditions as this controls the consumption and production of protons (Sung and Morgan, 1980; Engesgaard & Kipp, 1992; Appelo et al., 1998; Prommer & Stuyfzand, 2005; Greskowiak et al., 2005). Barcelona and Holm (1991) first studied the oxidation-reduction capacities in a sand-gravel aquifer and found that the groundwater contributed less than 1 % to it. They also point out that the manipulation of redox conditions, e.g. using hydrogen peroxide, might be hampered by this as hydrogen peroxide reduction by aquifer solids proceeds much faster than microbially mediated contaminant degradation. This factor is reiterated by Hartog et al. (2002) who studied the reactivity of sedimentary organic matter, pyrite and siderite and found even though those O_2-reducing components react on the same time scales, the fine fractions are more reactive. They concluded that the geological history of the site determines the amount of those reductants present but the pH and microbial activity control their reactivity. Iron minerals have a two-fold effect on the aquifer as they, on the one hand, form the source of electron acceptors (Vencelides et al., 2007), however on the other hand, especially oxidised iron sulphide minerals can impact water quality of the aquifer (Andersen et al., 2001; Prommer and Stuyfzand, 2005). Additional effects are the build-up of iron oxide encrustations in wells, thereby hampering water abstraction or injection (Houben, 2004) and the consumption of large amounts of oxidants leaving very little left for contaminant degradation (Thullner and Schäfer, 1999).

2.6 Quantification of biodegradation and mass fluxes

Nyer and Duffin (1997) summarised that the application of Natural Attenuation requires (i) documentation of a decrease of the contaminant concentrations with distance at the site under investigation, (ii) evidence of microbial activity on-site and (iii) the characterization of trends of hydrogeochemically relevant parameters. The latter referring to a decrease and increase of electron acceptors and degradation products, respectively. Evidence for NA has to be collected at each site individually as all of these factors are site-specific, especially the heterogeneity and composition of the contaminant and the conditions in the aquifer itself, as both affect the concentration and release rate of the contaminant into the aquifer. Early studies focused on the biodegradation of dissolved organic contaminants that occur at specific rates which can be quantified and form the basis for assessing the degradation potential in the subsurface and are used when modelling such reactions. These rates are function of the temperature and the availability of electron acceptors and electron donors and can be studied by applying laboratory batch and column studies as well as by analysing field data (Chapelle et al., 1996). Baker et al. (2000) measured the reaction rates of O_2 and CO_2 in a lab microcosm, while maintaining field conditions over time to estimate hydrocarbon biodegradation rates.

A different approach to describe plume extent and behaviour are mass flow rate approaches that average and integrate measured values and are defined as the movement of mass per unit time [$M\ T^{-1}$]. The most common approach includes point-scale concentration measurements and their interpolation. Examples include the measurement of compound-specific stable isotope ratios (Hunkeler et al., 1999), tracer tests with isotope-labelled contaminants (Therrin et al., 1995) or with conservative tracers (Wiedemeier et al., 1996) as well as the spatial and temporal monitoring of contaminant concentrations and electron acceptors (Chiang et al., 1989; Gieg et al., 1999; Davis et al., 1999). Blum et al. (2009) presented a comparison between different quantification approaches to estimate biodegradation rates (first-order decay models, Michaelis-Menten kinetics and stable carbon isotopes) and could show that Michaelis-Menten kinetics were most suitable, however, representing bulk attenuation, whereas stable carbon isotopes are more appropriate for the estimation of actual biodegradation. Beyer et al. (2007) compared different strategies using monitoring networks (1D centreline as well as 2D methods) to estimate first-order degradation rates using virtual heterogeneous aquifers and could show that overestimation of degradation rates was prevalent for both methods especially for narrow plumes but could be reduced when incorporating all downstream measurements in the 2D approximation. They also found that the number of observation wells was not correlated to the quality of the estimated degradation rate when using the 2D approach. Li and Abriola (2009) pointed out that applying multiple criteria decision making theory to the selection of optimal sampling locations can reduce the required sampling strategy quite considerably but still guarantee accurate quantification of mass discharge uncertainty. However, point measurements are very sensitive to temporal dynamics of groundwater, especially at the plume fringe even if the hydraulic conductivity is assumed to be homogeneous (Rein et al., 2009). Other methods might therefore be required to assess mass flux estimates, especially when spatial as well as temporal variations are expected.

The passive flux meter has been introduced by Hatfield et al. (2004) and consists of a medium which retains organic or inorganic substances present in the groundwater. At the same time, the medium is also impregnated with a water soluble tracer which is displaced by the sorbent at rates proportional to the groundwater flux. A special focus on landfill leachate and their complex organic composition was placed by Cornelissen et al. (2009) who employed an equilibrium passive sampler to determine the free and total dissolved concentrations in groundwater. Basu et al. (2009) integrated point monitoring data with on-line volatile organic compound samplers and passive flux meters to evaluate a trichloroethene source zone and the contaminant mass flux emerging from it.

Goltz et al. (2009) validated the tandem circulation well approach as well as the modified integral pumping test for quantifying contaminant mass flux by implementing both methods in an artificial aquifer.

Approaches to measure the flow and extent of non-aqueous phase liquids include single-well tracer dilution techniques to measure the flow of light non-aqueous phase liquid through the well and the adjacent surroundings (Sale et al, 2007) and synchrotron x-ray microtomography and interfacial partitioning tracer tests to determine the interfacial area between a non-aqueous phase liquid and the groundwater (Brusseau et al. 2008).

Another possibility are Integral Pumping Tests that enable the determination of the integrated mass flow rates of chemical components in the groundwater. Mass flow rate determination between two consecutive control planes gives rise to a quantification of natural attenuation rate constants (Bockelmann et al., 2001, 2003). Furthermore, the numerical evaluation of IPTs can aid in the investigation of the position of the contaminant plume, can quantify the individual source strengths by evaluating the mass flow rates at the downstream control planes and can thereby answer the question if suspected source zones are (still) active (Bauer et al., 2004). The mass flow rates can also be obtained with a vertical resolution if predefined segments of the aquifer are separately investigated by pumping only in the appropriate well screen parts (Ptak et al., 2004). Bayer-Raich et al. (2006) introduced multiple-well analysis of IPTs to include mass-balance considerations and showed that those results differed from single-well analyses which influences the estimation of natural attenuation rate estimates. Peter et al. (2004) combined compound-specific isotope analysis with IPTs to assess the mean biodegradation of o-xylene between consecutive control planes. Even though Zeru and Schäfer (2005) argued that strong concentration gradients might introduce a bias when analysing concentration-time series during an IPT, Jarsjö and Bayer-Raich (2008) presented an analytical expression to evaluate the prediction error and could show that the mass flow error remains small even for large first-order degradation rates. Recently, Bayer-Raich et al. (2009) introduced an analytical expression for the relationship between the initial concentrations in the aquifer and the measured concentration-time series if the contaminant plume is subject to degradation and sorption.

2.7 Reactive Transport Modelling

A way to understand processes acting in the environment are models, where analytical models are the least complex and most easily applied tool (Gutierrez-Neri et al, 2009; Zhang et al., 2009). However, as processes in the subsurface are usually more complex, even when artificial homogeneity is studied (Close et al., 2008), numerical solutions are frequently employed to model transport. Such approaches have been applied to study the effect of low hydraulic conductivity zones (Timms and Hendry, 2008), heterogeneous media (Fagerlund et al., 2008; Kuo et al., 2008), to simplify chemical reactions by using a particle tracking approach (Benson and Meerschaert, 2008) and to study the distribution of edible oil emulsions in heterogeneous aquifers (Clayton and Borden, 2009).

A contaminated site, especially one being actively remediated, is characterised by complex interactions of hydraulic, hydrogeochemical and microbial processes, that are often non-linear and cannot always be extrapolated from laboratory studies. The analysis of field data is therefore often supported by the application of multi-component reactive transport models to identify and understand the processes involved at contaminated sites. Such reactive transport models were employed to understand processes regarding natural attenuation (Gomez et al., 2008; 2009; Miles et al., 2008), river-groundwater interactions (Batlle-Aguilar et al., 2009; Yabusaki et al., 2008), sorption in soil columns (Bi et al., 2009), tidal influence on contaminated groundwater (Robinson et al., 2009), effects of precipitation on reactive transport in groundwater (Visser et al., 2009) and source zone depletion (D’Affonseca et al., 2008). These models have also been applied to sites contaminated with BTEX simulating possible remediation scenarios (Prommer et al., 2000) as well as enhanced natural attenuation using nitrate (Eckert and Appelo, 2002), in situ ozonation (Kim and Choi, 2002), air sparging and soil vapour extraction (Rahbeh and Mohtar, 2007), oxidation by potassium permanganate (Henderson et al., 2009), humic acids (Molson et al., 2002) and lactate addition (Henderson et al., 2009b). Other studies focused on the potential for natural attenuation (Mayer et al., 2001) and the identification of the governing processes within contaminant plumes (Brun et al., 2002: Hunter et al., 1998). A special focus on DNAPLs emanating from manufactured gas plants was placed by Birak and Miller (2009), whereas Falta (2008) presented a new approach to compare source and plume remediation alternatives.

2.8 Source delimiting

Identifying the source of a contamination is often the only effective way to achieve complete site clean-up but is, however, also quite demanding. The exact location as well as the timing of the contamination incident is usually unknown as is the amount and type of degradation undergone by the contaminant. Finding a solution to this problem is a mathematically demanding task and requires the solution of an inverse problem. This problem has traditionally been solved using a trial-and-error calibration process to reach an acceptable fit between the simulated and measured values. This process is rather subjective and very time consuming leading to the development of optimisation models for solving the inverse problem by employing statistical methods (Gorelick et al., 1983, Parker and Van Genuchten, 1984, Wagner and Gorelick, 1987). Wagner (1992) combined groundwater flow and contaminant transport parameter estimation and contaminant source characterisation to estimate unknown parameters such as the contaminant mass flux into the aquifer by applying non-linear maximum likelihood estimation. Skaggs and Kabala (1995) used the method of quasi-reversibility to solve the diffusion equation in reverse time and discovered that it offers improved generality but at the expense of accuracy. Snodgrass and Kitanidis (1997) applied a geostatistical approach to determine the source function by discretising it into components that are assigned a known stochastic structure with unknown stochastic parameters aiming to recover the release history of a conservative solute in a one dimensional homogeneous medium. A different approach was applied by Woodbury et al. (1998) who employed a method of statistical inference (Minimum Relative Entropy inversion) to recover the source release history in a three dimensional, steady and uniform groundwater flow system where transport parameters like dispersivity were assumed to be known. Datta et al. (2009) developed a methodology where a nonlinear optimisation model is linked to a groundwater flow and transport simulator to simultaneously identify pollution sources and estimate groundwater system parameters. Neupauer et al. (2000) compared two proposed inverse methods (Tikhonov regularisation and minimum relative entropy inversion) and concluded that assuming error-free data a smooth source history function could be reconstructed using both methods but differences are emerging if the source history function in nonsmooth. Neupauer and Wilson (1999) then introduced the concept of adjoint-derived backward location and travel-time probabilities where those probabilities provide information about the source of contamination. They applied it to an instantaneous point source (i) in a one-dimensional, semi-infinite domain, (ii) in a hypothetical two-dimensional domain (Neupauer and Wilson, 2001) and (iii) in a hypothetical one-dimensional model with a decaying solute (first-order decay) (Neupauer and Wilson, 2003). A further step was taken by Neupauer and Lin (2006) who could recover the source location or the release time of the observed contamination using a backward location probability density function conditioned on measured concentrations in a hypothetical, two dimensional, confined and heterogeneous aquifer with an instantaneous point source. Neupauer et al. (2007) then applied this to a solute that exhibits first-order decay and linear equilibrium or non-equilibrium sorption using data from a trichloroethylene plume. Neupauer et al. (2009) explored this concept further by developing forward and backward temporal probability distribution functions to determine the random time in the past that a contaminant was sorbed at a location of interest. A different approach was taken by Jarsjö et al. (2005) who used integral pumping tests (IPTs) to quantify different sources of uncertainties regarding field-scale mass flow and average concentration estimations. Their complex IPT evaluations were used to delineate possible source zones and source absence zones with the help of particle backtracking. This approach depends on the robustness and quality of the groundwater flow model it is based on, which was tested by applying different boundary conditions to quantify the uncertainty of the groundwater model. Additionally, they implemented empirical plume length statistics for benzene and chlorinated hydrocarbons to delimit the source and the source absence zones upstream of the measurement well even further. Troldborg et al. (2008) approached the subject by developing a modelling tool for prioritising known point sources according to their impact on groundwater quality. They suggest that unknown contaminant sources can be identified by comparing measured contaminant flux with the calculated mass flux, where a deficit could point towards the existence of still unknown sources. Once the position of the plume is located, Dridi et al. (2009) proposed using partitioning interwell tracer tests combined with an inverse modelling approach to characterise the distribution of a dense non-aqueous phase liquid in a virtual vertical plane of the source.

2.9 Heterogeneity and Uncertainty

Heterogeneity of the subsurface has been identified as the crux of hydrogeology and many a studies have been conducted to describe it and to study its effects on our understanding of the subsurface. The analysis of data from an investigation method can only yield information about a restricted part within the subsurface. Such a representative elementary volume (REV) is defined as the smallest sampling volume that still represents the overall conditions. Devlin and McElwee (2007) presented a study that showed that monitoring water levels in an area smaller than a certain size, which is determined by the measurement error, will lead to erroneous horizontal hydraulic gradient estimates and flow directions. Furthermore, Copty et al. (2008) could show how heterogeneity influences the interpretation of pumping tests in leaky aquifers due to lumping of the heterogeneous structure of the aquifer. Heterogeneity can be observed on all (hydro-)geological scales, beginning with fine soil layering up to large-scale preferential flow paths. There have been a number of methods proposed to handle the issue, including statistical (Hu and Chugunova, 2008; Nowak et al., 2008; Kourakos and Mantoglou, 2008; Perrin et al., 2008; Gotovac et al., 2009) and technical (Butler et al., 2002; Yeh and Lee, 2007; Labaky et al., 2009; Gehman et al., 2009; Greswell et al., 2009).

The inherent heterogeneity of aquifers has major implications, especially regarding issues such as dispersivity (Sun et al., 2008) and LNAPL recovery rates (Johnston and Trefry, 2009). Soil matrix heterogeneity also affects pollutant transfer through the unsaturated zone due to preferential flow processes (Bachmair et al., 2009). This makes modelling of transport in heterogeneous media a rather demanding task as homogeneous advection-dispersion models often cannot model the resulting tailing in tracer breakthrough curves, however, mass transfer models using memory offer a possibility to reproduce the tracer spreading in heterogeneous aquifers (Willmann et al., 2008). Technical approaches to tackle the issue of transport in heterogeneous media have been presented by Charette and Allen (2006), Singha et al. (2008) and Renard and Jeannée (2008). A heterogeneous distribution of sediments becomes also crucial when considering reactive contaminant transport as changing mineralogy (Zhu and Burden, 2001) as well as dispersive mixing (Bauer et al., 2009) influence (enhanced) natural attenuation of contaminants. However, before the heterogeneity of sediment and groundwater composition at a contaminated site is considered, questions regarding the influence of precipitation patterns (Zosseder et al., 2009), kinetic sorption and biodegradation in the vadose zone (Kuntz and Grathwohl, 2009) and the applicability of so-called background concentrations (Kelly and Panno, 2008) should be answered.

Unknown heterogeneity of sediments and groundwater constituents increases the uncertainty of groundwater models tremendously. Already the conceptual model is a source of uncertainty (Rojas et al., 2008) and simplifications such as depth-averaging (Simpson, 2009) and upscaling of equilibrium assumptions (Binning and Celia, 2008) can introduce errors. There have been many attempts to characterise and quantify the uncertainty in groundwater models (Clark et al., 2008; Götzinger and Bárdossy, 2008; Ross et al., 2009; Matott et al., 2009) where a special focus on remediation strategies has been placed by Bolster et al. (2009). Despite these challenges, it has been called into question if most groundwater models use too many lumped parameters that do not properly represent the relevant processes, simply due to historical restrictions on computing capabilities and a focus on calibration rather than prediction (Hunt et al., 2007).

2.10 References

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Chapter 3

Bestimmung der Schadstofffrachten an Kontrollebenen mithilfe von Punktkonzentrationsmessungen und Immissionspumpversuchen – ein Vergleich

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Kurzfassung

Die Quantifizierung der Schadstofffrachten an Kontrollebenen ist eine entscheidende Voraussetzung zur Bewertung von Grundwasserschadensfällen und zum Nachweis von Natural Attenuation. Hierzu können zwei verschiedene Erkundungsansätze, die Frachtbestimmung basierend auf der Interpolation von Punktkonzentrationsmessungen sowie Immissionspumpversuche, verwendet werden. Punktkonzentrationsmessungen haben den entscheidenden Nachteil, dass in der Regel nur eine ausreichend große Anzahl sicher stellen kann, dass die gesamte Abstromfahne erfasst wird. Immissionspumpversuche können wiederum relativ hohe Grundwasseraufbereitungs- und Entsorgungskosten verursachen und nur in ausreichend durchlässigen Grundwasserleitern durchgeführt werden. Ein Vergleich der Ergebnisse aus der Anwendung beider Erkundungsansätze kann eine Hilfestellung bei der Konzipierung von Erkundungsmaßnahmen bieten. Daher wurden die Resultate von vier Immissionspumpversuchen mit Messungen in 13, in kurzem Abstand zueinander errichteten Direct-Push-Messstellen auf dem Gelände eines ehemaligen Gaswerks verglichen. Es konnte festgestellt werden, dass die Vergleichbarkeit der Erkundungsergebnisse je nach Standortsituation stark von der Heterogenität der Verteilung der Schadstoffe im Grundwasserleiter abhängt. Die Studie legt nahe, dass insbesondere bei stark heterogenen Verhältnissen im Grundwasserleiter Immissionspumpversuche bei der Wahl der Erkundungsmethode bevorzugt werden sollten, da die Interpolation von Punktkonzentrationsmessungen selbst im Falle eines relativ engmaschigen Messstellennetzes zu einer großen Erkundungsunsicherheit führen kann.

Abstract

The quantification of contaminant mass flow rates at control planes is an essential prerequisite for assessing contaminated sites and for providing evidence of natural attenuation. Two different investigation approaches are usually implemented: mass flow estimation based on interpolation of point scale concentration measurements, and integral pumping tests. Point scale concentration measurements have the crucial disadvantage that in general, only a sufficiently dense monitoring network can ensure that the plume is completely covered. On the other hand, integral pumping tests may require expensive groundwater treatment and disposal and are only applicable in sufficiently conductive aquifers. A comparison of results from the application of both approaches can help with respect to the selection of a subsurface investigation method. A former gasworks site was chosen to compare the results of four integral pumping tests and measurements obtained from 13 direct-push wells, which were installed at a relatively close spacing. The comparison shows that the correlation of the two methods depends strongly on the heterogeneity of the contaminant distribution within the aquifer. The study suggests that especially in the case of heterogeneous settings, integral pumping tests should be chosen for subsurface investigations, as interpolated point scale concentration measurements, even if densely spaced, can still bear a prohibitively high degree of uncertainty.

3.1 Einleitung

Die Quantifizierung von Schadstofffrachten und der Abnahme der Schadstofffrachten zwischen zwei oder mehreren Kontrollebenen ist ein essentieller Bestandteil der Beurteilung von Schadensfällen in Grundwasserleitern, insbesondere wenn Natural Attenuation (NA) im Rahmen der Sanierungsplanung in Betracht gezogen wird. Sowohl das LABO-Positionspapier (2005) als auch die US-EPA (2004) betonen für die NA-Untersuchung die Notwendigkeit einer Charakterisierung der Schadenssituation, welche sowohl die räumliche als auch die zeitliche Ausbreitung der Schadstofffahne und den Austrag aus der Schadstoffquelle betrachtet. Die US-EPA betont insbesondere die möglichst dreidimensionale Charakterisierung der Fahne sowie die Beantwortung der Frage, ob es sich um eine stationäre oder instationäre Schadstofffahne handelt. Erst bei Vorliegen dieser Informationsgrundlage, welche sicher stellen muss, dass die gesamte Fahne erfasst wurde, kann es zu einer Einschätzung und Bewertung des Schadensfalls sowie der genauen Konzeption, Positionierung und Dimensionierung von Sanierungsmaßnahmen und der eventuellen Berücksichtigung von NA kommen. Dafür können die berechneten Schadstofffrachten als Eingangsgrößen für ein reaktives Strömungs- und Transportmodell verwendet werden, mit dessen Hilfe das NA-Potenzial des Standorts evaluiert und mögliche Sanierungsstrategien entwickelt werden. Ein Beispiel für die Bestimmung des NA-Potenzials durch Berechnung der Schadstofffrachten von Benzol, Toluol, Ethylbenzol und Xylol (BTEX) und Polyaromatischen Kohlenwasserstoffen (PAKs) an mehreren hintereinander liegenden Kontrollebenen findet sich z. B. bei Bockelmann et al. (2001) und Bayer-Raich et al. (2006). Weitere Anwendungsgebiete für die Berechnung der Schadstofffrachten ergeben sich (i) bei der Bewertung unterschiedlicher Schadstoffe in Bezug auf ihre Umweltverträglichkeit und damit deren Priorisierung (Einarson & Mackay 2001), sowie (ii) bei der Beurteilung von Sanierungsmaßnahmen an Schadstoffquellen (Soga et al. 2004). Sowohl die Zusammensetzung und Heterogenität der Schadensquelle als auch die Heterogenität des betroffenen Grundwasserleiters sind ausschlaggebend für die Freisetzung und Verteilung der Schadstoffe im Untergrund. In der Regel resultiert hieraus eine ungleichmäßige Verteilung der Schadstoffmasse innerhalb der Schadstofffahne. Erfahrungsgemäß ist die Berechnung der Schadstofffrachten an Kontrollebenen, insbesondere aufgrund möglicher Instationarität des hydraulischen Systems, keine triviale Aufgabe. Prinzipiell lassen sich hierzu zwei verschiedene Erkundungsansätze einsetzen, die Frachtbestimmung basierend auf der Messung von Punktkonzentrationswerten und deren Interpolation sowie der räumlich integrierende Ansatz, der zur Entwicklung von Immissionspumpversuchen (IPV) geführt hat. Ersterer umfasst neben der Messung von Konzentrationen an einzelnen Messstellen bzw. Brunnen auch die Bestimmung der hydraulischen Leitfähigkeit und des hydraulischen Gradienten, optimalerweise an jedem Messpunkt, wobei manche Interpolationsansätze tiefenhorizontierte Parameter benötigen. Abhängig von der Anzahl der Messstellen können dabei hohe Erkundungskosten entstehen, wobei eine relativ geringe Anzahl von Messstellen den entscheidenden Nachteil hat, dass nur ein relativ kleiner Teil des Untergrundes mit seiner Schadstoffverteilung direkt erfasst wird. Immissionspumpversuche stellen eine weitergehende Erkundungsmaßnahme dar, die mit einer umfassenden Vor- und Nachbereitung und je nach Standortsituation mit ggf. relativ hohen Wasseraufbereitungs- und –entsorgungskosten verbunden ist. IPV haben den Vorteil, dass weitere relevante Parameter wie z. B. die Transmissivität in einem Schritt erfasst werden und ermöglichen gleichzeitig die vollständige Erfassung der Schadstofffahne und somit eine verlässliche Berechnung der Schadstofffrachten. Hier kann (i) ein Vergleich der Ergebnisse aus der Anwendung beider Erkundungsansätze Stärken und Limitationen der Methoden aufzeigen und (ii) eine Analyse der methodentypischen Unsicherheiten ermöglichen, Empfehlungen zum Einsatz dieser Methoden geben zu können. Bisher sind mehrere verschiedene Vorgehensweisen, deren Ziel die Bestimmung des Massenflusses durch Interpolation von Punktkonzentrationsmessungen war, vorgestellt worden, wobei hier insbesondere die Unterschiede im Umfang und Qualität der Datengrundlage von Bedeutung sind. King et al. (1999), Borden et al. (1997) sowie Kao & Wang (2001) verfolgten aufgrund der guten Datengrundlage einen Ansatz, bei dem alle Parameter sowohl horizontal als auch vertikal aufgelöst in die Berechnung eingehen konnten. Hatfield et al. (2002, 2004) verwendeten Fluxmeter, um den spezifischen Massenfluss direkt an der Messstelle zu bestimmen. Einen ähnlichen Ansatz verfolgte Ballard (1996), der mit einem Durchflusssensor die Richtung und Stärke des Grundwasserflusses in drei Dimensionen bestimmte. Eher klassische Methoden setzten Newell et al. (2003) und Bockelmann et al. (2003) ein, wobei sich ihre Arbeiten durch die horizontale und vertikale Auflösung der verwendeten Datensätze unterscheiden. Bei Kübert & Finkel (2006) findet man einen Vergleich dieser verschiedenen Ansätze sowie die Empfehlung, bei zunehmend heterogenen Verhältnissen integrierende Methoden zu verwenden. Die Heterogenität des Untergrunds führt in der Regel zu stark unregelmäßig ausgebildeten Schadstofffahnen, wobei die Qualität der Bestimmung der Schadstofffracht wesentlich von der Anzahl und Positionierung der Monitoring-Messstellen abhängt. Ebenso bewirkt eine heterogene Verteilung der Schadstoffe im Schadensherd ungleichmäßig verteilte Schadstoffkonzentrationen im Abstrom. Nur ein ausreichend dichtes Messstellennetz könnte sicherstellen, dass die Fahne in ihrem ganzen Ausmaß erfasst wird. Da eine solche Erkundungsmaßnahme schnell an ihre finanziellen Grenzen stoßen kann und daher in der Regel keine ausreichende Erkundungssicherheit bieten kann, wurden räumlich integrierende Immissionspumpversuche (Teutsch et al. 2000, Ptak et al. 2000) entwickelt, die, angeordnet entlang einer oder mehrerer Kontrollebenen, im Abstrom des Schadensherdes durchgeführt werden. Hierbei handelt es sich um eine nicht notwendigerweise günstigere Erkundungsmaßnahme, die aber eine höhere Aussagesicherheit bietet, da sich durch das große Erfassungsvolumen an den einzelnen IPV-Brunnen die aus der räumlichen Konzentrationsvariabilität resultierende Erkundungsunsicherheit reduziert. Immissionspumpversuche basieren auf der Auswertung von Schadstoffkonzentrationsganglinien (C(t)), die während eines Pumpversuchs durch Beprobung des Grundwassers gewonnen werden können. Durch Anwendung eines Inversionsalgorithmus auf die gemessenen Schadstoffkonzentrationsganglinien erhält man dann eine räumliche Konzentrationsverteilung (C(x)) entlang einer Kontrollebene und daraus die gesamte Schadstofffracht und die mittlere Schadstoffkonzentration an der Kontrollebene.

