Interpreting Multiple Environmental Tracer Data with a Groundwater Model in a Perialpine Catchment

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Abstract

Environmental tracers are isotopic and chemical compounds which have been increasingly used in hydrological sciences to investigate the water cycle. Early studies in the seventies demonstrated the potential of environmental tracers also in groundwater investigations in providing information about groundwater age, travel times, streamline information, ratio of fluxes and recharge rates. Compared to artificial tracer tests over short time scales, transient environmental tracers released into the atmosphere since the early fifties provide a tool to investigate the groundwater flow and transport over time scales of up to 50 years.

A case study for the environmental tracers Tritium (³H), Helium-3 (decay product of ³H) and Krypton-85 in a small catchment in Northern Switzerland, near Baltenswil, is presented. It contains a sandy-gravel aquifer with groundwater residence times of two to fifteen years. Its small size (9 square kilometers) and its hydrogeology being well known, thanks to former groundwater investigations and local artificial tracer test campaigns, make this aquifer an excellent test site for environmental tracer modeling. During the years 2003 to 2006 a new sampling campaign, undertaken by EAWAG Dübendorf and IPB Bern for the present study, provided a new set of Tritium, Helium-3 and Krypton-85 data. In particular, Krypton-85 data show at some locations significant variations on a seasonal timescale without an apparent trend. Integrating the information coming from different tracers into a groundwater modeling effort is the main intention of this thesis.

Following a method from Gomez-Hernandez (1991), the transmissivity field is stochastically modeled. The groundwater flow model is identified by means of Stochastic Inverse Modeling in a transient regime. Available transient hydraulic head data together with local measurement of transmissivities (T) are used for calibration of the T-field, performed with the code INERTO (Hendricks-Franssen, 2001). The evaluation of the aquifer recharge by precipitation and discharge via drains (natural springs) is performed through comparison of the calculated and measured time-varying hydraulic heads after the inversion procedure. Despite a complete lack of knowledge about the aquifer's natural discharge rates, a fair reproduction of the observed water table variations for the last ten years is obtained. Stochastic inverse modeling allows a reliable estimate of the water budget of the aquifer system and selecting the ensemble of possible T-fields governing the real but unknown transient flow field. A number of equally-likely T-realizations honoring both T and time-varying head measurements are generated. The calibrated T-fields share common pattern features. Considering an ensemble of T-realizations,
which reproduce the head measurements, allows setting the calibration problem into
the framework of uncertainty assessment of predictions.

Following a study from Cook and Solomon (1995), the impact of the spatially-variable,
thick unsaturated zone (> 10 m) is investigated by means of a numerical solution to
the vertical advection-dispersion equation (ADE). The environmental tracers pass the
unsaturated zone either advectively ($^{3}$H), or by diffusion ($^{3}$He and $^{85}$Kr). Starting from
the more or less known tracer concentrations in the atmosphere, a numerical solution of
the vertical ADE in an unsaturated homogeneous porous medium is used to calculate
the tracer input to the saturated zone at different groundwater table depths. Sensitivity
analysis shows that the gas-phase effective diffusion coefficients (including physically
related quantities such as gas-phase tortuosity and saturation conditions) and the mea-
sured atmospheric tracer input function are the most sensitive parameters with respect
to the tracer concentrations at depth.

The behavior of environmental tracers in the saturated zone is investigated by using
selected calibrated T-fields as input into a deterministic transport model and by making
use of the tracer input history calculated at the groundwater table. Effects of tracer
transport in the saturated zone at the observation locations are simulated via the mod-
ule MT3DMS (Zheng, 1990) in Processing Modflow (Chiang and Kinzelbach, 2001) for
each transmissivity realization. The transport simulation results are in general fair and
can well reproduce the tracer data at most observation locations. However, the model
can account for only 20% of the amplitude of the high-frequency oscillations in Krypton-
85 concentrations observed at the pumping station Baltenswil. A range of possible alter-
native explanations are sought and analyzed for this unusual behavior of Krypton-85
data. Short term variations of the recharge rate (three days) and of the actual pumping
rate (over one day) can account for a further 10% each of the concentration fluctuations
amplitudes. Older water components are identified possibly coming from the unsatu-
rated hilly boundary of the domain. Tritium data are also fairly well reproduced by model
simulations. Daughter-product Helium-3 simulations instead largely overestimate the
observed concentrations at most locations. Helium-3 loss mechanisms are therefore
investigated to account for the model/data discrepancy. In particular, the model im-
plementation of Helium-3 back-diffusion to the atmosphere via the groundwater table
significantly reduces the above-mentioned discrepancy of up to 70%. Differential diffu-
sion of Helium-3 in less permeable soil lenses is also implemented but does not bring
the desired reduction, due to the nearly steady-state of Tritium and Helium-3 concen-
trations established in the groundwater in the last five and more years. This result is
found in agreement with Labolle and Fogg (2001).
Transmissivity does not play the expected primary role in determining the fate of tracers due to the small ratio between the groundwater residence times and the travel times in the unsaturated zone. Other parameters have a larger impact on uncertainty of tracer simulated time series in the groundwater: effective diffusion coefficient, atmospheric input function and saturated porosity. Local knowledge of these parameters is, although difficult to obtain, highly desirable, in order to reduce the associated uncertainty on model predictions. Environmental tracers can contribute to uncertainty mitigation by updating of the conceptual model following experimental evidence (Helium-3). They can provide additional information about the possible origin of water samples (Krypton-85). They can offer a useful validity cross-check (Tritium). In particular, gas tracers will be most useful in aquifers where groundwater residence times are larger than the travel times in the vadose zone. A combination of several tracers may make their application to groundwater investigations more reliable. Their integrated use allows separating the focus on different phenomena in the subsurface dynamics and provides information on water movement at different spatial and temporal scales. Especially in areas with spatially variable unsaturated zone thickness, this can only come at the price of new sources of uncertainty on the transport-related parameters. Finally, the chosen stochastic approach has the considerable advantage of naturally including the quantification of uncertainty in the model predictions.
Zusammenfassung


Der Einfluss des räumlich variablen mächtigen ungesättigten Bereichs (> 10m) wird analog zu Cook und Solomon (1995) mit Hilfe einer numerischen Lösung der vertikalen Advektions-Dispersionsgleichung (ADE) untersucht. Die Umwelttracer passieren die ungesättigte Zone entweder durch Advektion ($^3$H) oder durch Diffusion ($^4$He und $^{85}$Kr). Ausgehend von mehr oder weniger gut bekannten Tracerkonzentrationen in der Atmosphäre wird die numerische Lösung der vertikalen ADE dazu verwendet, den Tracerinput in die gesättigte Zone für verschiedene Grundwasserstände zu berechnen. Sensitivitätsanalysen zeigen, dass der effektive Diffusionskoeffizient für die Gasphase (enthält physikalisch relevante Eigenschaften wie Tortuosität und Sättigungsgrad) und der gemessene atmosphärische Tracerinput die sensitivsten Parameter in Bezug auf die Verteilung der Tracerkonzentration über die Tiefe sind.


alla Manu

e

al mio unico fratello

Un pensiero molto carino...
Il giorno che io esco di prigione
il mio unico fratello mi viene a prendere
con una macchina della polizia.

Jake
...La fortuna dell’acqua è che va sottoterra.

*Il Benzi*
Chapter 1

Introduction

In the context of water resources management, groundwater modeling is of primary importance. Models are needed to interpret observation data and, most importantly, to predict the effects of anthropogenic inputs (change in land use, in hydrological and hydraulic regimes, inputs of pollutants). This is done in order to evaluate whether the present situation in a catchment or watershed is sustainable both in terms of water quantity and quality and second, to test which type of measures are required to achieve sustainability.

The groundwater asset becomes crucial when the focus is on drinkable water. Protection measures have to be pursued to secure water quality and guarantee control on water pollution. Hydrogeologists, physicists, engineers, chemists, natural scientists, sociologists and economists are bringing contributions to the issue of the sustainable exploitation of the groundwater resource. In assessing the groundwater resources of any region from the hydro-geologist's point of view, knowledge of the water balance is as vital as the knowledge of parameters such as the porosity and permeability of the rocks or sediments, to mention a few, allowing and regulating the water movement in the subsurface. Management strategies and the consequential decision making process can only be supported starting from a detailed knowledge of the hydro-geological system.

1.1 Groundwater models

Groundwater models attempt to interpret available data in a holistic way for understanding the actual functioning of aquifers. This interpretation has the scope of
testing the reliability of the model tool in successfully reproducing the actual state (observed/measured) and in making trustworthy predictions about future behavior of the system, when subjected to known external stresses (such as reduced precipitation, augmented extraction rates, or pollutant input from the external environment). The extraction of sensible information from the model results allows to evaluate whether the present situation in a catchment or watershed is sustainable both in terms of groundwater quantity and quality and second, to test which type of measures are required to achieve sustainability.

Groundwater models serve also for risk assessment in different-from-actual conditions or to design engineering measures for well protection purposes, as well as to plan a sustainable management of the subsurface water resource between competing market actors and water use such as farmers, households, industry and eventually nature. Remediation measures for polluted aquifers and risk assessment for a nuclear waste repository also call upon reliable groundwater modeling, the latter being undoubtedly the most challenging field for scientists since predictions are needed for timescales in the order of geological eras.

The modeling effort aims at a simplification of the complexity of the hydrogeological system through the development of a conceptual model towards the interpretation of the available sparse data. The model must be capable of linking interesting quantities - with regard to the system response to given external excitations- to measurable quantities. Modeling is necessary because of the relative inaccessibility of the system to be investigated. It provides a cheap alternative to systematic direct investigation through extensive measurement campaigns, whose costs would be unacceptably high. Besides, the long timescales (years, decades or even centuries) typical of groundwater systems also require modeling as a prediction tool.

1.2 Lack of knowledge

Generally speaking, models are a representation of the real system and its processes. The scientist first develops a conceptual model to account for how the system operates and which are the relevant processes to be represented. The physical idea is then given in quantitative terms through a mathematical model.
Groundwater hydrology provides well established theories for the description of water and solute movement in the subsurface. The equations governing the system dynamics are well known and have been thoroughly studied in the last seventy years. Yet, complexity problems arise when one wants to consider the study of a site-specific aquifer. The application of the physical equations governing the dynamics of a particular hydro-geological system requires a quantitative knowledge of parameters describing site-specific features - like geology, soil properties and climatic conditions. The aquifer properties are highly variable over space, reflecting the heterogeneous character of the subsurface structure. An exact knowledge of:

- soil and aquifer parameters such as permeabilities, storativity, porosity,...
- the location of the physical boundaries of the aquifer system
- the amount of water recharging the aquifer (recharge) and naturally leaving it (discharge),

is clearly impossible. The knowledge of these essential parameters numerically quantifying the aquifer properties is usually based on a set of field measurement. These are scarce, expensive, unevenly distributed over time and space and prone to sensible measurements errors. They can only provide the scientist a far-from-complete knowledge of the aquifer parameters. A reliable model requires a spatially detailed and varied data input on the process scale, which will never be available to a satisfactory extent.

Groundwater models can be divided in flow models - describing the movement of the water in the subsurface by piezometric heads (modeled quantity) and flow velocities (derived) - and transport models, where the modeled quantity is the solute concentration and the solute flux $j$ is derived. These models generally require the solution of partial differential equations based on mass conservation (a general principle), Darcy’s Law and Fick’s Law of diffusion, which are empirical statements relating quantities of interest (energy/momentum and mass fluxes) to measurable state variables (piezometric heads and solute concentration). The groundwater flow equation in 3-dimensions on the spatial domain $\Omega$ is

$$\nabla \cdot (K(x) \cdot \nabla h(x, t)) + q(x) = S_s(x) \frac{\partial h(x, t)}{\partial t}$$

where $\nabla \cdot$ is the divergence operator, $\nabla$ is the gradient operator, $K(x)$ is the hydraulic conductivity of the aquifer $[\text{m}^2/(\text{m}^2 \text{s})]$, $h(x, t)$ is the unknown piezometric head $[\text{m}]$, $q$ is
the source/sink term \([m^3/s]\), \(S_s(x)\) the specific storage coefficient \([m^{-1}]\) and \(t\) is time \([s]\). It describes the subsurface movement of water driven by piezometric heads \(h\) via the Darcy velocity field \(U = -K \nabla h\), given the initial and boundary conditions defined on \(\Omega\) and its boundaries \(\Gamma_1, \Gamma_2\) and \(\Gamma_3\).

- **Initial condition at time** \(t = 0\)
  \[
  h(x, t = 0) = h_0(x) \quad x \in \Omega
  \]

- **Prescribed head boundary**: hydraulic head \(h\) is independent of the groundwater flow (Dirichlet condition): \(h_1(x, t)\) is given
  \[
  h(x, t) = h_1(x, t) \quad x \in \Gamma_1, \quad \forall t
  \]

- **Prescribed flux boundary**: the hydraulic head gradient normal to the boundary is imposed (Neumann condition). No-flux boundary (physically impermeable layer) for \(f(x, t) = 0\)
  \[
  \frac{\partial h(x, t)}{\partial n} = f(x, t) \quad x \in \Gamma_2, \quad \forall t
  \]

- **Cauchy condition**: a linear combination of the hydraulic head and its gradient normal to the boundary \(n\) is imposed
  \[
  h(x, t) + \alpha \frac{\partial h(x, t)}{\partial n} = g(x, t) \quad x \in \Gamma_3, \quad \forall t, \quad \alpha \in \mathbb{R}
  \]

The 3-dimensional solute transport equation is

\[
\nabla \cdot (n D(x) \cdot \nabla c(x, t) - U(x) \cdot c(x, t)) = n \frac{\partial c(x, t)}{\partial t}
\]  

where \(D(x)\) is the effective hydro-dynamic dispersion coefficient \([m^2/s]\), \(c(x, t)\) is the unknown solute concentration \([g/m^3]\), \(U(x)\) is the Darcy velocity \([m/s]\) as derived by solving flow equation (1.1) and \(n\) is the porosity \([\cdot]\). The equation shows an advective term (flux: \([c \cdot U]\)) as well as a diffusive/dispersive one (\([D \cdot \nabla c]\)). Equation 1.2 is subject to the initial condition and boundary conditions on \(\Gamma_4, \Gamma_5\) and \(\Gamma_6\) (boundaries of \(\Omega\))
1.2. Lack of knowledge

- Initial condition at time $t = 0$

$$c(x, t = 0) = c_0(x) \quad x \in \Omega$$

- Prescribed concentration boundary: solute concentration $c_1$ is specified (Dirichlet condition)

$$c(x, t) = c_1(x, t) \quad x \in \Gamma_4, \quad \forall t$$

- Prescribed concentration gradient boundary: concentration gradient along the normal $n$ to the boundary is specified (Neumann condition)

$$n \left( \mathbf{D}(x) \cdot \nabla c(x, t) \right) \cdot n = f'(x, t) \quad x \in \Gamma_5, \quad \forall t$$

where $f'(x, t)$ is the dispersive flux normal to the boundary $\Gamma_5$. Non-dispersive mass flux boundary corresponds to $f'(x, t) = 0$

- Cauchy condition: a combination of the concentration and its gradient normal to the boundary $\Gamma_6$ is specified

$$(n \mathbf{D}(x) \cdot \nabla c(x, t) - U(x) \cdot c(x, t)) \cdot n = g'(x, t) \quad x \in \Gamma_6, \quad \forall t,$$

where $n$ is porosity, $n$ is the vector normal to boundary $\Gamma_6$ and $g'(x, t)$ is the total flux (dispersive and advective) normal to the boundary $\Gamma_6$. No-flux (impermeable) boundaries for $g'(x, t) = 0$.

The spatially variable physical parameters ($K$, $S_s$, $D$ and $n$) and the boundary conditions in equations 1.1 and 1.2 have to be identified for any site-specific study. The lack of knowledge about the parameters’ values on the field scale and the associated uncertainty is the most serious problem of groundwater modeling.
1.3 Uncertainty

Exact solutions of equations 1.1 and 1.2 can be obtained analytically only in few, highly idealized cases, assuming homogeneous physical parameters and very simple boundary conditions. Parameter heterogeneity and complex boundary conditions which are always met in real groundwater systems can only be dealt with by making use of numerical solution techniques.

Approximate solutions can be obtained by means of a convenient discretization in space and time (e.g. finite elements or finite difference schemes). Numerical algorithms for solving the two partial differential equations can be implemented in computer codes through a site-specific definition of boundaries and stresses. The resulting site-specific groundwater model is the demanded tool for managing the groundwater resource.

Can an approximate solution be reliable and useful for risk assessment and the consequential decision-making task? The very fact of solving approximated linearized equations involves numerical (computational) errors arising in the equation solving algorithm. Truncation errors (due to linearization) and numerical dispersion often arise, giving non-physical solutions. Yet, numerical errors do not usually constitute the most serious problem. The equation parameters are often defined with non sufficient accuracy. Lack of information about the geometry, aquifer parameters, inflow and outflow in the model domain reflect into poor characterization of the input data which may result in a complete inadequacy of the numerical solution in reproducing the observed actual state of the groundwater system. Conceptualization errors may also arise, since some relevant processes may not be included in the conceptual model, while inappropriate processes may be represented. The lack of knowledge about parameters and boundary conditions represents the most serious problem in the modeling effort.

Several sources of uncertainty are thus inherently present in any modeling. The most threatening one is the uncertainty in model physical parameters. Inherent heterogeneity of the subsurface porous media where flow and transport take place makes the characterization of relevant aquifer parameters a hard task. Measurement errors in the data are the norm. More importantly, measurement values are often scale-dependent. The amount of locally measured data is often extremely small if compared to the
spatial extension of the investigated domain. Interpolation errors of parameter values in locations where no measurement is available are unavoidable. Possible errors in the local data interpretation may also arise: where measurements exist, these reflect the conditions at the point of measurement and cannot be considered as representative of regional conditions. Inadequate knowledge of the geological and hydrogeological setting impairs the determination of the exact location and characteristics of the aquifer boundary conditions, with particular regard to boundary fluxes. Groundwater models capable of incorporating different sources of uncertainty in its predictions would be highly preferable.

1.4 Parameter identification

The need for a predictive tool is, as already mentioned, the first aim of groundwater modeling. A predictive tool’s reliability must first of all be tested. Once the hydrogeological setting has been defined and the physical parameters \( K(x), S_s(x), q(x), \) etc., and boundary fluxes have been estimated for the specific site, piezometric heads \( h(x, t) \) and solute concentrations \( c(x, t) \) can be calculated by numerical solutions of equations 1.1 and 1.2. This problem is known as the forward problem of groundwater modeling. A reliable characterization of the model parameters for a specific aquifer is yet fundamental for any meaningful solution of the forward problem.

The lack of sufficient input data concerning the parameters forced groundwater modellers to take a reverse point of view. Assuming that the former unknowns \( h(x, t) \) and \( c(x, t) \) are known and given by the available measured data, the model physical parameters can be treated as dependent variables in a new formal boundary value problem. In this way, parameters that well reproduce the observed data can be estimated by solving the groundwater flow and transport equation. The solution to this boundary value problem is known as the inverse problem of groundwater modeling. In this perspective, the issue of interest is the identification of spatially distributed parameter values: measurements on state variables (heads and concentrations) have to be reproduced by the model, by modification of the input data. The inverse modeler seeks for parameter sets that reflect his actual knowledge of the aquifer. From this point of view, the characterization of the aquifer structure through parameter estimation is the new challenge.
Chapter 1. Introduction

"The solution of the inverse problem is of paramount importance. Without a satisfactory solution of this problem, the solution of any forecasting problem, and hence also of any management problem which is based on it, remains in doubt" [Bear, 1979].

For sake of simplicity, hydrogeologists first tackled the inverse problem of groundwater flow. Because of its mathematical character (parabolic equation - purely diffusive) and the simpler fluxes involved, the flow equation is easier to solve than the transport equation, which shows instead a parabolic/hyperbolic character (advective/diffusive). Moreover, a reliable flow model is a necessary basis for transport modeling purposes. Flow models are often not accurate enough for prediction of solute transport. Transport usually takes place on smaller spatial scales and larger time scales than flow. Simulating transport will thus allow accounting for smaller spatial scale effects of water movement in the subsurface and investigating them on a larger time span if compared to flow simulations alone. Transport is much more strongly influenced by parameter heterogeneity, primarily the effective dispersion coefficient $D$. Fluxes also are more complicated, in that they consist of an advective, a diffusive and a dispersive part. A poorly characterized velocity field $U(x)$, as derived from the flow model, will have serious consequences on the transport modeling. Hydraulic conductivity $K(x)$ is believed to be the most consequential parameter in determining the head and concentration trends in the subsurface. It directly enters the flow equations, determines the velocity field and water and solute mass fluxes. It is also the parameter which shows the highest spatial variability (even several orders of magnitude in few meters distance).

The groundwater flow inverse problem consists of solving equation 1.1 with respect to hydraulic conductivities $K(x)$ and specific storativities $S_i(x)$ with $h(x,t)$ and $q(x)$ being known. Since the number of observations (measurements $K(x)$ and $h(x,t)$ at different locations $x$ and times $t$) is finite and limited whereas the spatial domain is continuous, one will always deal with an infinite number of unknowns. The parameter space is said to have infinite dimension. In practice, the number of unknowns is reduced from the infinite to finite dimension by averaging over scale. The dimension of the parameter space is reduced by approximating space and time in a convenient finite-difference or finite-element scheme. The regional domain is divided into sub-zones with a constant parameter value. By the so-called ‘parametrization’ (or ‘regularization’) procedure, the model becomes a (spatially) distributed parameter model with finite dimension. Nonetheless, one will practically always deal with equations in which the number of unknowns exceeds the number of equations.
1.5. Stochastic approach

This intrinsic degree of indetermination of the inverse problem, often referred to as "non-uniqueness" or as "non-identifiability" of the inverse problem solution, is one of the major impediments to the question about the usefulness and reliability of groundwater models. The system is called "over-parameterized". Several parameter sets that equally well reproduce the observed data are likely to be found via the inversion procedure. There is no unique solution. The parameter value must be estimated at too many locations compared to the number of available data\(^1\). Insufficient information about the model parameters is the very limiting factor to our capability of distinguishing between alternative parameter sets that equally well reproduce the observed data (often referred to as \textit{ill-posedness} of the inverse problem).

The non-uniqueness in spatial oscillations of high frequency and amplitude in the estimated parameters values, to such a degree that they may have to be considered non-physical (purely numerical) solutions of the inverse problem. A second major peril in groundwater inverse modeling also manifests itself by high frequency oscillations. The problem of numerical instability stems from the mathematical structure of the equations. Since the $K$ parameter to be estimated is connected to the piezometric head derivatives $dh/dx$, small errors in the heads values will cause severe oscillations in the computed hydraulic conductivity values $K$ (Carrera and Neuman, 1986).

1.5 Stochastic approach

The need for accounting for extreme parameter values and explicit incorporation of uncertainty through the whole modeling process lead quite naturally to use statistical concepts (and techniques) already developed in hydrogeology into the inverse problem (Neuman and Yakowitz, 1979; Kitanidis and Vomvoris, 1983; Dagan, 1985; Kitanidis, 1986; Yeh, 1986; Kitanidis, 1996). Stochastic modeling of parameters could be of help in mitigating ill-posedness of the inverse problem, in describing the variability of the parameter field at different scales (regional to local) and in accounting for the intrinsic uncertainty associated with the parameter estimates. As it was recognized that the hydraulic conductivity parameter does not vary in a completely erratic manner, but shows a distinct spatial correlation structure with the correlation between two values depending on their distance, a new perspective was adopted.