Hierbei besteht die Schwierigkeit sicherzustellen, dass die gesamte Fahnenbreite erfasst wird. Falls nicht örtliche Gegebenheiten am Standort (z. B. die Position der seitlichen Aquiferbegrenzung, wie beim hier nachfolgend betrachteten Beispiel) oder IPV ohne messbare Schadstoffkonzentration diese Unsicherheit reduzieren, können dies Punktkonzentrationsmessungen bewirken. Die Inversion kann analytisch, unter Berücksichtigung der natürlichen Grundwasserströmung (Bayer-Raich et al. 2004) und numerisch, unter Einbindung eines Grundwasserströmungs- und Transportmodells (Bayer-Raich et al. 2003) erfolgen. Bei der analytischen Lösung wird von einem homogenen Grundwasserleiter mit stationärer Grundwasserströmung ausgegangen, wohingegen die numerische Lösung in Verbindung mit einem Strömungs- und Transportmodell heterogene geologische Verhältnisse sowie instationäre Grundwasserströmung berücksichtigt. Bayer-Raich et al. (2007) konnten zeigen, dass Konzentrationsgradienten, so weit sie parallel zur Grundströmung linear verlaufen, innerhalb des Entnahmebereichs des IPV keinen signifikanten Einfluss auf die Auswertung haben, sodass bei beiden Lösungen ein Transport ohne Abbau angenommen werden kann. Beispiele für solche Auswertungen findet man unter anderem bei Bockelmann et al. (2001, 2003), Bauer et al. (2004) und Rügner et al. (2004), wobei Ptak et al. (2004) eine höhere räumliche Auflösung durch vertikale Differenzierung der IPV-Konzentrationsganglinien erreicht haben. In der vorliegenden Studie werden beide Erkundungsansätze zur Quantifizierung von Schadstofffrachten an einem ehemaligen Gaswerksstandort (Testfeld Süd, Herfort et al. 1998) erstmals unter Feldbedingungen quantitativ miteinander verglichen, um ihre Eignung zur Erkundung heterogener Aquifere beurteilen zu können.

3.2 Standortbeschreibung

Das Testfeld Süd befindet sich auf dem Gelände eines ehemaligen Gaswerksstandortes im Neckartal in Süddeutschland und hat eine Nord-Süd-Ausdehnung von ungefähr 1.000 m und eine Breite zwischen 160 und 400 m. Es wird im Osten durch den Neckar und im Westen durch einen hydraulisch verhältnismäßig undurchlässigen Talrand begrenzt, der aus mesozoischen Mergeln und intermediären Hanglehmschichten besteht. Der hier untersuchte quartäre Grundwasserleiter mit einer Mächtigkeit von durchschnittlich 3,3 m besteht aus Mittelkies mit örtlich begrenzten feinkörnigen Lagen und wird entweder von Auesedimenten oder anthropogenen Auffüllungen überdeckt. Im Liegenden folgt eine 30 m mächtige Gipskeuperschicht und daraufhin der Obere Muschelkalk. Erstere stellen die Quelle von sulfatreichem Wasser dar, welches im untersuchten Grundwasserleiter nachgewiesen wurde. Die ausgeprägte Heterogenität des Grundwasserleiters ist durch die Sedimentationsbedingungen vor Ort, die Lage am Talrand (Ausstreichen und Auskeilen der Schichten), lokale Einsenkungen im Festgesteinsuntergrund (Störungen und Auslaugung) sowie anthropogene Einflüsse wie Baumaßnahmen (Aushub, Fundamente) bedingt. Der Grundwasserflurabstand beträgt im Mittel 4,1 m, wobei der Grundwasserleiter, abhängig von der Art der Überdeckung (Auesediment oder anthropogene Auffüllung), gespannt bzw. ungespannt ist. Die gemessenen Grundwasserpotenziale der letzten 10 Jahre schwanken nur geringfügig, und ein saisonaler Trend ist nicht erkennbar. Beides ist auf die regulierende Funktion des künstlich aufgestauten Vorfluters zurückzuführen. Erkundungsmaßnahmen ergaben einen Gradienten von 0,002 bei einer nach N-NW ausgerichteten Hauptströmungsrichtung (Herfort 2000) sowie eine mittlere Abstandsgeschwindigkeit von 2 md–1 (Bösel et al. 2000). Mit Tracerversuchen im Jahr 2007 wurde eine speichernutzbare Porosität von 16 % bestimmt (Trötschler et al. 2007). Eine große Anzahl von Pumpversuchen im zentralen und südlichen Teil des Geländes ergab einen mittleren Kf –Wert von 3,3 · 10 –3 ms–1 (Herfort 2000), und aus der hydraulischen Auswertung der Immissionspumpversuche in den Jahren 2004 und 2006 resultierte ein mittlerer Kf -Wert von 3,7 · 10 –3 ms–1 für den nördlichen Teil. Das Gaswerk war zwischen 1875 und 1970 in Betrieb, und Leckagen in Bereichen der Kohleverarbeitung, insbesondere aber die Zerstörungen im 2. Weltkrieg, haben zu einer großen Anzahl von Schadensherden geführt (Zamfirescu & Grathwohl 2001). Aus diesem Grund wird das Alter des Hauptschadensherdes auf ungefähr 60 Jahre geschätzt. Das Schadstoffspektrum umfasst gaswerkstypische Substanzen wie monoaromatische Kohlenwasserstoffe, polyzyklische aromatische Kohlenwasserstoffe (PAK), aliphatische Kohlenwasserstoffe, Phenole und heterozyklische aromatische Kohlenwasserstoffe (HET) (Zamfirescu 2000). In zahlreichen Bohrungen im südlichen Teil des Testfeldes wurde im Kapillarsaumbereich und an der Basis des Grundwasserleiters Öl in Phase gefunden. Weitere Bohrungen im zentralen und nördlichen Teil weisen auf die Ausbildung einer komplexen Schadstofffahne hin. Die vorherrschenden Bedingungen im Grundwasser sind sulfatreduzierend.

3.3 Methodik

3.3.1 Grundlagen zu Immissionspumpversuchen

Räumlich integrierende Immissionspumpversuche (IPV, Teutsch et al. 2000, Ptak et al. 2000) werden seit einigen Jahren eingesetzt, um Schadstofffrachten unterstromig von Schadstoffquellen zu bestimmen. Hierzu werden Pumpbrunnen entlang einer Kontrollebene angeordnet und entweder gleichzeitig oder sequenziell bepumpt. Die Positionierung der Brunnen sowie deren Pumpraten und Pumpdauer müssen so gewählt werden, dass optimalerweise der gesamte Abstrombereich der Verdachtsfläche erfasst wird. Hierfür sind a priori Kenntnisse über die Aquifergeometrie, Kf -Werte, Porositäten und Gradienten, bzw. ein Strömungs- und advektives Transportmodell notwendig. Während der Pumpmaßnahmen werden Konzentrationsganglinien der Schadstoffe und anderer relevanter Grundwasserqualitätsparameter gemessen, die Information über die Position und die Ausmaße der Fahne sowie über die Konzentrationen der Schadstoffe und die Verteilung der Grundwasserparameter geben. Die Konzentrationsganglinien werden dann unter Verwendung eines instationären Inversionsalgorithmus analytisch oder numerisch mithilfe eines Strömungs- und Transportmodells ausgewertet, um Konzentrationsverteilungen entlang der Kontrollebene und daraus Schadstofffrachten zu erhalten. Dieses Prinzip wird in Abbildung 1 (Figure 3.1) verdeutlicht.

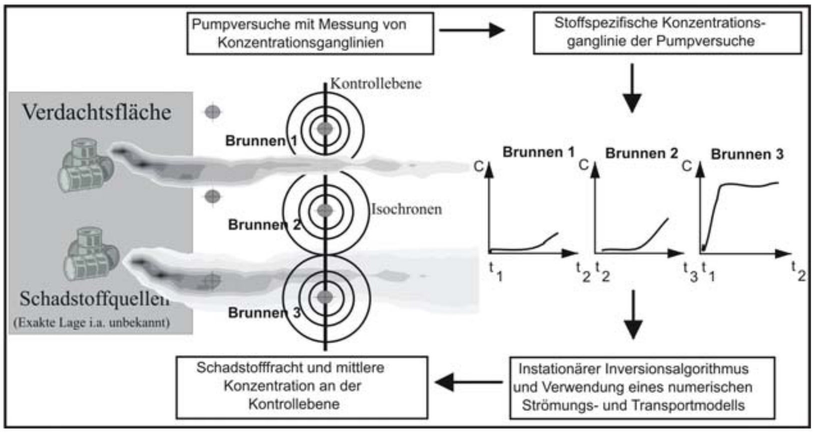

Figure 3.1: Prinzip der Immissionspumpversuche (IPV) (Ptak et al. 2004)

3.3.2 Numerische Auswertung

Der Inversionsalgorithmus, der zur numerischen Inversion der Konzentrationsganglinien verwendet wird, ist in dem Programm CSTREAM (Bayer-Raich et al. 2003, Bayer-Raich 2004) implementiert, welches eine Erweiterung der Inversionslösung von Schwarz (2002) darstellt. CSTREAM benötigt mindestens ein instationäres Strömungs- und advektives, nicht-reaktives Transportmodell des Untersuchungsgebietes, welches dazu dient, die Stromlinien und Isochronen zu bestimmen. Dieses Modell simuliert alle IPV unter Berücksichtigung der räumlichen Variabilität der hydraulischen Leitfähigkeit, der Porosität und der Mächtigkeit des Grundwasserleiters, wobei diese Parameter durch mehrere Pumpversuche, Markierungsversuche bzw. Bohrungen bestimmt wurden. Dadurch ermöglicht es die numerische Inversionslösung, im Gegensatz zur analytischen Lösung, die Einzugsbereiche der IPV unter Berücksichtigung der Heterogenität des Untergrunds und der Einflüsse des hydraulischen Gradienten abzubilden. Die Schadstofffracht über die Kontrollebene, M_{CP} [M T^{-1}], wird wie folgt berechnet:

$$M_{CP}(t) = \int_{\ell_{CP}(t)} C_0(x,0) q_{0y}(x,0) b(x,0) dx \qquad [1]$$

wobei $C_0(x,0)$ [M L^{-3}] die tiefengemittelte Konzentrationsverteilung vor der Pumpmaßnahme entlang der Kontrollebene in x-Richtung, $q_{0y}(x,0)$ [L T^{-1}] die Darcy-Geschwindigkeit vor der Pumpmaßnahme in y-Richtung senkrecht zur Kontrollebene, positioniert bei $y = 0$, $\ell_{CP}(t)$ die Länge der durch die Isochronen der IPV erfassten Kontrollebene zum Zeitpunkt t und $b(x,0)$ [L] die wassererfüllte Mächtigkeit des Grundwasserleiters darstellen. Zur Bestimmung der Konzentrationsverteilung $C_0(x,0)$ [M L^{-3}] werden Isochronen zu Zeitpunkten t der Probennahme in den Konzentrationsganglinien unter Berücksichtigung der natürlichen Grundwasserströmung im Modell berechnet. Die Abhängigkeit der Konzentrationsganglinien $C_w(t)$ [M L^{-3}] von der Konzentrationsverteilung vor Beginn der Pumpmaßnahme $C_0(x,y)$ [M L^{-3}] kann durch die folgende Massenbilanz (Bayer-Raich et al. 2004) dargestellt werden:

$$Q_w C_w(t) = -\oint_{\ell_I(t)} C_0(x,y) \vec{q}_w(x,y) \vec{n} b(x,y) d\ell \qquad [2]$$

wobei $\vec{q}_w(x,y)$ [L T^{-1}] als Darcy-Geschwindigkeit während des Pumpversuchs, $\vec{n}$ als nach außen zeigender Einheitsvektor rechtwinklig zur Isochrone, $b(x,y)$ [L] als wassergefüllte Aquifermächtigkeit, $Q_w = -\int_{\ell_I(t)} \vec{q}_w(x,y) \vec{n} b(x,y) d\ell$ [L^3 T^{-1}] als Pumprate am Brunnen und $\ell_I(t)$ als

Isochrone zum Probennahmezeitpunkt t definiert ist. Gleichung 2 wird für jeden Wert der Konzentrationsganglinie gelöst, wobei die Konzentrationsverteilung der vorausgegangenen Isochronen mit einbezogen wird. Details sind z. B. in Ptak et al. (2000), Bayer-Raich et al. (2003), Bayer-Raich (2004) und Herold et al. (2008) enthalten.

3.3.3 Frachtbestimmung mittels Punktkonzentrationsmessungen

Der für diese Studie verwendete Ansatz wurde von Bockelmann et al. (2003) übernommen:

$$M_{CP} = \sum_{n=1}^{n_{Brunnen}} \left(i_n \cdot C_n \cdot K_n \cdot A_n \right) \qquad [3]$$

wobei M_{CP} die Schadstofffracht an der Kontrollebene, i_n den Gradienten an der Messstelle n, C_n die Konzentration an der Messstelle, K_n den hydraulischen Durchlässigkeitsbeiwert an der Messstelle und A_n die Fläche, die durch die Probe bzw. Messstelle n repräsentiert wird, beschreiben. Bockelmann et al. (2003) wählten diesen Ansatz, da alle Messstellen voll verfiltert waren und keine Multi-Level-Daten zur Verfügung standen. In dieser Studie handelt es sich um dasselbe Testgelände, und wiederum standen nur tiefenintegrierende Proben zur Verfügung. Bei der Auswertung wurde Wert darauf gelegt, dass die Gesamtsumme ($\sum_{n=1}^{n_{Brunnen}} A_n$) der IPV- Kontrollebenenflächenanteile sowie die Summe der für die Punktkonzentrationsmessungen repräsentativen Teilflächen identisch sind. Die Konzentrationsganglinien wurden daher so gekürzt, dass es zu keiner Überlappung der Einzugsbereiche von nacheinander durchgeführten IPV kam.

3.4 Durchführung

Im Jahr 2006 wurden sechs IPV an den Brunnen der Kontrollebene CP2-3 (B97–B102, s. Abb. 2, Figure 3.2) innerhalb eines Zeitraums von 42 Tagen durchgeführt. Um gegenseitige Beeinflussung zu vermeiden, wurden nur maximal 2 Brunnen gleichzeitig bepumpt. Ebenso wurde eine möglichst lange Wiederanstiegsphase zwischen den Pumpkampagnen gewählt (3 Tage), um eine Wiederherstellung des natürlichen Strömungsfeldes zu ermöglichen, was durch fortlaufende Wasserstandsmessungen kontrolliert wurde. Für die Punktkonzentrationsmessungen wurden 13 Direct-Push-Messstellen im Abstand von 3 bis 11 Meter zwischen den Brunnen B97 und B100 errichtet (Abb. 2, Figure 3.2). Der Vergleich der Schadstoffmassenfrachten aus den IPV und der Interpolation von Punktkonzentrationswerten erfolgt somit an einem Teilstück der Kontrollebene CP2-3. Die Probennahmezeitpunkte während der Pumpdauer an den IPV-Brunnen von jeweils rund 100 Stunden ergaben einen Abstand zwischen den Isochronen von 2 m, was eine höhere räumliche Auflösung darstellt als bei den Direct-Push-Messstellen. Die Beprobung der Direct-Push-Messstellen erfolgte über Membranpumpen, wobei der Temperaturverlauf, die elektrische Leitfähigkeit, der pH-Wert, das Redoxpotenzial und die Konzentration an gelöstem Sauerstoff mithilfe einer Durchflusszelle im Förderstrom bestimmt wurden. Die Probennahme von zwei Litern Grundwasser erfolgte, nachdem das zweifache Brunnenvolumen abgepumpt worden war. Die Analyse der Grundwasserproben aus den IPV und aus den Direct-Push-Messstellen wird bei Herold et al. (2008) beschrieben.

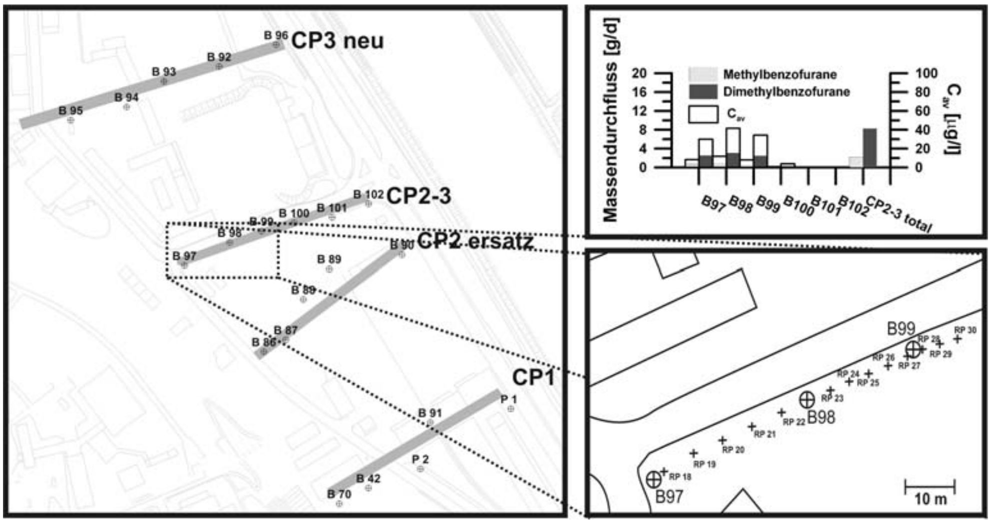

Figure 3.2: Position der Kontrollebenen und Brunnen im Testfeld Süd (links), Position der Direct-Push-Messstellen zur Bestimmung von Punktkonzentrationswerten (rechts unten), Schadstoffmassenfrachten und mittlere Konzentration (Cav) an Kontrollebene CP2-3 (IPV-spezifische Auftragung der Frachten) (rechts oben).

3.4.1 Modellierung von Strömung und Transport

Das in dieser Studie zur Inversion der IPV-Konzentrationsganglinien mittels CSTREAM (Bayer-Raich et al. 2003, Bayer-Raich 2004) verwendete numerische Strömungs- und Transportmodell basiert auf den Modellen von Bösel et al. (2000), Jarsjö et al. (2005) und Mak et al. (2006) und wurde in Richtung Norden erweitert, um die Schadstofffahne und alle Kontrollebenen abzudecken. Es handelt sich um ein mit MODFLOW (Harbaugh & McDonald 1996) und MODPATH (Pollock 1994) erstelltes zweidimensionales Modell. Ein 2D-Ansatz wurde gewählt, da der Grundwasserleiter geringmächtig und die Brunnen voll verfiltert sind. Die verwendeten Randbedingungen sind in Herold et al. (2008) dargestellt. Potenzialmessungen im Feld (im Rahmen von Stichtagsmessungen) ergaben nur geringe Grundwasserstands- und Fließrichtungsänderungen, was sich auf die versiegelte Oberfläche im Untersuchungsgebiet und den regulierenden Einfluss des gestauten Vorfluters zurückführen lässt. Dies führt zu der Annahme, dass es sich um ein stationäres System handelt. Weitere Details zum Modell und zur Auswertung mit CSTREAM sind in Herold et al. (2008) enthalten.

3.5 Ergebnisse

Tabelle 1 (Table 3.1) stellt die ermittelten Schadstofffrachten an dem untersuchten Teilstück der Kontrollebene (CP2-3) für die im Testfeld Süd dominierenden Schadstoffkomponenten dar, die (i) mittels Interpolation von Punktkonzentrationsmessungen entsprechend Gleichung 3 und (ii) mithilfe des Programms CSTREAM und des numerischen Standortmodells für das Gelände berechnet wurden. Die für die Interpolation von Punktkonzentrationsmessungen verwendeten Daten sind in Tabelle 2 (Table 3.2) dargestellt, wobei die hydraulischen Durchlässigkeitsbeiwerte an den Rammpegeln durch Interpolation der pumpversuchsbasierten Werte an den IPVBrunnen bestimmt wurden. Es ist deutlich zu erkennen, dass die Gesamtschadstofffrachten der zwei HET (Methylbenzofurane und Dimethylbenzofurane), unabhängig von der Methode, jeweils ähnliche Ergebnisse aufweisen. Die Gesamtschadstofffracht der Methylbenzofurane beträgt 1,36 bzw. 1,38 g/d und die der Dimethylbenzofurane 5,22 und 5,34 g/d, wobei die absoluten Unterschiede (0,02 und 0,12 g/d) und auch die relativen Abweichungen (–1,45 % und –2,25 %) minimal ausfallen. Ganz anders stellt sich das Bild bei Acenaphthen dar. Hier beträgt der quantitative Unterschied der durch die zwei unterschiedlichen Methoden bestimmten Gesamtschadstofffrachten 1,68 g/d und auch die relative Abweichung (–25,23 %) ist erheblich größer.