\(^1\)Although even in the case of a sufficient number of data the problem may be ill-posed.
In the early eighties the Theory of Random Fields (RF) was introduced in the parameter estimation procedure (Kitanidis and Vomvoris, 1983). In this framework, the spatially distributed values of an uncertain parameter are seen as the outcome of a random process governed by some statistical spatial law (the Random Field). The spatially variable parameter to be estimated is represented as a realization of an appropriately characterized RF with a given statistic. Instead of estimating the discretized function $K(x)$ at all nodes of the grid, the problem was cast in terms of the estimation of the RF first moments (typically, expectation value and covariance function), with a significant reduction in the number of unknowns. The real parameter distribution over space is too difficult if not impossible to obtain because of the scarcity of measurements.

The deterministic approach - seeking an optimal estimate - cannot account for small scale heterogeneity of the calibrated parameters and cannot explicitly model uncertainty in the predictions. Its outcomes will be over-smoothed representations of the real field with no quantification of the uncertainty in its estimates. In the probabilistic (or stochastic) approach the attention is shifted from the ill-posed problem of fitting the spatial $K(x)$ function to the estimation of the (few) parameters describing its statistical structure. These - expectation value and covariance functions - are in turn smooth functions and thus easier and less problematic to characterize. As the spatial distribution law of the RF $K(x)$ has been recognized, it can be used for parameter estimation over the study area by conditional simulation. With this technique, the parameter estimates $K(x_0)$ at all locations $x_0$ in the domain $\Omega$ are randomly drawn according to its spatial law $K(x)$. A set of spatial values at all locations $x_0 \in \Omega$ is called realization of the spatially distributed parameter $K$. This procedure can be iteratively repeated in order to obtain a set (or ensemble) of multiple equally-likely spatial realizations of hydraulic conductivity. In this way, the aim is not to determine the exact real configuration of the spatially distributed parameter, but to stochastically generate all the possible ones.

Each single realization in the statistical ensemble is one of the multiple possible realizations of the unknown reality. These, in turn, can be analyzed in a Monte-Carlo framework (Fig. 1.1), where the set of RF-realizations can be used to model the local uncertainty of the estimated parameter values (hydraulic conductivity) and other variables of interest (hydraulic heads and solute concentrations) over the study area. The large number of hydraulic conductivity realizations in the ensemble are analyzed via the solution of the flow (transport) equation. By superposition of the solutions (e.g. calculated hydraulic heads and concentrations) a distribution of results is obtained.
1.5. Stochastic approach

Fig. 1.1: Schematic illustration of the Monte-Carlo Method. A set of different realizations with identical geo-statistical parameters (possibly conditioned on measured data) is generated and simulations are performed for each realization. Averaging over all simulations gives the opportunity to evaluate the PDF of outcomes and related uncertainties for the quantity of interest. Reproduced from Hendricks-Franssen (2001)

and characterized by its expectation value and variance. Besides, the probability distribution of the input parameters can also be derived.

Uncertainty estimation of results is thus straightforward and naturally included in the stochastic/Monte-Carlo approach. The uncertainty concerning the values of the parameter $K(x)$ stems from the weakness of the available samples (in terms of both quantity and quality), and the probabilistic language provides a useful tool for managing and quantifying this uncertainty. Within this approach, the dimensionality of the parameter space is drastically reduced. The ill-posedness of the inverse problem is mitigated, since the modeler does not seek a single, smoothly varying, expected value which is believed 'optimal' in some sense, but a virtually infinite set of equally likely realization of the attributes. Unwanted non-physical oscillations in the solution due to the large dimensionality of the parameter space are also avoided.

The Monte-Carlo Method has a variety of benefits if compared to semi-analytical methods. No linear approximation is needed in solving the flow equation. Large
parameter variances, complex boundaries and configurations can be successfully handled. Complete Probability Density Function (PDF) estimation (with all moments) is possible. Various input variables with multivariate PDFs can be handled. The Monte-Carlo Method is a general and versatile tool which is always applicable. There are also a couple of drawbacks in this powerful tool. A large number of realizations may be necessary to get convergent statistics. This number is not known a-priori. Calculations can easily become CPU intensive and time consuming.

Uncertainty is not a bad thing in itself, as far as we can quantify and eventually reduce it. Limited knowledge about the state of the system - typical of Geosciences - results in uncertainty of predictions. The epistemic - due to limited knowledge - uncertainty in model results, contrary to aleatory uncertainty such as measurement errors, can be mitigated and eventually removed by further analysis and experimentation following a Bayesian approach. According to Bayesian Theory and in contrast to the classical frequentist definition, probability can be defined as the degree to which a person believes in an uncertain proposition. This approach gives up the notions of truth and falsity in favor of belief and misbelief, which are instead epistemic notions. In this respect the Bayesian interpretation of probability is more subjective, in contrast to the frequentist interpretation where probabilities are assumed to be a characteristic of nature. Frequentist and Bayesian interpretation disagree about the kind of events to which probabilities should be assigned in applications: frequentists assign probabilities according to revealed frequencies of occurrence in controlled repetitive experiments, while Bayesian do this according to propositions that are uncertain. Nonetheless, the Bayesian interpretation includes the frequentist one in the sense that the subjectively assigned probabilities may be based on the experience from previous experiments. As probabilistic models are based on both frequentistic and subjective information, these are Bayesian in nature.

The degree of belief in a certain state/scenario reflects the actual knowledge of the system. It is also referred to as prior belief - quantified in an a-priori (ex-ante) PDF - in the sense of prior to obtaining any further knowledge. When additional information becomes available, it is desired to update the prior probabilistic model on the basis of the new data. Bayesian Theory provides a mathematical framework to update prior probabilistic models by new information about the system, weighting the confidence in the prior model consistently with evidence provided by the new data. Bayesian inference, based on Bayes’ Theorem, is used to update evidence/observations about the system, ending up in an a-posteriori knowledge and quantified in an ex-post PDF.
The basic idea behind Bayesian statistics is that lack of knowledge is an uncertainty that should be treated by probabilistic reasoning in a similar way to other types of uncertainties. New information may allow to raise the modeler’s belief in the ex-post knowledge of the system. Bayesian concepts are of help and widely applied also in decision analysis. Decisions have to be made despite the lack of knowledge and statistical tools provide a great deal of help in this process.

Within the stochastic inverse modeling framework it is possible to capitalize on the advantages of Monte-Carlo and Bayesian approaches. Small scale variability and uncertainty are accounted for in the Random Fields formalism and analyzed by iterative solution of the groundwater flow equation for many realizations. New information such as hydraulic conductivity, head and tracer concentration data can be used for updating in a Bayesian formalism.

In the stochastic inverse modeling framework it is possible to define the ensemble of parameter realizations. By conditioning these realizations to more and different types of data, a subset of realizations can be identified which honors the available data. The data useful for conditioning are not any data, but the ones which make the parameter distribution narrower, i.e. less uncertain. Inclusion of prior information in the inversion procedure is clearly a key step in reducing the uncertainty of the parameter set. Adding new data allows to exclude impossible worlds, i.e. realizations which are in apparent contradiction with the observations.

This is the essence of the Bayesian Approach. Starting from an a-priori distribution, through conditioning of the system to new data, a new, narrower, a-posteriori distribution is obtained. The essential step is the extraction of information from the available measurements. The final goal is the reduction of parameter estimation uncertainty to a degree that allows operational decisions about the water resource management.

Scientific modeling of complex phenomena can live with uncertainty of predictions, since the prediction of future events should be understood to have a range of expected values, instead of a single true one. The concept of truth necessarily blurs into that of belief.
1.6 Scope and contents of the Dissertation

The scope of the present thesis is to bring new insights in the parameter estimation procedure exploiting the stochastic inverse modeling technique and the informational content of environmental tracers Krypton-85, Hydrogen-3 (Tritium) and Helium-3. Available data for conditioning are measures of hydraulic conductivity, geophysical data, piezometric heads and tracer concentrations. Head and tracer data offer, for groundwater investigations, alternative insights to be complemented with the information coming from hydraulic conductivity measurements. In particular, environmental tracers, unlike artificial and local tracers, rely on a sound and in-depth understanding of the whole water cycle and all processes affecting tracer concentrations in nature. Their limited application up to now in groundwater modeling stems from measurement time and cost considerations.

The study is performed on a small part of the Aathal aquifer, a sandy-gravel formation of the Riss ice age situated in Northern Switzerland, called Baltenswil aquifer. This relatively small aquifer was thoroughly studied over the last 15 years. Such studies provided a satisfactory knowledge of its hydro-geological conditions, that make the aquifer ideal for the present investigation purposes. Several transient head data are available thanks to intensive drilling and measurement campaigns. Krypton-85, Tritium and Helium-3 concentration measurements in groundwater samples have been provided by the Institute of Physics at Bern University and EAWAG Dübendorf. All the available knowledge about the Baltenswil aquifer makes it an ideal case-study for the testing of the model and techniques developed in the present work. The project area is presented in chapter 2.

The flow model is built following a stochastic/Monte-Carlo approach to inverse modeling of the groundwater flow equation. The focus is on the statistical characterization of hydraulic conductivity. The RF-formalism is used to deal with the problem. Other aquifer parameters such as storativity, porosity, recharge to groundwater and water extractions, although uncertain to some degree, do not usually show high spatial variability. Not all input parameters thus call for a RF-model. Hydraulic conductivity instead often shows the largest spatial variances and is thought to be the most consequential parameter to the uncertainty of the model results. Quantities derived from hydraulic conductivity will reflect its large uncertainty: groundwater flow velocities, dispersion coefficient and finally the solute concentrations.
To **quantify and reduce the uncertainty** in groundwater flow and mass transport it is crucial to reduce the uncertainty in the spatial variable $K(x)$, or transmissivity $T(x)$. Geo-statistical methods are used to incorporate information which reduces the uncertainty of the hydraulic conductivity field. Multiple equally likely realizations conditional to $T$ measurements are generated with a suitable Random Function Model. The second step is less trivial. Each realization from the ensemble is conditioned to available hydraulic head data. The hydraulic head state variable is non-linearly related to the stochastically modeled quantity $T$ and contains important information about the aquifer properties.

A clear advantage of the stochastic approach is its capability of including experimental information non-linearly related to the state variables. The Sequential Self-Calibrated Method (Sahuquillo et al., 1992; Gomez-Hernandez and Journel, 1993; Gomez-Hernandez et al., 1997; Capilla et al., 1997) and its code implementation INVERTO (Hendricks-Franssen, 2001) are used to obtain an ensemble of equally likely transmissivity fields made conditional to both hydraulic conductivity and hydraulic head observations.

The calibration procedure is performed in a **transient** regime, in contrast to the usual steady-state calibration. The use of transient head data provides a stronger constraint on the global water balance of the hydro-geological system than the use of steady-state head data. Not any parameter set describing the water balance (recharge and discharge) can be calibrated by a simple redefinition of the $T$ field. Making the realizations conditional to transient head data, storativities can also be estimated. The recharge parameter time-series has been estimated separately by means of a simple budget model, the Soil-Moisture Budget Model and calibrated within the inversion procedure. The stochastic inverse calibration of the flow model is presented in chapter 3.

A transport model for the **environmental tracers** Krypton-85, Tritium and its daughter-product Helium-3 is developed. In contrast to artificial tracers, which are injected point-like in space and time, environmental tracers were released into the atmosphere since the early fifties by man-made activities (nuclear testing and industry). These radioactive compounds were recorded at a net of stations worldwide since 1961. They are present in non-harmful but measurable concentrations all through the atmosphere. Since they were found in well measurable concentrations also in the groundwater body,
they have been used as tracers for hydro-geological purposes. The very fact that they are spread in space and also in time, allows the investigation of the hydrogeological system for a longer time span (typically 50 years) and larger spatial scale if compared to artificial tracers.

The discrepancy between the measured concentrations in the atmosphere (known as "atmospheric input function") and in the groundwater samples can be used to extract useful information about the water movement in the subsurface. Such information comprises travel times, geological structure, porosity and recharge rates and locations.

The role of the unsaturated zone in tracer transport was already stressed in an important paper which is one of the main pillars of the present thesis. Cook and Solomon (1995) pointed out the severe impact that the unsaturated zone can have on subsurface concentrations when non-shallow aquifers are considered. In case of water tables deeper than 5-10 meters, the tracer concentration in the subsurface becomes sensitively different from the one measured in the atmosphere. The aquifer under examination in this work is characterized by a hilly topography which gives rise to a spatially variable unsaturated zone thickness - predominantly made of moraine material - overlying a gravelly layer. The expected effect is that different thicknesses give rise to different tracer delays resulting in an integrated concentration signal at the groundwater table. A numerical code is developed to account for this effect and used for the reconstruction of the tracer input function at the groundwater table, starting from the more or less known atmospheric input function in the area. Environmental tracers and the transport model in the unsaturated zone are presented in chapter 4.

After conditioning the realizations to hydraulic conductivity and head data, the potential information content of environmental tracers is tested in a Monte-Carlo framework. Flow and transport simulations in the groundwater are performed for each realization of the ensemble, making use of MODFLOW (McDonald and Harbaugh, 1988) and MT3DMS (Zheng and Wang, 1999b). The reconstructed input function at the groundwater table is used as input for the transport simulations in the saturated zone. Hydraulic conductivity realizations are not calibrated to concentration data. The distribution of concentration of the output could nonetheless be built. A set of possible realizations honoring the concentration data can be selected and realizations not consistent with tracer data can be excluded. The stochastic set-up of the transport model, the transport model results and sensitivity analysis on transport parameters are
presented in chapter 5.

Chapter 6 presents further studies on Helium-3 back-diffusion from the groundwater table to the atmosphere (Helium-3 loss) and the differential diffusion of Helium-3 relative to Tritium. These additional transport phenomena, involving only Helium-3, are modeled and discussed in order to mitigate the discrepancies between model results and experimental evidence, as observed for transport modeling of Helium-3 only in Chapter 5. The final chapter describes the major conclusions and findings of the thesis.
Chapter 2

The project area

The Baltenswil site is situated in the Middle Glatt valley, about 10 kilometers North-east of the city of Zürich (Switzerland, Fig. 2.1). It belongs to the Water Works ‘Lattenbuck’, which provides drinking water to the villages of Bassersdorf, Wangen-Brüttisellen, Dietlikon, Illnau, Lindau, Nürensdorf and Wallisellen by means of 12 pumping stations and 6 springs.

The Aathal aquifer has been long studied by the Canton of Zürich in the last 20 years in the framework of nitrate pollution and remediation. In the eighties it was realized that the tolerance value of 40 mgNO₃/liter was by far exceeded in the groundwater, due to fertilizer utilization in agricultural activities. After preliminary studies, a four year action program aiming at the reduction of nitrate content in the Baltenswil aquifer began in 1993. Hydrological conditions were investigated and better assessed through the drilling of new boreholes and artificial tracer (Eosin, Fluorescein and Pyranine) tests by the company Dr. Heinrich Jäckli AG. Goal of the project was the reduction down to 25 mgNO₃/liter (drinking water standard) of the nitrate content in the groundwater in the medium and long run. The study concluded that nitrate use in agricultural activities had to be reduced in order to reduce nitrate contents in the groundwater (Jäckli AG, 1998).

According to the Swiss Law on Water Protection, protection zones for the water body must be defined through the assessment of the water well catchment’s extension. An assessment based on tracer tests was performed by Dr. Heinrich Jäckli AG during the years 1994-1997 (Jäckli AG, 1998). A Semester Work performed in 2001 by ETH-diploma students assessed through a numerical model the quasi-steady state extension of the Baltenswil pumping station catchment under different external stresses (pumping rate and recharge to groundwater) (Fehlmann et al., 2000). Meteorological data
and results from hydro-geological analysis in the Baltenswil domain were collected to characterize the water balance in the area. In the study, parameter calibration was performed, the water balance estimated and aquifer boundaries localized. The two works mentioned above provide the informational basis for the present study on the Baltenswil site.

2.1 Hydro-geological setting

During the relatively warm period (150000 to 20000 years ago) between the last two ice ages in the Pleistocene Era - the Riss and Wurm ice ages - the water melting from retreating glaciers in the Upper Glatt valley left extensive gravelly glacio-fluvial deposits (SGK, 1986).

The so-called ‘Aathal-gravel’ was later further reworked by the advancing of the Alpine
2.1. Hydro-geological setting

Fig. 2.2: Groundwater resources in Kanton Zürich: Aathal gravel corridor and Baltenswil site. Reproduced from AWEL (2006) and modified (colors and legend)

Glaciers during the following Wurm ice age (20000 to 11000 years ago). Today, the Aathal-gravel is present in the form of an elongated gravel corridor running for about 50 kilometers from Hinwil in the Zürcher Oberland in North-west direction up to Bassersdorf in the Middle Glatt valley. It covers an area of about 30 to 40 square kilometers and is on average 1.5 to 2 kilometers wide and 30 to 40 meters thick. The Baltenswil aquifer is situated at the North-western end of the Aathal-gravel corridor, in the Middle Glatt valley (Fig. 2.2).
Chapter 2. The project area

Superficial layers (post ice-age. Holocene): loam, sand, peat
Deltaic sediments (Late Würm): predominantly sand
Average groundwater level and conductive layer
Lake sediments rich in fossils, interglacial
Lake sediments (Late Würm): sand, silt and clays
Gravel (Late Würm): sandy-gravel and gravelly sands, granular
Aathal-gravel (Riss and Early Würm): predominantly coarse sandy-gravel, conglomerate
Obere SüßwasserMolasse (OSM) upper boundary: clay and sandstone, subordinated conglomerate
Aathal aquifer - close to Baltenswil - Springs

Fig. 2.3: Geological profile 1. Middle Glatt valley. Quaternary sediments fill the Paleo-valley incised in the Obere SüßwasserMolasse (OSM). Reproduced from SGK (1986).
The Quaternary sedimentary cover in this area overlies an impervious bedrock consisting of brown and greyish sandstones of the Obere SüsswasserMolasse (OSM). The bedrock, which is shallow close to the aquifer Northern boundary, was deeply incised by erosion towards the South, with associated formation of a valley, subsequently filled up by thick lacustrine deposits during the Riss period (Fig. 2.3). The bedrock and the Riss deposits form together the bottom layer of the aquifer. During the intra-glacial period (Post-Riss), the above-mentioned sequence was extensively covered by the Aathal-gravel complex, including heterogeneous, highly conductive brownish-grey sandy gravels with silt, with sparse pebbles up to 15 cm in size. The Aathal-gravels were successively covered by younger moraine material ('Vorstoss-gravel'), deposited during the Last Glacial Maximum (LGM - Würm ice-age). The moraine deposits consist of less conductive sandy silts with clay, locally forming lenticular layers (SGK, 1986).

At the Southern and Western boundary the entire sequence was subsequently deeply eroded after the LGM and filled up with a sequence of moraine, glacio-fluvial, deltaic and lacustrine deposits. The Aathal and Vorstoss gravel sequences are here abruptly interrupted by these less conductive deposits. On the North-eastern boundary of the study area, both the Aathal and the Vorstoss gravels meet the impermeable OSM bedrock which wedges upwards (Fig. 2.4).
2.2 Groundwater

The Aathal-gravel forms the conductive layer in which the groundwater is stored. The aquifer is unconfined. It consists predominantly of sandy-gravels with pebbles and is generally characterized by high hydraulic conductivity values (order $K \sim 10^{-3}$ m/s). Characteristic of the area is the occurrence of sparse cemented sandstones in the gravel layer. The main water-bearing gravel layer seldom outcrops to the surface, being covered almost everywhere by the mentioned moraine layer. The complex structure of the moraine layer, as revealed by borehole drilling, may result here and there in un-localized perched aquifers and local high-lying natural surface springs. Moraines give rise to a characteristic hilly forested landscape, and form a heterogeneous layer with spatially variable thickness, for the most part unsaturated, between a few meters (close to the aquifer Western boundary) to tens of meters in the North-eastern hilly part of the domain (SGK, 1986).

The North-eastern aquifer boundary is located on the hilly slopes, where the OSM is uplifted interrupting the Aathal and Vorstoss gravel layers (see Fig. 2.4). Here infiltrating water slopes down the impermeable bedrock, giving rise to a thin (< 2 meters) layer, that finally enters the groundwater body as boundary flux (brown-blue edge in Fig. 2.5). The thickness of the unsaturated soil layer in the inflow area to the North is considerably larger (up to 40-50 meters) than in the rest of the domain.

The North-western as well as the South-eastern boundaries are taken along steady-state flow streamlines, taken from available groundwater maps (Fig. 2.6). The South-western boundary is identified with the sharp lithological change between the gravel layers and subsequent lacustrine deposits. Here the boundaries of the Aathal and Vorstoss gravel layers are determined by a vertical sharp cut which laterally confines the groundwater. Here the groundwater table lies far above the impermeable basement (OSM) of the Glatt valley: about 15 to 20 meters. The hydraulic conductivity barrier provides a natural subsurface dam acting as a geological lateral wall for the groundwater and constraining the aquifer to a characteristic pan-shaped geometry. The barriers outcrop to the surface only locally, leading to the occurrence of natural springs in the domain. Most of them are located along the Southern and Western boundaries of the study area, from Wangen and Brütisellen up to Baltenswil. The Aathal aquifer finds its end a few hundred meters to the East of Baltenswil, where it spills out to the surface through a number of springs.
2.2. Groundwater

Fig. 2.5: Geography of the Baltenswil area. The blue region coincides with the modeled domain, in which five pumping stations (red squares) are operative. Straight lines indicate the geological profiles of Fig. 2.3 and Fig. 2.4. Land use in the area is 45% agricultural, 40% is covered by forests and 15% by urban settlements.

Fig. 2.6: Groundwater map of the Baltenswil area. Several springs are present at the Southern and Eastern boundaries. On the North-east, a thin groundwater layer (brown) provides the lateral boundary inflow to the aquifer proper (blue). Groundwater thickness varies from a few meters close to the NE boundary up to more than 20 m downstream. Reproduced from AWEL (2006) and modified.
The groundwater flow direction in the area mainly follows a North-east/South-west axis, from the NE inflow boundary on the hilly moraines towards the SW and West geological boundaries. The 5 pumping stations (Baltenswil, Brüttisellen, Büel, Girhalden I and II) operating in the domain under study contribute to significant deviations of the undisturbed flow direction towards the East-West axis. The hydraulic gradient is roughly varying between 0.1% and 0.5%. The saturated zone thickness is on average 5 to 8 meters thick in the Northern part, increasing to 15 to 20 meters close to the SW boundary (Fig. 2.7).

Fig. 2.7: Baltenswil model geometry, as reconstructed from available topographical data. The thickness of the unsaturated zone displays a high spatial variability due to hilly moraines. The saturated layer increases in thickness southwards, due to the sloping of the impermeable bottom OSM layer. The model reconstruction correctly accounts for natural springs in the domain, where the groundwater table meets the soil surface at the Southern and Western boundaries.
2.3 Precipitation and groundwater level monitoring

The region belongs to the Swiss Plateau, where a temperate climate prevails, with a mean annual temperature of about 10°C. Monthly averages vary from 2°C above zero in January and 18°C in July\(^1\). Prevailing westerly winds transport mild and moist air masses from the Ocean, which in turn determine most of the precipitation on the Swiss plateau, 90% of which in the form of rainfall. Precipitation in the Baltenswil catchment is about 1200 mm annually. Precipitation distribution is akin to a bell-shaped curve, centered on late spring and early summer months. Significant precipitation can also take place in autumn months, while winter months are mostly drier. Meteorological data are available at the Swiss Meteo Service station installed at the Zürich-Kloten airport, 6 kilometers to the North-west of the Baltenswil domain (BMK, 2006).

Precipitation events in the domain for the period from 1994 to 2006 are shown in Figures 2.8 and 2.9. In the year 1995 precipitation was above normal. It was followed by the relatively dry years 1996 and 1997. Year 1998, although in agreement with the long-term yearly average, was poor in precipitation during the summer months (60% of the long-term monthly average in July and August) but received exceptionally high rainfall in the autumn and winter months (September to February 1999, 700 mm total rain). Extraordinary rainfall took place in 2001, especially in January, March and September, with 9 months out of 12 above the long-term monthly averages. Year 2002 was also wet, especially from August to November. Year 2003 was recorded as the driest year since 1971, with a dramatic decrease in precipitation in winter and summer months.

The groundwater is recharged by infiltrating precipitation, which provides both direct recharge to the groundwater table and lateral inflow from the hilly moraines in the North-east. Most of the water stored in the aquifer is pumped as drinkable water for domestic use, while a part flows out via the numerous springs at domain boundaries. Only little information is available about the discharge rates of these springs. The water table fluctuates on average by one to two meters during the year, with high water table levels in summer (after winter recharge) and low levels in autumn, following the summer months with increased Evapo-Transpiration (Fig. 2.8). The presence of poorly sorted and thick moraines filters away pollutants and bacteria from the seepage water. The water quality

\(^1\)Average monthly values for 1971-2006, based on measured average daily temperatures. Data from Meteoschweiz (BMK, 2006)
Fig. 2.8: Precipitation and groundwater table level variation in 1994-2003, as measured at four boreholes in the Baltenswil catchment (see map in Fig. 2.11). The red line indicates the precipitation monthly average on the long run (1994-2003).

Fig. 2.9: Yearly precipitation and average on the long run (1994-2006) at the meteorological station of Kloten (ZH)
of the aquifer is high, threatened only by nitrate pollution from agriculture.

2.4 Soil conditions

Soil information is derived from the soil map of Kanton Zürich and work performed by the Hydrology group (Dr. F. Naef) at the Institute of Environmental Engineering, ETH-Zürich (FAL, 1997). Available maps describe the geology and soil parameters like grain size distribution, soil aggregation and soil structure in the first 30 cm and 150 cm of the soil. Dominant runoff processes like Subsurface Flow (SSF), Saturated Overland Flow (SOF) or Deep Percolation (DP) were derived automatically with GIS from information like soil water balance, grain-size distribution, permeability of bedrock, tile drains and land-use (Margreth and Naef, 2006; Schmocker-Fackel, 2006). These maps provided important information for many key hypotheses which were assumed in the recharge-to-groundwater estimation (see section 3.5). Other geological features in layers deeper than 5 meters could be derived from the drilling profiles at the pumping stations and observation locations across the modeled domain (Wyssling, 1981).

In general, two geological formations are present in the domain: the hilly moraines and the gravel plain. In more than half of the domain, moraine deposits overlay the gravel bed. The moraine cover is strongly heterogeneous. It is made up of loamy and sandy-loamy materials with some sparse clay lenses. The gravel bed, which is very shallow in correspondence to the valleys, is instead less heterogeneous and in general highly permeable.

The root zone is at least 70 cm deep and can reach in some forested parts a depth of supposedly 4 meters. It is made up of fine structured loam and sandy-loam, which indicates, that the matrix permeability is high for the most part of the domain. Water can infiltrate there directly into the soil or the underlying bedrock (DP) during low and intense rainfall. On SOF3- and SSF3- areas, a precipitation event amounting to at least 100 mm rainfall is needed for saturation and runoff production. On SOF2-areas, which cover an area of about 10%, runoff occurs for rainfall events larger than 40 mm. The threshold amount of rainfall after which runoff takes place is called soil retention capacity. In most parts of the Baltenswil domain, the soil retention capacity exceeds 200 mm (Fig. 2.10).
Chapter 2. The project area

Fig. 2.10: Map of relevant surface and subsurface processes in the Baltenswil domain, classified in terms of soil retention capacity. The blue square indicates the location of Baltenswil pumping station. HOF - Hortonian Flow: fast and intense runoff, occurring on sealed surfaces (from 0 to 30 mm soil retention) or compacted soils. SOF - Saturated Overland Flow: slightly delayed runoff, occurring on soils with small storage capacity and slow drainage (30 to 100 mm). SSF - Subsurface Flow: delayed and moderate runoff, occurring in soils with a large infiltration capacity (100 to 200 mm). DP - Deep Percolation: storage of water in soil and recharge to groundwater, occurring in permeable soils (more than 200 mm). The numbers associated with each runoff process account for the degree of process (1. low 3. high)

Streams are completely missing, with the exception of lateral spring outflow. This shows that during rainfall of low to middle intensity, the whole amount of water can infiltrate into deeper layers. In case of strong precipitation most of the runoff developing on the SOF2-areas can re-infiltrate later on in higher hydraulic conductivity areas still inside the domain. Surface runoff and shallow subsurface flow only occur during rare precipitation events of high intensity. Runoff processes were therefore not considered in the water balance assessment (Margreth and Naef, 2006).
2.5 Pumping stations and observation locations

In the domain 5 pumping stations (Baltenswil, Brüttisellen, Büel, Girhalden I and II) are operative and 7 observation locations (Kb 94-1, Kb 94-2, Kb 14, Kb 85-1, Kb 84-1, Kb 84-3 and Kb 84-4) are selected, carrying either head and/or environmental tracer concentration data (Fig. 2.11). From former tracer investigations it is shown that boreholes Kb 94-1, Kb 94-2, Kb 14 do not belong to the catchment of the pumping station Baltenswil. The other boreholes may instead belong to catchments of one or another pumping station according to local pumping conditions. Data of water abstraction by pumping are well documented on a yearly basis from 1991 to 1998, and on a daily basis from 1999 onwards (Fig. 2.12). The saturated zone thickness as derived from drilling profiles is about 5 to 8 meters in the PW Baltenswil area, rising up to 20 at the South-east boundary (Fig. 2.13).

Fig. 2.11: Baltenswil model geometry, with pumping stations (red squares), springs (yellow squares) and observation boreholes (red stars). Boundary inflow from the North-east zone is indicated with arrows.
Fig. 2.12: Monthly averaged pumping rates at the 5 stations in the domain (before 1999, yearly averages)

Fig. 2.13: Saturated zone thickness [m]
Chapter 3

The groundwater flow model

Investigation of transport processes in the subsurface requires a reliable flow model. The groundwater velocity field which is obtained from the calibrated flow model will drive the environmental tracers through the subsurface. This chapter presents how the flow model for the Baltenswil aquifer is established. As mentioned in the introduction, the focus will be on the stochastic characterization of the spatially variable hydraulic conductivity parameter $K$, which is believed to be the most consequential for groundwater model uncertainty. The proposed method is based upon the Random Function Theory, presented in Section 3.1.

The Sequential Simulation Technique is used for the generation of multiple, independent equally likely realizations of the hydraulic conductivity field, conditional to the available $K$ data, and the Sequential Self-Calibrating Method to further inverse-condition these realizations to transient hydraulic head data $h$. These techniques and methods are presented in Section 3.2 and 3.3. Application of the above-mentioned techniques and methods to stochastic inverse modeling of groundwater flow in the Baltenswil real case-study is presented in Section 3.4.

The conditioning of realizations to transient head data calls for an accurate determination of the water budget. The recharge to groundwater is independently estimated via a simple budget model, the Soil-Water Budget Model, presented in Section 3.5. The inverse-calibration results are presented and discussed in Section 3.6.
Chapter 3. The groundwater flow model

3.1 The Random Function

Mathematical models of physical phenomena are often subject to significant uncertainties. As it is often the case in soil physics, uncertainties are not completely aleatory, but may show a spatial correlation, which can be characterized in a statistical way. The spatially distributed values of an uncertain parameter can be seen as the outcome of a random process governed by some statistical spatial law. The real but unknown parameter spatial field is regarded as one particular outcome - or realization - of the random process. By accounting for all the possible realizations, a distribution of parameter values can be obtained at each location and the parameter local uncertainty can be modeled. A random process is mathematically idealized in a Probabilistic Random Function Model.

The concept of Random Variable (RV) refers to a variable $Z$ which can take a series of values according to the probability distribution governing the random process (Goovaerts, 1997). For spatially distributed phenomena and for a particular outcome $\theta$ of the random process, a distributed parameter value (or spatial function) $Z(x) = z(x, \theta)$ can be obtained for all $x$ in the domain $\Omega$, called realization. The set of all possible realizations defines the Random Function. A Random Function (RF) $Z$ is defined as a set of RV $Z(x, \theta)$ for each location $x$ in the domain $\Omega$ and for all outcomes $\theta$. The variable $\theta$ will be from now on omitted unless necessary. The attribute $Z$ modeled as RF can be any uncertain variable like temperature, water content or hydraulic conductivity.

To any set of $N$ locations $x = \{x_1, \ldots, x_N\}$ corresponds a vector of $N$ RVs $\{Z(x_1), \ldots, Z(x_N)\}$. The probability that the RF $Z$ at the $N$ locations is less than any given threshold $z = z_1, \ldots, z_N$ is defined as $N$-variate (or $N$-points) cumulative distribution function (CDF) (Goovaerts, 1997)

$$F(z_1, \ldots, z_N; x_1, \ldots, x_N) = \text{Prob}(Z(x_1) \leq z_1, \ldots, Z(x_N) \leq z_N)$$ (3.1)

The spatial derivative of the $N$-variate CDF with respect to $\{z_1, \ldots, z_N\}$ defines the $N$-variate probability density function (PDF)

$$f(z_1, \ldots, z_N; x_1, \ldots, x_N) = \frac{\partial^N F(z_1, \ldots, z_N; x_1, \ldots, x_N)}{\partial z_1 \ldots \partial z_N}$$ (3.2)
A RF is fully characterized by the multi-variate CDFs/PDFs for all choices of \(z, \mathbf{x}\) and \(N\). The set of all such \(N\)-variate CDFs/PDFs constitutes the spatial law of the RF \(Z(\mathbf{x})\). In practice, only a limited number of measurements is usually accessible and the entire distribution is thus not known. It becomes thus necessary to infer or parameterize the Random function from available measurements. For sake of simplicity, one pairs the measurements of two points and assumes that the spatial law is dependent only on the separation distance \(h = x - x'\). The assumption (or decision) of RF-invariance under translation is referred to as stationarity hypothesis\(^1\). Stationarity ensures that the RF does not show spatial trends in mean and higher statistical moments (Goovaerts, 1997).

For practicality, one limits the stationarity requirement to the two-points covariance (second-order stationarity). With these assumptions, the spatial law analysis is restricted to PDFs involving no more than 2 locations at a time \((N = 2)\) and their corresponding moments: the mean or expected value (Veneziano, 1978)

\[
m(x) = E\{Z(x)\} = \int_{-\infty}^{+\infty} z \cdot f(z; \mathbf{x}) \, dz
\]

and the two-point covariance function

\[
C(x_1, x_2) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} [z_1 - m(x_1)] \cdot [z_2 - m(x_2)] \cdot f(z_1, z_2; x_1, x_2) \, dz_1 \, dz_2
\]

The second-order stationarity decision implies that the mean is constant

\[
E\{Z(x)\} = m
\]

and its covariance function depends only on the separation distance \(h = x_1 - x_2\)

\[
C(x_1, x_2) = C(h)
\]

\(^1\)Stationarity is a property of the RF model needed for statistical inference. It is not a characteristic of the phenomenon under study. Stationary processes are important since stationarity is a necessary condition for the ergodicity hypotheses, used in the inference process (see later on in this section). Stationarity (and later, ergodicity) will be both model decisions rather than assumptions or hypothesis. It must be reminded that there is no actual RF behind the observations (Goovaerts, 1997).
Chapter 3. The groundwater flow model

In some cases the second-order stationarity may not be satisfied by the data, e.g. when the experimental variance increases with the size of the area under study, the mean of the attribute $Z$ is not constant and the variance not finite. In this case the two-point covariance function is not defined. It is thus convenient to use the variogram, defined as variance of the increments (Goovaerts, 1997)

$$2\gamma(x_1, x_2) = Var\{Z(x_1) - Z(x_2)\}$$

In case of second-order stationarity, the variogram is also depending only on the separation distance and has its covariance counter-part

$$C(h) = C(0) - \gamma(h)$$

where $C(0) = \sigma^2$ is the variance.

By the estimation of a few distribution parameters (expected value and covariance function/variogram) it is possible to describe the major spatial features of the attribute over the domain. *Statistical inference* is the process of estimating the RF model parameters from the sample information available over the study area (Goovaerts, 1997). The statistical property (or assumption) whereby this is possible is called *ergodicity*. *Ergodicity* holds when the statistical parameter can be inferred from one single realization, namely the measured (or experimental) one. In other words, ergodicity tells whether the single realization of an aquifer will exhibit the same statistical properties as the ensemble.

Statistical inference for the attribute $Z$ can be performed by calculating a *sample variogram*. The attribute measurements at the different locations are divided in *distance classes*, whose number and length must be chosen such that a sufficient number of data are represented in each class. A set of *experimental* values $\gamma(h)$ for a finite number of lags (or distance classes) $h_k, k = 1, \ldots, N(h)$ between data locations $x_\alpha$ can be obtained (Goovaerts, 1997)

$$\gamma(h) = \frac{1}{N(h)} \sum_{\alpha=1}^{N(h)} [Z(x_\alpha) - Z(x_\alpha + h)]^2$$

(3.3)
3.1. The Random Function

The accuracy of the variogram estimation depends to a large extent on the number of measurements available. A major issue in geo-statistics is that sample data are representative of the population over the study area. A scarce data set would result in a poor estimation of variance and correlation length (Journel and Huijbregts, 1978).

The experimental variogram (3.3) has to be fitted by a continuous function with some statistical parameters, typically the correlation range. The function-type (or variogram model) is chosen depending on the phenomenon under study and the variability observed across the domain. There are several mathematically feasible models, respecting the positive-definiteness condition that ensures the non-negativity of the RF covariance function (De Marsily, 1986)

- **Spherical**
  \[
  \gamma(h) = C \left[ \frac{3}{2} \frac{h}{a} - \frac{1}{2} \left( \frac{h}{a} \right)^3 \right] \quad \text{for } h \leq a
  \]
  \[
  \gamma(h) = C \quad \text{for } h > a
  \]

- **Exponential**
  \[
  \gamma(h) = C \left[ 1 - \exp \left( -\frac{h}{a} \right) \right]
  \]

- **Gaussian**
  \[
  \gamma(h) = C \left[ 1 - \exp \left( -\frac{h}{a} \right)^2 \right]
  \]

- **Power law**
  \[
  \gamma(h) = C \cdot h^\lambda \quad \text{for } 0 < \lambda < 2
  \]

- **Nugget**
  \[
  \gamma(h) = \text{const.} = c_0
  \]

where \( C \) and \( c_0 \) are constants [-], \( h \) is the separation distance [L] and \( a \) is the correlation length [m]. Each model displays different behaviors at the origin (small separation distance \( h \)) and at infinity (Fig. 3.1). Bounded variogram models stem from the stationarity decision. They asymptotically reach their limit (or sill value) at a distance called range and have their covariance counterpart. Unbounded models show instead a monotonically increasing variance and thus sill (and range) are not defined. The sill is defined as the sum of variance and (possibly) nugget. The Gaussian model
is usually preferred when highly continuous phenomena are under investigation (parabolic behavior near the origin), otherwise when linear behavior in the origin proximity is expected, the modeler may prefer the exponential or the spherical model (the first one showing a faster increase in the origin neighborhood). A combination of different models is also a possibility. The principle of parsimony (small number of basic structures and preference for simple ones) should nonetheless be followed. The nugget model is often nested in to account both for small scale variability and uncorrelated measurement errors and to avoid numerical instabilities in the interpolation algorithms.

3.2 Conditioning to hydraulic conductivity.

Sequential Simulation Technique

The characterization of hydraulic conductivity $K$ as RF allows to model its spatial variability and local uncertainty. The advantage is that the problem of assessing uncertainty of $K$ at location $x$ is reduced to that of modeling the PDF of the Random Field at that location. By the estimation of a few statistical parameters (variogram range, sill and nugget) it is possible to give estimates of the parameter values at unsampled locations and to associate an uncertainty to these values. To obtain such estimations, geo-statistical interpolation (such as kriging) and simulation techniques
3.2. Conditioning to hydraulic conductivity. Sequential Simulation Technique

can be used.

Small-scale spatial variability of the K field is crucial for solute transport in the groundwater. Resulting very high and very low flow velocities might have a decisive impact on the solute transport. Extreme values of hydraulic conductivity would be averaged out if interpolation techniques are used. The use of kriged input K fields into the groundwater flow equation will result in biased estimates of groundwater flow velocity. Kriging techniques tend to give a smoothed representation of the K field, by systematic overestimation of the low values and underestimation of the high ones. Uncertainties in the hydraulic conductivity K(x) will also be reflected in the subsurface solute concentrations.

While kriging aims at obtaining a best local estimate of the attribute, simulation techniques focus instead on global patterns (through statistical description) rather than on local accuracy. Simulation techniques allow a better account of spatial variability of hydraulic conductivity and related physical variables. Uncertainty is also better accounted for through the whole modeling process (groundwater flow and transport). Geo-statistical simulation techniques are thus preferable to interpolation techniques when transport modeling is the issue of interest.

Geo-statistical simulation of the Random Function Z(x) refers to a technique that allows drawing one attribute spatial realization at random from its PDF, as modeled by the sample variogram (Journel, 1985; Gomez-Hernandez, 1991; Gomez-Hernandez and Journel, 1993). From the same PDF a large number of spatial realizations of the attribute can be obtained. Realizations can be unconditional or conditional to measurements: in the latter case they are forced to take fixed values at some locations, e.g. where measurements are available.

We first consider the issue of drawing realizations at random from the ensemble of unconditional realizations. According to the axiom of conditional probability (Papoulis, 1986), the joint PDF of two Random Variables Z(x₁) and Z(x₂) (also called second-order joint PDF) can be written as the product of the conditional PDF of Z(x₁) given Z(x₂) times the unconditional PDF of Z(x₂).

\[ f(z_1, z_2; x_1, x_2) = f(z_1; x_1 \mid z_2; x_2) f(z_2; x_2) \]
By recursive application of the axiom, any $N$-th order joint PDF of $\{Z(x_i) : i \in (N)\}$ at $N$ locations $\{x_1, \ldots, x_N\}$ can be calculated. The $N$-th joint unconditional PDF $f_{(N)}$ can be written in terms of $(N-1)$ conditional PDF and the unconditional PDF of $Z(x_1)$ (Gomez-Hernandez, 1991)

$$f_{(N)}(z_i; x_i, i \in (N)) = f_{N|(N-1)}(z_N; x_N | z_i; x_i, i \in (N-1)) \cdot f_{N-1|(N-2)}(z_{N-1} | z_i; x_i, i \in (N-2)) \cdot \ldots \cdot f_{2|1}(z_2; x_2 | z_1; x_1) \cdot f(z_1; x_1) \tag{3.4}$$

where $f_{N|(N-1)}$ is the $N$-th order PDF of $Z(x_N)$ conditional to the set of $(N-1)$ values $Z(x_i, i \in (N-1)) = z_i$, $f_{N-1|(N-2)}$ is the $(N-1)$-th order PDF of $Z(x_{N-1})$ conditional to the set of $(N-2)$ values $Z(x_i, i \in (N-2))$ and so on. The last term of the product line is the unconditional PDF of $Z(x_1)$. Within this theoretical framework, a random realization of $Z(x_\alpha, \alpha \in (N))$ can be generated by sequentially drawing from the PDF of $Z(x_1)$ and the $(N-1)$ uni-variate conditional PDFs in equation (3.4).

The Sequential Simulation Technique (Journel, 1985; Gomez-Hernandez, 1991) takes the direct approach of directly drawing the realizations at random from the multi-variate unconditional PDFs of $Z(x)$. Given the multi-variate PDF of $Z(x)$, the sequential simulation algorithm for the generation of multiple equally likely realizations consists of the following steps (Gomez-Hernandez, 1991)

1. Draw at random the attribute value $z_1$ at location $x_1$ from the marginal density of $Z(x_1)$

2. Determine the conditional density of $Z(x_2)$ given $Z(x_1) = z_1$. Draw from it $z_2$

3. Determine the conditional density of $Z(x_3)$ given $Z(x_1) = z_1$ and $Z(x_2) = z_2$. Draw from it $z_3$

```
  ...
```

4. Determine the conditional density of $Z(x_N)$ given $Z(x_i) = z_i, i = 1, \ldots, (N-1)$. Draw from it $z_N$
3.2. Conditioning to hydraulic conductivity. Sequential Simulation Technique

The procedure is completely general and can be used for simulation of any Random Function. Each sequential simulation can be looped \(n\) times for as many realizations as necessary.

In case of conditional realizations, the procedure remains the same, just the \(N\)-th joint PDF of \{\(Z(x)\)\} conditional to the \(N_0\) measurements \(Z(x_\alpha) = z_\alpha\) at locations \(x_\alpha\) must be used for sequential simulation (Gomez-Hernandez, 1991). The conditional statistics of \(Z(x \mid (N_0))\) is thus determined by the conditional PDFs of \(Z(x)\). As example, the second-order PDF conditional to \(N_0\) data \(Z(x_\alpha) = z_\alpha, \alpha \in (N_0)\) is given by the joint PDF of \(Z(x_1), Z(x_2)\) and the data \(Z(x_\alpha)\), divided by the unconditional PDF of the \(Z(x_\alpha)\) alone

\[
f(2)(z_1, z_2; x_1, x_2 | Z(x_\alpha) = z_\alpha, \alpha \in (N_0)) = \frac{f(z_1, z_2, x_1, x_2, x_\alpha)}{f(z_\alpha; x_\alpha)}
\]

In a similar fashion as for the unconditional case, the \(N\)-th joint conditional PDF \(f_{(N)(N_0)}\) can be expressed as a product of uni-variate PDFs conditional to the \(N_0\) data (Gomez-Hernandez, 1991)

\[
f_{(N)(N_0)}(z_i; x_i, i \in (N)) = f_{N|(N-1)\cup(N_0)}(z_N; x_N | z_i, z_\alpha; x_i, x_\alpha, i \in (N-1), \alpha \in (N_0)) \cdot f_{N-1|(N-2)\cup(N_0)}(z_{N-1}; x_{N-1} | z_i, z_\alpha; x_i, x_\alpha, i \in (N-2), \alpha \in (N_0)) \cdot \ldots \cdot f_{2(1)\cup(N_0)}(z_2; x_2 | z_1, z_\alpha; x_1, x_\alpha, \alpha \in (N_0)) \cdot f_{1(N_0)}(z_1; x_1 | z_\alpha; x_\alpha, \alpha \in (N_0))
\]

(3.5)

where \(f_{N|(N-1)\cup(N_0)}\) is the \(N\)-th order PDF of \(Z(x_N)\) conditional to the set of \((N-1)\) values \(Z(x_i, i \in (N-1)) = z_i\) and to the \(N_0\) data \(Z(x_\alpha) = z_\alpha\). All the following conditional probabilities \(f_{n|(n-1)\cup(N_0)}\) are calculated including the \(N_0\) data \(Z(x_\alpha) = z_\alpha\). The Sequential Simulation algorithm remains the same, but the first value \(z_1\) is instead drawn from the conditional PDF of \(Z(x_1)\) given the \(N_0\) data rather than from the marginal unconditional PDF of \(Z(x_1)\). The conditional PDF of \(Z(x_2)\) will be determined given \(Z(x_1) = z_1\) and \(N_0\) data and so on.