Table 3.1: Vergleich der Schadstoffmassenflüsse entlang Kontrollebene CP2-3

	Methylbenzofurane		**Dimethylbenzofurane**		**Acenaphthen**	
	MF [g/d]	**MF [g/d]**	**MF [g/d]**	**MF [g/d]**	**MF [g/d]**	**MF [g/d]**
	Punkt	IPV	Punkt	IPV	Punkt	IPV
B97	0,34	0,42	1,28	1,54	0,35	1,38
RP18	0,09		0,33		0,17	
RP19	0,06		0,24		0,05	
RP20	0,11		0,46		0,70	
RP21	0,14	0,67	0,51	2,43	0,88	4,34
RP22	0,14		0,46		0,38	
B98	0,08		0,31		0,91	
RP23	0,06		0,20		0,35	
RP24	0,07		0,30		0,43	
RP25	0,08		0,32		0,41	
RP26	0,07	0,28	0,28	1,44	0,12	0,94
RP27	0,06		0,21		0,16	
B99	0,03		0,11		0,08	
RP28	0,02		0,09		0,00	
RP29	0,01		0,07		0,00	
RP30	0,00		0,01		0,00	
B100	0,01	0,00	0,05	0,02	0,00	0,00
Summe	**1,36**	**1,38**	**5,22**	**5,34**	**4,98**	**6,66**

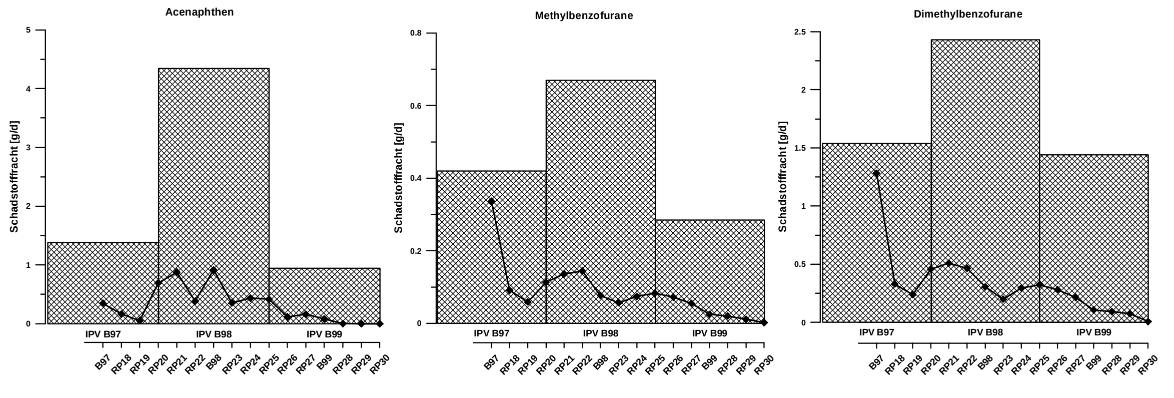

Figure 3.3: Schadstoffmassenfrachten für Methylbenzofurane, Dimethylbenzofurane und Acenaphthen: Bestimmung mit IPV (graue Balken, Breite entspricht Einzugsbereich) und über Punktkonzentrationsmessungen (schwarze Linie)

Abbildung 3 (Figure 3.3) stellt die Daten aus Tabelle 2 (Table 3.2) dar, wobei deutlich wird, dass beide Methoden das Fahnenzentrum hervorheben und einen erneuten Anstieg der Schadstofffrachten am westlichen Rand verzeichnen (vgl. Herold et al. 2008). Aus den Daten geht hervor, dass die Summe der aus Punktkonzentrationsmessungen berechneten Schadstofffrachten der zwei HET (Methylbenzofurane und Dimethylbenzofurane) im Erfassungsbereich des IPV am Brunnen B97 einen relativen Anstieg von 43 % bzw. 50 % gegenüber dem entsprechenden IPV-Ergebnis aufweisen, wohingegen die Summe der Punktkonzentrationsmessungen im Erfassungsbereich der anderen zwei IPV (B98 und B99) eine relative Abnahme verzeichnen. Das legt die Vermutung nahe, dass die für Brunnen B97 aus der Interpolation berechnete außergewöhnlich hohe Schadstofffracht ein von einer einzelnen Schadstoffkonzentration überprägtes Bild darstellt. Die Variabilität der Schadstoffmassenfrachten an den Punktmessstellen nimmt in Richtung Osten ab, wobei die im Einzugsbereich des IPV an Brunnen B97 summierten ungewöhnlich hohen Schadstofffrachten durch eine relative Abnahme im Einzugsbereich der anderen beiden IPV, über die Kontrollebene betrachtet, ausgeglichen werden.

Table 3.2: Daten für die Interpolation der Punktkonzentrationsmessungen (C_{ACE} = Konzentration Acenaphthen, C_{MBF} = Konzentration Methylbenzofurane, C_{DMBF} = Konzentration Dimethylbenzofurane, K_f = hydraulischer Durchlässigkeitsbeiwert, A = Fläche und i = Gradient).

	C_{ACE} [µg/L]	C_{MBF} [µg/L]	C_{DMBF} [µg/L]	K_f [m/s]	A [m^2]	i[-]
B97	12	11,7	44,5	2,84E-03	48,96	0,0024
RP18	23	12,6	45,9	3,01E-03	11,53	0,0024
RP19	4,9	5,7	22,7	3,18E-03	15,87	0,0024
RP20	65	10,5	42,6	3,34E-03	15,44	0,0024
RP21	80	12,4	46,4	3,51E-03	15,04	0,0024
RP22	35	13,1	42,4	3,68E-03	14,36	0,0024
B98	98,1	8,3	32,8	3,85E-03	11,65	0,0024
RP23	45	7,3	25,5	3,60E-03	10,43	0,0024
RP24	55	9,4	37,6	3,35E-03	11,32	0,0024
RP25	52	10,4	40,7	3,11E-03	12,32	0,0024
RP26	14	9,0	35,3	2,86E-03	13,46	0,0024
RP27	30	10,4	40,5	2,61E-03	9,77	0,0024
B99	26,7	8,5	35,8	2,36E-03	6,08	0,0024
RP28	0,19	4,2	19,3	2,40E-03	9,59	0,0024
RP29	0,01	1,9	12,2	2,43E-03	11,91	0,0024
RP30	0,01	0,1	0,5	2,47E-03	26,12	0,0024
B100	0,03	0,4	3,1	2,50E-03	28,21	0,0024

Die Ursache für die Unterschiede der Gesamtschadstofffracht bei Acenaphthen wird deutlich, wenn die während der IPV gemessenen Konzentrationsganglinien betrachtet werden (Abb. 4, Figure 3.4). Am Beispiel der Abbildung 4 (Figure 3.4) ist zu erkennen, dass die HET-Konzentrationsganglinien einen nahezu konstanten Verlauf aufweisen, wobei Methylbenzofuran im Vergleich zu Dimethylbenzofuran eine geringere Schwankungsbreite zeigt. Im Gegensatz dazu variiert die Konzentrationsganglinie von Acenaphthen über den betrachteten Zeitraum von

99 Stunden zwischen 110 und 70 µg/l, d. h. mit einer deutlich größeren Schwankungsbreite. Entsprechend den theoretischen Überlegungen zur Auswertung von Konzentrationsganglinien aus Immissionspumpversuchen (z. B. Ptak et al. 2000, Bockelmann et al. 2001, Bayer-Raich et al. 2004) indiziert eine relativ große Schwankungsbreite in der Konzentrationsganglinie eine relativ heterogene Verteilung der Schadstoffmasse innerhalb der Schadstofffahne. In diesem Fall werden für eine zuverlässige Quantifizierung der Schadstofffracht, im Vergleich zu einer Konzentrationsganglinie mit konstantem Konzentrationsverlauf, relativ mehr Punktkonzentrationsmessungen benötigt.

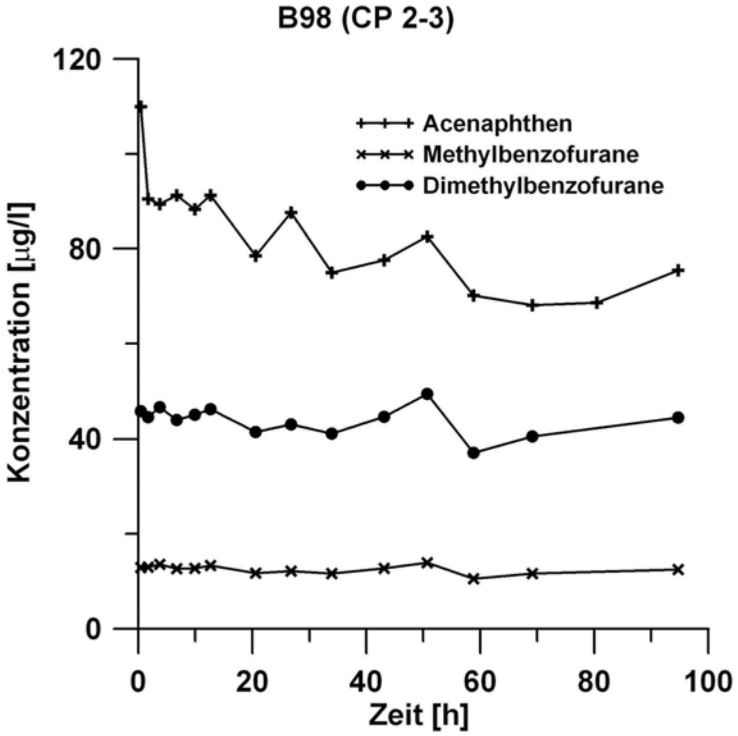

Figure 3.4: Konzentrationsganglinien von Methylbenzofuranen, Dimethylbenzofuranen und Acenaphthen am Beispiel des IPV-Brunnens B98

Die relative Größe der Unterschiede der Schadstofffrachten aus der Interpolation von Punktkonzentrationsmessungen und aus den Immissionspumpversuchen bestätigt dieses Postulat. Für Methylbenzofuran beträgt der Unterschied der Frachten nur 0,02 g/d, hier ist die Konzentrationsganglinie nahezu konstant (s. Abb. 4, Figure 3.4). Für Dimethylbenzofuran ist im Vergleich zu Methylbenzofuran der Unterschied mit 0,12 g/d etwas größer, ebenso wie die Schwankungsbreite der Dimethylbenzofuran-Konzentrationsganglinie. Dagegen führt die große Schwankungsbreite der Acenaphthen-Konzentrationsganglinie und entsprechend die große räumliche Variabilität der Acenaphthen-Masse innerhalb der Schadstofffahne dazu, dass mit der Interpolation von Punktkonzentrationsmessungen die Gesamtfracht im vorliegenden Fall deutlich unterschätzt wird (4,98 g/d für die Frachtbestimmung mittels Punktkonzentrationsmessungen im Gegensatz zu 6,66 g/d für die IPV). Die Ergebnisse des Vergleichs legen nahe, dass das Direct-Push-Messstellennetz trotz des relativ geringen Messstellenabstandes von bis zu 3 m noch nicht dicht genug war, um die Verteilung der Acenaphthen-Masse im Aquifer mittels Interpolation von Punktkonzentrationswerten hinreichend genau quantifizieren zu können. Offensichtlich konnten mit den Punktkonzentrationsmessungen einzelne Bereiche relativ hoher Konzentrationen nicht erfasst werden. Die Bestimmung der Anzahl der erforderlichen Punktkonzentrationsmesswerte als Funktion einer zulässigen Abweichung der Ergebnisse aus den beiden Frachtbestimmungsmethoden war nicht Inhalt der durchgeführten Untersuchungen. Sie ließe sich z. B. über eine Szenariomodellierung zur Verdichtung des Messstellennetzes unter Verwendung der aus den IPVs ermittelten räumlichen Konzentrationsverteilung ableiten, oder aber durch eine systematische Verdichtung des Messstellennetzes im Testfeld bestimmen. Es sei hier angemerkt, dass bereits die im Testfeld jetzt implementierte Messstellendichte unter Praxisbedingungen in der Regel wohl nicht realisierbar wäre. Eine Multilevelbeprobung in den Messstellen zur Gewinnung von tiefenorientierten Punktkonzentrationsmesswerten und deren anschließenden Interpolation (3D-Ansatz) würde die Situation nicht zwingend verbessern, da auch in diesem Fall der Aquiferbereich zwischen den Messstellen, im Gegensatz zum IPV, nicht erfasst werden würde. Auch würde der 3D-Ansatz einen unter Praxisbedingungen in der Regel nicht vertretbaren Erkundungsaufwand (tiefenorientierte Bestimmung von Kf -Werten, hydraulischen Gradienten, Analytik etc.) erfordern. Aus den beiden Methoden ergeben sich Unsicherheiten, welche ebenfalls die Ergebnisse beeinflussen können. Die Ergebnisunsicherheit der IPV sowie der Frachtbestimmung über Punktkonzentrationsmessungen ergibt sich aus der Analytik und aus der Anwendung physikalischer Messverfahren. Für die Analytik von Acenaphthen, Methylbenzofuranen und Dimethylbenzofuranen ergibt sich jeweils eine Unsicherheit von 5 %. Die Unsicherheit aufgrund von physikalischen Messungen beträgt in beiden Fällen etwa 10 %. Die den Punktkonzentrationsmessungen inhärente Unsicherheit infolge der Interpolation wird bei der IPV-Methode durch die integrale Natur der Methode aufgehoben. Retardation kann bei den IPV berücksichtigt werden (Bayer-Raich et al. 2006, Herold et al. 2008). Es stellt sich auch die Frage inwieweit Konzentrationsgradienten, z. B. hervorgerufen durch NA, das Ergebnis der IPV beeinflussen können. Jarsjö & Bayer-Raich (2008) haben nachgewiesen, dass konstante Konzentrationsgradienten in Richtung der Grundwasserströmung keinen nennenswerten Effekt auf das Ergebnis haben. Somit kann gefolgert werden, dass die Unterschiede bei der Frachtbestimmung mittels der beiden Methoden nicht durch Messfehler bzw. Fehler aufgrund vereinfachender Annahmen bei der IPV-Auswertung dominiert werden.

3.6 Schlussfolgerungen

Der hier vorgestellte Vergleich von Schadstofffrachten aus Immissionspumpversuchen und aus der Interpolation von Punktkonzentrationsmessungen hat gezeigt, dass auch hochaufgelöste Punktkonzentrationsmessungen je nach Standortsituation und Heterogenität der Schadstoffverteilung im Untergrund zu Unsicherheiten bei der Frachtbestimmung führen können. Die Erkundungsunsicherheit nimmt dabei mit dem Grad der Heterogenität der Schadstoffverteilung zu, da die Wahrscheinlichkeit, Bereiche mit relativ hoher Schadstoffkonzentration zu verfehlen oder aber hohe Konzentrationswerte durch die Interpolation über in Wirklichkeit gar nicht oder nur wenig kontaminierte Bereiche zu verteilen, zunimmt. Ein dichteres Direct-Push-Messstellennetz, bei dem Schadstoffkonzentrationen und hydraulische Durchlässigkeitsbeiwerte ggf. auch vertikal aufgelöst gemessen werden, könnte die Verlässlichkeit der Frachtbestimmung basierend auf Punktkonzentrationsmessungen erhöhen, wobei allerdings die Limitierungen bei der Verfügbarkeit von Bohransatzpunkten und die zu erwartenden Installations- und Beprobungskosten berücksichtigt werden müssten. Hier können Immissionspumpversuche aufgrund des mit der Zeit zunehmenden Probennahmevolumens und ihrer integrierenden Wirkung einen wichtigen Beitrag zur sicheren Bestimmung von Schadstofffrachten und Konzentrationsverteilungen entlang von Kontrollebenen leisten, auch an Standorten mit eingeschränkter Zugänglichkeit, z. B. infolge von Bebauung und Nutzung. Dabei hilft die Anwendung eines numerischen Strömungs- und Transportmodells, durch das es möglich wird, auch hydraulisch und hydrogeochemisch heterogene Standortbedingungen und reaktiven Transport zu simulieren. Die Erhöhung der Erkundungsgenauigkeit ist insbesondere bei der Standortbeurteilung sowie bei der Planung und Durchführung von Sanierungsmaßnahmen von Bedeutung. Des Weiteren kann durch die gesamte Erfassung des mobilen Anteils an Schadstoffen im Einzugsgebiet eines IPV-Brunnens bestimmt werden, welche Schadstoffe aufgrund ihrer Mobilität priorisiert werden müssen. Letztendlich kann die erhöhte Erkundungssicherheit auch eine genauere Beurteilung der Effizienz von bereits implementierten Sanierungsmaßnahmen ermöglichen.

Danksagung

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Chapter 4

Integral quantification of contaminant mass flow rates in a contaminated aquifer: Conditioning of the numerical inversion of concentration-time series

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Abstract

A series of integral pumping tests (IPTs) has been conducted at a former gasworks site to quantify the contaminant mass flow rates and average concentration in groundwater along three control planes across the groundwater flow direction. The measured concentration-time series were analysed numerically with the help of the inversion code CSTREAM and a flow and transport model representing the highly heterogeneous aquifer. Since the control planes cover the entire downstream width of the potentially contaminated area, they allow conclusions to be drawn about the current location and spread of the contaminant plume. Previous evaluations of integral pumping tests could calculate three scenarios concerning the spread of the plume around the IPT well: (i) the plume is located to the right of the pumping well, (ii) to the left, or (iii) is distributed symmetrically around it. To create a more realistic picture of the plume position, a series of direct-push monitoring wells were installed along one control plane. The concentrations found in these wells were included in the numerical analysis to condition the numerical inversion results, and allowed the identification of a more pronounced plume centre and fringe, which supports the development of optimised remediation strategies.

4.1 Introduction

Mass flow-based assessments of contaminant plumes give rise to averaged or integrated values that meaningfully describe plume extent and behaviour. They can be utilized to design remediation measures, including Natural Attenuation (NA), as well as to bring forth a better understanding of the processes governing contaminant release and distribution in the subsurface. NA has received more and more attention in recent years when remediation of large-scale contamination sites was considered. The reason is that, compared to other remediation measures such as Pump-and-Treat, NA sets a financial cost limit, and in many cases can result in overall lower costs. NA requires (i) documentation of a decrease of the contaminant concentrations with distance at the investigated site, (ii) the characterization of trends of hydrogeochemically relevant parameters, such as the increase and decrease of degradation products and electron acceptors, respectively, and (iii) evidence of microbial activity on-site (Nyer and Duffin, 1997). Evidence of a decrease of contaminant mass flow rates, defined as the movement of mass per unit time [$M\ T^{-1}$], is in most cases very difficult to obtain, and mass flow rate investigations are not generally performed at remediation sites. The individual proof of NA is essential as NA is completely controlled by the conditions on-site. Composition and heterogeneity of the contaminant source as well as the heterogeneity of the affected aquifer are crucial to the release and distribution of the contaminants. Both factors influence the distribution and concentration of the contaminant within the aquifer significantly but are, however, still not easily quantified. This is due to the fact that most investigation techniques applied today, e.g. spatial and temporal monitoring of contaminant concentrations and electron acceptors (Chiang et al., 1989; Gieg et al., 1999; Davis et al., 1999), tracer tests with isotope-labelled contaminants (Therrin et al., 1995) or with conservative tracers (Wiedemeier et al., 1996), measurement of compound-specific stable isotope ratios (Hunkeler et al., 1999), or calculation of contaminant mass fluxes at control planes (King et al., 1999; Borden et al., 1997), are all based on point-scale measurements or the interpolation of point-scale concentration measurements. This can often give an incomplete view of the contaminant distribution in the subsurface. Subsurface heterogeneity leads to generally very irregularly shaped contaminant plumes, therefore making delineation highly dependent on the number and positioning of the monitoring wells and sampling points. In addition, heterogeneous distribution of contaminants within a source zone causes an accordingly irregular contaminant mass distribution within a plume downstream. Only a sufficiently dense monitoring network can ensure that a plume is appropriately defined. However, the costs for such an investigation become in many cases prohibitively high. A spatially integrating investigation technique has been developed — the Integral Pumping Test (IPT) Technique (Teutsch et al., 2000; Ptak et al., 2000). The pumping tests are conducted along one or more control planes, positioned downstream of a contaminant source. The integrating sampling volume at each of the IPT wells, which increases with pumping time, reduces investigation uncertainty caused by the spatial variability of plume concentrations. A control plane of pumping wells positioned and designed correctly can cover the entire plume. Applying an inversion algorithm to the concentration-time series measured during IPTs provides the total contaminant mass flow rate and the average contaminant concentration at the control plane. The inversion can be carried out analytically, taking natural groundwater flow into account (Bayer-Raich et al., 2004), or numerically by including a flow and transport model of the investigated site (Bayer-Raich et al., 2003). Examples of such evaluations can be found in Bockelmann et al. (2001, 2003), Bauer et al. (2004) and Rügner et al. (2004), whereas Ptak et al. (2004) achieved a higher spatial resolution through vertical differentiation of the IPT concentration-time series. Using two or more control planes positioned downstream of each other can aid in determining NA rates as demonstrated for benzene, toluene, ethylbenzene and xylene (BTEX) and polycyclic aromatic hydrocarbons (PAHs) by Bockelmann et al. (2001) and Bayer-Raich et al. (2006), respectively. Interpreting simple IPTs has had the disadvantage so far that the contaminant load (flow rate) could only be determined for three specific cases: either by assuming a symmetrical distribution around an IPT well, or by assuming the plume flows either to the left or to the right side of the well (e.g. Jarsjö et al., 2005), unless a complex investigation design with multiple IPTs and sequentially overlapping capture zones was employed (Ptak et al., 2000). This problem can be dealt with by conditioning the inversion solution with point-scale concentration measurements. In this approach, information gathered by e.g. a direct-push technique regarding contaminant concentration along the control plane close to the IPT well is incorporated into the evaluation. This enables a far more precise and accurate determination of the plume position and of the mass flow rates. In the current study, this new approach is tested for the first time to determine the exact position of a nitrogen, sulphur, oxygen-heterocycles (NSO-HET) contaminant plume at a former gasworks site (Herfort et al., 1998). At this site, IPTs without conditioning were already used to design an innovative remediation measure (H_2O_2 injection by means of a groundwater circulation well) by providing the contaminant mass flow rates as input parameters (Trötschler et al., 2008). Exact knowledge of the plume position and extent is a fundamental requirement for further studies concerned with locating the contaminant source and reactive transport modelling in connection with the H_2O_2 based remediation measure.

4.2 Site description

The site is situated on the premises of a former gasworks site in the Neckar valley in southern Germany. It has an extent of 1000 m from North to South and a width between 160 and 400 m. The western flanks are defined by the edge of the valley, and the river Neckar is confining it in the east. The Quaternary aquifer under investigation has a thickness of approximately 3.3 m and consists of medium gravel with locally confined fine-grained layers. It is overlain with either floodplain sediments or anthropogenic fillings, and is underlain by 30 m of Gipskeuper sediments which cover Muschelkalk carbonates. The pronounced heterogeneity of the aquifer at the site is determined by the sedimentation conditions on-site, the location close to the valley edge (outcrops of layers), lowering of bedrock (faults and lixiviation) as well as anthropogenic influences such as civil works (foundation excavation). The average groundwater level is 4.1mbelowground surface. The aquifer is locally either confined or unconfined, depending on the type of cover, floodplain sediments or anthropogenic filling, respectively. The measured groundwater heads in the aquifer were fluctuating only minimally over the last 10 years, and a seasonal trend is not observable. The steady water levels are attributable to the regulating function of an artificially retained receiving stream. Subsurface investigations yielded a hydraulic gradient of 0.002, the main flow direction was determined as N–NW (Herfort, 2000), and the transport velocity is 2 md^{-1} (Bösel et al., 2000). The effective porosity, determined using tracer tests, is 15%. A large number of pumping tests were conducted in the southern and central part of the site, yielding average hydraulic conductivities of $3.3 \cdot 10^{-3}$ ms^{-1} (Herfort, 2000), whereas the evaluation of the integral pumping tests performed 2004 and 2006 resulted in an average hydraulic conductivity of $3.7 \cdot 10^{-3}$ ms^{-1} for the northern part.

The gasworks were in operation between 1875 and 1970, and leakages in the area of coal processing and particularly the partial destruction during World War II lead to a large number of contaminant sources (Zamfirescu und Grathwohl, 2001). For this reason, the age of the main contamination is estimated to be close to 60 years. The contaminant spectrum comprises substances typical for gasworks, such as monoaromatic hydrocarbons, PAHs, aliphatic hydrocarbons, phenols and heterocyclic aromatic hydrocarbons (HETs) (Zamfirescu, 2000). In several borings in the southern part of the site non-aqueous phase liquids were found at the top and bottom of the aquifer. Further borings in the central and northern part of the site point towards the formation of a complex contaminant plume. The groundwater is dominated by sulphate-reducing conditions.

4.3 Methodology

4.3.1 Integral pumping tests

At the field site, IPTs (Teutsch et al., 2000; Ptak et al., 2000) have been implemented for a couple of years to determine contaminant mass flow rates downstream of contaminant sources. A number of pumping wells were located along a control plane and were either pumped sequentially or simultaneously. Positioning of the wells as well as their pumping rates and pumping times were selected in order to obtain capture zones ideally covering the whole area downstream of the potentially contaminated area. Concentration-time series of the target contaminants and other relevant groundwater parameters were recorded during pumping to provide information about the position and extent of the plume as well as about the spatial distribution of contaminant concentrations and other relevant groundwater parameters. The concentration-time series were analysed analytically or numerically with the help of a transient inversion algorithm and a flow and transport model of the investigated site, yielding contaminant concentration distributions along the control plane and the respective contaminant mass flow rates. This principle is shown in Figure 4.1.

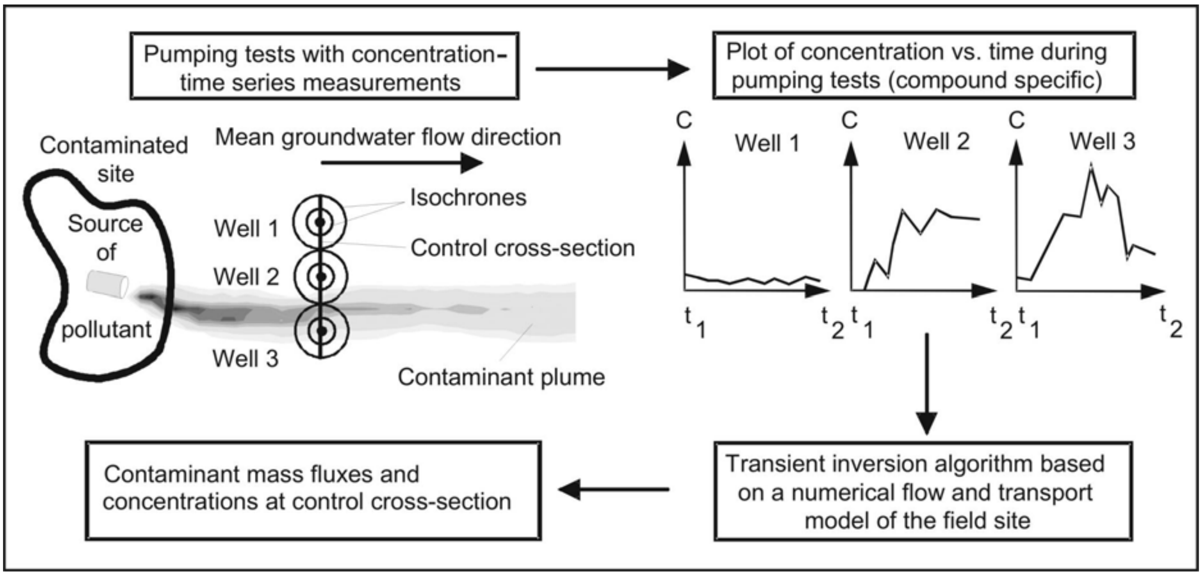

Figure 4.1: Principle of the integral pumping tests (Ptak and Teutsch, 2000)

4.3.2 Numerical evaluation

The inversion algorithm applied for the numerical inversion of the concentration-time series is implemented in the program CSTREAM (Bayer-Raich et al., 2003, Bayer-Raich, 2004), which

represents an extension to the inversion solution by Schwarz (2002). CSTREAM requires a transient and advective flow and transport model of the site. This model simulates all IPTs while taking the spatial variability of hydraulic conductivity, porosity and thickness of the aquifer into account. It thereby enables the numerical inversion solution, in contrast to the analytical solution, to reproduce the capture zone of an IPT by taking the heterogeneity of the subsurface and the influence of the hydraulic gradient into account.
The contaminant mass flow rate at the control plane, M_{CP} [M T^{-1}], is calculated as follows:

$$M_{CP} = \int_{\ell_{CP}} C_0(x,y) q_{0y}(x,y) b(x,y) dx \tag{1}$$

where ℓ_{CP} [L] is the control plane extent at pumping time t, $C_0(x,y)$ [M L^{-3}] the concentration distribution, $q_{0y}(x,y)$ [L T^{-1}] the Darcy velocity in the y-direction and $b(x,y)$ [L] the water-saturated thickness of the aquifer. Isochrones are being defined according to the sampling process and the natural course of the streamlines in the model to determine the concentration distribution (Fig. 4.2). The dependency of the concentration-time series $C_w(t)$ on the concentration distribution prior to pumping $C_0(x,y)$ can be represented by the following mass balance (Bayer-Raich et al., 2004):

$$Q_w C_w(t) = -\oint_{\ell_I(t)} C_0(x,y) \vec{q}_w(x,y) \vec{n} b(x,y) d\ell \tag{2}$$

where $\vec{q}_w(x,y)$ [L T^{-1}] is the Darcy velocity during pumping, $\vec{n}$ a unit vector pointing outward perpendicular to the isochrone, $Q_w = -\int_{\ell_I(t)} \vec{q}_w(x,y)\vec{n} b(x,y) d\ell$ [L^3 T^{-1}] the pumping rate at the well and $\ell_I(t)$ the isochrone at time t.
For obtaining the concentration distribution $C_0(x,y)$ on the basis of $C_w(t)$, the aquifer is discretised into $2n-1$ streamtubes, with n being the total number of samples taken, as indicated in Figure 4.2. Then $C_0(x,y)$ can be expressed as

$$C_0(x,y) = C_0(x_j)\xi_j(x,y) \tag{3}$$

where $\xi_j(x,y)$ is an indicator function defined as

$$\xi_j(x,y) = \begin{cases} 1 & \text{if } (x,y) \text{ belongs to streamtube } j \\ 0 & \text{otherwise} \end{cases} \tag{4}$$

Using (3) it is assumed that initial concentrations are constant and equal to $C_0(x_j)$ within each streamtube j.

Inserting (3) into (2) we obtain n equations, one for each sampling time, as

$$C_w(t_i) = \sum_{j=n-i+1}^{n+i-1} C_0(x_i) g_{ij} \tag{5}$$

where the matrix g_{ij} is defined as

$$g_{ij} = \frac{-1}{Q_w} \oint_{\ell_I(t_i)} C_0(x,y)\xi_j(x,y)\vec{q}_w(x,y)\vec{n}b(x,y)d\ell\,. \tag{6}$$

This matrix can be physically interpreted as the water volume of sample i, initially located within streamtube j, divided by the total water volume of sample i. Written in matrix notation, equation (5) can be expressed for 4 samples, i. e. with $n = 4$, and hence 2n-1 = 7 streamtubes, as (e. g. Bayer-Raich, 2004; Jarsjö et al., 2005)

$$\begin{bmatrix} 0 & 0 & 0 & g_{14} & 0 & 0 & 0 \\ 0 & 0 & g_{23} & g_{24} & g_{25} & 0 & 0 \\ 0 & g_{32} & g_{33} & g_{34} & g_{35} & g_{36} & 0 \\ g_{41} & g_{42} & g_{43} & g_{44} & g_{45} & g_{46} & g_{47} \end{bmatrix} \begin{bmatrix} C_0(x_1) \\ C_0(x_2) \\ C_0(x_3) \\ C_0(x_4) \\ C_0(x_5) \\ C_0(x_6) \\ C_0(x_7) \end{bmatrix} = \begin{bmatrix} C_w(t_1) \\ C_w(t_2) \\ C_w(t_3) \\ C_w(t_4) \end{bmatrix} \tag{7}$$

where (in the matrix g_{ij}) the number of rows is the number of samples taken, and the number of columns is the number of streamtubes.

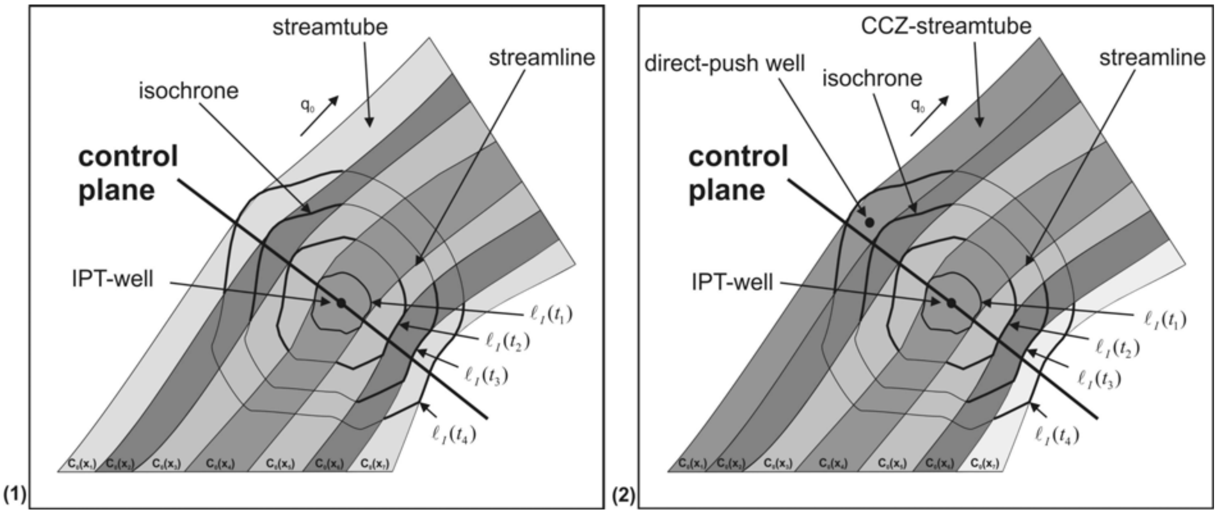

Figure 4.2: Definition of isochrones, streamlines and streamtubes in CSTREAM; case (1) describes symmetrical evaluation, case (2) describes conditioned evaluation

4.3.3 Conditioning

Since in equation (7) there are $2n-1$ unknowns and only n equations, the solution of the system is non-unique. In previous work, e. g. Bauer et al. (2004); Jarsjö et al. (2005), the non-uniqueness of equation (7) is dealt with by computing total mass flow rates for 3 different extreme situations: (a) all contaminant mass is located to the left-hand side of the well (in the flow direction); (b) contaminant concentration is symmetrical with respect to the streamtube containing the first isochrone and (c) all contaminant mass is located to the right-hand side of the well.

This non-uniqueness gives rise to the question about the true plume position. Conditioning of the CSTREAM inversion solution using point-scale concentration measurements could aid in narrowing the non-uniqueness down. CSTREAM offers, after some modification, the possibility to define so-called Constant Concentration Zones (CCZ) incorporating point measurements, obtained e.g. via direct-push-methods or other point-scale concentration measuring approaches. A visual comparison helps in matching georeferenced streamtubes to georeferenced point-scale concentration measurement locations in order to condition values of concentration for some of the streamtubes. Implementing conditioning, equation (7) can be generalized as

$$\begin{bmatrix} 0 & 0 & 0 & g_{14} & 0 & 0 & 0 \\ 0 & 0 & g_{23} & g_{24} & g_{25} & 0 & 0 \\ 0 & g_{32} & g_{33} & g_{34} & g_{35} & g_{36} & 0 \\ g_{41} & g_{42} & g_{43} & g_{44} & g_{45} & g_{46} & g_{47} \\ 0 & 0 & \alpha_3 & 0 & \alpha_5 & 0 & 0 \\ 0 & \alpha_2 & 0 & 0 & 0 & \alpha_6 & 0 \\ \alpha_1 & 0 & 0 & 0 & 0 & 0 & \alpha_7 \end{bmatrix} \begin{bmatrix} C_0(x_1) \\ C_0(x_2) \\ C_0(x_3) \\ C_0(x_4) \\ C_0(x_5) \\ C_0(x_6) \\ C_0(x_7) \end{bmatrix} = \begin{bmatrix} C_w(t_1) \\ C_w(t_2) \\ C_w(t_3) \\ C_w(t_4) \\ \beta_3 \\ \beta_2 \\ \beta_1 \end{bmatrix} \qquad (8)$$

where $2n-2$ indexes α_j with $j =$ 1, 2, $.....,n-1,n+1,n+2,....,2n-1$ and $n-1$ indexes β_i with $i = 1, 2, ...,n-1$ are defined as

$$\alpha_k = \begin{cases} -1 & \text{for } k > n \text{, if both streamtubes } k \text{ and } 2n-k \text{ are not CCZ} \\ 0 & \text{if streamtube } 2n-k \text{ is CCZ} \\ 1 & \text{otherwise} \end{cases}$$

$$\beta_k = \begin{cases} C_{DP} & \text{if measurement } C_{DP} \text{ corresponds to streamtube } k \text{ or } 2n-k \\ 0 & \text{otherwise} \end{cases} \tag{9}$$

For instance, for the case $n = 4$ depicted in Figure 4.2, if streamtube 1 is fixed to a value C_{DP1} and streamtube 5 to C_{DP2} we will have: $\alpha_1 = 1$, $\alpha_7 = 0$, $\beta_1 = C_{DP1}$ to condition streamtube 1, i.e. $C_0(x_1) = C_{DP1}$; $\alpha_2 = 1$, $\alpha_6 = -1$, $\beta_2 = 0$ to apply the symmetrical solution to streamtubes 2 and 6, i. e. $C_0(x_2) = C_0(x_6)$ and $\alpha_3 = 0$, $\alpha_5 = 1$, $\beta_3 = C_{DP2}$ to condition streamtube 5, i. e. $C_0(x_5) = C_{DP2}$. Conditioning can not be applied to the streamtube corresponding to the first isochrones (i.e. streamtube n). Another restriction is that two opposite streamtubes (i.e. streamtubes k and $2n-k$) can not be simultaneously conditioned. For those streamtubes where no conditioning applies, the symmetrical solution is used.

4.4 Application

A total of four control planes (Figures 4.3 and 4.4) are situated on the test site, positioned perpendicular to the main groundwater flow direction and at a distance of 140 m (CP1), 240 m (CP2), 330 m (CP2-3) and 450 m (CP3) from the presumed contaminant source. A first set of IPTs has been conducted in 2003 (CP2) and 2004 (CP3), followed by a second set in 2006 with 8 IPTs at the wells of control plane CP2-3 (B97-B102), as well as at B86 und B96. Long-time observations at the test site lead to the conclusion that the plume is at steady state, allowing the assumption that the time difference between the IPTs should not be of any concern. As a means of avoiding mutual interference of the IPTs, a maximum of two not directly neighbouring wells were pumped simultaneously. Furthermore, a recovery phase long enough to allow a full recovery of the natural groundwater flow field was introduced between pumping campaigns, which was checked by continuous water level measurements. The parameters of the integral pumping tests, which were used as input for the inversion solution are presented in Table 4.1.

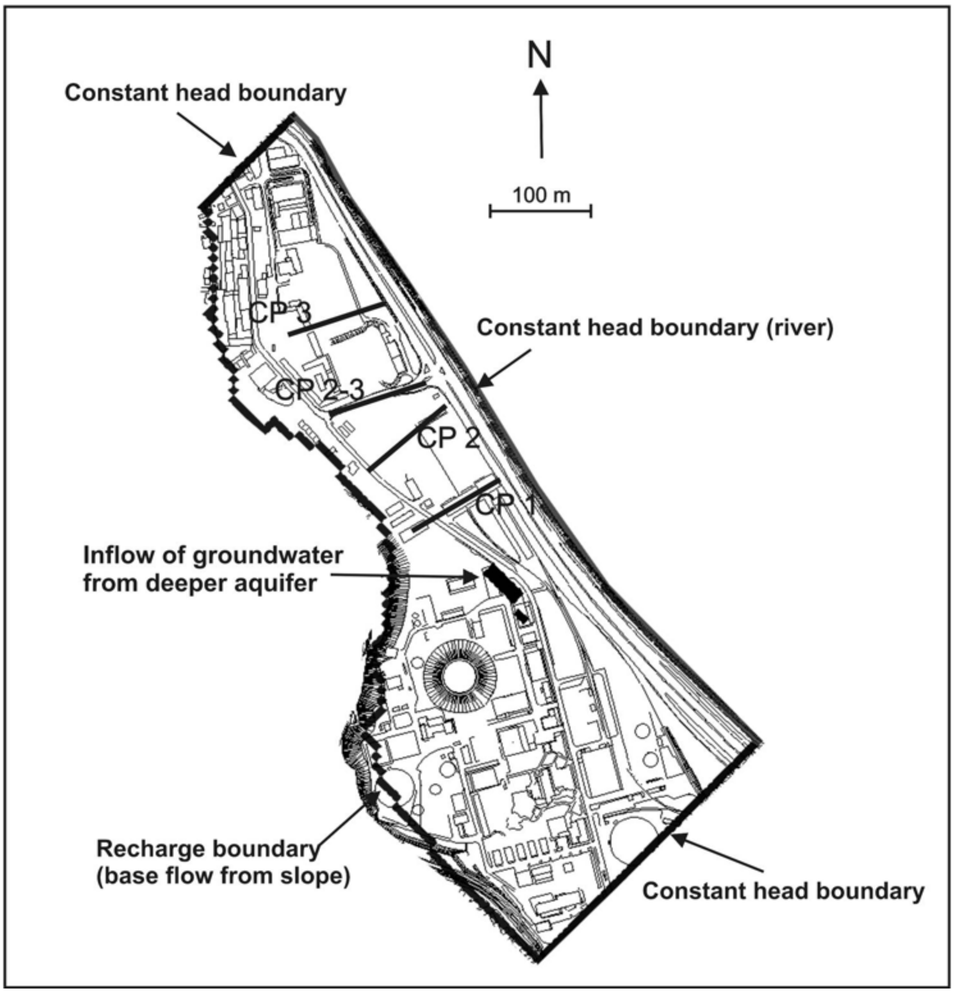

Figure 4.3: Position of control planes at the test site, and boundary conditions of the numerical flow and transport model.

Groundwater sampling was mainly concerned with HET, PAH and BTEX to obtain both the concentration-time series required for the IPT inversion solution and the point-scale concentration measurements for conditioning of the inversion solution. Groundwater temperature, electrical conductivity, pH, redox potential and the concentration of dissolved oxygen were measured continuously at the discharge of each IPT well. The water samples were stored airtight in amber bottles with laminated Teflon sealings at 4°C. Within 24 hours, the groundwater samples for BTEX analyses were concentrated via Purge&Trap and analysed with HP 6890 GC-MS (MSD 5972 A by HP). The groundwater samples for PAH analyses were extracted with the help of liquid-liquid extraction (LLE) and analysed with HP 5890 GC-MS (MSD 5972 by HP). HET analyses were conducted by using SPE cartridges to concentrate HET from the groundwater, then eluting them with solvent and finally analysing the extracts using HP 5890 GC-MS (MSD 5972 by HP). Figure 4.5 shows an example of the above mentioned concentration-time series for one PAH (acenaphthene) and two HET compounds (methylbenzofurans and dimethylbenzofurans) at IPT well B97.

Table 4.1: Hydraulic parameters of the integral pumping tests

well	aquifer thickness [m]	transmissivity [m^{2}s^{-1}]	gradient [-]	pumping rate [m^{3}s^{-1}]	duration of pumping [h]	max. radius of capture zone [m]	number of data-points
Control plane CP2							
B86	3.5	6.6E-03	0.002	0.0035	118	29.9	15
B87	1.9	7.91E-03	0.002	0.0036	99	37.85	7
B88	3.0	4.28E-03	0.002	0.0041	99	32.15	7
B89	0.9	4.33E-04	0.002	0.00051	99	25.35	7
B90	3.09	2.31E-02	0.002	0.0046	99	33.55	7
Control plane CP2-3							
B97	2.4	6.8E-03	0.0024	0.0035	93	31.05	15
B98	2.0	7.7E-03	0.0024	0.0025	95	27.9	15
B99	3.4	8.04E-03	0.0024	0.004	117	31.02	15
B100	2.6	6.4E-03	0.0024	0.003	103	29.01	15
B101	2.78	5.4E-03	0.0024	0.004	80	27.7	15
B102	3.32	2.7E-03	0.0024	0.0045	118	34.8	15
Control plane CP3							
GWM11	3.3	3.19E-02	0.0028	0.005	99.9	34.00	18
B95	2.9	3.77E-02	0.0028	0.004	74.4	28.00	15
B94	3.0	2.37E-02	0.0028	0.004	77.0	28.01	15
B93	3.7	2.30E-02	0.0028	0.004	116.3	30.99	16
B92	2.3	2.78E-03	0.0028	0.003	92.0	30.28	16
B96	3.7	1.05E-03	0.0028	0.0045	93.0	25.6	14

In addition, it should be kept in mind that the capture zone of groundwater and contaminants are only identical if a retardation factor of 1 applies. In the case of $R > 1$ the capture zone for the contaminant is smaller than that for groundwater. In the course of the project, the retardation factors for acenaphthene, methylbenzofurans and dimethylbenzofurans were determined using column experiments containing material similar to that of the test site. Therefore, the sampling times of the concentration-time series were adjusted, following the procedure described in Bockelmann et al. (2001), using the retardation factors $R_{Ace} = 2.8$, $R_{MBF} = 1.2$ and $R_{DMBF} = 1.96$.

Conditioning of the numerical inversion solution in CSTREAM was aided by the installation of 13 direct-push wells at horizontal intervals of 3 to 11 m between well B97 and B99 (Fig. 4.4). The groundwater samples from these wells were analysed for the same contaminants as the integral pumping tests to obtain point-scale concentration measurements.