Multi-Gaussian PDFs are a preferred choice in geostatistics. The RF \(Z(x)\) is in this case fully characterized by its mean and covariance, which is mathematically appealing. Besides, hydraulic conductivity is often log-normally distributed. This does not
Chapter 3. The groundwater flow model

imply, however, that the $N$-variate PDF is Multi-Gaussian. Multi-Gaussianity is instead a modeler’s decision, also depending on bivariate (or higher order) data analysis and geological considerations. *Sequential Multi-Gaussian Simulation* allows to generate multiple, independent conditional realizations of an attribute with a Multi-Gaussian RF Model. The generation of one random realization with this technique consists of the following steps:

1. The experimental data set is normal-score transformed

2. The first grid cell is randomly chosen. Ordinary kriging estimate and variance are calculated from the normal-scored data set.

3. Kriging estimate and variance are used to calculate a CDF conditional to the data set, by recursive application of Bayes’ Theorem. A value is drawn from the conditional CDF and added to the data set. This is the simulated value of the attribute for the first grid cell.

4. The next grid cell is visited following a random path. Kriging estimate and variance are calculated by the normal-scored data plus the values simulated at each previously visited cell. A new conditional CDF is built. The simulated value for the cell is drawn from the new conditional CDF.

5. The grid cell is changed according to the random path and the simulation continues until all cells are visited

6. Simulated normal scored values for all grid cells are normal-score back-transformed into physical space. The first realization is obtained.

A drawback of Multi-Gaussian probabilistic models is that they do not allow for any significant spatial correlation of extreme values. This property of the Gaussian RF model reflects the tendency of the variogram range to decrease for very low and very high values of the variable (Hendricks-Franssen, 2001). Modeling the LogT field with Gaussian RF, although mathematically convenient, may impair the reproduction of high and low LogT channels. Non-Gaussian simulation algorithms, such as Sequential Indicator Simulation, may better account for spatial continuity of extreme values (Gomez-Hernandez and Shrivastava, 1990).
Sequential simulation is a completely general, direct and computationally fast method for the generation of conditional realizations. In this dissertation, the code implementation of conditional Multi-Gaussian Sequential Simulation GCOSIM3D (Gomez-Hernandez, 1991) is used to generate an ensemble of multiple equally likely conditional realizations of the hydraulic conductivity \( Z = \ln K(x) \).

### 3.3 Conditioning to heads. Sequential Self-Calibrated Method

Conditioning realizations to data is a special issue in risk and reliability analysis, as this forms the basis for the updating of probability estimates based on new information, knowledge and evidence. Geo-statistical simulation techniques allow the incorporation of different types of conditioning information, which might reduce the uncertainty of the hydraulic conductivity. Hydraulic conductivity data are usually sparse while expensive if compared to hydraulic head measurements. Moreover, being the \( K \) data scale-dependent, they are not of easy interpretation. A large deal of information about the hydraulic conductivity spatial features can be extracted if the \( K \)-conditional realizations are made conditional also to head measurements.

In the present dissertation the Sequential Self-Calibrating Method (SSCM) is used (Sahuquillo et al., 1992). SSCM is a stochastic inversion procedure which, by iteratively solving the full (i.e. non-linearized) groundwater flow equation, allows the calibration of multiple stochastic realizations to head measurements. As reported by the authors (Gomez-Hernandez et al., 1997), this can be considered as the first inverse stochastic simulation method aiming at the direct generation of \( K \)-field realizations conditional to both \( K \) and piezometric head measurements, achieved without destroying the spatial pattern of the \( K \) realization, i.e. displaying the same spatial variability as observed in the field. The main difference with before-existing methodologies is the generation of multiple equally likely solutions to the inverse problem in a Monte-Carlo framework and the parameterization of the \( K \) field. The advantage of the SSCM is that each calibrated \( K \) field displays a 'natural' variability.

The theoretical basis of the SSCM method was given by Gomez-Hernandez et al. (1997); Capilla et al. (1997), including testing on a 2-D steady-state inverse flow prob-
lem. The numerical methods used to solve the groundwater flow equation have been implemented for a confined aquifer in the inverse modeling code INVERTO (Hendricks-Franssen, 2001).

The essential steps of the SSCM are (Hendricks-Franssen, 2001):

1. A seed field is generated - e.g. by the Sequential Simulation Technique - honoring the $K$ data

2. The full groundwater flow equation is numerically solved for given boundary conditions and specified input parameters (storativity, recharge, boundary conditions,...). The numerical solution of the groundwater flow equation is achieved in a finite difference scheme. The numerical scheme allows to deal with large LogK-variances (higher than one) realizations and complex boundary conditions. The calculated solution is fully implicit and is achieved without any linearization of the groundwater flow equation.

3. The mismatch between simulated and observed hydraulic heads is calculated by means of the objective (or penalty) function $J$, defined as the sum of squared deviations between measured and simulated heads plus the sum of squared deviations between updated and prior values $Y_p$, $p = 1, \ldots, n_p$ for the parameter type $p = K, S, \ldots$

$$J = \sum_{t=1}^{N_t} \sum_{i=1}^{N_h} \xi_{i,t} (h_{i,t}^{sim} - h_{i,t}^{meas})^2 + \psi_p \sum_{p=1}^{n_p} \sum_{i=1}^{N_{Y_p}} (Y_{i,p}^{sim} - Y_{i,p}^{meas})^2 \quad (3.6)$$

where $N_h$ is the number of head measurements, $N_t$ the number of transient head measurement at each location, $\xi_{i,t}$ are the weights related to head measurements errors, $N_{Y_p}$ the number of measurements of the $p$-th parameter and $\psi_p$ the covariance matrices of the corresponding parameter. The definition (3.6) of the penalty function has been shown to maximize, under certain assumptions (e.g. covariances of prior head errors and prior parameters errors is fixed), the likelihood that estimated values are true, given the measurements (Carrera and Neuman, 1986). We will consider the case $\psi_p = 0$, i.e. no penalty for $Y_p$.

4. Perturbations $\Delta K$ of the seed field are sought that can produce the largest reduction in the $J$ value, given constraints (see equation 3.7). The $K$ field to be


updated is parameterized as the sum of the 'seed' field plus perturbation $\Delta K$:

$$K_{\text{updated}} = K_{\text{seed}} + \Delta K.$$ 

The search for $\Delta K$ that minimizes the penalty function (3.6) is performed by the calculation of a gradient vector, containing the partial derivatives of $J$ with respect to perturbation of parameters under calibration. This is done by means of the CPU-efficient Adjoint State Method (Carrera et al., 1990), where the Lagrangian of $J$ instead of $J$ itself is minimized with the Lagrange multipliers method.

An updating direction is derived from the vector gradient. Four different non-linear optimization algorithms are alternatively used in INVERTO (Steepest Descent, Hestenes-Stiefel and Fletcher-Reeves Conjugate Gradient, Davidson-Fletcher-Powell Quasi-Newtonian Method) to improve the searching efficiency of the gradient/updating direction (Hendricks-Franssen, 2001).

For CPU-time economy, perturbations are calculated at a limited number of selected locations only - called master blocks. Master-block locations will be randomly changed at each iteration.

5. The optimized perturbations $\Delta K_{\text{update}}^k$ at the $N$ master blocks are interpolated to each grid cell $(i, j)$ in the domain $\Omega$ by ordinary kriging

$$\Delta K_{i,j}^{\text{update}} = \sum_{k=1}^{N} \lambda_{ij}^k \Delta K_{k}^{\text{update}}$$

where $\lambda_{ij}^k$ are the kriging weights. Constrained optimization is used in the procedure to improve numerical stability of the solution: the allowed departure of the updated $K$ field is limited to plus/minus three times the kriging standard deviation $\sigma_{\text{krig}}$

$$K(i, j) - 3 \sigma_{\text{krig}}(i, j) \leq \Delta K(i, j) \leq K(i, j) + 3 \sigma_{\text{krig}}(i, j)$$

(3.7)

In a similar fashion, other parameters such as recharge, storativity and boundary conditions can be updated.

6. The groundwater flow equation is solved for the updated $K$ field. The objective function (3.6) is re-evaluated. Two possibilities exist at this stage:
(a) The iterative procedure is stopped if the updated $J$ value falls below a modeler pre-defined value, if a number of maximum iterations is exceeded or if the relative change in $J$ is too small. The $K$ realization is considered conditional to the head measurements.

(b) If $J$ is larger than a pre-defined value or if the number of maximum iterations is not exceeded yet, steps 4 and 5 are repeated and the head field is updated again.

7. The procedure continues iteratively until the updated $K$ field is found that minimizes the penalty function.

During the inversion procedure, the realization is maintained conditional to hydraulic conductivity data. The $K$ data are automatically matched in the algorithm by assigning perturbations $\Delta K = 0$ at measurement locations. There is also the possibility to account for measurement errors on $K$ by allowing some variability at measurement locations within a proportion related to the assigned measurement error.

The Sequential self-Calibrated Method was extended and formulated to include 2-D transient groundwater flow, with additional joint calibration of storativities (Hendricks-Franssen et al., 1999), as well as joint calibration of transmissivity and recharge (Hendricks-Franssen et al., 2004). Further research has been devoted to inverse modeling of 3-D flow in fractured media (Gomez-Hernandez et al., 2001; Hendricks-Franssen and Gomez-Hernandez, 2002) as well as to coupled inverse modeling of flow and transport equations, making use of concentration data (Hendricks-Franssen et al., 2003). The code has been tested in several case-studies (Hendricks-Franssen et al., 1997; Gomez-Hernandez et al., 2001; Hendricks-Franssen and Gomez-Hernandez, 2002; Hendricks-Franssen and Stauffer, 2005).

### 3.4 Baltenswil case-study

The Baltenswil area (3x3 km²) is discretized on a 60x60 cells grid (1 cell = 50x50m²). Since water table fluctuations amount to less than 15% of the average saturated zone
3.4. Baltenswil case-study

Fig. 3.2: Baltenswil model geometry, with pumping stations (red squares), springs (yellow squares) and observation boreholes (red stars). Boundary inflow from the hills in the North-east is indicated with arrows.

Fig. 3.3: Example of LogT realization (Nr.99) conditional to transmissivity measurements.
Chapter 3. The groundwater flow model

thickness (see chapter 2, Fig. 2.8), the aquifer can be modeled as 2-D confined. Seventeen hydraulic conductivity measurements are available at pumping stations (indicated as 'PW') and observation boreholes ('Kb') in the modeled domain. Data are spread over the area in an irregular fashion. There is a lack of data especially in the South-western part of the domain, mostly hilly and covered by deep forest (Fig. 3.2). The observed variability is high, varying over three orders of magnitude from $K = 10^{-2}$ to $10^{-5}$ m/s.

Due to the small number of available data, a good fit of the sample variogram (equation (3.3)) could not be achieved. The variogram model and relevant parameters have thus been chosen following rules of thumbs and direct experience. A nested nugget-exponential model variogram is used with nugget equal to the measurement error ($c_0 = \sigma^2_{nugget} = 0.25$), sill equal to experimental variance ($\sigma^2_{LogT} = 0.5$) and practical range equal to one tenth of the domain size ($r=300$ m). The geometric average of the transmissivity field is ($LogT = -3.3$). GCOSIM3D (Gomez-Hernandez, 1991) is used to generate by Sequential Simulation an ensemble of 100 equally-likely LogT realizations conditional to transmissivity measurements (Fig. 3.3).

In addition, these realizations were conditioned to transient head data with the help of INVERTO (Hendriks-Franssen, 2001). The following groundwater flow equation in two dimensions was numerically solved

$$\nabla \cdot (T(x) \cdot \nabla h(x, t)) + q(x) = S(x) \frac{\partial h(x, t)}{\partial t}$$

where $\nabla \cdot$ is the divergence operator, $\nabla$ is the gradient operator, $T(x)$ is transmissivity [m$^2$/s], $h(x, t)$ is the unknown piezometric head [m], $q$ is the source/sink term [m$^3$/s], $S(x)$ the storage coefficient [-], $x$ is the vector of the spatial coordinates [m] and $t$ is time [s].

The variogram model for LogT-calibration is the same as defined for Sequential Simulation (nested nugget-exponential) but, in addition, two zones are identified in the domain and characterized with different variogram parameters

- First zone: the part of the aquifer with a saturated zone thickness of more than 2 m. The variogram practical range is set to one-tenth of the domain length $r = 300$ m.
3.4. Baltenswil case-study

- Second zone: the North-eastern hilly area, where the saturated zone is less than 2 m thick. In the aim to provide an accurate estimation of the boundary inflow from this area, this zone is included in the calibration procedure as virtually saturated zone, e.g. as a thin saturated layer of 0.1 m thickness. We assume the average LogT value in this zone to be at least one order of magnitude lower than in the aquifer ($\log T = -4$) and allow it to vary two orders of magnitude during the calibration process. An artificially high value of the variogram range is chosen to allow a smoother (less spatially variable) calibrated LogT value across the NE inflow zone.

Three different ensembles of 100 realizations each are calibrated to transient heads. Because of the variogram uncertainty, we will use the experimental variance as well as higher and lower values of the Log$^2$-variance (the sill value)

1. moderate variance: $\sigma^2_{\log T} = 0.25$
2. large variance: $\sigma^2_{\log T} = 0.5$
3. very large variance: $\sigma^2_{\log T} = 1$

Corresponding to total sill (experimental plus nugget variance) $c = 0.5$, $c = 0.75$ and $c = 1.25$ respectively. The larger variance results also in higher small-scale variability and more preferential flow paths (high T-conduits). It should be reminded, however, that the Multi-Gaussian RF models are not well suited to account for connectivity in extreme Log$^2$ values.

Each realization of the ensemble is inversely conditioned to transient head data, maintaining the realizations conditional to 17 LogT measurements. A small departure from the measured value is nonetheless allowed by measurement error.

The LogT measurement locations are also regarded as master blocks, i.e. locations where the field perturbations $\Delta T$ are calculated and then spread through the domain by kriging. At these locations the perturbations are limited by the measurement errors. Additional 50 master blocks are included in zone one and 16 master blocks in the (smaller) zone 2. Master blocks are isotropically located on a regular grid with random starting point in zone 1, and randomly located in zone 2. Eight master blocks are used to krige the perturbation for each grid-cell. Two master-blocks per (effective)
correlation range are placed throughout the domain and redistributed at each iteration (Hendricks-Franssen, 2001).

INVERTO has two criteria to stop the inversion procedure. First, the calibration stops when the objective function falls below what is estimated to be an acceptable error. In our case study, 96 transient head data are available for each of the 5 pumping stations (years 1999-2006), and 120 for each of the 4 boreholes (years 1994-2003). Assuming as acceptable a residual error of 10 cm for each measurement, the lower limit of the objective function $J$ is set to $J_{\text{stop}} = (96 \times 5 + 120 \times 4) \times (0.1)^2 = 9.6 \text{ m}^2$. Alternatively, the calibration procedure is stopped when a user-defined maximum number of iterations is reached (1500 in our case, including inner and outer iterations).

### 3.4.1 Modeling approach

We aim at the calibration of the Log$T$ field to transient head measurements, as the transmissivity field is identified as the most consequential parameter on the uncertainty of the model (groundwater flow and, most importantly, solute transport) predictions (local transmissivity data vary over 3 orders of magnitude). Nonetheless transmissivity is not the only uncertain parameter. Recharge and discharge to/from groundwater and the storativity parameter are also uncertain, although their spatial variability is smaller than that of the transmissivity parameter. Besides, recharge and discharge are not only spatially but also temporally variable parameters. Since we are aiming at a 'dynamic' calibration of the system (by the honoring of transient head data), the uncertainties that affect the system variables controlling its temporal behavior have also to be properly handled.

The fact that all parameters (except, if wanted, storativity, whose uncertainty is not large for known geological and soil conditions) show significant uncertainties, prevents their joint calibration. Transmissivity and recharge are so highly correlated that their joint identification becomes difficult. Storativity, controlling the system storage together with water input and output from the aquifer, shows smaller uncertainty if compared to the more important uncertainties regarding the water balance. Joint calibration of storativity and transmissivity is thus not performed.

Then, we first establish a physically-based model to calculate the recharge rate in time
(see next section). The same is done to evaluate the discharge rate, where natural springs are modeled as drains (and not fixed heads) according to the physics that governs the discharge mechanism. Fixed heads may not be suited to model discharge locations in a transient regime, since they may add water to the aquifer in case of low groundwater tables.

The parameters governing recharge (field capacity, actual evapotranspiration and crop coefficients, delay - see next section), discharge (drain height and conductance - see next section) and storage (storativity) are all independently estimated based on physical knowledge and prior information. The drain height is chosen to allow the drain to run most of the time (which happens according to private information) and their conductance is determined according to the dynamic response of the aquifer system (e.g. after intense precipitation events) is reproduced, where this could not be handled by modifying storativity alone. Storativity is manually calibrated instead, by judging whether the aquifer response is in phase with the observed groundwater table fluctuations records.

In addition, and most importantly, their estimation is made consistent with the reproduction of transient head data by running - in a trial and error framework - inverse simulations with INVERTO (Hendricks-Franssen, 2001) for selected transmissivity fields. For this purpose, discharge via drains has been implemented in a new version of the code INVERTO. When a realistic (i.e. honoring transient heads in the best achievable way) set of the water balance parameters has been found for the selected inverse-calibrated realizations, stochastic inverse modeling is finally performed on the transmissivity parameter for all the $T$-realizations of the ensemble.

3.5 Groundwater recharge and discharge

3.5.1 The Soil-Water Budget Method

Due to the high spatial and temporal variability of the phenomena involved (precipitation, evaporation and transpiration, free surface overflow, percolation through the subsurface, topography, soil type and vegetation cover, preferential flow paths,...), groundwater recharge is also subject to significant uncertainties, although to a smaller extent than transmissivity. An exact characterization of the spatial and temporal distribution of recharge is usually very difficult to obtain. Moreover, recharge is not
measurable with sufficient accuracy on any spatial scale. We give an independent estimate of this parameter by means of the Soil-Moisture Balance Method (Blau et al., 1983), a box-model model that, starting from meteorological data, allows estimating the aquifer recharge as residual of all other fluxes (Fig. 3.4).

Soil moisture budgeting models were originally developed for humid climates, such as the temperate climate of Central Europe. They become less reliable in arid and semi-arid climates, where precipitation and Evapo-Transpiration become almost equal. Budget models work best for seasonal patterns of recharge, well developed soils which do not dry completely, where potential and actual ET are of similar sizes and with uniform and widespread precipitation. Although simple and prone to sensible errors, budget methods can be useful to give independent estimates of recharge by exploiting further available physical knowledge about the system, such as information coming from soil physics and meteorological data.

The unsaturated zone receiving precipitation is divided in two zones. The upper zone is used as control/buffer volume for water budget calculations of exchanged fluxes (precipitation, actual evapotranspiration and run-off), ideally representing the root zone. The amount of water which is stored in the upper zone is referred to as soil moisture. Each time the soil moisture exceeds the soil field capacity, the surplus water is allowed to
3.5. Groundwater recharge and discharge

leave towards the lower zone, where deep percolation takes place, which enters the groundwater as recharge. The balance equation in the buffer zone for a time interval $\Delta t$ is

$$B(t + \Delta t) = B(t) + (N(t) - E_{\text{act}}(t) - R(t) - DP(t)) \cdot \Delta t$$

where $N$ is precipitation, $E_{\text{act}}$ is actual Evapo-Transpiration (ET), $R$ is runoff, $B$ is soil-moisture content and $DP$ is deep percolation. These quantities are all expressed with length units [m] for each time interval $\Delta t$. The control volume is assumed to be 2 m thick, in accordance with the average depth of the root zone (section 2.4). Budget calculations are performed on a daily basis, using daily meteorological data available at the meteorological station Kloten (Canton Zürich), six kilometers away from the modeled domain. All these quantities are related to unit horizontal area and unit time. As discussed in section 2.4, runoff can be neglected in the study area, $R(t) = 0$.

3.5.2 Estimation of Actual Evapo-Transpiration

The estimation of actual Evapo-Transpiration is one of the most consequential with regard to the reliability of calculated recharge. Evaporation from soil surfaces and transpiration from growing plants are major processes essentially driven by the energy input from the sun. Potential Evapo-Transpiration ($E_p$) can be estimated via an energy/radiation balance taking place in the coupled atmosphere/soil system (ASCE, 2000). One of the most commonly adopted methods in hydrological science is the simplified Penman-Monteith empirical formula (Penman, 1948, 1963; Montheit, 1965), generally considered very efficient in humid climates. We make use of a simplified version of the formula (Wendling, 1996)

$$E_p = 2.3 \cdot \frac{T + 22}{T + 123} \left[ \frac{0.6 \cdot K_{\text{day}}}{L(T)} + 0.66 \cdot (1 + 1.08 \cdot v) \cdot \left(1 - \frac{U}{100}\right) \cdot S_d \right] \left[ \frac{\text{mm}}{\text{day}} \right]$$

The formula requires the knowledge of several atmospheric and soil parameters: global radiation $K_{\text{day}}$ [J/cm²], air temperature $T$ [°C], wind velocity $v$ [m/s], relative humidity $U$ [%] latent evaporation heat $L = L(T)$ [J/cm²/mm], relative sunshine duration $S_d$ [\%]. All these relevant quantities have been continuously measured at the meteorological station Kloten (ZH) since 1971.
By application of equation (3.8), the daily potential ET values can be calculated. Actual ET is derived from potential ET taking into account the soil moisture deficit in the buffer zone and the land use through a simple threshold scheme

\[
ET_{act}(t) = \begin{cases} 
0, & B(t-1) < \theta_{wp} \\
K_c \cdot \frac{B(t-1) - \theta_{wp}}{\alpha \theta_{FC}} \cdot ET_p(t), & \theta_{wp} \leq B(t-1) < \alpha \theta_{FC} \\
K_c \cdot ET_p(t), & \alpha \theta_{FC} \leq B(t) < \theta_{FC}
\end{cases}
\]

where \( \theta_{wp} \) is the wilting point (minimum water content [mm] needed for plant survival) and \( \theta_{FC} \) is the field capacity (threshold water content [mm] stored in the control volume above which deep percolation takes place). Both quantities can be derived from soil maps and specific tables and diagrams relating soil water content \( \theta \) and matric potential \( \Psi(\theta) \). Characteristic curves are available for different soil types (sand, silt and clay). According to the soil types in the Baltenswil domain (section 2.4) and considering a control volume of 2 m thickness, field capacity has been estimated to be \( \theta_{FC} = 250 \) mm. Wilting point is at \( \theta_{wp} = 20 \) mm and the constant \( \alpha = 0.7 \) indicates a standard proportion of field capacity for the definition of dry soils.

Land use is also accounted for by the crop coefficients \( K_c \) in the actual ET calculation.