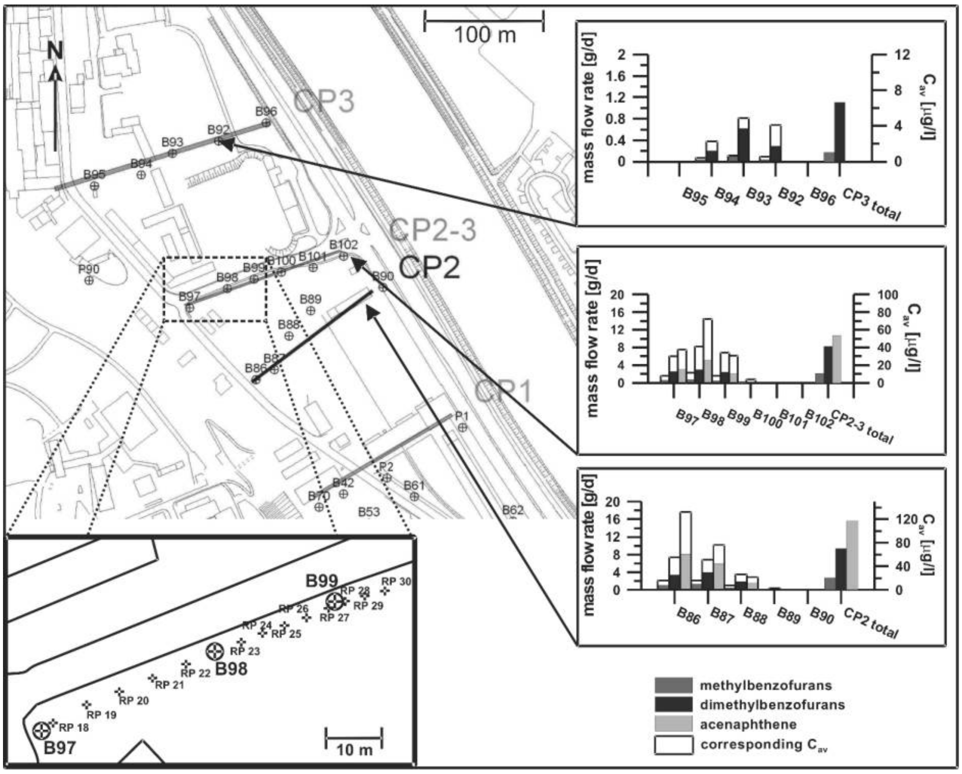

Figure 4.4: Contaminant mass flow rates and average concentrations (C_{AV}), note different scale, at 3 control planes (IPT-specific application and sum of mass flow rates, applied to the right, respectively) as well as position of direct-push wells for conditioning of the numerical inversion solution with point-scale concentration measurements (enlargement), Section 1 describes the area between CP2 and CP2–3 and Section 2 delineates the area between CP2–3 and CP3.

4.4.1 Flow and transport modeling

In the course of previous studies at the test site, several hydraulic models of the central and southern areas were developed, which partly built on one another (Bösel et al., 2000; Jarsjö et al., 2005; Mak et al., 2006). Furthermore, a conservative transport model was developed in connection with the analysis of carbon isotope ratios of benzene, toluene and o-xylene to define in situ degradation rates (Mak et al., 2006). The models were created using MODFLOW (Harbaugh and McDonald, 1996) and MODPATH (Pollock, 1994).

The numerical flow and transport model used in the current study for inversion of the IPT concentration-time series using CSTREAM was based on the already mentioned models, especially the one by Mak et al. (2006). It was extended to the north to cover the plume and all control planes. In the present study, a two-dimensional model was applied, as the aquifer is relatively thin and all wells were fully screened. This 2D model consists of one confined/unconfined layer with 190 rows and 216 columns with a cell size of 5 by 5 m with local refinements (up to 1 by 1 m at the wells). The boundary conditions applied are shown in Figure 4.3. The sealed surface at the investigation area and the regulating effect of the receiving stream give rise to the conclusion that the system was at steady-state. The inflow at the eastern valley boundary in the central and southern parts was adopted from Mak et al. (2006).

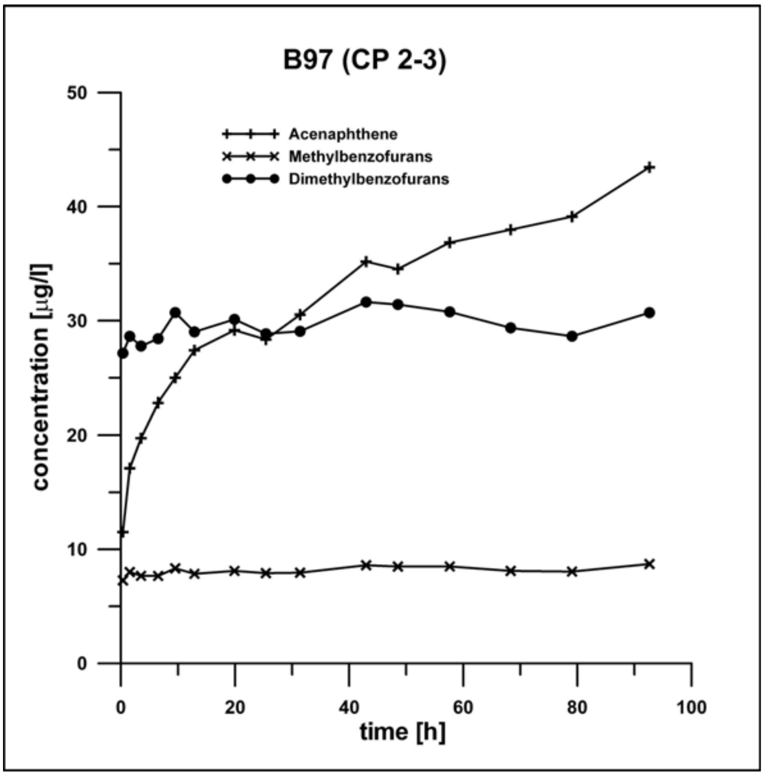

Figure 4.5: Example of acenaphthene, methylbenzofurans und dimethylbenzofurans concentration-time series at IPT well B97

4.5 Results

Table 4.2 presents the contaminant mass flow rates determined at the three control planes for the contaminants dominating on-site, i.e. methylbenzofurans, dimethylbenzofurans and acenaphthene, which were computed using the software CSTREAM and the numerical site-model.

Table 4.2: Contaminant mass flow rates at control plane CP2, CP2–3 and CP3

CP2 [gd^{-1}]	B86	B87	B88	B89	B90		Total
acenaphthene	8.1	5.92	1.61	0.000539	0.000813		15.63
methylbenzofurans	1.01	1.24	0.563	0.0113	n.d.		2.82
dimethylbenzofurans	3.41	3.98	1.95	0.0403	n.d.		9.38
CP2-3 [gd^{-1}]	B97	B98	B99	B100	B101	B102	Total
acenaphthene	3.18	5.29	2.23	0.0196	0.000822	0.00631	10.73
methylbenzofurans	0.706	0.86	0.565	0.0454	n.d.	n.d.	2.18
dimethylbenzofurans	2.54	3.04	2.45	0.236	n.d.	n.d.	8.7
CP3 [gd^{-1}]	B95	B94	B93	B92	B96		Total
acenaphthene	n.d.	n.d.	0.00237	0.000779	0.000408		0.0036
methylbenzofurans	n.d.	0.0385	0.0887	0.0417	n.d.		0.17
dimethylbenzofurans	n.d.	0.203	0.618	0.292	n.d.		1.11

n.d. = not detectable

The results from all pumping campaigns are also shown in Figure 4.4. The total contaminant mass flow rate at the individual control planes decreases from south to north, i.e. with increasing distance from the suspected contaminant source. The decrease from CP2 to CP2-3 (section 1) is considerably less than from CP2-3 to CP3 (section 2). This becomes especially apparent when looking at the methylbenzofurans (decrease: 0.64 g d^{-1} for section 1 and 2.01 g d^{-1} for section 2) and dimethylbenzofurans (decrease: 0.68 g d^{-1} and 7.59 g d^{-1}, respectively). Acenaphthene shows a much less pronounced difference (decrease: 4.9 g d^{-1} and 10.73 g d^{-1}, respectively). It is possible to distinguish a definite trend along the individual control planes, where the main flow of contaminants is concentrated at one to three wells (Fig. 4.4). At CP2 this area is situated around B86 to B89 with the maximum flow at B86 for acenaphthene and the maximum flow at location B87 for methyl- and dimethylbenzofurans, although the flow rates for these two compounds are similar at B86 and B87 at this control plane. The second control plane CP2-3 shows the highest contaminant mass flow rate at wells B97 to B99 with the maximum at B98. The third control plane (CP3) is marked by very low concentrations (and therefore mass flow rates) of all contaminants, with the plume centre located around B93. Aligning the maximum flow locations on each of the control planes suggests that the plume centreline is located at B86/87 and continues north through B98. The wells adjacent to B86/87 and B98 show decreases in lateral directions.

The evaluation of the IPTs has shown that along one control plane the highest average concentration, representative for a single IPT, C_{AV} (defined as the contaminant mass flow rate [M T^{-1}] divided by total groundwater flow rate [L^3 T^{-1}] across the capture zone extent of the IPT) does not necessarily have to coincide with the largest contaminant mass flow (Fig. 4.4, especially B86 and B87 at CP2). This can be explained by the influence of the spatially variable groundwater flux in the aquifer caused by the heterogeneous distribution of hydraulic conductivity, i.e. a zone with a high hydraulic conductivity will have a larger contaminant flow than a zone with the same average concentration but a lower hydraulic conductivity.

The concentrations for the wells B97, B98 and B99, as calculated in CSTREAM for the individual stream tubes (amounting to 27 concentration values for well B97, 29 for B98 and 29 for B99, respectively) are presented in Figure 4.6a, c and e. Thereby, the symmetrical inversion solution was chosen at first (symmetrical around each of the IPT wells). Here, the outer stream tubes do not overlap with the ones from adjacent wells. The symmetry caused by the unconditioned inversion solution becomes obvious. Already in this case, due to the selection of wells, the unconditioned solution pronounces the postulated plume centre at B98, when comparing the inversion results at B97, B98 and B99.

The results of conditioning of the numerical inversion solution using point measurements at direct-push wells are presented in Figure 4.6b, d and f. In particular, conditioning can help to narrow down the plume fringe, as the concentrations using the unconditioned symmetrical solution even tend to increase towards the fringe (cf. Fig. 4.6a). In this case the conditioned solution shows (Fig. 4.6b) that the eastern plume fringe at B99 can be much better narrowed down than the western fringe at B97, as there are fewer direct-push wells positioned there than close to B99. This leads to the fact that (i) streamtubes that are not conditioned on either side of the IPT well will keep the concentrations from the symmetrical solution and that (ii) the concentrations in streamtubes which are conditioned on either side of the IPT well will either increase or decrease to fulfil the mass balance. This effect is particularly noticeable from streamtube concentrations located at the fringe of the control plane where mass balance considerations lead to solitary peak values (cf. Fig. 4.6f) caused by conditioning of the streamtube concentration on the opposite side of that particular IPT well.

The concentrations of all three contaminants measured in the direct-push wells close to the postulated plume centre all lay distinctly above the levels of the fringe area, disregarding one exception each (direct-push wells RP22 and RP23, respectively). This confirms the assumption of the plume centre being located around well B98 as well as the pronounced small-scale contaminant concentration variability within the plume. Combining this information with the IPT evaluation allows for a more realistic quantification of the mass flow rates compared to the distinction into a symmetrical, left-side and right-side distribution around the IPT well.

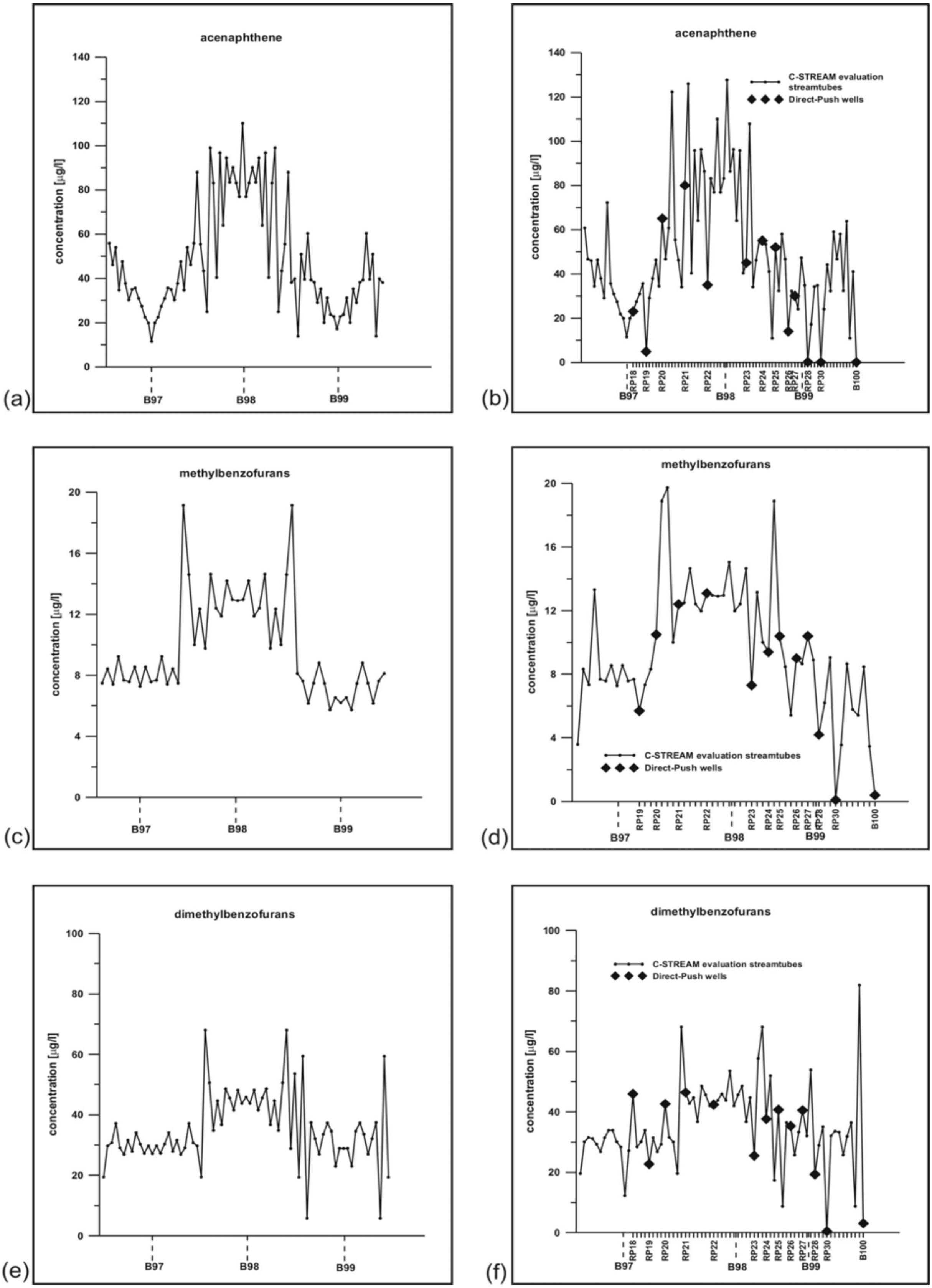

Figure 4.6: Results of symmetrical (a, c and e) and conditioned (b, d and f) IPT evaluation: concentration profiles at control plane CP2–3.

4.6 Conclusions

Integral pumping tests can, as already shown in previous studies, make a valuable contribution towards reliable estimation of contaminant mass flow rates and concentration distributions at control planes due to the integrating nature of the method, compared to approaches that are based on the interpolation of point measurements and therefore sensitive to the density of the monitoring well network. Applying the method to several control planes situated downstream of one another allows a much more exact determination of natural attenuation rates. Here, the application of a numerical flow and transport model of the investigated site enables the simulation of hydraulically and hydrogeochemically heterogeneous site conditions. However, up to now it was only possible to determine the approximate position of the contaminant plume along control planes, unless several IPTs with sequentially overlapping capture zones were employed. Conditioning the numerical IPT inversion solution using point-scale concentration measurements, taken, e.g., from direct-push wells, as described here, can aid in narrowing down the plume position and reduce the non-uniqueness of the inverse determination of contaminant mass flow rates and the spatial contaminant concentration distribution along control planes, respectively. The increase in site investigation accuracy is especially helpful for planning and implementation of remediation schemes and to improve our knowledge about source zone-plume interactions.

Conditioning shows for the case of the present test site that more information from the fringe zones of the test site is necessary to lead to more precise statements to the west of well B97.

As a next step, the results of the IPT evaluation will be implemented in a reactive transport model of the test site to use the contaminant distribution prior to and after the implementation of an innovative remediation measure (using H_2O_2) as boundary conditions. In addition, the results of the conditioned IPT evaluation will contribute to source zone delineation using backtracking methods.

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Chapter 5

Modelling of an enhanced PAH attenuation experiment and associated biogeochemical changes at a former gasworks site in Southern Germany

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Abstract

Former manufactured gas plant sites often form a widespread contaminant source in the subsurface, leading to large plumes that contain a wide variety of tar-oil related compounds. Although most of these compounds eventually degrade naturally, the relevant processes tend to be slow and inefficient, often leaving active remediation as the only viable option to eliminate the risks of toxic substances to reach potential receptors such as surface waters or drinking water wells. In this study we use a reactive transport model to analyse the fate of a contaminant plume containing acenaphthene, methylbenzofurans and dimethylbenzofurans (i) prior to the installation of an active remediation scheme and (ii) for an enhanced remediation experiment during which O_2 and H_2O_2 were added to the contaminated groundwater through a recirculation well. The numerical model developed for this study considers the primary contaminant degradation reactions (i.e., microbially mediated redox reactions) as well as secondary and competing mineral precipitation/dissolution reactions that affect the site's hydrochemistry and/or contaminant fate. The model was calibrated using a variety of constraints to test the uncertainty on model predictions resulting from the undocumented presence of reductants such as pyrite. The results highlight the important role of reactive transport modelling for the development of a comprehensive process understanding.

5.1 Introduction

Tar-oil subsurface contaminations are a common feature of industrial areas that formerly accommodated manufactured gas plants, and they might pose a threat to nearby drinking water supplies or other receptors. They typically consist of a complex mixture of contaminants, comprising benzene, toluene, ethylbenzene and xylene (BTEX), polycyclic aromatic hydrocarbons (PAH), heterocyclic aromatic hydrocarbons (HET) and phenols (Zamfirescu, 2000). These compounds are characterised by a wide range of physical and chemical properties and therefore typically present a significant challenge for remediation efforts. Most former manufactured gas plant (MGP) sites have unique features with respect to their release history and/or their geochemical, mineralogical and (hydro)geological characteristics. Any remediation efforts, especially those involving (enhanced) natural attenuation (ENA), will therefore require a thorough understanding of the processes that control the feasibility as well as the efficiency of the remediation approach. ENA techniques were, initially at lab-scale, implemented and investigated, e.g., by Odencrantz et al. (1990) and became successively more widely applied at the field-scale. Hunkeler et al. (2002), for example, studied the active remediation of a diesel-fuel contaminated aquifer and found that natural attenuation processes continued to remove the petroleum hydrocarbons even after the injection of oxygen and nutrients had ceased. The performance of a sequential anaerobic and aerobic in-situ treatment system was evaluated for an emplaced source of chlorinated solvents by Devlin et al. (2004) who found this system to be more effective than natural attenuation alone. Their findings confirm that the identification and understanding of rate-limiting processes and reactants, such as water rock interactions and competing reductants is decisive for the site-specific performance of ENA measures. Where ENA is initiated to stimulate oxidative degradation of contaminants a clear understanding of the presence and reactivity of competing reductants (Hartog et al., 2002, Johnston and Desvignes, 2003, Descourvieres et al., 2010a,b), such as organic matter or reduced-form minerals, can be crucial. Reactions involving these reductants might consume a substantial fraction of the ENA-added oxidants, leaving little oxidation capacity for the targeted contaminant degradation processes (Thullner and Schäfer, 1999, Prommer and Barry, 2005). To advance from a qualitative understanding of reductant competition to a process-based quantification the use of a numerical modelling framework with advanced geochemical capabilities is required. Modelling studies that specifically investigated ENA measures have previously been applied to a variety of problems, including a hypothetical BTEX contamination and the evaluation of possible remediation schemes for enhanced biodegradation using nitrate as a terminal electron acceptor (TEA) (Prommer et al. 2000). Subsequently Eckert and Appelo (2002) studied the effects for a field-case where active remediation of a BTEX contaminated aquifer was stimulated via addition of nitrate. They specifically evaluated the competition of the hydrocarbon compounds for nitrate by reduced iron species/minerals (dissolved ferrous iron, Fe^{2+} and FeS). Schäfer and Therrien (1995) quantified the observed biodegradation of xylene and found the efficiency to be in the same order as the previously installed pump-and-treat remediation measure. Rahbeh and Mohtar (2007) modelled the enhanced natural attenuation of a BTEX plume using air sparging and included soil heterogeneities and multiphase transport. Remediation of chlorinated solvents by potassium permanganate addition was modelled using a multicomponent reactive transport model by Henderson et al. (2009a), whereas Wood et al. (2006) modelled the bioremediation of these compounds by addition of hydrogen release compounds (HRC). Goel et al. (2003) studied the effectiveness of electrolytic aeration in comparison to oxygen release compounds (ORC) addition in a simulated aquifer. An approach taking several factors into account was demonstrated by Henderson et al. (2009b) who considered partial source removal and plume remediation and studied its effects on the presence of specific contaminants dissolving from a leaded gasoline plume. A different approach was taken by Schäfer and Kinzelbach (1992) who could show that switching the locations of active well injection of dissolved oxygen increases the robustness of the hypothetical remediation scheme.

Kim and Choi (2002) modelled gaseous ozone transport in a soil column contaminated with PAHs to study the feasibility of an in situ application. A comprehensive review of chemical oxidation treatments (application of ozone, hydrogen peroxide and high-temperature pressurised water) applied to PAH contaminated soils has been presented by Rivas (2006). Molson et al. (2002) numerically simulated humic acid-enhanced remediation of BTEX and naphthalene based on a pilot scale experiment and could compare these results to the field case without further model adjustments. Bockelmann (2002) studied via modelling the sorption behaviour of BTEX and PAHs at the same site under investigation in the current study. Finkel et al. (1999) presented a 1D streamtube-based reactive transport model and applied it to surfactant-enhanced remediation of PAHs. None of these studies, while only partially based on field data, have yet investigated the combined effect of decade-old multiple source, multiple compound subsurface contamination on enhanced remediation via targeted injection of electron accepting capacity. The present paper reports the results from such a study, where numerical modelling was used to analyse a remediation scheme that was applied to an old and extensive hydrocarbon plume situated below and downstream of a former MGP site. Enhanced remediation at this site was carried out via the injection of O_2 and H_2O_2 through a specifically designed groundwater circulation well (Trötschler et al. 2008) that was aimed at accelerating the naturally occurring degradation processes that were previously shown to persist under the site's anaerobic redox conditions (Bockelmann et al. 2001). ENA schemes that rely on transient injection schedules appear attractive as (i) the dynamic flow-field may lead to enhanced mixing between oxidants and contaminants and (ii) may reduce the risk of bioclogging. On the other hand the occurrence of microbial lag times und potential inhibition effects may deteriorate these advantages. To illustrate and investigate such issues we employ reactive transport modeling and identify, integrate and quantify the key hydraulic, chemical and biological processes that occurred at the site prior and during the enhanced remediation experiment. The study investigates specifically the hydrogeochemical changes, including reductant competition (e.g., oxidation of ferrous iron) that occurred during the injection of O_2 and H_2O_2, and the stimulated biodegradation of the contaminants of concern.

5.2 Site description

5.2.1 Hydrogeology

The study was performed at a former manufactured gas plant site located in the Neckar River valley near Stuttgart, South Germany. The Eastern side of the study site is bounded by the Neckar River while hillslopes form the Western boundary (Figure 5.1). The uppermost Quaternary aquifer is approximately 3.3 m thick and consists of medium gravel with locally confined fine-grained layers. It is underlain by 30 m of mostly impermeable Gipskeuper sediments, followed underneath by Muschelkalk carbonates that serve as the source of sulphate-rich waters that locally rise through the Gipskeuper (cf. Figure 5.1).

The sedimentological heterogeneity of the investigated aquifer is caused by several factors, such as lowering of bedrock (lixiviation and faults), its location close to the valley edge (outcrops of layers) and anthropogenic influences such as civil works (foundation excavation). The groundwater table is located approximately 4.1 m below the surface and the aquifer is considered to be locally either unconfined or confined, depending on the overlaying sediments, anthropogenic filling or floodplain sediments, respectively. Groundwater flow conditions at the site were intensely investigated over the last 10 years. It was shown that the groundwater levels fluctuate only marginally and no specific seasonal trend was observed. This is attributed to the regulated, steady water levels of the Neckar River. Pumping tests in the central and southern parts yielded an average hydraulic conductivity of $3.3 \cdot 10^{-3}$ ms^{-1} (Herfort, 2000). Additional investigations in more recent years in the northern part yielded a comparable hydraulic conductivity of $3.7 \cdot 10^{-3}$ ms^{-1}. A tracer test conducted in the contaminated zone of the aquifer (Bösel et al., 2000; Trötschler et al., 2008) showed the effective porosity to be 15 %. A longitudinal dispersivity of

2.5 m was estimated from the analysis of this test. The flow velocity was estimated to be 2 md^{-1} (Bösel et al., 2000) and the overall hydraulic gradient was found to be 0.002 with a general flow direction to the north-north west (Herfort, 2000). The site investigations have generated a set of four control planes perpendicular to the main groundwater flow direction. They are located at distances of 140 m (CP1), 240 m (CP2), 330 m (CP2-3) and 450 m (CP3) from the presumed contaminant source (Figure 5.1).

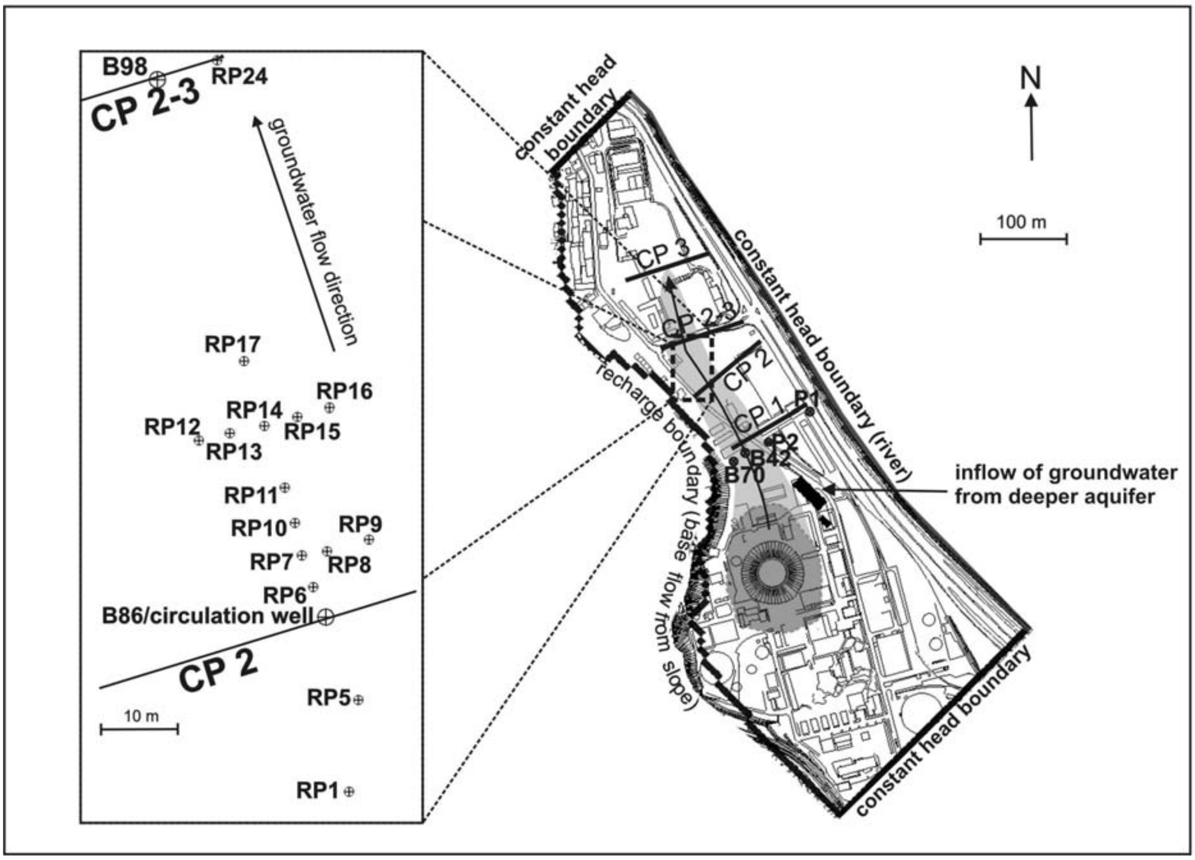


Figure 5.1: Site overview showing positions of wells, direct-push wells, control planes (CP) and inflow of groundwater from deeper aquifer (black boxes), as well as boundary conditions applied in the flow and transport model. Dark shaded area indicates observed NAPL phase, light shaded area indicates observed contaminant plume. Arrows in north-westerly direction indicate groundwater and plume flow direction.

5.2.2 Contamination history and distribution

The plant was in operation between 1875 and 1970, storing coal processing by-products on-site. The bombing of the site during World War II as well as continued leakages led to various contamination sources in the subsurface (Zamfirescu and Grathwohl, 2001). Therefore it is suspected that the main contamination at the site occurred about 60-70 years ago, and therefore it is assumed that the site is characterised by equilibrium conditions regarding sorption nowadays.

The contamination comprises monoaromatic hydrocarbons, polyaromatic hydrocarbons (PAH), aliphatic hydrocarbons, phenols as well as heterocyclic hydrocarbons (HET) (Zamfirescu, 2000). These contaminants are found today as non-aqueous phase liquids at the top and bottom of the uppermost aquifer, as well as dissolved in the groundwater. Of these, acenaphthene (PAH), methylbenzofurans (HET) and dimethylbenzofurans (HET) are the most prominent compounds in the downstream plume. They are the main focus of the present study. Information on the lab analytical procedures are reported by Herold et al. (2008). The evaluation of integral pumping test results (IPTs; Teutsch et al., 2000; Ptak et al., 2000, Ptak and Jarsjö, 2008) located the plume centre at well B86 at control plane 2 and well B98 at control plane 2-3 (Herold et al., 2008). The groundwater on-site is highly influenced by the decades old contamination. Indeed, pristine groundwater can essentially not be found within the study area.

5.2.3 Pre-remediation hydrogeochemistry

The aquifer matrix is composed of limestone with minor quartz and sandstone components, determined using scanning electron microscopy (SEM) (Proß, 1998), maintaining near neutral pH conditions. The hydrogeochemistry of the target aquifer is characterised by anaerobic, reducing conditions. Typically both oxygen and nitrate were depleted by contaminant degradation processes. Sulphate and iron reduction are the dominating redox processes in the southern and middle part, respectively (Weber et al., 2000). The analysis of sediments in the southern part has shown up to 15 mg/g dry weight of ferric iron, determined using 6 M HCl (boiling) (Proß, 1998), indicating the potential for iron minerals to act as electron acceptors.

Sorption behaviour was studied in column experiments using clean sands, thereby excluding the gravel fraction which features considerably at the current study site (Piepenbrink et al., 2005). In these experiments HETs displayed only little sorption whereas acenaphthene showed significant retardation ($R > 5$). This value should, however, not be viewed as representative of the current site situation as the gravel fraction was omitted in the experiments and the age of the contamination implies that sorption is in equilibrium as opposed to the conditions created in the column studies. Samples collected close-by, approximately 180 m upstream of the groundwater circulation well, contained up to 1 wt % pyrite determined using SEM (Proß, 1998). It remained unclear whether these concentration levels extend over a larger area, in particular whether pyrite was present near CP2 and CP2-3.

Ferrous iron and sulphate concentrations vary temporally and spatially in the area upstream of the injection well, masking any clear evidence of pyrite oxidation that would occur downstream of the injection well.

5.2.4 Remediation via groundwater circulation well and previous research

The groundwater remediation measures were emplaced in well B86, as it was found to be located on the centre line of the plume (Figure 5.1; Herold et al., 2009). Prior to the implementation, laboratory batch and column studies using on-site groundwater investigated and confirmed the effectiveness of H_2O_2 generated dissolved oxygen as an electron acceptor for the microbially mediated degradation of the target compounds (Sagner and Tiehm, 2005). Experiments using a large experimental basin filled with homogeneous sand aided the design of the operational scale groundwater circulation system, which was installed into well B86 (Trötschler et al., 2008). During the remediation, water was pumped out of the well from the uppermost well compartment, augmented with O_2 or H_2O_2 and reinjected in the lowermost compartment. The compartments were hydraulically separated and equipped with filter screens. The circulation well design (Trötschler et al., 2008) was shown to deliver and mix additional electron accepting capacity to a substantial portion of the aquifer zone in a radius of 7 – 8 m around the circulation well. Table 5.1 shows the different stages of remediation with regard to their duration and the type of injection, following Trötschler et al. (2008).

Table 5.1: Stages of remediation

stage I	pre-remediation	no injection
stage II	28 days	O_2-injection
stage III	105 days	no injection
stage IV	203 days	H_2O_2-injection
stage V	post-remediation	no injection

The effectiveness of the remediation measure was evaluated by an intense hydrochemical monitoring of the trial injection. In previous work, contaminant mass flow rates and compound-specific effective first-order natural attenuation rate constants λ $[T^{-1}]$ were quantified by Bockelmann et al. (2001) using the results of several integral pumping tests (IPTs). The same approach was used here using the results of two dedicated IPTs that were carried out after the groundwater circulation well was shut down (Table 5.2). The two IPTs were conducted (i) at injection well B86 to determine the contaminant mass flow rates associated with unremediated water (after a time assuring that all remediated water had migrated sufficiently downstream of well B86), as well as (ii) at downstream well B98 to quantify the contaminant concentrations in the remediated water just after the shut-down of the recirculation well, and the evaluation of the two IPTs was restricted to the aquifer domain (streamtubes) influenced by the groundwater circulation well.

Table 5.2: Natural attenuation rate constants of three main contaminants before and during remediation

contaminant	degradation rate constant (λ) pre-remediation [day^{-1}]	degradation rate constant (λ) during remediation [day^{-1}]
acenaphthene	0.00187	0.00413
methylbenzofurans	0.00512	0.01143
dimethylbenzofurans	0.00275	0.00448

Analysis of the collected data showed that the injection of O_2/H_2O_2 resulted in increased O_2 levels (1.5 -16 mg/L) up to 25 m downstream of the groundwater circulation well, while also having locally a profound effect on the aquifer geochemistry. During the remediation phases, ferrous iron had to be continuously filtered off within the circulation well. It proved to cause severe clogging problems, which resulted in highly variable injection rates. Sediment samples taken at several locations near the circulation well suggested that the total iron content did not increase significantly compared to background values. However, concentrations were higher close to the injection part of the well compared to the abstraction part, probably due to the immobilisation of Fe^{2+} by oxidation and precipitation as amorphous ironhydroxides. Highly variable sulphate concentrations in the background water prevented reliable identification of the occurrence of pyrite oxidation, during O_2 and H_2O_2 injection.

5.3 Numerical modelling

The investigated site is characterised by geological and hydrogeochemical heterogeneities and is subject to distinct hydrogeochemical changes in response to the injection of O_2 and H_2O_2. These dynamic changes can only be modelled with a complex process-oriented model. We chose a step-wise approach in which first, a flow and conservative transport model was set up and calibrated. Thereafter, a reactive transport model was set up which incorporates mechanistic descriptions of microbial degradation processes as well as of the key mineral reactions. The calibrated reactive transport model was then used to explore the different remediation scenarios and to study the impact of additional competing reductants on the robustness of our predictions.

5.3.1 Flow and Conservative Transport Modelling

The flow and transport model for the site is an extension of various previous modelling efforts (Bösel et al., 2000, Jarsjö et al., 2005, Mak et al., 2006). These modelling studies investigated specifically the central and southern part of the current study domain. Mak et al. (2006) used a conservative transport model to determine biodegradation rates of benzene, toluene and o-xylene using carbon isotope ratios. All models, including the present, were constructed using MODFLOW (Harbaugh and McDonald, 1996) and MODPATH (Pollock, 1994).

The model presented here is largely based on the work of Mak et al. (2006), but was extended to the north to cover the full contaminant plume extension determined by the four control planes. The flow and conservative transport model was constructed as a vertically integrated, two-dimensional model, which was thought to be a reasonable approximation for the relatively shallow aquifer.

It consists of one confined/unconfined layer with 190 rows and 216 columns with a cell size of 5 by 5 m. The boundary conditions applied are presented in Figure 5.1. The regulating effect of the receiving stream and the sealed surface underpin the assumption that the system is hydraulically at steady state. The final flow and transport model was then calibrated by adjusting the hydraulic conductivity values gathered from the pumping tests performed at the control planes to fit both the heads measured in the field and the results of the tracer test (Bösel et al., 2000; Trötschler et al., 2008), i.e. the dominant flow direction and the longitudinal dispersivity. The horizontal transverse dispersivity was estimated to be 0.25 m, i.e., 1/10 of the longitudinal dispersivity. As these tests have been conducted on a scale smaller than the total plume length they can only give an indication and presumably a lower limit of the plume scale dispersivity.

5.3.2 Reactive Transport Modelling

The biogeochemical transport model is based on the flow and transport model which was extended into a 3D model, by evenly subdividing the single layer of the 2D model in three separate layers, to allow for the effects of the groundwater circulation well. The current study employed the code PHT3D (Prommer et al., 2003) which couples the transport simulator MT3DMS (Zheng and Wang, 1999) with the geochemical model PHREEQC-2 (Parkhurst and Appelo, 1999). For the model application discussed in this study the original PHREEQC-2 database was extended to incorporate site-relevant kinetic reactions, in particular the microbial degradation of the contaminants and the kinetically controlled dissolution of minerals. Using the modified method of characteristics (MMOC) advection scheme the grid discretisation of three layers in vertical and of 5 by 5 m in horizontal directions was found to provide sufficiently accurate results. Tests with a finer discretisation have shown to have a negligible influence on the simulation results.

5.3.2.1 Reaction Network

Groundwater samples from the site showed the presence of iron and sulphate reducing bacteria prior to the implementation of the remediation measure and outside the zone influenced by the groundwater circulation well during remediation. These samples also contained no sulphate reducing bacteria within the radius of influence of the groundwater circulation well during the remediation, and an increase in iron reducing bacteria just downstream of the radius of influence, perhaps due to mineral phases containing ferric iron. It is therefore assumed that anaerobic microbial degradation is decreasing the contaminant concentrations downstream of the source. However, the mass removal rates are not significant enough to allow monitored natural attenuation to become a viable option for this site. The injection of O_2 or H_2O_2 into the aquifer supplies the groundwater with dissolved oxygen (DO) which then serves as an electron acceptor for the aerobic degradation of hydrocarbons. In addition, the dissolved oxygen will also react with the other reductants such as dissolved ferrous iron and reduced iron minerals (cf. Figure 5.2).

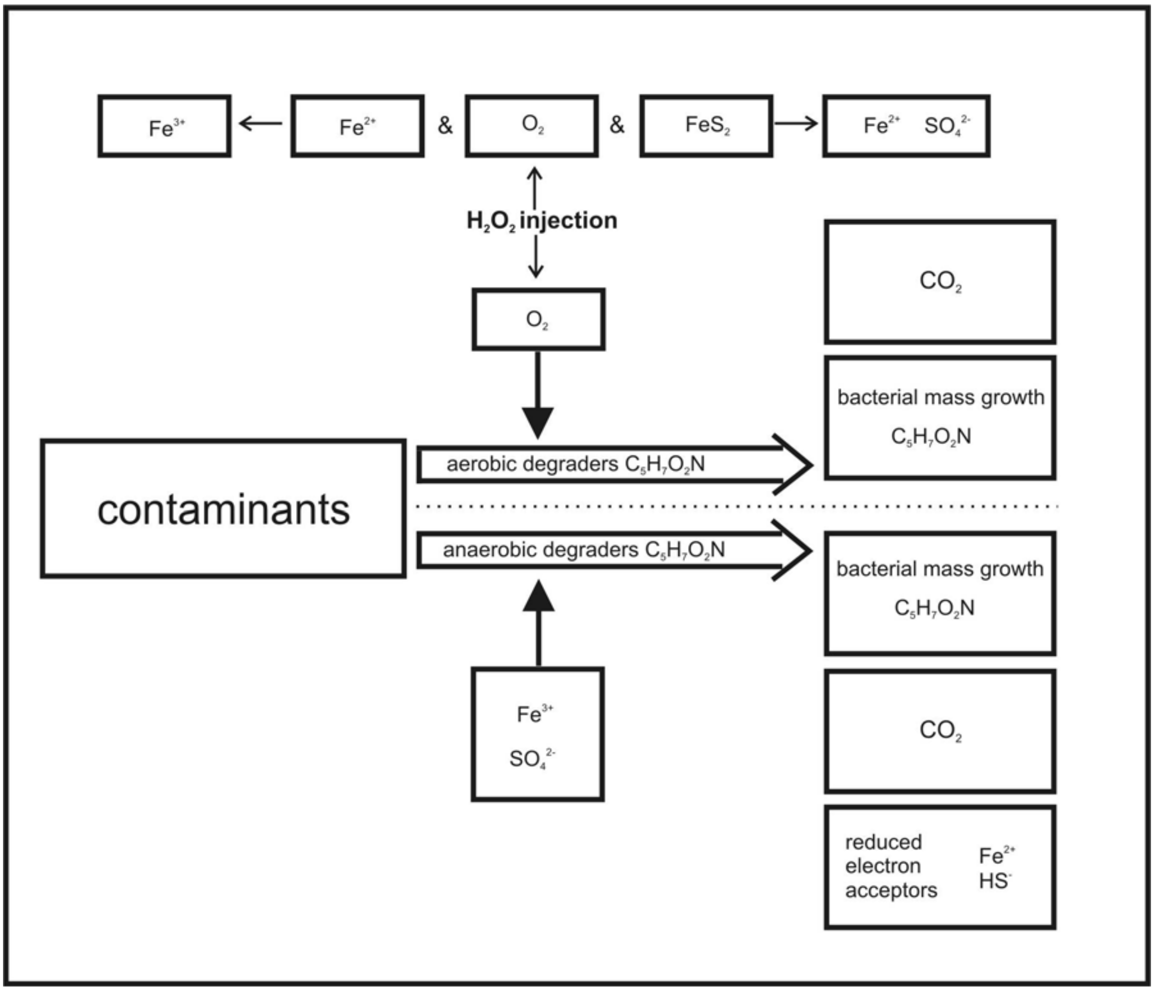


Figure 5.2: Overview of reaction network.

5.3.2.2 Microbially Mediated Contaminant Degradation

As discussed elsewhere (e.g., Barry et al., 2002), biodegradation reactions of oxidisable contaminants may be modelled by a single step or a two step approach. The latter is referred to as the partial equilibrium approach (PEA) (Brun and Engesgaard, 2002) as it separates the electron donating step from the electron accepting step and assumes the former to be rate-limiting. This allows the latter to be modelled through geochemical equilibrium reactions. The formulation of a partial equilibrium approach of microbial contaminant degradation requires (i) appropriate kinetic rate expressions as well as (ii) reaction stoichiometries of the relevant reactions. The current scenarios consider dynamic changes in microbial activity, which requires formulation of suitable reaction rate expression for microbial growth and decay processes and to define the stoichiometries of the reactions.

The latter depend on the estimated microbial efficiency e_m (Rittmann and VanBriesen, 1996; Prommer et al., 2002), which controls how much of the organic carbon is incorporated into biomass and what fraction is incorporated into CO_2. Two different microbial communities, both being attached to the aquifer matrix, were considered in the present model. The first microbial group contains aerobic bacteria that use oxygen and have a microbial efficiency (e_m) of 60 %. The stoichiometry of the reaction is, for example for methylbenzofurans under aerobic conditions:

$$C_9H_8O + 5.1O_2 + 1.08NH_4{}^+ + 1.76H_2O \rightarrow 1.08C_5H_7O_2N + 3.6HCO_3{}^- + 4.68H^+ \tag{1}$$

The second bacterial group consisting of anaerobic degraders was assumed to have a much lower microbial efficiency (10 %). Their growth is inhibited in the presence of elevated oxygen concentrations. The degradation reaction using sulphate as an electron acceptor is then:

$$C_9H_8O + 4.8SO_4^{2-} + 0.18NH_4^+ + 4.46H_2O \rightarrow 0.18C_5H_7O_2N + 4.8HS^- + 8.1HCO_3^- + 3.48H^+ \tag{2}$$

The mass balance for the first microbial group is:

$$\frac{\partial X_1}{\partial t} = \left.\frac{\partial X_1}{\partial t}\right|_{growth} + \left.\frac{\partial X_1}{\partial t}\right|_{decay} \tag{3}$$

where X_1 describes the concentration of the aerobic bacteria. The first term on the right hand side specifies the microbial growth rate

$$\left.\frac{\partial X_1}{\partial t}\right|_{growth} = \sum_{i=1,n_{org}} Y_{i,1} \times r_{i,1}, \tag{4}$$

which depends on the sum of the mineralisation rates of the n_{org} compounds, i.e., the three contaminants, and the stoichiometric factors Y_i, while the second term on the right hand side can be described as the product of a first-order decay rate (ν_{decay,X_1}) and the microbial concentration (X_1).

The mineralisation rate, for example of methylbenzofurans is computed from:

$$r_1 = \left(r_{ox} \frac{C_{ox}}{K_{ox} + C_{ox}} \right) \left(\frac{C_{NH_4^+}}{K_{NH_4^+} + C_{NH_4^+}} \right) \left(\frac{C_{MBF}}{K_{MBF} + C_{MBF}} \right) I_{bio} X_1 \tag{5}$$

where K_{ox}, $K_{NH_4^+}$ and K_{MBF} are the Monod half saturation constants for oxygen, ammonium and methylbenzofurans, respectively. r_{ox} is the maximum degradation rate for methylbenzofurans with respect to oxygen. Zysset et al. (1994) proposed an inhibition factor (I_{bio}) which can be devised as

$$I_{bio} = \frac{X_{\max} - X_1}{X_{\max}} \tag{6}$$

where X_1 is the microbial concentration that is limited to a maximum concentration $X_{\max}$. The second microbial group was assumed to follow kinetic rate expressions analogue to equations (3)-(6), whereby the potential electron acceptors to be used by this group were assumed to be ferrihydrite (Fe(OH)$_3$) and sulphate. No inhibition term was employed to control the order at which either ferrihydrite or sulphate was used. Instead, employing the partial equilibrium approach, the thermodynamically more favourable electron acceptor was automatically selected (cf. Postma and Jakobsen, 1996; Greskowiak et al., 2005).

5.3.2.3 Mineral Reactions

A range of mineral reactions were included in the simulations. Pyrite and its kinetically controlled oxidation (Williamson and Rimstedt, 1994; Eckert and Appelo, 2002; Prommer and Stuyfzand, 2005) was included in the model to study the competitive effect on contaminant degradation. Consuming dissolved oxygen, pyrite oxidation releases sulphate and dissolved iron. In the presence of excess oxygen the dissolved iron can subsequently reprecipitate as ferrihydrite (Fe(OH)$_3$) :

$$FeS_2 + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \tag{7}$$

The oxidation of pyrite was modelled as (Williamson and Rimstedt, 1994; Prommer and Stuyfzand, 2005):

$$r_{pyr} = C_{O_2}^{\ 0.5} C_{H^+}^{\ -0.11} \left(10^{-10.19} \frac{A_{pyr}}{V}\right) \left(\frac{C}{C_0}\right)_{pyr}^{0.67} \tag{8}$$

where C_{O_2} is the dissolved oxygen concentration, C_{H^+} is the proton concentration, A_{pyr}/V is the ratio of pyrite surface area to solution volume and C/C_0 is a factor that accounts for changes in surface area resulting from the progressing reaction (Appelo and Postma, 2005). Calcite (CaCO$_3$) and Fe(OH)$_3$ were both included as equilibrium reactions, with ferrihydrite locally and temporally acting as electron acceptor, while calcite was acting as potential buffer during pyrite oxidation.