Fig. 3.5: Calculated actual ET for agricultural land use \( (K_c = 0.8) \). According to available measurements, the average yearly actual ET rate lies between 500 and 600 mm/yr in the area, about 1.4 to 1.6 mm/day (Menzel et al., 1997). Actual ET is often equal to potential ET, but for instance in 2003 it was smaller. Significant discrepancies between the two quantities can take place on a daily basis.
3.5. Groundwater recharge and discharge

The crop coefficient \( 0 \leq K_c \leq 1 \) is a multiplication factor that can be estimated by Bragov’s Method (Wendling, 1996). Three constant values are selected for three different surface soil types and land use types in the study domain. Forest: \( K_c = 1 \), agriculture: \( K_c = 0.8 \) and \( K_c = 0.3 \) for urban areas to account for green areas in villages (Fig. 3.5).

3.5.3 Deep percolation

Deep percolation \( DP(t) \) is calculated as a residual between fluxes involved in the buffer zone.

\[
DP(t) = \begin{cases} 
0 & \text{if } B(t-1) + P(t) - ET_{act}(t) < \beta \cdot \theta_{FC} \\
\gamma \cdot (P(t) - ET_{act}(t)) & \text{if } \beta \cdot \theta_{FC} \leq B(t-1) + P(t) - ET_{act}(t) < \theta_{FC} \\
B(t-1) + N(t) - ET_{act}(t) - \theta_{FC} & \text{if } B(t-1) + P(t) - ET_{act}(t) \geq \theta_{FC} 
\end{cases}
\]

(3.9)

Constants \( \beta = 0.7 \) and \( \gamma = 0.1 \) have reference values defined in literature (Blau et al., 1983). Sensitivity analysis shows that the constants \( \alpha, \beta \) and \( \gamma \) have a small effect on the calculated deep percolation. According to the threshold scheme in equation (3.9), when the input \( (P - ET_{act}) \) increases the stored water volume \( B \) above the soil field capacity, the water in excess leaves the control volume as percolation. A small percolation fraction \( \gamma \cdot (P - ET_{act}) \) is also allowed when soil moisture is below the field capacity. The calculated deep percolation shows important sensitivity only to the field capacity \( \theta_{FC} \) and crop coefficient \( K_c \). The larger the values of these two parameters, the smaller the calculated deep percolation.

3.5.4 Delayed recharge to groundwater

Natural recharge to groundwater may differ from calculated deep percolation \( DP(t) \) by a time-delay in case of deep groundwater tables (Fig. 3.6). A single linear reservoir model can be used to account for this effect. The complete de-watering of the control volume by a quantity \( DP(0) \) is described by an exponential law

\[
DP(t) = DP(0) \cdot e^{-\alpha t}
\]
where \( \alpha \) [1/s] is a characteristic time of the de-storing process. This constant can be made dependent on the thickness of the unsaturated zone \( z \) [m], to allow a slow de-watering process in case of deep groundwater tables and fast dynamics for shallow ones

\[
\alpha(z) = -\frac{K_{\text{uns}}}{n z}
\]

where \( K_{\text{uns}} = 10^{-5} \text{ m/s} \) is the unsaturated zone hydraulic conductivity [m/s], estimated to be two orders of magnitude lower than the average saturated hydraulic conductivity and \( n = 0.15 \) is porosity. At the same time, the delayed seepage water must satisfy mass conservation. By introduction of a normalization constant \( C(z) \) this condition can be written as

\[
\int_0^\infty C(z) \cdot DP(t) \, dt = DP(0)
\]

The recharge delay to groundwater can be obtained as

\[
DP(t) = \left(e^{\alpha(z)} - 1\right) \cdot DP(0) \cdot e^{-\alpha(z) \cdot t}
\]

The maximum delay obtained with the chosen parameters is 6 months. This value is dependent on the calculated \( \alpha(z) \) parameter for a particular cell. Large values of \( \alpha(z) \)
3.5. Groundwater recharge and discharge

result in smaller delay and smoothing effect.

3.5.5 Groundwater discharge

Groundwater discharge is simulated via three drain locations representing the several natural springs distributed at the aquifer boundaries (see Chapter 2, Fig. 2.6). At a drain grid-cell water is allowed to flow out the domain when the hydraulic head is above an assigned height. The drain discharge law is linearly dependent on the difference between actual hydraulic head and the given drain height \( h_d \) [m] (Fig. 3.7)

\[
Q = \begin{cases} 
C_d \cdot (h - h_d) & \text{if } h > h_d \\
0 & \text{otherwise}
\end{cases}
\]

where \( C_d \) is the equivalent hydraulic conductance \([\text{m}^2/\text{s}]\), a quantity which measures the drain resistance to water flow. Drain locations, in the high conductance limit \( C_d \to \infty \) behave like fixed heads. The difference between these two boundary conditions lies in the fact that drains are pure discharge locations, activated only when \( h > h_d \). An estimation of a drain height could be drawn from topographical maps, while equivalent hydraulic conductivity had to be calibrated manually. Springs were not directly accessible since many of them are located in private houses.

![Fig. 3.7: Time-varying head simulated at drain Nr2, close to PW Girhalden, as example of drain functioning. Discharge does not take place during the years 1997-1998 as well as after the dry summer in 2005](image-url)
The three drains have been calibrated manually together with recharge to achieve a satisfactory match between simulated and measured heads. Drain Nr.1, close to the Baltenswil pumping station, has been estimated to be at \( h_d = 459 \) m.a.s.l. with an equivalent hydraulic conductance \( C_d = 10^{-2} \) m\(^2\)/s. Drains Nr.2 and Nr.3, close to the Southern boundary, are both set at \( h_d = 447 \) m above sea level with \( C_d = 10^{-3} \) m\(^2\)/s.

### 3.5.6 Results

Because of tracer transport model requirements, recharge is calculated for the time interval 1961-2006. Monthly averages of recharge - calculated from the daily values - during years 1991-2006 are used as input for the groundwater flow inverse modeling and are shown in Figs. 3.8 and 3.9.

The calculated monthly-averaged recharge is capable of reproducing seasonal variations of the groundwater table, and specifically reproduces very well the drought (low recharge) of the extremely dry summer 2003 (Fig. 3.8). Calculated average yearly values for deep percolation amount to 516 mm for forest, 637 mm for agricultural and 181 mm for urban areas. The system response to precipitation is almost immediate for shallow groundwater (about 10 m deep), while at larger depths recharge becomes smoother and more delayed (up to 4 months). The calculated recharge to groundwater is also in good agreement with the measured head variations at observation boreholes in the PW Baltenswil catchment, where the groundwater is relatively shallow, in terms of both amplitude and phase (Fig. 3.9).

The model parameters determining the water balance of the aquifer (recharge, discharge and storativity) have been calibrated manually by direct integration of calculated recharge and discharge set-up as input into the inversion procedure for selected calibrations. Due to lack of direct measurements, their automatic calibration within the inversion procedure was not performed. Based on the achieved match between calibrated and observed transient heads, a realistic water balance could be achieved. The same water balance values are used during calibration of all \( T \)-realizations. A constant storativity value \( S = 0.2 \) - realistic for a sand/gravel unconfined aquifer - has been assigned. The calibration of water balance, affected by uncertain input (recharge), output (discharge mechanism) and storage (storativity value) was found to be a key and not trivial step towards the reproduction of a satisfactory match of the
3.5. Groundwater recharge and discharge

Fig. 3.8: Calculated recharge to groundwater for different depths of the unsaturated zone, years 1991-2007

Fig. 3.9: Measured head time series in 1994-2003 in four boreholes in the PW Baltenswil catchment versus calculated recharge (blue histogram) at a reference depth of 15 m. Boreholes locations are shown in Fig. 3.2
transient hydraulic heads. Water abstraction from the five pumping stations is also accounted for in the water budget. Pumping data are given on a yearly basis from 1991 to 1998, and on a monthly basis later (see chapter 2, Fig. 2.12).

### 3.6 Groundwater flow simulations results

#### 3.6.1 Conditioning to transmissivity

One hundred realizations conditioned to transmissivity measurements were generated by means of Sequential Gaussian Simulation with the code GCOSIM3D (Gomez-Hernandez, 1991). The North-east inflow zone is given a constant LogT=-4 value, which will be later inversely-calibrated. Realizations conditional only to transmissivity show a distinct amount of spatial variability, but do not display any particular global pattern. The match with observed transient heads at this stage is very poor, as can be seen from the high objective function values (Fig. 3.10).

#### 3.6.2 Conditioning to hydraulic heads

The flow model is calibrated in a transient regime for the years 1991-2006 by means of the code INVERTO (Hendricks-Franssen et al., 1999). Calculated recharge to groundwater and pumping data are given for this period on a monthly basis. Time discretization for the solution of the groundwater flow equation is 3 days, resulting in 1920 time-steps. The harmonic mean is used to calculate inter-block transmissivity averages. Monthly-averaged head data - calculated from daily head records at pumping stations - were used for conditioning at the pumping stations. Ninety-six monthly-averaged head data (years 1999-2006) at each of the five pumping stations (PW) are available. At the four observations boreholes (Kb94-1, Kb94-2, Kb14 and Kb85-1) located in the neighborhood of PW Baltenswil, 120 monthly head data (years 1994-2003) are used for conditioning at each borehole. In total, 960 transient head data were used. The numerical simulation starts 3 years (360 time-steps) earlier than the first head data are available to reduce the influence of uncertain initial conditions.

The transient inversion procedure takes on average 24 hours CPU-time for each realization. Calibration of 3 ensembles of each 100 LogT-realizations to transient
heads needed 300 calculating-days, distributed on eight CPU processors (PowerPC G5 970FX, 2.3 GHz each) operating in a Mac-OS Xserve5 G5 cluster.

Fig. 3.10: Three LogT realizations conditioned to the transmissivity measurements: LogT spatial distribution (left) and LogT histogram (right). Calculated objective function values for all realizations are still very high.
Fig. 3.11: Head-time series for 100 realizations calibrated to T and head data. The objective function value [m^2] for each observation location is shown.

### Heads [m] for Various Locations

<table>
<thead>
<tr>
<th>Location</th>
<th>Heads [m]</th>
<th>Objective Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW Girhalden</td>
<td>J = 74.66</td>
<td></td>
</tr>
<tr>
<td>PW Bruttisellen</td>
<td>J = 56.33</td>
<td></td>
</tr>
<tr>
<td>PW Buel</td>
<td>J = 74.66</td>
<td></td>
</tr>
<tr>
<td>PW Baltenswil</td>
<td>J = 49.63</td>
<td></td>
</tr>
<tr>
<td>Kb 94-1</td>
<td>J = 49.68</td>
<td></td>
</tr>
<tr>
<td>Kb 94-2</td>
<td>J = 73.94</td>
<td></td>
</tr>
<tr>
<td>Kb 14</td>
<td>J = 82.51</td>
<td></td>
</tr>
<tr>
<td>Kb 85-1</td>
<td>J = 49.63</td>
<td></td>
</tr>
</tbody>
</table>
3.6. Groundwater flow simulations results

Fig. 3.12: Head-time series at borehole Kb94-2. The two high-lighted realizations show the difficulty of INVERTO in reproducing the water table fluctuations in terms of both phase and amplitude. Conceptual uncertainties on the water budget, and especially on short temporal scale, prevented a better fit of the complete data time-series.

Fig. 3.13: Head scatter diagrams for one realization at selected observation locations. Significant deviations take place in all cases, especially at the pumping stations.
Simulation results for the ensemble $\sigma^2_{\log T} = 1$ are shown in Fig. 3.11. INVERTO could achieve LogT realizations that allow a reasonably good fit at all observation locations. The drought of the dry summer 2003 is especially well reproduced. Water table variations are also correctly accounted for, except for the period 1999-2002 at the boreholes location Kb94-1, Kb94-2, Kb14 and Kb85-1 (Fig. 3.11, below). After the continuous drop in hydraulic heads which took place until 1998, groundwater table levels started to rise in 1999 and resumed fluctuating with a more or less seasonal character (high water tables in autumn/winter and low ones in spring/summer). The fast water table fluctuations in 1999-2001 could not be reproduced by the calibrated LogT-field. INVERTO calibrates the LogT-fields by honoring the observed water table variations in phase, but cannot always fully account for their amplitude (Fig. 3.12). Nonetheless, reproduction of water level fluctuations could be achieved for the period 2002-2006, which is the period of greatest interest for the transport modeling (environmental tracer data available for years 2003-2006, see chapter 5).

3.6.3 Discussion

Clear patterns characterize the LogT-fields when made conditional to transient hydraulic head measurements. Increased small scale variability, appearance of patterns of high and low transmissivity and change in the actual LogT distribution takes place for each realization. After conditioning to heads, the original Gaussian-shaped LogT distribution, as obtained with GCOSIM3D, partly loses its Gaussian character. The boundary inflow is also calibrated by a suitable constant LogT value in the North-east zone, adapted to each realization (Fig. 3.14).

Objective function values after calibration to head values range from a minimum of nearly $J=600 \text{ m}^2$ to a maximum of $J=3000 \text{ m}^2$. Realizations with $J<1000 \text{ m}^2$ have been judged as satisfactorily calibrated (Fig. 3.15). Comparison of LogT calibrated realizations and related simulated head time-series with the three different statistics postulated for the LogT variances ($\sigma^2_{\log T} = 0.25$, $\sigma^2_{\log T} = 0.5$ and $\sigma^2_{\log T} = 1$) show that the flow model is almost insensitive to this parameter. Zones with higher and lower than average LogT can be reproduced. Preferential flow paths however do not clearly emerge, the reason probably being the underlying Gaussianity of the realization ensemble. The ensemble statistics of the calibrated results shows nonetheless that slightly better calibration is achieved allowing maximum LogT-variance (Fig. 3.15, right).
3.6. Groundwater flow simulations results

Fig. 3.14: Effects of calibration to heads on the Log\(T\) field and distribution. The sample population Log\(T=-4\) (left) stems from the un-calibrated grid cells in the North-east zone (zone 2 - left). This value, governing the boundary inflow to the aquifer proper (zone 1), is re-calibrated according to the simulated/measured head match.

Fig. 3.15: Objective function \(J\) distribution before (left) and after (right) calibration to hydraulic heads. Statistics for three different a-priori variances are reported. The objective function value drops one to two orders of magnitude after conditioning to heads (note the different scales of the two graphs).
Fig. 3.16: Examples of LogT realizations made conditional to transient head data. Realizations #15 and #25 are subject to severe oscillations in the solutions and display a non-realistic T-field. The related objective function values are respectively $J=807$ and $J=2469$. In particular, realization #43 shows a credible LogT field and has a low objective function, but was discarded due to numerical oscillations of the head solution at some observation locations. A low $J$ value can mislead the modeler’s judgement. Most realizations show objective function values below 1000 and are regarded as conditional (or calibrated) realizations.

LogT realizations conditioned to head data show a variety of patterns, and are able to reproduce the small scale variability as observed by field measurements (Fig. 3.16). Only 25 of the initial 100 T-conditional realizations could not achieve a satisfactory match with the observed heads. The judgement is based either on objective function value or on plausibility of the obtained LogT-field patterns. Especially in case of numerical oscillations, extreme patterns can be obtained for the calibrated LogT-field even when a low objective function value may indicate calibration has been achieved.
3.7. Conclusions

Numerical oscillations are likely to take place especially at discharge locations, and from there propagate through the aquifer. These non-physical solutions have to be discarded. Uncertainties in the conceptual model, with special regard to the water balance (recharge estimation, drain location and discharge rates) can be responsible for these numerical instabilities.

The calibrated transmissivity fields give rise to transient head fields that are capable of reproducing the observed water table conditions in periods of high recharge (winter months) and low recharge (summer months, Fig. 3.17). The ensemble average LogT and ensemble LogT-variance were calculated making use of the 75 realizations which resulted conditional to the data, both for ensembles conditioned only to LogT data and the inverse conditioned ensemble (Fig. 3.18). Ensemble statistics for LogT fields conditional only to the transmissivity data do not display significant patterns in transmissivity. The spatial average over the 100 realizations is comparable to the measurement LogT average ($\overline{\text{LogT}} = -3.3$). The LogT-variance field before calibration to heads is also smooth and on average is equal to the experimental variance $\sigma_{\text{logT}}^2 = 0.58$ (Fig. 3.18, left). After calibration to transient heads global patterns in the ensemble average LogT-field become apparent. Zones with higher and lower than average LogT values appear. The LogT-mean over all inverse conditioned realizations ($\overline{\text{LogT}} = -2.3$) is lower than the measurements LogT average, while LogT-variance ($\sigma_{\text{logT}}^2 = 0.58$) over the ensemble did not change much although it is clearly spatially redistributed. Larger uncertainties characterize areas where no transmissivity or head measurements are available for calibration.

3.7 Conclusions

A careful determination of the global water balance in the area proved a key step towards the full reproduction (amplitude and phase) of the observed groundwater table fluctuations. Not any independently estimated recharge allows to reproduce the observed heads with correct amplitude and phase, nor do any drain configuration or storativity value. Despite the model uncertainties, the transient hydraulic head data allow a better account of the heterogeneity of the transmissivity fields. The Monte-Carlo analysis of the stochastic realizations showed a tendency towards similar transmissivity spatial patterns, e.g. the presence of a transmissivity ‘dam’ in the middle of the domain separating the Northern and the Southern parts of the aquifer (Fig. 3.18). The parameters governing the water balance are sensibly constrained by the
observed transient heads. Besides, it was also possible to exclude about 25% of the calibrated transmissivity realizations from the conditional ensemble as they did not honor the transient head data. Besides, the stochastic/Monte-Carlo approach allowed to estimate - and reduce, via the conditioning to data - the uncertainties in the simulated head fields and in the calibrated transmissivity realizations. Finally, the achieved calibration of a stochastic LogT field provides a satisfactory modeling of flow for future tracer transport modeling purposes.

Significant errors in transient forcing such as recharge and discharge are probably the reason for the only partially successful head match. Although the reconstruction of the recharge to groundwater seems reasonable, as it correlates extremely well with the piezometric head variations at the observation boreholes, an improved division between soil evaporation, season-dependent transpiration and water interception (e.g. by leaves) may have allowed to achieve a better match. Drains in particular are difficult to calibrate in absence of clear hydrogeological knowledge about the drain locations and discharge efficiency. They nonetheless provide a more correct physical modeling of the discharge process via springs if compared to fixed heads. Drains are purely discharge locations, while steady-state prescribed heads are often unrealistic in transient conditions, by leading to inflows.

The uncertainty on recharge rates and its effects on the achieved fit between observed and measured transient heads has been investigated by using meteorological data from three different stations in the modeled domain vicinity (less than 10 km. far) for the calculation of the recharge rates to be feeded into the inverse calibration for one \( T \)-realization conditional to \( T \)-data only. Calculated recharge time series from the three stations data show discrepancies as large as 20% and have quite different time evolution. Such experimental uncertainty is reflected in up to 20% uncertainty on the simulated head time series (Fig. 3.19) and more importantly in different \( T \)-calibrated spatial fields (Fig. 3.20). In particular, uncertainties on recharge/discharge rates even on a limited temporal scale (e.g seasonal, Fig. 3.21) prevent the calibration of the complete \( h \)-data series. The reproduction of extreme water table fluctuations thus depends on a correct water balance calculation.

The un-accounted-for spatial variability of the storativity parameter (constant \( S=0.2 \), although displaying smaller variance than transmissivity, might also play a role. Joint calibration of recharge and transmissivity was not attempted since the two parameters
3.7. Conclusions

are difficult to identify jointly, joint identification leading to an ill-posed problem. Besides, the estimation of recharge by a physically based model is more reliable than calibrating it, when both transmissivity and recharge are uncertain. Uncertainties of recharge imply nonetheless the identification of $S$. Water table fluctuations have been addressed by trial and error of different recharge and storativity values as input to the inverse modeling. The parameter governing the Soil-Moisture Budget Model, the drain discharge parameters and a storativity constant value have been adapted in the inverse modeling procedure to the best achievable head fit, based on known geological, meteorological and physical information about the domain.

Greatest difficulties were found in honoring the observed heads at pumping stations, especially where short-term intense pumping rates lead to significant water table variations. Although a good match could be achieved at PW Baltenswil, fast water table fluctuations lead to calibration problems at PW Buel, Girhalden 1 and 2. A possible option is to exclude pumping stations' measurements from the calibration procedure, to reduce extreme transient forcing on the calibrated LogT field. As to our case, pumping stations' head data have been kept since they provide the only available information on hydraulic heads in the South-west part of the modeled domain.

Errors in the conceptual model are most probably the reason for the discrepancies in the full reproduction of the water table variations. Different possible improvements of the conceptual model have been addressed with the aim of correcting local deviations of simulated heads from the measured values. As example, the delay model for recharge has been successfully introduced for this purpose. Unsuccessfully other improvements have also been addressed. Exceptional water abstraction from a construction site close to the aquifer boundary SW of PW Baltenswil has been simulated with a pumping line active only during 2002. Refined evaluation of evapotranspiration was tried, by modification of controlling parameters (global incoming radiation at surface level, crop coefficients and field capacity). Particular attention was devoted to the drainage mechanism. A parabolic (instead of linear) discharge law for the drains has been implemented by modification of the MODFLOW code. The drain efficiency has also been improved by allowing independent calibration of the 8 drain-neighboring cells (by definition of additional variogram zones). These latter additional models are here omitted since they did not bring any substantial improvement in the observed vs. measured hydraulic head match. Further possibilities could be to make the drain conductance $C_d$ explicitly dependent on time and/or on the $T$-realizations.
Fig. 3.17: Selected examples of ensemble averaged calibrated hydraulic head fields [m.a.s.l.] for selected time steps. Ensemble average is calculated over the 75 conditional realizations.
3.7. Conclusions

Fig. 3.18: Log-T ensemble statistics calculated over the 75 conditional realizations: before conditioning to transient heads (GCOSIM3D - left) and after conditioning to transient heads (INVERTO - right)
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Fig. 3.19: Comparison of simulated vs. observed head time series obtained after inversion with the Effretikon precipitation data (standard simulation, Fig. 3.11) and data from two other stations (Opfikon and Kloten) to calculate the recharge rate time series for years 1991-2007.
3.7. Conclusions

Fig. 3.20: Different calibrated $T$-realizations making use of Effretikon - Opfikon - Kloten precipitation data
Fig. 3.21: Calibration with Effretikon precipitation data (standard simulation) and Effretikon data with artificial modification of recharge during years 1998-99
Chapter 4

Environmental tracer transport in the unsaturated zone

Environmental tracers are chemical and isotopic substances released to the atmosphere in the last 50 years by human activities such as above-ground testing of nuclear devices, nuclear power production and other industrial activities. Their atmospheric concentrations have been measured at reference sites across the world, showing in most cases a steadily increasing trend in the last decades. Being soluble in water (or part of it, as in the case of Tritium), these tracers have also been found deep in the subsurface, with non-negligible concentrations in the groundwater body. Environmental tracers have thus been applied as hydrologic tracers in groundwater investigations. Compared to artificial tracers, which are applied locally in time and space by the investigator, environmental tracers are present and distributed in the near-surface environment since the early fifties or even before. This means that their use allows investigating the water movement over a larger time span and an extended spatial domain.