5.3.2.4 Boundary and initial conditions

The concentrations of anions and cations vary distinctly in time and spatially across the test site, therefore complicating the clear identification of contaminant degradation from other processes. For example, ferrous iron (Figure 5.3) had highly variable concentrations across the monitoring wells and downstream of the groundwater circulation well (B86 – CP2). The concentrations at the direct-push wells show that the well closest to the groundwater circulation well (RP6) had consistently low ferrous iron concentrations. However, all other direct-push wells had a more variable behaviour. The observed high variability of elemental concentrations was most likely caused by both aquifer heterogeneity and anthropogenic influences. For simplicity an averaged groundwater composition from wells B86 and B98 was used as an initial concentration as well as inflow concentration at all model boundaries, including recharge.

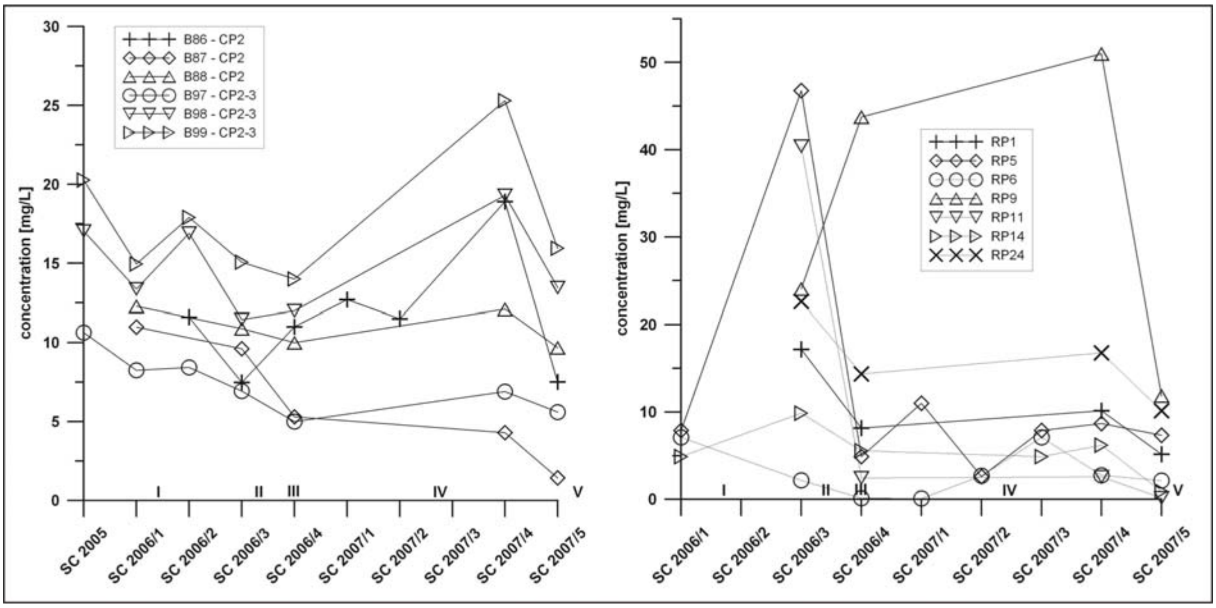


Figure 5.3: Concentration of ferrous iron in groundwater samples from control plane wells (left) and direct-push wells (right) at the test site during different sampling campaigns (SC). Roman numbers above abscissas refer to the mid-point of the various stages of pre-remediation (I), O2-injection (II), no injection (III), H2O2-injection (IV) and post-remediation (V) (see also Table 5.1).

Both initial and boundary solutions were equilibrated with respect to calcite and ferrihydrite, while charge imbalances were corrected by adjusting the chloride concentrations (Table 5.3). The mineral concentrations were estimated based on previous sediment analyses from the central part of the current site and are assumed to be present everywhere.

Injection well concentrations during O_2/H_2O_2 injection were set to a DO concentration equivalent to the combined (with respect to its oxidation capacity) O_2 and H_2O_2 concentration. The mass flow rates determined using IPTs were used to define the boundary conditions for the contaminant concentrations.

Table 5.3: Measured (average from wells B86 and B98) and equilibrated groundwater composition (pre-remediation)

Aqueous component	Measured [mmol/L][a]	Equilibrated [mmol/L][a]
O(0)	0	0
Ca	8.89	7.55
Mg	3.04	3.01
Na	4.55	4.57
K	0.30	0.30
Fe(2)	0.26	0.26
Fe(3)	0	0
Mn(2)	0.02	0.02
Mn(3)	0	0
Cl	7.35	7.44
C(4)	12.47	11.15
C(-4)	0	0
S(6)	5.65	5.66
S(-2)	0	0
N(5)	0	0
N(3)	0	0
Ammonium	0.12	0.12
pH	7.07	6.72
Aerobes/denitrifying bacteria[b]	NA	10^{-7}
Iron/sulphate-reducing bacteria[b]	NA	10^{-7}
calcite	NA	14440
ferrihydrite	NA	180
pyrite	NA	240

[a] except pH

[b] assumed concentrations

5.3.2.5 Model calibration and scenario modelling

A manual model calibration was carried out for all remediation stages by adjusting rate constants and other parameters (Table 5.4) in order to reproduce the mass flow rates derived from the IPTs. Visual comparison between simulation results and observed data served as constraint during calibration. Thereby a separate manual calibration was carried out for each of two alternative conceptual models: (i) assuming pyrite to be present and (ii) pyrite to be absent in the aquifer. During calibration it was found that the maximum degradation rates were by far the most sensitive parameters. Pre-modelling indicated that the half saturation constants and X_{max} were least sensitive, which was in agreement to previous modelling studies (e.g., Watson et al., 2003;

Greskowiak et al., 2005, 2006). Therefore these parameters have been set constant to typical literature values and were not further adjusted during calibration. Once the two conceptual models were calibrated, subsequent scenario modelling was carried out to study the efficiency of two types of remediation scenarios. Scenario A represents a model that incorporates a groundwater circulation well that aerates the aquifer via H_2O_2 injection without interruption for a total period of two years (cf. Table 5.5). In contrast, Scenario B assumes an alternating bimonthly H_2O_2 injection/no injection period, each period lasting one month, also over a period of two years (cf. Table 5.5). The latter scenario was used to test the hypothesis if the neo-precipitated (amorphous) iron found close to the groundwater circulation well during H_2O_2 injection could potentially be used by anaerobic bacteria during injection-free periods, thus allowing degradation to proceed in the absence of a direct supply of oxygen. The injection times during the field experiment, selected by Trötschler et al. (2008), were determined by operational constraints and the technical limits of the groundwater circulation well. In scenario B two stages of injection (as in the experimental stages II and IV) were separated by a stage in which injection was interrupted (as in the experimental stage III) (cf. Table 5.1). The effectiveness of scenarios A and B on contaminant degradation are compared and discussed.

The uncertainty in modelled aerobic biodegradation in these two scenarios due to the unclear presence of pyrite at the site was evaluated by considering four different cases during the scenario modelling (cf. Table 5.5 and 5.6) using the two calibrated conceptual models (i.e., with and without pyrite):

- *Case 1*: The model is calibrated under the assumption that pyrite is absent in the aquifer. The subsequent scenario simulations consider that indeed the aquifer does not contain pyrite in “reality”.
- *Case 2*: The model is calibrated under the assumption that pyrite is absent in the aquifer. However, the subsequent scenario simulations consider the case that in “reality” pyrite is present.
- *Case 3*: The model is calibrated assuming that pyrite is present. The subsequent scenario simulations consider that the aquifer does also contain pyrite in “reality”.
- *Case 4*: The model is calibrated assuming pyrite is present. However, the subsequent scenario simulations consider the case that in “reality” the aquifer does not contain any pyrite.

Table 5.4: Estimated values of adjustable reaction model parameters (Monod half saturation constants (K), bacterial concentration (X), maximum degradation rates (r), decay rates (V), exponents of pyrite oxidation (exp), for details please refer to text) during calibration of models, with and without pyrite, and parameter values reported in the literature

parameter	unit	value	Literature values	References[a]
K_{ox}	[mol/L]	$1*10^{-4}$	$^{b}0.9*10^{-4}, 1*10^{-6}, 1.2*10^{-5}, 1*10^{-4}$	1, 2, 3, 4
$K_{Fe(OH)3}$	[mol/L]	$1*10^{-4}$	$^{b}\ 1.9*10^{-4}, 1*10^{-6}, 1.1*10^{-5}, 1*10^{-4}$	1, 2, 3, 4
$K_{Sulphate}$	[mol/L]	$1*10^{-4}$	$^{b}\ 1.03*10^{-4}, 1*10^{-6}, 2.2*10^{-3}, 1*10^{-4}$	1, 2, 3, 4
K_{NH4+}	[mol/L]	$1*10^{-4}$	$^{b}\ 1.1*10^{-4}$	1
$K_{Ace}/\ K_{Mbf}/\ K_{DMbf}$	[mol/L]	$1*10^{-4}$	$^{b,c}\ 1.44*10^{-4}, 10^{-6}, 2*10^{-2}, 10^{-4}$	1, 2, 3, 4
X_{max}	[g/L]	1.13	$0.68, 1.2, 10, 50, 17.6^{d}$	1, 7, 6, 8, 9
r_{ox_Ace}	[1/d]	12	$^{b}\ 9.69, 3, 0.1, 10^{-3}, 10$	1, 2, 3, 4, 5
r_{ox_Mbf}	[1/d]	12	$^{b}\ 9.69, 3, 0.1, 10^{-3}, 10$	1, 2, 3, 4, 5
r_{ox_DMbf}	[1/d]	7	$^{b}\ 9.69, 3, 0.1, 10^{-3}, 10$	1, 2, 3, 4, 5
r_{ox_Ace} *	[1/d]	32.22	-	-
r_{ox_Mbf} *	[1/d]	21.84	-	-
r_{ox_DMbf} *	[1/d]	10.35	-	-
$r_{Fe/Sulph\_Ace}$	[1/d]	3.86	$^{b}\ 0.47, 0.1/0.25, 0.1/0.1, 10^{-4}/10^{-4}$	1, 2, 3, 4
$r_{Fe/Sulph\_Mbf}$	[1/d]	2.75	$^{b}\ 0.47, 0.1/0.25, 0.1/0.1, 10^{-4}/10^{-4}$	1, 2, 3, 4
$r_{Fe/Sulph\_DMbf}$	[1/d]	2.31	$^{b}\ 0.47, 0.1/0.25, 0.1/0.1, 10^{-4}/10^{-4}$	1, 2, 3, 4
$V_{decay\_Aerobes}$	[1/d]	0.06	$^{b}\ 1.03*10^{-2}, 0.3, 10^{-2}, 10^{-6}, 7*10^{-2}$	1, 2, 3, 4, 6
$V_{decay\_Iron/Sulph.\ Reducers}$	[1/d]	0.01	$^{b}\ 1.09*10^{-2}, 10^{-2}, 10^{-2}, 10^{-6}$	1, 2, 3, 4
exp_{pyr_1}	[-]	1	0.5	10
exp_{pyr_2}	[-]	-0.8	-0.11	10
exp_{pyr_3}	[-]	-10.19	-10.19	10
exp_{pyr_4}	[-]	0.1	0.67	10

*model with pyrite

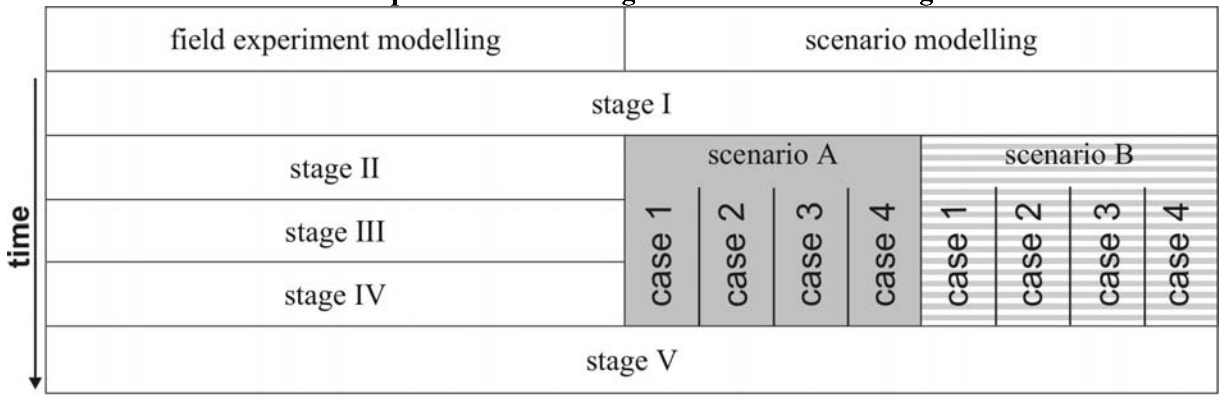
[a] References are 1, Greskowiak et al. (2005); 2, Schäfer et al. [1998]; 3, Schäfer [2001]; 4, Brun et al. [2002]; 5, MacQuarrie and Sudicky [2001]; 6, Kissel et al. [1984]; 7, Zysset et al. [1994] ; 8, Odencrantz et al. [1990]; 9, Rinck-Pfeiffer et al. [2000]; 10, Prommer and Stuyfzand [2005]

[b] Degradation constants refer to bulk DOC (references 1,4 and 5), lactate (reference 2) and xylene (reference 3)

[c] all K_{DOC}

[d] Derived from experimental data

Table 5.5: Overview of field experiment modelling and scenario modelling



field experiment modelling	scenario modelling							
stage I								
stage II	scenario A				scenario B			
stage III	case 1	case 2	case 3	case 4	case 1	case 2	case 3	case 4
stage IV								
stage V								

Table 5.6: Overview of four different cases during scenario modelling

case	calibrated with pyrite	pyrite present
1	**-**	**-**
2	**-**	+
3	+	+
4	+	**-**

5.4 Results and Discussion

5.4.1 Field experiment modelling

Both calibrated models (i.e., with and without pyrite) were able to reproduce the observed mass flow rates of the three investigated contaminants determined by the IPTs (Figure 5.4, results only shown for the model assuming no pyrite in the aquifer). The simulation of Stage I mimics the conditions before the start of the remediation activities. During this period anaerobic microbial degradation causes a 12% to 32% decrease of the contaminant mass flow rates between control planes CP2 and CP2-3. In the model acenaphthene, methylbenzofurans and dimethylbenzofurans oxidise partially while simultaneously using amorphous iron oxides and sulphate as electron acceptor. Due to the rather slow rate of degradation (cf. Table 5.2) the geochemical changes induced by the degradation are not very pronounced. No noticeable decrease in modelled SO_4^{2-} concentrations was apparent and only a minor increase in ferrous iron concentrations occurs during stage I (Figure 5.5). An increase in pH occurs in response to the significant proton consumption that is associated with the reduction of amorphous iron oxides (results not shown). The simulated growth of anaerobic bacteria (results not shown) is slow and consequently it takes approximately four years until steady state mass flow rates are established.

Stage II and IV describe the O_2 and H_2O_2 injection phases, respectively, separated by an intermission phase (stage III) during which no oxygenation takes place. The model results, especially the minimal decrease of contaminant mass flow rates and an only insignificant increase in aerobic bacteria, suggest that the duration of Stage II was too short and that the injected oxygen capacity was insufficient to create a lasting effect on the oxidation state of the groundwater and sediments and thus on contaminant removal. However, during stage IV the aquifer zones that became sufficiently exposed to the injected oxygen were able to facilitate the growth of aerobic degraders, associated with a faster degradation of the contaminant compared to anaerobic degradation. In the model simulations the dissolved oxygen in the injectant is primarily used to oxidise the contaminants. However, it is also consumed by the oxidation of dissolved ferrous iron (Figure 5.5). The aerobic degradation is accompanied by a decrease in pH (results not shown) due to the proton formation that is indicated by Eq. (1).

Stage III and V represent periods where anaerobic conditions are re-established while no further O_2 or H_2O_2 is injected and iron reduction once again becomes the dominant electron accepting process. The degradation efficiency, is, however, hampered by the abruptness of the shift, i.e., the time-scale of the operational changes is shorter than the predicted time-scale for (re-)adaptation of the microbes. This then leads to a sudden increase in the contaminant mass flow rates as soon as the oxygenation of the aquifer becomes interrupted at the beginning of stages III and V respectively (Figure 5.4).

Despite the high variability in point scale concentration measurements that were observed prior and during the remediation (as shown for Fe und SO_4 in Figure 5.3), which is attributed to the heterogeneity of the subsurface (Herfort, 2000) and the irregular distribution of contaminants within the source zone, it is possible to discern a general trend of decreasing contamination levels once the remediation enters stage IV (H_2O_2-injection). On the other hand, the magnitude of the observed major ion variability makes the distinction between changes induced by either anaerobic or aerobic degradation and the natural background fluctuations rather difficult. The majority of the modelled ferrous iron concentrations fall within the range of the observed (IPT-)values and their sampling and methodological error. Concentrations of SO_4^{2-}, pH, Ca^{2+} and HCO_3^- also show no discernible trend in the field that could be unanimously attributed as being a geochemical response to or indicator of contaminant degradation.

Overall the parameter values that were employed for the present simulations (Table 5.4) are fitting reasonably well into the range found by comparable studies. Interestingly the calibrated degradation rate constants for aerobic and anaerobic degradation (r_{ox} and $r_{Fe/Sulph}$) for the individual contaminants differ less than expected. However, this can probably be attributed to the generally rather low effectiveness of the remediation measure (cf. Table 5.2). On the other hand, the differences between the aerobic rate constants for the model calibration with and without pyrite (cf. Table 5.4 and Table 5.6, and see also below) are quite striking, and they indicate that the presence of pyrite has a major effect on model simulations and the associated uncertainty.

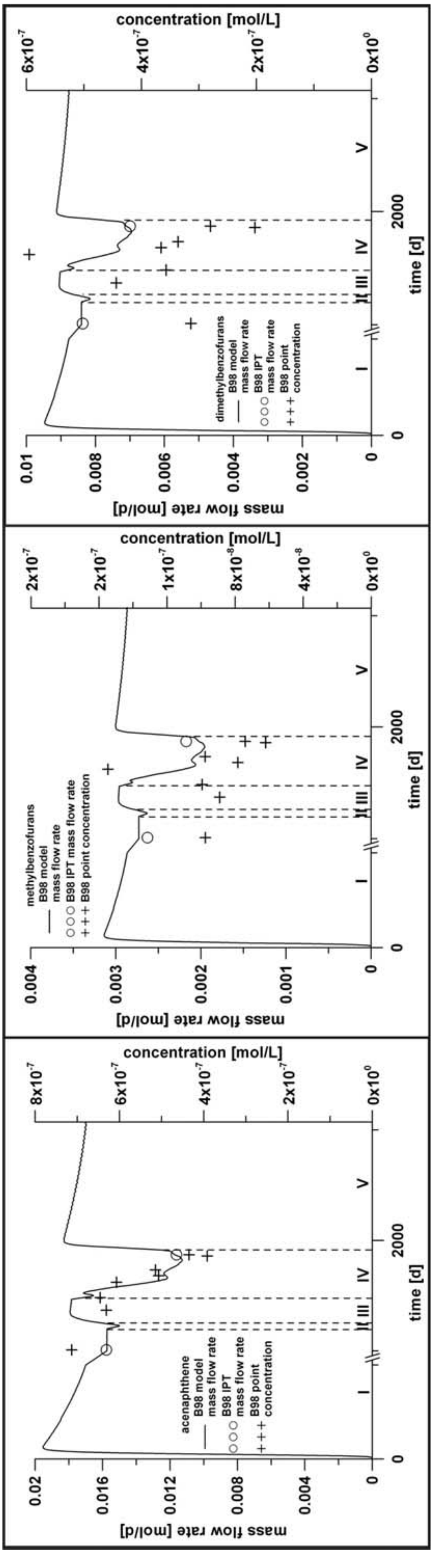


Figure 5.4: (left) Comparison of model results of mass flow rate for main contaminants (acenaphthene, methylbenzofurans, dimethylbenzofurans) with measured field (IPT) mass flow rate at well B98. Additionally, point scale concentrations are provided to show their variability (concentration ordinate at right). Roman numerals refer to different stages of remediation (cf. Table 5.1).

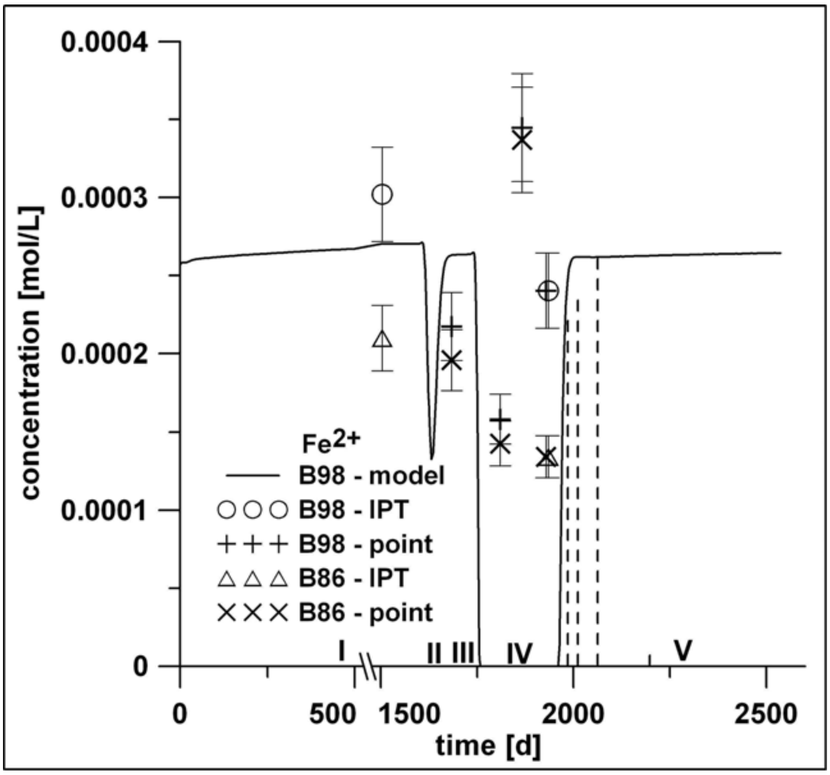


Figure 5.5: Comparison of concentration model results for ferrous iron with measured concentration data (IPT and point measurements) at well B98 and B86, including the relative methodological standard deviation (± 10 %). Roman numerals refer to different stages of remediation (cf. Table 5.1).

5.4.2 Remediation scenarios

Reactive transport modelling offers the possibility to explore a variety of remediation design parameters such as injection durations, injection rates and reactant concentrations. For example, a discontinuous injection of electron acceptor capacity may offer the possibility of an indirect enhancement of the natural ability of the aquifer to degrade contaminants. To illustrate the investigation of remediation scenarios the calibrated reactive transport model of the present site was used to simulate two remediation scenarios that eventually lead to very different results.

Figure 5.6 shows the difference between simulated methylbenzofurans concentration at well B98 between the two scenarios considered here (constant injection, scenario A, and bimonthly, scenario B) using *Case 1*. The simulated bimonthly injections are shown to be too short to aerate the groundwater sufficiently to improve aerobic degradation in the long run.

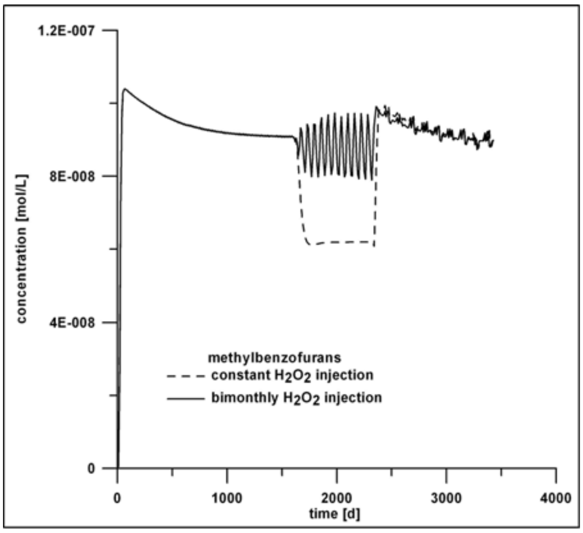


Figure 5.6: Comparison of methylbenzofurans concentration at well B98 due to constant and bimonthly H_2O_2 injections

For methylbenzofurans the difference in the decrease of contaminant mass between both scenarios during the injection period(s) is considerable. While in the constant injection scenario the average reduction in the concentration of methylbenzofurans due to degradation was 0.26 mg/L, only 0.03 mg/L were on average degraded during the bimonthly injection (referenced to a no-action scenario). While the modelled precipitation of amorphous iron oxides in principle increases the oxidation capacity of the zone surrounding the injection well, it appears that during the injection interruptions it remains unused as an electron acceptor. This is because the predicted microbial lag time for anaerobic degraders is too long relative to the proposed length of the interruption. As indicated in Figure 5.6, the average concentration levels are predicted to remain higher in the case of the interrupted injection, compared to a continuous injection scenario, which can mostly be attributed to the lower efficiency of the anaerobic degradation processes. The other contaminants (acenaphthene and dimethylbenzofurans) behave in a similar fashion. The simulations suggest that unless the contaminant release is reduced, e.g., by source removal, or unless bacterial activity (under anaerobic conditions) can adapt more quickly to changing hydrochemical conditions, only a constant or prolonged injection will lead to significant mass removal and a measurable improvement of the downstream groundwater quality.

5.4.3 Impact of presence of pyrite

Applying the four different cases (Table 5.6) to both injection scenarios A and B demonstrates the uncertainty in the model results with respect to the consideration of reactive, reduced sediments such as pyrite. The differences in the calibrated aerobic rate constants for the model with and the one without pyrite (Table 5.4) provide a good indication of the influence of an additional competitor for oxidation capacity on the degradation of the target contaminants. This can be seen in Figure 5.7, which presents the concentration of dimethylbenzofurans in each of the four cases for the constant injection scenario.

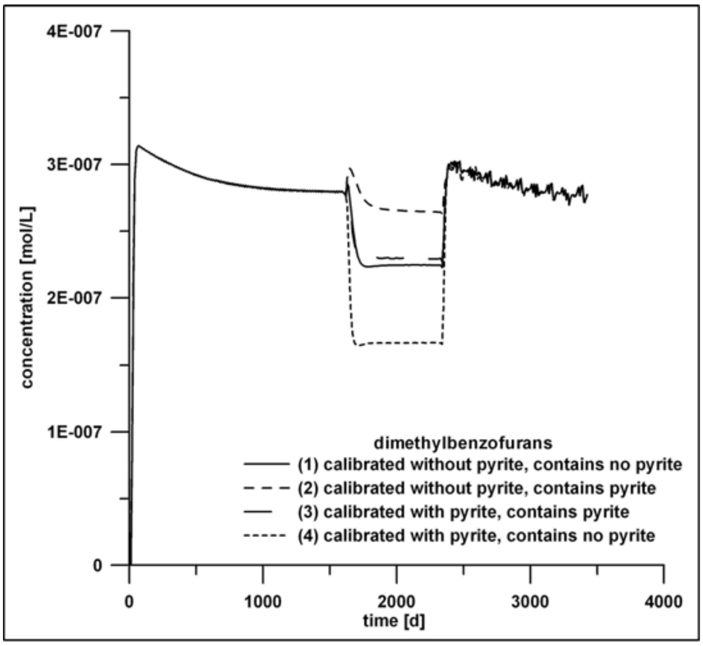


Figure 5.7: Concentration of dimethylbenzofurans during scenario A (constant injection) for four different cases at well B98

Case 1 (calibrated without pyrite, contains no pyrite in the scenario) and *Case 3* (calibrated with pyrite, contains pyrite in the scenario) can be considered as models where prior knowledge about the aquifer is adequately implemented in the model. The slight difference between the simulated concentrations of *Case 1* and *Case 3* can be attributed to differences in calibration results. *Case 2* (calibrated without pyrite, contains pyrite in the scenario) and *Case 4* (calibrated with pyrite, contains no pyrite in the scenario) represent the uncertainty that arises when knowledge about the aquifer either does not exist or is disregarded, and an inadequate conceptual hydrochemical model setup is selected. *Case 2* underestimates the aerobic degradation of dimethylbenzofurans by about 66 % and *Case 4* overestimates the same process by around 155 %. The uncertainty for the other two contaminants is equally significant: acenaphthene and methylbenzofurans concentrations were underestimated by 86 % and 83.3 %, respectively, for *Case 2*, and acenaphthene and methylbenzofurans concentrations were overestimated by 123 % and 125 %, respectively, for *Case 4*. The ferrous iron concentrations for the four cases using scenario A are not influenced by the calibration of the model but only by the presence of pyrite. In the case that pyrite is not present (*Case 1* and *Case 4*), all dissolved ferrous iron is oxidised (cf. Figure 5, stage IV), in the opposite case where pyrite is implemented in the model (*Case 2* and *Case 3*), oxygen is consumed by both pyrite oxidation and ferrous iron oxidation leaving too little oxygen for complete ferrous iron oxidation (results not shown).

Figure 5.8 presents the cumulative mass of acenaphthene for the four different cases during constant and bimonthly injection (scenarios A and B, respectively), transported across CP 2-3 within the extent of the whole plume width, approximately 94 m. Changes in mass accumulation over time can only be observed during the injection period(s) between day 1600 and 2330. Constant injection leads in all four cases to a decrease in mass accumulation, while intermittent bimonthly injection leads to an increase in contaminant mass accumulation (Figure 5.8 a-d). During the proposed bimonthly injection, anaerobic bacteria decay when dissolved oxygen is injected and start to grow again once injection is interrupted. However, these latter phases are too short for full recovery of the anaerobic bacteria population and transverse dispersion is too small to mix the aerobic water with anaerobic water from outside the plume to re-establish an anaerobic degradation zone downstream of the injection point within this limited time frame. When oxygen is injected, aerobic conditions are established but, once again the proposed injection cycle is too short to establish sufficient growth of aerobic bacteria. Constant injection, however, induces considerable growth of aerobic bacteria downstream of the injection well where aerobic degradation leads to a significant contaminant mass flow rate decrease at CP 2-3. The differences between *Case 1* (Figure 5.8 a) and *Case 3* (Figure 5.8 c) for constant and bimonthly injection are comparable. In both cases the accumulation of mass is slower during constant injection, whereby bimonthly injections leads to a faster accumulation. The latter leads to an increase of the total contaminant mass passing through the control plane. In comparison, *Case 2* (Figure 5.8 b) exhibits a contaminant mass accumulation similar to pre-remediation conditions during constant injection and an increase of the accumulation rate during bimonthly injections. The opposite occurs in *Case 4* (Figure 5.8 d), where bimonthly injections display a mass accumulation similar to that before the start of the injection, and a permanent injection leads to a slower accumulation of contaminant mass. It shows that the constant injection may change the aquifer chemistry more profoundly, which then results in a larger uncertainty if the conceptual model does not represent the situation in the field. The variation between the changes in mass accumulation of the other two contaminants (results not shown) is again directly proportional to the difference in degradation rates between the model calibrated with and the one without pyrite (cf. Table 5.4). These results highlight a pronounced sensitivity of the degradation efficiency to the presence of pyrite.

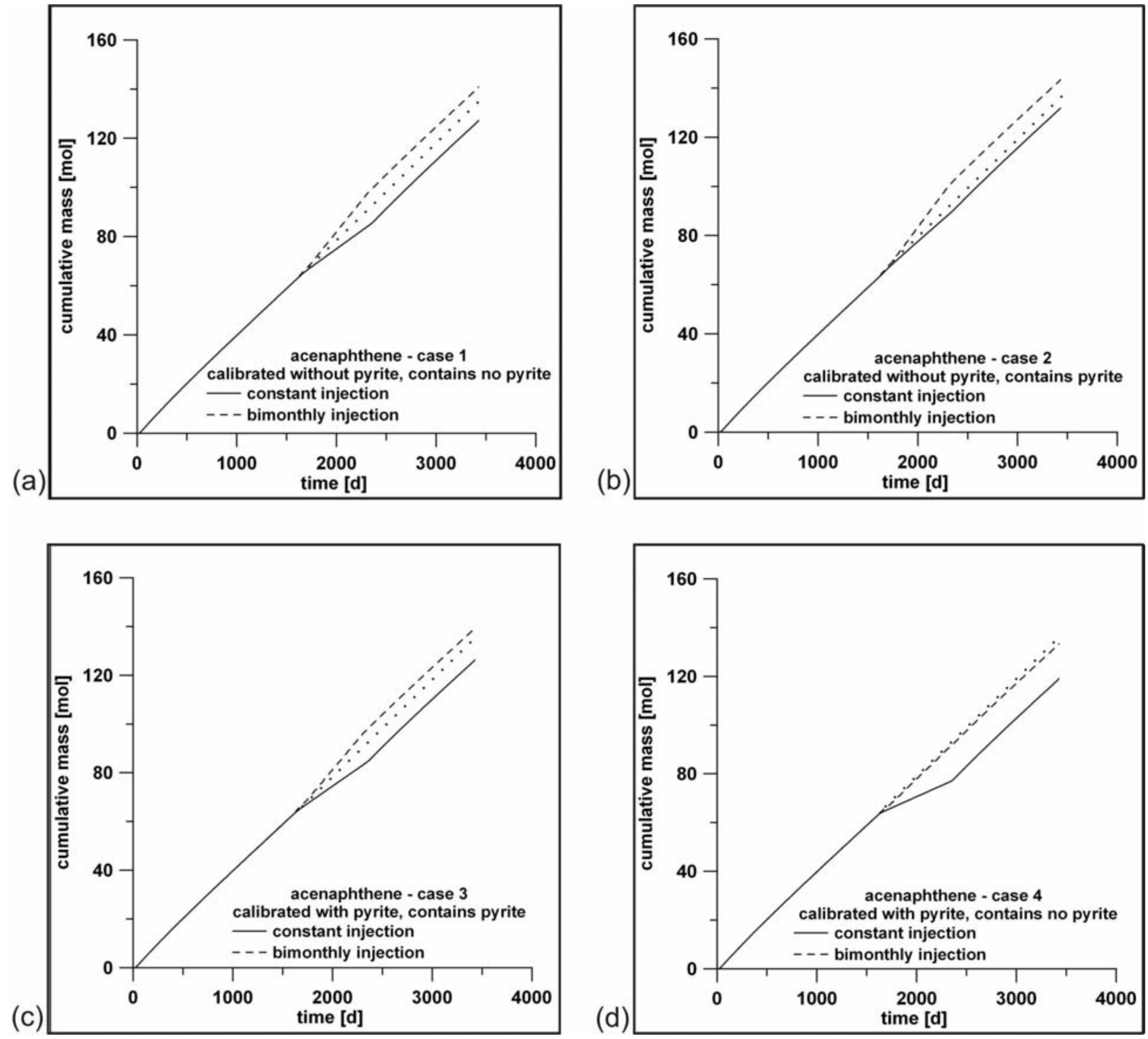


Figure 5.8: Mass accumulation of acenaphthene during constant and bimonthly injection for *case 1* (a, calibrated without pyrite, contains no pyrite), *case 2* (b, calibrated without pyrite, contains pyrite), *case 3* (c, calibrated with pyrite, contains pyrite) and *case 4* (d, calibrated with pyrite, contains no pyrite); dotted line represents no-action scenario

5.5 Conclusions

In this study we employed reactive transport model simulations to conceptually investigate the key biogeochemical processes that governed groundwater quality before and during a remediation experiment at a former gasworks site where O_2/H_2O_2 was injected using a groundwater circulation well. The calibrated model reproduces the major hydrochemical features and in particular the observed mass flow rate changes of the three investigated PAH compounds quite well. The ambiguous field data, which indicate substantial spatial and temporal variability of hydrogeochemical parameters, emerged as a substantial challenge for the modelling study. Eventually considerable uncertainty remained, specifically with respect to the effect of competing reactions with sediment bound reductants.

The calibrated model was used to explore the feasibility and efficiency of a limited set of remediation scenarios. In these scenario simulations the groundwater circulation well was operating for a total period of two years either in a constant or, alternatively, in a bimonthly alternating injection mode. The simulation results indicate that when a dynamic ENA scheme (e.g., alternating H_2O_2 injection) is employed or a consequence of operational constraints (e.g., well clogging), microbial lag times can be a crucially detriment to effectiveness. This suggests that if the contaminant flux released at the source is not clearly decreased, by at least a partial source removal, only constant injection of electron accepting capacity will lead to a noticeable improvement of groundwater quality.

Further, the simulations highlight the uncertainties that results from the insufficient characterisation of the hydrogeochemical heterogeneities. In particular, quantification of the reductive capacity of the sediment (Descourvieres et al., 2010) and detailed mineralogical analysis in an adequate spatial resolution is often not routinely employed during site investigations (Zhu et al., 2001), although extensive mineral reactions have caused the failure of remediation schemes in the past (Wood, 2000). Neglecting secondary reactions involving sedimentary reductants can lead to wrong assumptions for stoichiometric calculations and degradation rates during remediation design. To illustrate the effect of the reductive minerals on the effectiveness of the remediation scheme we carried out comparative simulations for two alternative conceptual models where pyrite, acting as a ‘model’ reductant, was either present or absent in the aquifer. For the investigated scenarios the calibrated aerobic degradation constants differed considerably between the two alternative conceptual models, as pyrite consumed a significant fraction of the injected oxidation capacity. This shows that enhanced natural remediation via O_2/H_2O_2 injection is highly sensitive to the reductive capacity of the aquifer, i.e., concentrations and reactivity of reductants such as pyrite or sedimentary organic matter.

Despite the numerous simplifications made in the conceptualisation and numerical modelling of microbial dynamics, the modelling study demonstrated the ability of a model-based analysis to detect key processes that can be crucial for the effectiveness of an ENA remediation scheme.

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Chapter 6

General conclusions and perspectives

Aquifers represent a readily available source of drinking water to a large proportion of the world's population. It is therefore vital to protect this resource also for future generations. This aim, however, is hampered by the lack of knowledge regarding these systems, caused by the heterogeneous distribution of sediments in the subsurface. Therefore hydrogeologists have developed specific methods in order to characterise these systems adequately. The application of these methods as well as the analysis and interpretation of the results can aid the interpretation of the current state of the system and help predicting possible effects of over exploitation and contamination scenarios. Field investigations are often obstructed by the presence of infrastructure leading to the implementation of often less than desired groundwater observation points. Integral investigation techniques offer a possibility to survey large areas while only installing and using a limited observation well network. The current work gives an indication where integral pumping tests offer advantages over the traditional point measurements. Integral investigation techniques have so far been hampered by the limited range of scenarios regarding the contaminant plume position. This work presents an approach to employ point measurements during the analysis of integral pumping tests to narrow down the plume position.

Mathematical models play an important role in simulating and understanding complex flow and transport phenomena of a hydrogeological system. Such an understanding is required before any human interference should take place. One of the biggest threats faced by drinking water resources is contamination caused by leaking landfills or underground storage tanks. Enhanced Natural Attenuation (ENA) offers a possibility to alter at least parts of the system to improve water quality possibly even back to background concentrations. This, however, often affects more parts of the system than intended leading to possibly adverse effects, therefore making a thorough understanding of the processes involved essential.

A comparison of mass flow rate estimates based on point scale and integral measurements

This comparison between contaminant mass fluxes based on integral pumping tests and the interpolation of point measurements showed that the distribution of contaminants in the subsurface can increase the uncertainty in mass flux estimates even when concentration point measurements are taken in high resolution. This uncertainty increases with the degree of heterogeneity of the contaminant distribution. This is due to the fact that parts of the contaminant plume might be missed or single high concentrations might be used for interpolation over large areas that actually might be characterised by lower concentrations. A possibility to improve the reliability of concentration point measurements could be to increase the number of measurements horizontally as well as vertically. However, infrastructure restrictions as well as increased costs might hamper such developments. Integral pumping tests can offer a possibility to estimate contaminant mass fluxes even in rather inaccessible areas. The estimation of mass fluxes can then be aided by the implementation of a flow and transport model, where the existing control planes as well as the heterogeneous hydrogeochemical distribution can be simulated. The reduction in uncertainty is especially valuable when evaluating the current state of the system, during the planning and implementation of ENA measures, when prioritising contaminants and when assessing the effectiveness of already existing remediation measures.

Conditioning of the numerical inversion of concentration-time series

Applying integral pumping tests to several control planes situated downstream of one another and using them to estimate contaminant mass flow rates allows to roughly determine the position of the plume as well as the natural attenuation rates. However, the IPTs could up to now be analysed for three separate scenarios only: the plume is situated to the left of the well, to the right of the well or is distributed symmetrically around it. Though the contaminant mass flow rate estimates are very reliable due to the integrating nature of the method, a clearer picture of the plume position might be especially valuable when remediation measures are considered and source zone-plume interactions are studied. The presented approach that employs point-scale concentration measurements, taken, e.g., from direct-push wells, to condition the numerical IPT inversion solution, can aid in narrowing down the plume position. It thereby reduces the non-uniqueness of the inverse determination of contaminant mass flow rates. When comparing the unconditioned results with the conditioned results, the plume centre can be narrowed down, however, additional information is necessary at the western fringe to lead to even more precise statements. These results would be valuable information if backtracking methods are employed. These aim to delimit the source of the contamination where a reliable estimation of contaminant mass flow rates and concentration distributions at control planes as well as the narrowed down plume position would be very useful.

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Modelling of a remediation measure and subsequent biogeochemical changes

The contaminant mass flow rates are then implemented in a reactive transport model of the test site to use the contaminant distribution prior to and after the implementation of an innovative remediation measure as boundary conditions. With the help of this model, the proposed biogeochemical processes before and during a remediation where H_2O_2 was injected using a pilot-scale groundwater circulation well could be confirmed. Processes such as microbial degradation of contaminants are most often non-linear and the presented framework could reproduce the observed changes quite well. This modelling study has shown that the heterogeneity of the system under investigation and represented by the model might be critically different from the average sampling volume. Samples taken at the current study site have shown large variability concerning hydrochemical components, which could only be represented in the model to a certain degree. This variability could be due to factors, such as upwelling from lower aquifers, which were not taken into account during modelling. The pilot-scale groundwater remediation well is not able to supply constant injections over long time spans, however, assuming an improved circulation system, two scenarios of injection were then simulated and compared: constant and bimonthly injections over a period of two years. The results showed that without source treatment only constant injections would lead to an improvement of groundwater at the site.

An aquifer component, like the mineral pyrite, consumes oxidation capacity and affects the model results quite dramatically. As pyrite was found outside of the current model area it was implemented in the model. The results showed contaminant mass flow rates to be strongly affected. In the case of bimonthly injection, the contaminant mass flux was even increased compared to the scenario where no H_2O_2 was injected, as bacterial growth during anaerobic phases was too slow and transverse dispersion was not sufficient to establish conditions comparable to the pre-remediation phase. Additionally, constant injection showed greater uncertainty in contaminant mass fluxes compared to bimonthly injections due to the large impact the former has on the aquifer. Such an increase in uncertainty should be taken into consideration when studying and possibly even attempting to influence a possibly under-characterised groundwater system.

Further perspectives

Characterisation of aquifers is still hampered by their heterogeneity and inaccessibility. Therefore, most investigations will require the combination of several methods. Coupling integral pumping tests with concentration point measurements appears to be a promising approach to gather reliable data on contaminant mass flow rates as well as narrowing down the plume position. Concentration point measurements alone should be primarily used to obtain an overview of the contamination situation at a site, especially if the heterogeneity of the aquifer is unknown and funds are too restricted to implement a dense monitoring network. Many sites are usually already equipped with a small number of groundwater wells which can be used for a first assessment, however, later on contaminant mass flow rates should be estimated using integral pumping tests.

Additionally, the narrowed down plume combined with reliable mass flow rates estimates along with knowledge about the degradation mechanisms involved are an excellent basis for delimiting the source by applying backtracking techniques. These degradation pathways as well as other hydrogeochemical processes can be studied by employing a reactive transport model of the site. A better understanding of the processes at such sites could also be achieved when utilising isotope-based techniques that can help clarifying the relevant degradation processes. Though laboratory data forms a good basis for such studies, quite often processes proceed differently on other scales. Reactive transport models offer an unprecedented insight into the biogeochemical evolution of a site characterised by geological as well as hydrochemical heterogeneities.

Appendix

List of publications authored or co-authored by me and related to the current work

Journals

Herold, M., Ptak, T., Bayer-Raich, M., Wendel, T., Grathwohl, P. (2009) Integral quantification of contaminant mass flow rates in a contaminated aquifer: Conditioning of the numerical inversion of concentration-time series. Journal of Contaminant Hydrology, 106(1-2), pp. 29-38.

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Submitted

Herold, M., Greskowiak, J., Ptak, T., Prommer, H., Grathwohl, P. (2009) Modelling of a remediation measure and subsequent biogeochemical changes at a former gasworks site in Southern Germany.

Extended abstracts

Herold, M., Ptak, T., Prommer, H., Greskowiak, J., Wendel, T., Grathwohl, P. (2008) Process-oriented Reactive Transport Modelling of Heterocyclic Hydrocarbons at a former Gasworks Site in Southern Germany. MGP Europe, 4.-6- März 2008, Dresden, Germany:255-261.

Abstracts

Herold, M., Ptak, T., Prommer, H., Greskowiak, J., Wendel, T., Grathwohl, P. (2008) Reaktive Transportmodellierung heterozyklischer Kohlenwasserstoffe im Grundwasser eines ehemaligen Gaswerks in Süddeutschland. In: SDGG – Schriftenreihe der Deutschen Gesellschaft für Geowissenschaften, Heft 57, Grundwasserressourcen – Charakterisierung, Bewirtschaftung, Prognosen. Tagung der Fachsektion Hydrogeologie in der DGG (FH-DGG) (Kurzfassungen der Vorträge und Poster), Göttingen, 21.-25. Mai 2008:52.

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Reports

Ptak, T., Grathwohl, P., **Herold, M.**, Wendel, T., Piepenbrink, M., Dietze, M., Tiehm, A., Sagner, A., Schulze, S., Koschitzky, H.-P., Haslwimmer, T., Trötschler, O. (2008) Förderschwerpunkt 'KORA' Themenverbund 2, Projektverbund 2.4 'ENA' "Enhanced Natural Attenuation" zum In-situ-Abbau von heterozyklischen Kohlenwasserstoffen. Abschlußbericht, BMBF Förderkennzeichen 02WN0361, 02WN0362 und 02WN0363, 274 pp.

Ptak, T., Grathwohl, P., **Herold, M.**, Wendel, T., Piepenbrink, M., Dietze, M., Tiehm, A., Sagner, A., Schulze, S., Koschitzky, H.-P., Haslwimmer, T., Trötschler, O. (2006) Förderschwerpunkt 'KORA' Themenverbund 2, Projektverbund 2.4 'ENA' "Enhanced Natural Attenuation" zum In-situ-Abbau von heterozyklischen Kohlenwasserstoffen. Zwischenbericht, BMBF Förderkennzeichen 02WN0361, 02WN0362 und 02WN0363, 66 pp.

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