In the present chapter, we introduce a particular class of tracers (the environmental tracers) which will be used in our case study. Environmental tracers, compared to artificial ones, are the only realistic alternative to local investigations with artificial tracers when time-scales of years to decades and more are under study. We address the importance of the transport in the unsaturated zone and propose a method for the reconstruction of the tracer input to the groundwater table by means of numerical simulations of tracer transport in the unsaturated zone. The simulation of tracer transport in the saturated zone will be presented in Chapter 5.
4.1 Classification

Tracers are classified according to their physical and chemical properties as well as their origin (Cook and Herzog, 2000). Ideal tracers possess desirable tracer properties for environmental investigations. These are mobile and soluble, hydraulically, chemically and biologically inactive, non-sorbing and conservative (i.e. not retarded by soil or aquifer matrix). Ideal tracers can provide information on porosity, streamlines, ratio of fluxes, variability of flow field heterogeneity and travel times.

Natural tracers (e.g. \(^{222}\text{Rn}\), salinity, \(^{39}\text{Ar}\), \(^{81}\text{Kr}\), \(^{14}\text{C}\) and also \(^{3}\text{H}\) (Tritium) before the nuclear era) are substances originating from natural processes (diffuse geochemical or biogenic sources) within the geological time-scale.

Artificial tracers (e.g. fluorescent dyes (uranine) or the radioactive tracer \(^{131}\text{I}\)) are substances which are purposefully released at specific locations and times into the environmental system to be investigated. They show pore velocity and dispersion coefficients and are most suited for short time and small spatial scale investigations.

Conservative tracers are characterized by no sources or sinks within the system. These tracers can yield information on the physics of the system and serve for the determination of residence times and mixing ratios, whereas reactive tracers (such as \(^{13}\text{C}\)) can help to study the nature of chemical or biological processes, giving information on average adsorption and degradation parameters.

Environmental tracers are natural and anthropogenic compounds or isotopes widely distributed in the near-surface environment. Man-induced release occurred mostly because of catastrophic events such as thermonuclear bomb testing and nuclear reactor accidents. Release was also caused by leakage from industrial production and waste disposal. Some of these tracers are less abundant isotopes (either stable or radioactive) of common elements. Examples of this kind are Tritium (\(^{3}\text{H}\)), \(^{85}\text{Kr}\), freons used in refrigerator devices (CFCs), SF\(_6\) and \(^{14}\text{C}\). Among these, noble gases isotopes (such as Helium and Krypton) are of major interest, being chemically inert. Being more widely distributed in time and space than any other tracer, environmental tracers are the most suited for the investigations of transport processes on large and different temporal and spatial scales, according to decay rate and emission period in the atmosphere. Some of them - called transient tracers, like Tritium, \(^{85}\text{Kr}\) and CFCs -
4.1. Classification

Fig. 4.1: Annually averaged atmospheric concentrations of some environmental tracers used to determine ages of groundwater, illustrating a variety of input functions. CFC-12, $^{85}\text{Kr}$ and SF$_6$ have monotonically increasing input function from low background level owing to industrial production and release. $^3\text{H}$ and $^{36}\text{Cl}$ illustrate episodic production and release with relatively little natural production. $^{14}\text{C}$ data are given in percent modern carbon. SF$_6$ data in parts per trillion. Note that scaling factors have been added to units for SF$_6$ and $^{36}\text{Cl}$. [Reproduced from Cook and Herzog (2000)]

have a time-dependent input function (Fig. 4.1 and 4.4). Tracers with a time-dependent and well known input function can be used as event-markers for recent waters, by comparing the tracer concentrations in the groundwater samples with the concentration history in the free atmosphere. Time resolution is better for $^{85}\text{Kr}$, CFCs and SF$_6$ than for $^3\text{H}$ and $^{36}\text{Cl}$, because the former have monotonically increasing input functions and measured concentrations in groundwater samples can be uniquely assigned a groundwater age.

Radioactive tracers (like Tritium and Krypton-85) also provide a useful dating method. The ratio of the stable daughter to the radioactive parent is a direct measure of the time elapsed since the water parcel was in last contact with the atmosphere. This will hold in a closed system, where all isotopic changes stem only from radioactive decay. Changes in the ratio daughter to parent concentration can be used to infer timescales of water movement, as in the case of parent-daughter pair tritium - Helium-3. By measuring the isotope proportion (or ratio) to the main stable isotope within a groundwater sample,
the apparent water age \( t \) can be derived from the (known) initial concentration \( c_0 \) (Cook and Solomon, 1997)

\[
t = \frac{\tau_{1/2}}{\ln 2} \ln \left( \frac{c_0}{c_{meas}} \right)
\]

(4.1)

Groundwater dating with Krypton-85 follows this method (see Fig. 4.4). Several practical difficulties may arise in groundwater dating with the isotope method. The atmospheric input function is most of the times not known with sufficient accuracy. Variations in the production rate (e.g. for tritium, by varying solar activity or cosmic radiation) as well as local anthropogenic sources (as is the case for tritium, \(^{85}\)Kr and \(^{36}\)Cl) may result in large uncertainties. Spontaneous radioactive decay in the deep subsurface may also affect groundwater isotope concentration (as is the case for Helium).

In recent years noble gas radio-isotopes were introduced as potential environmental tracers for groundwater investigations. They were found in small (trace) concentrations in the groundwater. Although complicated measuring procedures and above all large sample volumes are needed for sampling and measurements, they provide an additional dating tool for a wide range of time-scales: \(^{37}\)Ar (\( \tau_{1/2} = 35 \) days), \(^{85}\)Kr (\( \tau_{1/2} = 10.32 \) yrs.), \(^{39}\)Ar (\( \tau_{1/2} = 269 \) yrs.) and \(^{81}\)Kr (\( \tau_{1/2} = 229000 \) yrs.). Most widely used radioactive environmental tracers operate in two time windows between about 40000 and 2000 years and less than 50 years, depending on the tracer half-life.

### 4.2 Environmental tracers

Environmental tracers thus provide a natural tool to investigate the groundwater flow and transport over time scales from 0 to 50 years. They involve the observation of the transport chain from the known measured atmospheric concentration, through the sub-surface, to the concentration in the groundwater which can be measured at sampling locations such as boreholes and pumping stations. With such characteristics, the environmental tracers offer the hydro-geologist a complementary approach to the usual hydraulic analysis, involving measurements of hydraulic head and conductivities in combination with Darcy’s Law, to estimate solute transport rates. Despite the large amount of sources of uncertainties (sample contamination, hydrodynamic dispersion...
along the flow path, estimations of several parameters to characterize the flow field), combining the two methods can provide feedback and cross-validation that may improve the understanding and quantification of the flow in shallow aquifers (Solomon et al., 1993b; Zoellmann et al., 2001).

Tracers as modeling tool for groundwater have been introduced in the late seventies. The most important information which can be derived from tracer transport modeling is the residence time of the water in the aquifer, or groundwater age (Poreda et al., 1988; Schlosser et al., 1989; Solomon and Sudicky, 1991; Cook and Solomon, 1997).

Tracer derived-ages can be on the order of months to decades for ‘young’ groundwater and up to $10^3 \div 10^7$ years for ‘old’ and ‘fossil’ groundwater. Tracer-derived water ages can be used for indirect evaluation of several aquifer-specific features, such as flow velocities, recharge rates and locations (Solomon et al., 1993b; Solomon and Sudicky, 1991; Solomon et al., 1993b, 1995; Cook et al., 1995). Groundwater ages at different locations can in turn provide estimates of the rate and direction of groundwater movement in the domain and are thus helpful in the assessment of the potential impact of contamination sources from land surface (e.g. nitrate from agricultural land use) and related well protection strategies for groundwater quality management (Zoellmann et al., 2001; Manning et al., 2005).

In the case of gaseous tracers (e.g. Krypton-85, Helium-3, CFCs), according to Henry’s law, if a water parcel is in gas exchange with the atmosphere the actual concentration reflects its atmospheric partial gas pressure at this time. The concentration of the water parcel thus reflects the time elapsed between the last gas exchange with the atmosphere (when the water parcel entered the saturated zone) and the sampling date. By direct comparison of the tracer concentrations in a groundwater sample with the concentrations in the water recharging the aquifer over time (measured and known as atmospheric input function) it is in principle possible to determine the groundwater age (water age or residence time), i.e. the time of infiltration in the saturated zone.

Care must nonetheless be taken when dating groundwater by means of the above mentioned comparison. The assumption that recharge waters are at equilibrium with atmospheric concentrations is usually a good approximation for shallow groundwater, since diffusion and barometric pressure fluctuations in a thin unsaturated zone provide a sufficient mixing of the tracer concentrations. The tracer input function at the
groundwater table can in that case be assumed to be equal to the atmospheric input function. As the flow velocity of seepage water in the unsaturated zone is often one or two orders of magnitude smaller than in the saturated zone, the equilibrium assumption does not hold anymore when considering aquifers overlain by thick unsaturated zones. Depending on the tracer used, tracer-derived water age can include also the time spent in the unsaturated zone before reaching the groundwater table. Neglecting this part of tracer transport can lead to overestimation of the water age, especially when deep groundwater tables are under examination (Cook and Solomon, 1995; Engesgaard et al., 2004). The time spent by the tracer in the unsaturated zone must in this case be accounted for in the calculation of the groundwater age. The subsurface dynamics of the hydraulic system is split in two components, accounting for the travel time in the unsaturated zone (also called \textit{time-lag}) and in the saturated zone. Up to now, a range of tracers have been used in groundwater studies, such as Tritium, Helium-3, Krypton-85, Chlorofluorocarbons and SF\textsubscript{6}. Several studies have shown the important role of the unsaturated zone in the tracer movement in the subsurface (Cook and Solomon, 1995; Engesgaard et al., 2004; Cook and Solomon, 1997; Zoellmann et al., 2001).

While the tracer movement in the saturated zone is almost the same for all conservative tracers, different environmental tracers usually show different timescales due to different transport mechanisms in the unsaturated zone: water-bound tracers such as Tritium will move advectively following the seepage water, while gas tracers such as Helium-3, Krypton-85, CFCs, SF\textsubscript{6} will move faster by diffusion in the soil-air. This difference in behavior could be in theory exploited to separate subsurface transport processes in the two zones (Zoellmann et al., 2001).

A major problem with the interpretation of tracer-derived ages is that, depending on the aquifer heterogeneity and dynamics, a distribution of travel times, rather than one single tracer age, will be obtained (Gelhar et al., 1992; Manning et al., 2005). Water ages are usually calculated assuming that all molecules in a sample moving along a streamline have the same age (i.e. no mixing and negligible dispersion: \textit{piston-flow} conditions). In many situations piston-flow may not apply and water with different tracer concentrations (and thus ages) will mix together (Engesgaard et al., 1996; Castro and Goblet, 2005). Inherent heterogeneity of the velocity flow field may increase hydrodynamic dispersion effects. The tracer-derived water age in such cases will represent a weighted average of the ages ‘carried’ by each streamline. Neglecting mixing effects in the saturated zone may lead to significant errors when modeling tracer...
4.2. Environmental tracers

Despite the above-mentioned complications and although the solution of the transport equation will require the quantification of additional parameters such as porosity, dispersivity and other soil parameters, there is the hope that tracer data may be useful to gain additional knowledge on the aquifer system and its dynamics. Tracer data may be used to exclude transmissivity realizations that do not allow to match the observed tracer concentrations at observation locations, as well as for the calibration of uncertain parameters with regard to water flow and transport both in the unsaturated and saturated zone. Tracer data should thus be understood in terms of potential information sources to be integrated in the calibrated groundwater flow model.

Tracer methods allow an independent quantitative description of system parameters and processes in complex systems that would be very difficult to estimate by other means. Tracers are essential tools for the investigation of physical, chemical and biological processes in groundwater systems. The tracers to be used must be consistently chosen for any specific study, with the appropriate dating range.

A combination of different tracer and dating methods may constrain the residence time estimation and provide feedback and cross-check in the investigation of mixing processes between waters of different origin and ages (Cook and Solomon, 1997; Cook et al., 1995; Castro and Goblet, 2005; Waugh et al., 2003; Ekwurzel et al., 1994). Feedback from multiple tracers with different input functions can improve the conceptual understanding of the groundwater flow system, provide increased resolution and finally help to reduce uncertainty. For such integrated investigations, spatially and time distributed concentration data on the aquifer must be available.

In most shallow aquifers, such as Baltenswil, residence times lie between months and decades. In this dissertation the environmental tracers Tritium, Helium-3 and Krypton-85 are used. The Tritium/Helium-3 method has been one of the most widely used methods among environmental tracers and is nowadays regarded as a standard tool in tracer hydrology (Solomon et al., 1995; Portniaguine and Solomon, 1998). Tritium and Helium-3 are considered as ideal tracers because they move practically at the same velocity as the water carrying them and are not affected by chemical reactions. They can be regarded as conservative tracers when dissolved in the groundwater, although this assumption may in certain cases be inappropriate, e.g. in...
case of significant Helium-3 back-loss to the atmosphere across the groundwater table (Schlosser et al., 1989) or differential diffusion to low conductivity lenses (Labolle and Fogg, 2001). Tritium and Helium-3 distributions in the aquifer can be utilized to calibrate groundwater flow and transport models either by using the two isotopes as separate tracers, or by using the $^{3}\text{H}/^{3}\text{He}$ ages. Krypton-85 has recently gained special attention because of the relatively well-known and monotonically increasing input function (Cook and Solomon, 1997; Ekwurzel et al., 1994; Jacob et al., 1987). These three tracers provide the calibration targets for the Baltenswil groundwater flow and transport models.

### 4.3 Tritium and Helium-3

Tritium ($^{3}\text{H}$) is the mutually radioactive isotope of hydrogen, with half-life $\tau_{1/2}=4500$ days (12.43 years) (Lucas and Unterweger, 2000). It is naturally produced by interaction of cosmic rays with nitrogen and oxygen in the upper atmosphere (cosmogenic production). $^{3}\text{H}$ production rate is latitude dependent, being largest near the poles. To a minor extent, $^{3}\text{H}$ is also produced in the subsurface by decay of $^{6}\text{Li}$, a by-product of $\alpha$-particle induced nuclear reactions from the U-Th series.

$^{3}\text{H}$ concentrations are expressed in terms of Tritium Units [TU], defined as the ratio of tritium to hydrogen (one $^{3}\text{H}^{1}\text{HO}$ - tritiated water molecule per $10^{18}$ $^{1}\text{H}_{2}\text{O}$ water molecules), or $6.686 \times 10^{7}$ $^{3}\text{H}$ atoms/Kg. One TU equals $1.11 \times 10^{16}$ mol/Kg or $2.488 \times 10^{-15}$ cm$^{3}$/g at Standard Temperature Pressure (STP). $^{3}\text{H}$ concentrations are also defined according to its radioactivity, one TU being equal to 0.118 Bq/Kg, or 3.19 pCi/Kg (Cook and Herzog, 2000).

Pre-bomb (1945) values of atmospheric concentrations (natural background) were between 3 and 5 TU in the Northern hemisphere (up to 15 TU at the poles). Regular measurements in precipitation began in 1953 in Ottawa (Canada). Since 1961, $^{3}\text{H}$ concentrations have been recorded at an international network of stations (IAEA, 1998). After the United States started atmospheric thermonuclear hydrogen bomb testing in 1951, followed by the URSS and United Kingdom, concentrations of 1300 TU were measured in the Northern hemisphere, locally up to 5000 TU. In 1963 the Limited Test Ban Treaty came into force, which banned above-ground nuclear tests. The early sixties thermonuclear fallout was spread and mixed by atmospheric
4.3. Tritium and Helium-3

Fig. 4.2: Tritium atmospheric input function at different measurement stations in Central Europe. Data are shown where and when available. Missing values in the input function can be reconstructed via correlation with other measurement stations, where data may be available [Data from IAEA (1998), International Atomic Energy Agency]. The three stations shown are separated by the following distances: Bern (CH) - Stuttgart (D) = 250 Km, Bern - Konstanz (D) = 150 km, Stuttgart - Konstanz = 120 km.

Circulation and high $^3$H levels were soon recorded also in the Southern hemisphere. Although China and France performed underground nuclear bomb tests from 1967 onwards, the atmospheric global $^3$H concentrations have been steadily decreasing down to the present-day concentrations of 10-20 TU (IAEA, 1998). $^3$H concentrations in meteoric waters worldwide are still today one order of magnitude larger than the natural background level (Fig. 4.2, right).

Seasonal, latitude and also longitudinal (due to proximity to test sites) variations in the global $^3$H inventory have been detected (IAEA, 1998). Continental effects are also present, the oceans acting as sinks. $^3$H release by human activities - such as nuclear power plants, nuclear fuel reprocessing facilities and industries (watches, luminous signs, dials and paint) - can be locally elevated and may be considered while modeling (Cook and Herzog, 2000). As example, $^3$H concentrations in Bern (Switzerland) are twice as high as those measured in Konstanz station (Germany), the two locations being only 150 km apart (Fig. 4.2, right).

The $^3$H daughter-product Helium-3 ($^3$He) is a stable conservative isotope. $^3$He is naturally present in the atmosphere. It is also present at the Earth crust and mantle by underground spontaneous nuclear reactions and may emanate from solid earth to the atmosphere, e.g. along crustal plate boundaries. The presence of subsurface sources may impair the reliability of the tracer-derived water age, if one is not able
to efficiently separate the tritiogenic $^3$He from other components (e.g. terrigenic from mantle and crustal sources and excess air). While the former two components may contribute in case of deep groundwater, shallow aquifers are mostly affected by the latter. The excess-air component deserves particular care. Air bubbles entrapped and dissolved in groundwater, as a consequence of fast water table variations or rapid recharge events, may result in higher dissolved $^3$He concentrations than expected at solubility equilibrium (Solomon et al., 1993b; Ekwurzel et al., 1994; Heaton and Vogel, 1981; Solomon et al., 1993a). Research on this topic is ongoing (Klump et al., 2007a,b).

In a system closed off from the atmosphere - such as groundwater - the sum of $^3$H and $^3$He is usually assumed to be conserved. If the initial $^3$H concentration at the groundwater table is known, an apparent water age can be derived independently of the $^3$H atmospheric input function (e.g. Cook and Solomon, 1997)

$$t = \frac{\tau_{1/2}}{\ln 2} \ln \left(1 + \frac{^3He_{tri}(t)}{^3H(t)} \right)$$ (4.2)

The $^3$H/$^3$He-derived (or apparent) water age measures the time since the water parcel was closed off from the atmosphere. It is thus different from the $^3$H age, which instead measures the time since water was formed as precipitation. The $^3$H/$^3$He-derived age is thus zero at the surface of open waters such as lakes and oceans and at the groundwater table. Groundwater ages between 5 and 50 years can be determined with an analytical uncertainty of about 10% (Solomon et al., 1993b).

Due to the low solubility of $^3$He in water and its large diffusion coefficient in soil air, $^3$He produced within the soil water in the vadose zone quickly emanates to the soil air. The exchange process between soil air and the atmosphere is usually assumed fast in comparison to the decay constant of $^3$H (Klump et al., 2008). $^3$He abundance in the vadose zone is dominated by gas transport. Air-phase diffusion and barometric pumping sufficiently mix the gases in the unsaturated zone, at least for not-too deep (< 10 m) ones, allowing tritiogenic $^3$He to be diffusively lost to the atmosphere and keep $^3$He partial pressure within the vadose zone at atmospheric levels. $^3$H instead is physically bound to the water molecule (tritiated water $^3$H$^1$HO). It is transported by advection in the unsaturated zone until it reaches the groundwater table.

In the groundwater, $^3$H and $^3$He produced by decay will move in the saturated zone by both advection and dispersion-diffusion. In these conditions, $^3$H/$^3$He ratio is regarded
as a conservative tracer. Confinement of $^3$He in groundwater is usually assumed, although diffusive loss of $^3$He from groundwater back via soil air to the atmosphere is likely to take place in shallow groundwater and under low-recharge conditions (Cook and Herzog, 2000; Schlosser et. al., 1988). This effect is usually neglected for $^3$H because it is water bound and due to its small diffusion coefficient in air (see Tab. 4.5.3). Another potential subsurface sink of $^3$He are aquitards and low conductivity lenses in the saturated zone. $^3$He may better diffuse than $^3$H to adjacent low conductivity lenses due to its larger diffusion coefficient in water (see Tab. 4.5.3). Differential diffusion behavior of $^3$H and $^3$He may also lead to temporary $^3$He depletion in the groundwater (Labolle and Fogg, 2001; Labolle et al., 2006).

All the above mentioned $^3$He components and fluxes may alter the tracer-derived groundwater age. Effects of macro-dispersion will also lead to discrepancies between hydraulic and apparent water ages, most notably in correspondence to sharp peaks of the atmospheric input function. The effects of dispersion on $^3$H/$^3$He-age decreases as the $^3$H input becomes constant in time, as is the case for the last decade.

### 4.3.1 Groundwater samples

Groundwater samples from Baltenswil aquifer were taken and analyzed by the Water Resources and Drinking Water Group at EAWAG Dübendorf (Swiss Federal Institute of Aquatic Science and Technology).

Groundwater samples for noble gas and tritium analyses were filled into copper tubes which can be sealed gas-tight using pinch-off clamps. All samples were analyzed for noble gas concentrations and the isotope ratios $^3$He/$^4$He, $^{20}$Ne/$^{22}$Ne, and $^{36}$Ar/$^{40}$Ar using noble gas mass spectrometry in the Noble Gas Laboratory at ETH Zurich (Beyerle et al., 2000). Tritium was analyzed applying the $^3$He-ingrowth method. After complete degassing of the samples for the analysis of the dissolved noble gases, the copper tubes were re-closed and stored for several months. During this time, Tritium decayed to $^3$He, which was then measured using a high-sensitivity compressor-source noble gas mass spectrometer (Beyerle et al., 2000; Baur, 1999). The measured $^3$He concentrations originating from the decay of tritium, could then be converted into the tritium concentrations at the time of sampling using the known dates of sampling and sample degassing, and the half-life of tritium.
Concentrations of tritiogenic $^3$He component must be separated from the atmospheric equilibrium and excess air fractions of the total measured $^3$He concentrations. The atmospheric equilibrium fraction results from the equilibration of the seepage water with the atmosphere-soil air during infiltration. The formation of excess air, i.e. the excess of dissolved atmospheric gases with respect to the atmospheric solubility equilibrium, is usually attributed to the (partial) dissolution of entrapped air within the quasi-saturated zone (or capillary fringe) (Heaton and Vogel, 1981). For the interpretation of dissolved noble gases in terms of infiltration temperature, amount of excess air, and radiogenic-tritiogenic $^3$He, several conceptual excess air models have been developed. The most commonly applied model, which is also used here, is the closed-system equilibration model of Aeschbach-Hertig et al. (2000). This model assumes equilibration of a finite water volume with a finite entrapped gas volume at increased hydrostatic pressure. The entrapped gas phase is dissolved partially or completely depending on the local pressure enhancement. The excess air component can be calculated for all the five atmospheric noble gases (He-Xe, see Kipfer et al., 2002).

### 4.4 Krypton-85

Krypton-85 is a radioactive isotope of Krypton, with half life $\tau_{1/2} = 10.76$ years (Cook and Herzog, 2000). This isotope has been predominantly released from nuclear fuel reprocessing plants, mainly in the Northern hemisphere (e.g. Sellafield - U.K. and La Hague - France, Jacob et al., 1987). Apart from the above mentioned sources no others contribute to the release into the environment. Near reprocessing plants, elevated concentration may be observed during time periods when the gas is released to the atmosphere (Loosli, 1983).

Krypton concentrations are expressed in terms of activity [Bq/m$^3$]. Krypton activity is usually measured by the ratio of $^{85}$Kr to stable Krypton [dpm/ccKr], decays per minute and cubic centimeter of Krypton at Standard Temperature and Pressure (STP). The activity in the atmosphere has been steadily increasing over the last 45 years and is actually (in 2006) about 90 dpm/ccKr in the Northern hemisphere. The lack of significant sources in the southern hemisphere results in about 15% lower concentrations than in the Northern hemisphere (Weiss et al., 1992). Recorded values at a number of stations worldwide are available since 1973. Previous atmospheric concentrations have been
4.4. Krypton-85

Atmospheric input functions are shown for Freiburg i.B. and Schauinsland (Germany) and Jungfraujoch station (Switzerland) (Fig. 4.3). The Krypton-85 concentration gradient depends on the actual weather conditions and wind direction relative to the main emission sources. Generally, Krypton-85 is well mixed below 3500 m.a.s.l. (lower troposphere). In winter, the well-mixed boundary layer is lower than in summer (often, only a few hundreds meters, but it varies from winter to winter). Therefore “clean” tropospheric air can be measured during winter months at the Jungfraujoch station (3554 m.a.s.l.). At higher altitudes Krypton-85 decreases to about 25 km and then stabilizes (Weiss et al., 1992; Winger et al., 2005).

Krypton-85 can be used to determine the water-age distribution as described in (Loosli, 1992). The half-life of 10.76 years and the atmospheric input function define the dating range of this isotope which is suitable for residence times in the range 5 to 50 years. The back extrapolation of the measured activity to the atmospheric activity yields an estimate of the residence time of the water since it entered the unsaturated zone. If
mixing of waters with different age is not occurring, a \textit{piston-flow} age can be calculated, with an overall accuracy of $\pm 2$ years (Loosli and Purtschert, 2005), by simply applying the exponential decay law (Fig. 4.4).

As Helium-3 is a noble gas, no chemical reactions or degradation have to be taken into account for the conversion into groundwater residence times. Calculated model ages are relatively insensitive to hydrodynamic dispersion due to the continuously increasing input function (Corcho et al., 2004; Engesgaard et al., 2004). Another important advantage of the method arises from the fact that an isotope ratio $[^{85}\text{Kr}/\text{Kr}]$ is measured. Therefore degassing or gas stripping do not affect $^{85}\text{Kr}$-tracer ages, in contrast to other gas-based methods. For the same reason, recharge conditions such as recharge temperature, infiltration height and excess air do not have to be known. The main limitation of the $^{85}\text{Kr}$ method is the large sample volume required and the
relatively high analytical demands and the uncertainty in the atmospheric input function.

Krypton-85 is a low solubility gas (Weiss and Kyser, 1978) and will thus move faster by diffusion in soil air than by advection in the water phase. Soil gas immediately above the water table may be in equilibrium with atmospheric concentrations only in case of shallow groundwater. At the groundwater table, Krypton-85 in soil air dissolves in water and moves passively with the flow of groundwater and hence it is subject to advection and dispersion-diffusion.

4.4.1 Groundwater samples

Groundwater samples from Baltenswil aquifer were taken and analyzed by the Climate and Environmental Physics Group at Bern University. The University of Bern is currently one of the few laboratories worldwide which is capable to measure Krypton-85 in groundwater. When the water is sampled all dissolved gases are extracted from the water. In the laboratory pure Krypton is separated and the specific Krypton-85 activity is measured. Because only about 4 litres of gas are dissolved in 200 litres of water the analytical requirements are considerable in order to measure Krypton-85 in reasonably sized water samples (Loosli and Purtschert, 2005). 200 liters of water have to be degassed in the field or in the laboratory. The $^{85}\text{Kr}$ activity is measured after Krypton separation by gas chromatography in proportional counters ranging in volume from 10 to 20 cm$^3$ (Loosli and Purtschert, 2005).

4.5 Tracer transport model for the unsaturated zone

Depending on the unsaturated zone properties (thickness, permeability and soil air and water content) the different behavior of water-bound and gas tracers can be used to separate the subsurface transport in the unsaturated and saturated parts. Tritium and Krypton-85 transport will reflect the whole travel time through the unsaturated and saturated zone, while Helium-3 shows the residence time solely in the groundwater (e.g. saturated conditions).

A common assumption in transport modeling of shallow aquifers is to take the
atmospheric composition of the soil air at the groundwater table as the same as in the free atmosphere. However, deep vadose zones suppress the complete gas re-equilibration with the atmosphere. Therefore, in case of deep groundwater tables transport in the unsaturated zone may lead to relevant changes in the input function at the groundwater table. Cook and Solomon (1995) found travel times in the unsaturated zones (also called time-lag) as large as 7 years at 40 meters depth. Moreover, spatially variable unsaturated zone thickness and other soil properties related to the saturation conditions will result in different time lags at different depths in the vadose zone. The effects of tracer transport in the unsaturated zone on subsurface concentrations have also been reported in other studies (Engesgaard et al., 2004; Busenberg and Plummer, 2000; Engesgaard et al., 1996).

Accounting for unsaturated zone transport and the consequential time-lag can be crucial even for not-very-deep (10-20 m) groundwater tables. The unsaturated zone dynamics of tracers gains importance in groundwater dating for thicker unsaturated zones. The tracer concentrations at the groundwater table can be significantly different from the atmospheric ones (measured input function) in case of deep water tables (> 10 m below surface, Cook and Solomon, 1995). Cook and Solomon (1995) also discussed the importance in variations in the unsaturated zone thickness. The presence of “valleys” (e.g. zones with shallower groundwater table) will result in younger water at the unsaturated/saturated zone interface and may thus lead to a more complex geometry of tracer concentrations at the groundwater table. In case only pure atmospheric input functions are known, the resulting time-lag for tracer transport in the unsaturated zone becomes a key issue in the evaluation of the correct groundwater age.

4.5.1 Theory

Tracer transport in the unsaturated zone can occur both in the liquid and gas phase. Due to the high spatial variability of the unsaturated zone thickness and the high temporal variability of the atmospheric input function, we model tracer transport in the unsaturated zone via a numerical solution of the advection-dispersion equation for radioactive tracers in a 1-D column (see Cook and Solomon, 1995).

\[
\frac{\partial (\theta^* \cdot c_g)}{\partial t} = D^* \cdot \frac{\partial^2 c_g}{\partial z^2} - q^* \cdot \frac{\partial c_g}{\partial z} - \theta^* \cdot \lambda \cdot c_g
\]  

(4.3)
4.5. Tracer transport model for the unsaturated zone

where \( c_g(z, t) \) is the gas concentration [moles/Kg] as a function of depth \( z \) [m] and time \( t \) [s] and

\[
\lambda = \frac{\ln 2}{\tau_2} \\
\theta^* = \epsilon_a + \theta \cdot \rho_l \cdot K_w + (1 - \theta - \epsilon_a) \cdot \rho_s \cdot K_w \cdot K_d \\
D^* = D_g + D_l \cdot \rho_l \cdot K_w \\
q^* = q_g + q_l \cdot \rho_l \cdot K_w
\]

\( \lambda \) being the decay constant [s\(^{-1}\)] of the gas tracer, \( \tau_{1/2} \) its half-life [s] and \( \theta^* \) [-], \( D^* \) [m\(^2\)s\(^{-1}\)] and \( q^* \) [m·s\(^{-1}\)] the effective parameters describing soil pore geometry and its gas/water content, dispersion and velocity field: \( \theta \) is the water content [-], \( \epsilon_a \) the gas-filled porosity [-], \( \rho_l \) and \( \rho_s \) the liquid and solid phase density [Kg·m\(^{-3}\)], \( K_w \) and \( K_d \) water/gas and solid/liquid partitioning coefficients [-], \( q_l \) and \( q_g \) the mean liquid and gas fluxes [m·s\(^{-1}\)], \( D_g \) the effective gas diffusion coefficient [m\(^2\)s\(^{-1}\)] and \( D_l \) the effective liquid phase dispersion coefficient [m\(^2\)s\(^{-1}\)] (definitions and nomenclature after Cook and Solomon, 1995)

\[
D_g = D_g^0 \tau_g \epsilon_a \\
D_l = D_l^0 \tau_l \theta + \alpha_L \frac{q_l}{\theta}
\]

where \( D_g^0 \) and \( D_l^0 \) are the self-diffusion coefficients of the species in air resp. water [m\(^2\)s\(^{-1}\)], \( \tau_g \) and \( \tau_l \) the air resp. liquid phase tortuosity [-] and \( \alpha_L \) is the longitudinal dispersivity [m].

It is usually assumed that infiltration of water in the unsaturated zone takes place under piston flow conditions. The water flux is thus vertical and no mixing takes place. Tracer transport is thus described by a simple 1-D model.

Due to fast equilibration between the water and the air phase (Klump et al., 2008), instantaneous local equilibrium between the gas and the water phases is assumed everywhere. The exchange between tracer concentrations in gas, water and solid phases is defined by Henry’s law
Chapter 4. Environmental tracer transport in the unsaturated zone

\[ c_w = K_w c_g \]
\[ c_s = K_d c_w \]

where \( c_w \) and \( c_s \) are the species concentrations in the liquid resp. solid phase [moles/m\(^3\)]. Since Tritium is water-bound and Helium-3 and Krypton-85 are noble gases and thus inert, the solid/water phase partitioning coefficient \( K_d = 0 \) is null in all transport simulations. In this way, the transport equation is expressed only in terms of the tracer concentration in the gas phase, while the concentration in the water phase is calculated assuming instantaneous equilibrium and the concentration in the solid phase is neglected.

We obtain a numerical solution to equation (4.3) in one dimension by means of a MATLAB script. The 1-D numerical solution to the advection-dispersion equation (4.3) is obtained by a forward-time and central-in-space finite difference scheme. A Conjugate Gradient Solver is used to get the solution of the implicit system.

### 4.5.2 Krypton-85

The gas tracer \(^{85}\)Kr is used as a case study to establish a correct numerical solution to the transport equation in one dimension for gaseous tracers. Based on the available geological information, related hydraulic properties of the porous media under examination and the physical characteristics of the tracer in use, the following hypotheses are assumed:

- **Spatially and temporally homogeneous porous medium**: constant values for the physical parameters describing the unsaturated zone structure (homogeneous porous medium). Default values are shown in Tab. 4.1

- **Solubility equilibrium** at the surface between atmospheric and aqueous tracer concentrations: water/air partitioning coefficient for Krypton-85 is \( K_w = 0.01 \) (Cook and Solomon, 1995; Weiss and Kyser, 1978)

- **Negligible sorption**: solid/water partitioning coefficient: \( K_d = 0 \)
4.5. Tracer transport model for the unsaturated zone

| \( \epsilon_a = 0.15 \) | gas filled porosity |
| \( \theta = 0.1 \) | water content |
| \( \tau_g = 0.25 \) | gas phase tortuosity |
| \( \tau_l = 0.25 \) | liquid phase tortuosity |
| \( n = \epsilon_a + \theta = 0.25 \) | porosity |

Table 4.1: Default parameter set for Krypton-85 transport simulations in the unsaturated zone

- Advection of the gas phase is important only in the few upper meters of the unsaturated zone (Cook and Solomon, 1995). Therefore, the advective transport in the gas phase is neglected. The gas transport mechanism is diffusion-dominated: \( q_l = q_g = 0 \)

With these assumptions, the Krypton-85 transport is controlled by the following parameters:

\[
\begin{align*}
\theta^* & \approx \epsilon_a \\
D^* & \approx D_g = D_g^0 \cdot \epsilon_a \cdot \tau_g \\
q^* & = 0
\end{align*}
\]

where \( D_g^0 = 440 \text{ m}^2 \cdot \text{yr}^{-1} \) is the diffusion coefficient for \(^{85}\text{Kr}\) in free water and \( \tau_g = 10.76 \) years its half-life (Cook and Solomon, 1995). With the above hypothesis, the most important parameters controlling the transport equation (4.3) are thus the gas-filled porosity \( \epsilon_A \) and the gas-phase tortuosity \( \tau_g \) (controlling the effective diffusion coefficient \( D_g \)).

The unsaturated 1-D soil column is discretized with \( \Delta z = 1 \text{ m} \) and \( \Delta t = 3 \text{ days} \). The calculated numerical solution is first compared to the known exact analytical solution for a \( \delta \)-pulse input function in a semi-infinite unsaturated column as derived by Van Genuchten (1981) (Fig. 4.5). A second comparison is performed between the analytical and numerical solution for the complete \(^{85}\text{Kr}\) atmospheric input function in a semi-infinite unsaturated column (Fig. 4.6). Perfect agreement is obtained in both simulations.

The unsaturated zone is modeled as a \( N \)-cell homogeneous 1-Dimensional finite column with upper boundary condition as time-varying concentrations (Dirichlet-type
Chapter 4. Environmental tracer transport in the unsaturated zone

Fig. 4.5: Analytical (left) and numerical (right) solution for a $\delta$-pulse at different depths of the unsaturated zone - pulse input

Fig. 4.6: Analytical (left) and numerical (right) solution at different depths of the unsaturated zone for the atmospheric input function as measured at Freiburg im Breisgau (D) for years 1950-2004, [data from IAEA (1998), International Atomic Energy Agency]
boundary condition, see 1.2), set equal to the atmospheric measured concentration $c_{atm}(t)$ at the reference station Freiburg im Breisgau (Germany). This station is chosen since it provides the most complete atmospheric input function time-series and describes the Krypton-85 atmospheric concentrations below the well-mixing boundary for Krypton-85 (located below 3000/3500 m.a.s.l.). For the latter reason, the Jungfraujoch station (3554 m.a.s.l.), although closer to the modeled domain, has not been used. The lower boundary at depth $z_L$ ($z_L$ being spatially variable) is modeled as a time-varying outgoing flux (Neumann boundary condition, see 1.2) set equal to the advective flux $q(t)$ or deep percolation as calculated in section 3.5 and neglecting the dispersive flux.

No diffusion at the lower boundary is considered since, for the actual recharge rate values, diffusive effects are negligible. They may, however, become important in low recharge conditions. To avoid any dependence of the numerical solution on the initial concentration value, the atmospheric input function is considered since the beginning of Krypton-85 emission in the atmosphere in 1950 (atmospheric concentration $c_{atm} = 0$). At any time $t$, boundary conditions for tracer concentrations $c(z, t)$ are thus

- Upper boundary: soil surface at $z = 0$. Constant concentration (Dirichlet condition)

$$c(z, t)|_{z=0} = c_{atm}(t) \quad \forall t$$

- Lower Boundary: groundwater table at $z = z_L$. Outgoing flux only advective, dispersive flux set to zero (Neumann condition)

$$\frac{\partial c(z, t)}{\partial z}|_{z=z_L} = 0 \quad \forall t$$

- Initial condition in the soil column at time $t = 0$

$$c(z, t) \mid_{t=0} = 0 \quad \forall z$$
The complete numerical solution (from 1950 to 2006) is calculated for each depth of the unsaturated zone, where the lower boundary for each simulation is set at a depth equal to the unsaturated zone depth. A stable solution is easily achieved with a relatively small number of time-steps, since advection is set to zero and no numerical dispersion problem arises in the iterative solution of the linear system.

Given the known tracer concentration in the atmosphere in Freiburg i.B. (Germany, data from IAEA (1998) - International Atomic Energy Agency), the numerical solution is used to calculate the input concentrations to the saturated zone. We calculate the tracer concentrations in the subsurface for different groundwater table depths. Our 1-D model allows reconstructing the tracer concentrations at the ground-water table of the whole aquifer since the beginning of environmental tracer emissions into the atmosphere (1950) up to now (2005). The concentration time series at different depths of the unsaturated zone column are shown in Fig. 4.7.

The concentration time series at different depths follow the atmospheric input function close to the soil surface, but become smoother and lose details with increasing depth. The noise in the time-series at depths (small wiggles) is due to time varying outgoing flux $q_l$ at the lower boundary. At 40 m depth only the increasing trend of the input function survives, but not any smaller detail. This is a direct consequence of Krypton-85 half-life. The typical timescale of diffusive transport can be calculated as $\tau_D = \frac{z^2}{D_g}$. While at $z = 5$ m depth $\tau_D \simeq 1.5$ years, at $z = 40$ m depth it becomes two times larger than the half-life of Krypton-85 ($\tau_D \simeq 24$ years) allowing natural decay of $^{85}$Kr to smear out almost completely the step-like atmospheric input. However, the time delay between the atmospheric input function peaks at the soil surface and the subsurface signal becomes apparent in the shift to the right of the concentration profiles (Fig. 4.7).

Vertical Krypton-85 concentration profiles in the unsaturated zone at fixed times are shown in Fig. 4.8. Due to the monotonic increase of the atmospheric input function, the vertical concentration profiles do not overlap with each other. They show higher concentration values close to the soil surface than at depth, resulting in a negative concentration gradient. Concentrations at depth also show an increase with time.
4.5. Tracer transport model for the unsaturated zone

Fig. 4.7: Krypton-85 time series at different unsaturated zone column depths

Fig. 4.8: Krypton-85 concentration profiles over depth for different times
Sensitivity analysis

Sensitivity analysis on the parameter values was performed to assess the most relevant simulation parameters controlling the transport process. A remarkable sensitivity to gas-phase tortuosity $\tau_g$, especially at larger depths (green and red time series respectively at 30 m and 40 m depths, Fig. 4.9 - bottom right) was found. Increasing gas tortuosity and the effective diffusion coefficient $D_g$ result in higher concentrations at depth, and thus in a faster tracer dynamics in the subsurface.

![Graphs showing sensitivity analysis](image)

Fig. 4.9: Krypton-85 sensitivity to gas-phase tortuosity $\tau_g$ for years 1950-2006 (in abscissa). The overlap of the first three graphs is reproduced in the bottom-right box for comparison. Due to space reasons, the legend is omitted in the following figures: it remains the same as in Fig. 4.7.

No sensitivity with respect to $\epsilon_a$ nor to $\theta$ (subject to the constant $n = \epsilon_a + \theta = 0.25$) is found. Gas-filled porosity $\epsilon_a$ is canceled out in equation (4.3), while the effect of water content $\theta$ is counterbalanced due to low Krypton-85 solubility in water ($K_w = 0.01$). We stress nonetheless that gas-phase tortuosity is a function of porosity and consequently of water content and gas filled porosity $\tau_g = \tau_g(\epsilon_a, \theta)$. Though no direct dependence of the time series at depth is shown on water content and gas-filled porosity, these two
quantities will come into play indirectly in the tortuosity coefficient. A correct characterization of the water content, the spatial and temporal variability of the gas-filled porosity and the tortuosity coefficient are thus of primary importance for a correct modeling of tracer transport in the unsaturated zone. However, this kind of measurements is notoriously difficult to obtain. Due to the high spatial and temporal variability, a large amount of such measurements would be needed to be fruitfully exploited in the modeling procedure.

When dealing with aquifers with overlying undulating topography, i.e. variable unsaturated zone thickness, the position of the lower boundary of the system changes. This strongly affects the concentration time series at depth: a remarkable sensitivity to the \( z \)-position of the lower boundary is apparent in Fig. 4.10: the deeper the boundary, the lower the concentration time series at depth, the slower the tracer dynamics.

![Graph showing concentration vs. time for different lower boundaries](image)

**Fig. 4.10:** Sensitivity to \( z \)-position of the lower boundary. Results are shown for 10 m, 30 m and 50 m deep unsaturated soil columns. See also Fig. 4.6, where the lower boundary is set at infinite depth

The lower boundary condition is also investigated with regard to the advective flux at the lower boundary. Sensitivity analysis was performed for a 50 m soil column with
three different flux rates, corresponding to 50%, 100% and 150% of the actual flux rate. Small sensitivity is found with respect to the constant outgoing flux rate at the lower boundary (Fig. 4.11). Sensitivity to the lower boundary outgoing flux is less than the sensitivity to its $z$-position. This dependence becomes apparent only at large depths (Fig. 4.11 - bottom-right, concentration time-series at 50 m depth). Raising the flux rate value, i.e. letting more water out of the system at the lower boundary, only results in slightly lower concentration time series.

Finally, sensitivity to the atmospheric input function variations was performed and found to be quite remarkable at all depths. Three different simulations were performed, assuming 80%, 100% and 120% of the original input function from Freiburg i.B. (D), (Fig. 4.12). An error of 20% is justified by the uncertainty in the input function for different reference stations (see Fig. 4.3). The actual reference station (Freiburg i.B.) is at a distance of about 100 km from the Baltenswil domain.

**Conclusions**

Krypton-85 shows strong sensitivity to the gas-phase tortuosity and to the time evolution of the atmospheric concentrations. The effective gas-phase diffusion coefficient $D_g$ thus governs almost completely the Krypton-85 transport in the unsaturated zone. Gas-phase tortuosity is highly variable in space as well as in time, according to the space and time-varying saturation conditions in the vadose zone. Less permeable lenses in the unsaturated zone can lead to very small tortuosity factors ($\tau_g = 0.01$). Consequently, the effective diffusion coefficient can vary in unsaturated soils over one or two orders of magnitude. Its impact on tracer transport is the most severe among all transport and soil parameters.

The atmospheric input function is also a source of uncertainty. As already mentioned, spatial variability is mainly due to local input sources. Variations of up to 20% have been recorded in Central Europe over a distance of a few hundred kilometers (see Fig. 4.3), as reported by (IAEA, 1998). Its impact on the tracer transport is thus smaller than the effective diffusion coefficient.

The thickness of the unsaturated zone also plays an important role. This parameter is nonetheless well known in the Baltenswil case study. It is calculated as difference
4.5. Tracer transport model for the unsaturated zone

Fig. 4.11: Sensitivity to recharge rate \( r \) at lower boundary \( z = 50 \) m

Fig. 4.12: Unsaturated zone time series sensitivity to atmospheric input function
between the terrain elevation (from Digital Elevation Models) and the elevation of the groundwater table (derived from steady state inverse modeling of the groundwater flow), both on a 50x50 m$^2$ grid. The associated uncertainty is reasonably smaller compared to those of the effective diffusion coefficient and the atmospheric input function.

### 4.5.3 Tritium and Helium-3

The Tritium ($^3$H) input to the subsurface occurred in a series of spikes following periods of atmospheric testing of nuclear devices that began in 1952 and reached a maximum in 1963-64 ($^3$H bomb-peak). Since then, $^3$H concentrations in precipitation have decreased (see section 4.3). Tritium being also released by industrial sources, its input function is characterized by a strong spatial variability (see Fig. 4.2, right). Radioactive decay of $^3$H produces the noble gas Helium-3 ($^3$He).

$^3$H and $^3$He are modeled solving the advection-dispersion equation (4.3). $^3$He is the stable daughter product of $^3$H (half-life $\tau_1 = 4500$ days, or 12.43 years). $^3$H bound water molecule moves mainly by advection, while $^3$He gas diffuses through soil air. Due to a large self-diffusion coefficient in free air, $^3$He in the unsaturated zone is usually assumed to be completely lost to the atmosphere via the soil air (Cook and Herzog, 2000). Here, such an assumption is not made and the $^3$He production and diffusion in the unsaturated zone are investigated.

The transport equation is (4.3), modified with a source term describing the $^3$He production from $^3$H decay. The two equations are thus coupled and must be solved simultaneously

$$\begin{align*}
\frac{\partial \theta^* c_{3H}}{\partial t} &= D^* \frac{\partial^2 c_{3H}}{\partial z^2} - q^* \frac{\partial c_{3H}}{\partial z} - \theta^* \lambda c_{3H} \\
\frac{\partial \theta^* c_{3He}}{\partial t} &= D^* \frac{\partial^2 c_{3He}}{\partial z^2} - q^* \frac{\partial c_{3He}}{\partial z} + \theta^* \lambda c_{3H}
\end{align*} \tag{4.4}$$

where $c_{3H}$ and $c_{3He}$ are the tracer concentrations in the gas phase and $\lambda = \ln 2 / \tau_{1/2}$ is the decay constant [s$^{-1}$] of Tritium. Coupling to the water phase is defined by the equilibrium
partitioning coefficients (see below). Based on the available geological information, related hydraulic properties of the porous medium under examination and the physical characteristics of the tracer in use, the following hypotheses are assumed:

- **Spatially and temporally homogeneous porous medium**: constant (effective) values for the physical parameters describing the soil (see Krypton-85 study, Tab. 4.1)

- **Solubility equilibrium** at the surface between atmospheric and aqueous tracer concentrations: water/air partitioning coefficient is $K_{3He}^{w} = 0.0093$ for $^{3}He$ (Weiss, 1971). $^{3}H$ is instead physically bound to the water molecule: $K_{w}^{3H} = 1$

- **Negligible sorption**: solid/water partitioning coefficient: $K_{d} = 0$ for both $^{3}H$ and $^{3}He$

- Advection in the liquid phase is the driving transport phenomenon for $^{3}H$: $q_{l}(t) = r(t)$, where $r(t)$ is the calculated recharge rate for the Baltenswil case-study (see section 3.5). $^{3}H$ advection in the gas phase can thus be neglected: $q_{g} = 0$. No mixing is assumed (longitudinal dispersivity is $\alpha_{L} = 0.5$ m, i.e. to one-tenth of the minimum unsaturated zone thickness in the Baltenswil domain).

- Advection in the gas phase is important only in the few upper meters of the unsaturated zone (Cook and Solomon, 1995). The gas transport mechanism is *diffusion-dominated*: $q_{l} = q_{g} = 0$ for $^{3}He$.

With these assumptions, the transport phenomena are controlled by the following parameters:

$$
\begin{align*}
^{3}H & \\
\theta^{*} & \approx \theta \\
D^{*} & \approx D_{l} = D_{l}^{0}(\theta + \alpha_{L} \frac{q^{*}}{\theta}) \\
q^{*} & = r(t)
\end{align*}
\begin{align*}
^{3}He & \\
\theta^{*} & \approx \epsilon_{a} \\
D^{*} & \approx D_{g} = D_{g}^{0} \cdot \epsilon_{a} \cdot \tau_{g} \\
q^{*} & = 0
\end{align*}
$$

where (Cook and Solomon, 1997; Cook and Herzog, 2000)
Chapter 4. Environmental tracer transport in the unsaturated zone

<table>
<thead>
<tr>
<th></th>
<th>$^3$H</th>
<th>$^3$He</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_l^0$</td>
<td>0.0495 m$^2$·yr$^{-1}$</td>
<td>0.207 m$^2$·yr$^{-1}$</td>
</tr>
<tr>
<td>$D_g^0$</td>
<td>0</td>
<td>2179 m$^2$·yr$^{-1}$</td>
</tr>
</tbody>
</table>

With the above hypothesis, tritium transport is thus controlled by water content $\theta$, dispersion in the water phase $D_l$ and advective flux $q^*(t)$, while $^3$He is controlled by the gas-filled porosity $\epsilon_a$ and the gas-phase tortuosity $\tau_g$ (controlling the effective diffusion coefficient).

The initial $^3$He concentration is set to zero in the unsaturated zone. The upper boundary condition is the atmospheric concentration for both $^3$H and for $^3$He. The lower boundary at finite depth $z_L$ ($z$ being spatially variable) is modeled as a time-varying outgoing flux (Neumann boundary condition, see 1.2) set equal to the advective flux $q(t)$ or deep percolation as calculated in section 3.5 and neglecting the dispersive flux. Concentrations are expressed in Tritium Units [TU] for both tracers.

- Upper boundary: soil surface at $z = 0$. Constant concentration - Dirichlet condition

$$c_{^3H}(z, t)|_{z=0} = c_{atm}(t) \quad \forall t$$

$$c_{^3He}(z, t)|_{z=0} = 0 \quad \forall t$$

- Lower Boundary: groundwater table at $z = z_L$. Outgoing flux for both $^3$H and $^3$He

$$\frac{\partial c(z, t)}{\partial z}|_{z=z_L} = 0 \quad \forall t$$

- Initial condition in the soil column at time $t = 0$

$$c_{^3H}(z, t) \mid_{t=0} = 5 \text{ TU} \quad \forall z$$

$$c_{^3He}(z, t) \mid_{t=0} = 0 \quad \forall z$$
Spatial discretization is $\Delta z = 1$ m, while time discretization is smaller than in the Krypton-study, $\Delta t = 1.5$ days, resulting in 11040 timesteps for a simulation time of 46 years, from 1961 to 2006. A larger number of time-steps - compared to the solution of the purely diffusive transport equation (as for Krypton-85) - is now necessary to get a stable solution: advection is nonzero and numerical dispersion is reduced with smaller time-steps. As already mentioned, a reliable $^3$H atmospheric input function is a key issue for modeling purposes. Here we make use of the Konstanz [D] $^3$H input function (data from IAEA, 1998), located only 50 km away from the Baltenswil area and providing data since 1978. Values from 1961 to 1977 have been reconstructed by linear regression with the measured atmospheric concentration at the Stuttgart station in Germany (IAEA, 1998).

The concentration time series for $^3$H and $^3$He at different depths of the unsaturated zone column are shown in Fig. 4.13 and 4.15. Compared to the other tracers, tritium time series at depth show a less pronounced decrease in their absolute value. A time delay effect is apparent when looking at the “propagation” of the 1963 $^3$H peak as depth increases in Fig. 4.14 - left or at the position of the 1963 peak at depth in Fig. 4.13 - left.

The time delay effect and the smoothing of the concentration time series are more and more apparent as depth increases. At 40 m depth, the delay of the 1963 bomb-peak is about ten years. Its movement in the unsaturated zone is clearly visible in Fig. 4.14 - left. The monotonically decreasing trend of the $^3$H input function results in nearly steady-state $^3$H concentrations at all depths in the last 10 years (Fig. 4.13 and 4.14 - right). The details of the input function - including its decreasing trend - are completely smeared out already at a depth of 20 m.

By contrast, the amount of tritiogenic $^3$He increases with depth, i.e. with increasing distance from the upper boundary at constant zero concentration (Fig. 4.15). $^3$He time series show at the different depths an increasing trend in the sixties and early seventies, due to the high $^3$H content in the unsaturated zone. The maximum concentrations correspond to the peak production of $^3$He by $^3$H.

The delay effect is recorded at each depth (Fig. 4.15 - left and Fig. 4.16 - left). After mid-seventies, $^3$He simulated concentrations at depth show a decreasing trend because of the continuously decreasing amount of $^3$H input. For thin unsaturated zones, $^3$He can be assumed to be lost by diffusion to the atmosphere. At larger
Chapter 4. Environmental tracer transport in the unsaturated zone

Fig. 4.13: Tritium time series at different unsaturated zone column depths

Fig. 4.14: Tritium concentration vertical profiles for different times
4.5. Tracer transport model for the unsaturated zone

$^3$He input function $c(t)$ at different depths

![Graph showing $^3$He input function $c(t)$ at different depths](image1)

Fig. 4.15: Helium-3 time series at different unsaturated zone column depths

$^3$He concentration profile $c(z)$

![Graph showing $^3$He concentration profile $c(z)$](image2)

Fig. 4.16: Helium-3 concentration vertical profiles for different times.
depths, $^3$He produced by $^3$H cannot escape via soil air and relevant concentrations are expected by model simulations. In the last 10 years $^3$He concentrations have stabilized towards a constant value, following the $^3$H atmospheric input function trend.

In deep unsaturated zones, $^3$He is therefore not completely lost to the atmosphere. However, it does not reach the groundwater table because of its small water/air partitioning coefficient. Gas phase $^3$He joins the water phase (solubility equilibrium is assumed) in crossing the unsaturated/saturated zone boundary. In order to get the correct $^3$He concentration in water, the calculated concentration values at the bottom of the unsaturated zone are multiplied by the water/gas partitioning coefficient $K_{^3He}^{w} = 0.093$. The calculated $^3$He concentration of the water input at the groundwater table is negligible (Fig. 4.17), being one order of magnitude smaller than the measurement and analytical errors of the Baltenswil samples (see chapter 5). This input could become important when modeling the unsaturated zone in aquifer systems with long travel times (more than 50 years), where the 1960-1970 water could still be moving. In the Baltenswil study, tracer-derived groundwater ages are between 2 and 12 years (young waters), and the 1960-1970 signal cannot be detected anymore.
4.5. Tracer transport model for the unsaturated zone

Fig. 4.18: Sensitivity to gas filled porosity $\epsilon_A$ and water content $\theta$ for years 1978-2006 (in abscissa). Legend is omitted, remaining as in Fig. 4.13 and 4.15

Fig. 4.19: Sensitivity to $\epsilon_A$ and $\theta$ at depth $z = 40$ m
Chapter 4. Environmental tracer transport in the unsaturated zone

Fig. 4.20: Sensitivity to mean water flux $q_L$

Fig. 4.21: Sensitivity to longitudinal dispersivity $\alpha_L$
4.5. Tracer transport model for the unsaturated zone

Sensitivity analysis

Sensitivity analysis was performed to assess the importance of simulation parameters controlling the transport process. Sensitivities with respect to gas filled porosity and water content are shown in Fig. 4.18. Fig. 4.19 shows the simulation results at one single depth in order to better appreciate the details of the concentration time series.

In contrast to the gas tracers, $^3$H (and consequently its daughter $^3$He) time series are directly influenced by water content (subject to the constrain $\epsilon_a + \theta = n$, see Tab. 4.1 and Fig. 4.19). Variations in the $^3$H and $^3$He concentration time series are important only after sharp peaks of the $^3$H input function. These variations becomes negligible in case of nearly steady-state $^3$H input function, as during the last 10 years.

$^3$H was not found to be sensitive to water phase tortuosity. Being a gas tracer as Krypton-85, $^3$He transport shows a sensitivity of its transport to the gas-phase tortuosity $\tau_g$, i.e. to the effective diffusion coefficient $D_g$.

Sensitivity to the advection parameter $q_l$ in the unsaturated zone is apparent as expected (Fig. 4.20), a larger $q_l$ resulting in slightly higher concentration values and steeper breakthrough curves, i.e. in faster tracer dynamics, for $^3$H. In general concentrations are not sensibly affected by mean water flux variations for $^3$H, especially during the last 15 years. Due to the decreasing trend of its input function, only a small sensitivity with respect to the dispersion coefficient in the unsaturated zone is found (Fig. 4.21).

The comments about sensitivity to physical parameters made in section 4.5.2 for Krypton-85 are still valid for both $^3$H and $^3$He: remarkable sensitivity with respect to lower boundary depth $z$ and small sensitivity with respect to recharge rate at the lower boundary is found.

Conclusions

$^3$H is not sensitive to all soil and transport parameters because of the monotonically decreasing trend of its atmospheric input function. Consequently $^3$He concentrations will also show little sensitivity to these parameters. The modeling of $^3$He concentrations in the unsaturated zone reveals that Helium-3 is lost by diffusion through soil air for
Chapter 4. Environmental tracer transport in the unsaturated zone

not too deep groundwater tables (< 20 m.), while non-negligible $^3\text{He}$ concentrations can be present in the deeper unsaturated zone > 30 m. Besides, Helium-3 has a small partitioning water/air coefficient which makes its dissolution in the groundwater small also in case of relevant Helium-3 concentrations in the deep unsaturated zone.

4.6 Travel and residence times

The travel times in the unsaturated zone for Krypton-85 can be roughly estimated by

$$\tau_D = \frac{z^2}{D_g}$$

where $\tau_D$ is the typical timescale of diffusive transport, $z$ is the unsaturated column depth and $D_g = D_0^g \cdot \epsilon_a \cdot \tau_g$ is the Krypton-85 effective diffusion coefficient in the unsaturated zone. With the default parameter values in Tab. 4.1, the effective diffusion coefficient is $D_g = 16.5 \text{ m}^2 \cdot \text{yr}^{-1}$. By considering the unsaturated zone thickness of each cell of the domain, the average travel times spatial distribution and its frequency distribution can be obtained (Fig. 4.22).

The spatial distribution of the Krypton-85 travel times in the unsaturated zone strictly follows the spatial distribution of the unsaturated zone thickness. Input to the groundwater table will be delayed of 40 years and more in the hilly zones, where the unsaturated zone thickness is larger. On the other hand, delays ranging from a few up to 10-20 yrs can be expected where the groundwater table is more shallow (blue zones in Fig. 4.22 - middle). On average, the calculated Krypton-85 delay is about 43 yrs across the modeled domain with a standard deviation of 34 yrs. The frequency distribution shows that travel times of less than 20 yrs and around 50 yrs are more frequent (Fig. 4.22 - bottom).

In a similar fashion, $^3\text{H}$ travel times in the unsaturated zone can be estimated by the formula

$$\tau_A = \frac{z \theta}{\tau}$$

where $\tau_A$ is the typical timescale of advective transport, $z$ is the unsaturated column depth, $\theta$ is the water content and $\tau$ is the mean liquid flux in the unsaturated zone.
4.6. Travel and residence times

Fig. 4.22: Average travel time spatial and frequency distributions for Krypton-85 transport in the unsaturated zone. Pumping stations are marked with squares, boreholes with crosses.
Assuming a water content $\theta = 0.1$ (see Tab. 4.1) and a mean liquid flux equal to the average calculated recharge rate $r = 0.520$ m·yr$^{-1}$ (see chapter 3), the average travel times distributions in the unsaturated zone for $^{3}$H can be obtained (Fig. 4.23).

The travel time spatial distribution for $^{3}$H in the unsaturated zone also follows the unsaturated zone thickness spatial distribution, being linearly related to it (Fig. 4.23 - top). The delays accumulated in the hilly zones are smaller than in the case of Krypton-85, being around 10-15 yrs. Calculated travel times for Tritium are about one tenth of Krypton-85 travel times, with an average of 4.6 yrs and a standard deviation of 2.8 yrs. The frequency distribution shows differences when compared to that of

![Spatial and frequency distributions of travel times for Tritium transport in the unsaturated zone](image)

Fig. 4.23: Spatial and frequency distributions of travel times for Tritium transport in the unsaturated zone
4.6. Travel and residence times

Krypton-85. The $^3$H distribution is gaussian-shaped with the median located around 5 years (Fig. 4.23 - bottom). Tritium transport in the water phase in the unsaturated zone is much faster than Krypton-85 transport via soil-air.

Residence times in the groundwater can be estimated for comparison purposes by means of PMPATH (Chiang and Kinzelbach, 1994), a purely advective transport model which uses a semi-analytical particle-tracking scheme (Pollock, 1988) to calculate the groundwater paths and travel times. One solute particle is placed in each cell and then advectively transported within the flow field. Residence time in the groundwater is calculated as the time needed for the particle at each cell to leave the domain either via a pumping station or a drain. Particle tracking derived travel times for two different realizations and two different quasi-steady state flow conditions are shown in Fig. 4.24 and Fig. 4.25. The average residence time in the saturated zone is about 2 years, i.e. ten times smaller than the average residence time in the unsaturated zone. This fact may reduce the impact of a spatially-variable transmissivity distribution on the simulated tracer concentrations in the groundwater (see Chapter 5).

The spatial distribution of residence times in the groundwater is rather heterogeneous. In the case of PW Baltenswil it strictly reflects the spatial extension of its quasi-steady state catchment (Fig. 4.26 and Fig. 4.27) and is characterized by residence times of 2 to 3 years. These ages agree well with the $^3$H/$^3$He derived groundwater ages, which account for the residence time in the saturated zone alone (see next chapter, Tab. 5.2). In Fig. 4.24 and 4.25 the domain appears divided in two zones: the PW Baltenswil catchment, with average groundwater residence times smaller than 4 years, and the other four wells catchments, which show larger residence times. The model correctly reproduces the observed residence times in the saturated zone.

The quasi-steady state catchment of the five pumping stations and of the three drains in the domain can be obtained by means of PMPATH. The extension of such catchments varies in time, according to the actual recharge and pumping conditions and, also, depending on the transmissivity distribution (Fig. 4.26 and Fig. 4.27). The velocity fields are also heterogeneous, with values ranging from $10^{-4}$ to $10^{-6}$ m/s (Fig. 4.26 and Fig. 4.27). Being determined mainly by the transmissivity field rather than by recharge, they do not vary much in time but more on the spatial scale. The velocity field will be nevertheless modified to a larger extent in the neighborhood of the pumping stations, according to the actual pumping rate.
Fig. 4.24: Spatial and frequency distributions of residence times for Krypton-85 transport in the saturated zone. Particle tracking results for two different realizations (left and right column) at different times (quasi-steady state approximation - March 2000 and October 2001)
4.6. Travel and residence times

Realization # 11

March 2003

Residence times distribution

Average = 2.07 yrs
Standard dev, = 3.23 yrs

October 2003

Residence times distribution

Average = 2.17 yrs
Standard dev, = 3.32 yrs

Realization # 19

Residence times distribution

Average = 2.02 yrs
Standard dev, = 3.14 yrs

Average = 2.22 yrs
Standard dev, = 3.31 yrs

Fig. 4.25: Spatial and frequency distributions of residence times for Krypton-85 transport in the saturated zone. Particle tracking results for two different realizations (left and right column) at different times (quasi-steady state approximation - March and October 2003)
Fig. 4.26: Quasi steady-state extension of the five pumping stations' catchments and velocity fields in different flow regimes for two different realizations March 2000 and October 2001
4.6. Travel and residence times

Fig. 4.27: Quasi steady-state extension of the five pumping stations’ catchments and velocity fields in different flow regimes for two different realizations March 2003 and October 2003
Chapter 5

Transport simulations

The groundwater flow model for the Baltenswil aquifer was established making use of conditioning information. The problem was tackled in a Monte-Carlo framework, i.e. by generating a large number of transmissivity realizations conditioned to the transmissivity and transient head measurements.

Any additional information (or knowledge) about the aquifer system state can be used to identify and retain only the solutions accounting for the observed data. Environmental tracers data can be used for this purpose. The solution of the transport equation for a given transmissivity realization is hoped to reproduce environmental tracer data. All realizations that do not allow to match the measured tracer concentrations should be discarded as model parameterizations in apparent disagreement with the actual observations of the aquifer system or, in other words, as 'impossible representations of the real world'.

It is widely recognized that the natural heterogeneity and the large spatial variability of the hydraulic conductivity predominantly controls the flow field variability in space and time and hence the transport and spread of contaminants in the groundwater (Gelhar, 1986; Dagan, 1986). No automated self-calibration of the hydraulic conductivity field to the concentration measurements is implemented in the following tracer modeling. The concentration data are not used for inverse modeling, e.g. by iteratively modifying the transmissivity realizations in order to minimize some penalty function defined for concentrations (see Chapter 3, Equation 3.6).

However, by following a stochastic approach, the realization ensemble may still be used
for further sieving of the transmissivity realizations by exclusion. This corresponds to using the concentration data to minimize uncertainty of results, by reduction of the number of the plausible transmissivity realizations in the ensemble and/or the modification of the conceptual model. The impact of spatial uncertainty on transmissivity can be finally estimated by the spread of the model results, e.g. the bandwidth of the different calculated concentration time-series.

The chosen approach is to model directly the tracer concentrations instead of water-ages. In this way, it is possible to obtain a more sophisticated interpretation of spatially and temporally available multi-tracer data than is possible with conventional box model methods. Information gained from different tracer methods can be used to separate individual segments of the whole transport process (e.g. unsaturated and saturated zones). Multiple tracer and hydraulic methods enable a coherent explanation of the flow paths and rates of movement while indicating weaknesses in the understanding of the system that will require further data collection and refinement of the conceptual model.

In this chapter we present the transport simulation results in the saturated zone. Based on the flow model established in Chapter 3, transport simulations for the environmental tracers Krypton-85 and Tritium/ Helium-3 are performed for each transmissivity realization of the ensemble. The tracer input at the groundwater table is reconstructed after its passage in the unsaturated zone by means of the numerical code developed in Chapter 4, according to the spatially variable depth of the groundwater table in the studied domain. It is then used as boundary concentration input flux to the transport simulations in the saturated zone.

### 5.1 Environmental tracer data

The Krypton-85 data show a distinct temporal variability at different locations in the domain (Tab. 5.1). The largest variability is observed at the pumping station (PW) Baltenswil (about 20 dpm/ccKr variation in a time interval of 3 years). The data at this location show an oscillating trend that is in contrast with the monotonically increasing trend of the atmospheric input function (see Fig. 4.3). Krypton-85 concentration data are not apparently correlated with the atmospheric input also at the PW Büel and at the
### Table 5.1: Krypton-85 data collected in the Baltenswil aquifer for the period 2003-2006 and derived groundwater apparent ages, calculated for Piston Flow conditions (i.e. tracer-derived ages equals hydraulic ages) according to equation 4.1. Concentration and age errors are expressed as one standard-deviation errors.

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>Sampling date</th>
<th>$^{85}$Kr [dpm/ccKr]</th>
<th>$^{85}$Kr-error [dpm/ccKr]</th>
<th>PF-age [yrs]</th>
<th>Age-error [yrs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW Baltenswil</td>
<td>28/05/2003</td>
<td>27.9</td>
<td>1.4</td>
<td>12.59</td>
<td>0.46</td>
</tr>
<tr>
<td>PW Baltenswil</td>
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<td>40.0</td>
<td>1.4</td>
<td>9.47</td>
<td>0.16</td>
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<tr>
<td>PW Baltenswil</td>
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<td>4.2</td>
<td>10.50</td>
<td>0.55</td>
</tr>
<tr>
<td>PW Baltenswil</td>
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<td>36.7</td>
<td>1.6</td>
<td>10.69</td>
<td>0.27</td>
</tr>
<tr>
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<td>39.3</td>
<td>2.3</td>
<td>9.59</td>
<td>0.32</td>
</tr>
<tr>
<td>PW Baltenswil</td>
<td>09/05/2006</td>
<td>44.4</td>
<td>2.2</td>
<td>11.06</td>
<td>0.30</td>
</tr>
<tr>
<td>PW Baltenswil</td>
<td>02/08/2006</td>
<td>35.7</td>
<td>1.9</td>
<td>11.38</td>
<td>0.30</td>
</tr>
<tr>
<td>Kb 94-1</td>
<td>12/03/2004</td>
<td>39.7</td>
<td>1.4</td>
<td>9.72</td>
<td>0.16</td>
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<td>Kb 94-1</td>
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<td>1.7</td>
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</tr>
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<td>2.0</td>
<td>9.87</td>
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<td>Kb 94-1</td>
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<td>1.9</td>
<td>11.38</td>
<td>0.30</td>
</tr>
<tr>
<td>Kb 94-2</td>
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<td>2.0</td>
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<td>Kb 94-2</td>
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<td>48.7</td>
<td>1.6</td>
<td>8.35</td>
<td>0.34</td>
</tr>
<tr>
<td>Kb 14</td>
<td>06/10/2004</td>
<td>41.0</td>
<td>3.3</td>
<td>10.07</td>
<td>0.37</td>
</tr>
<tr>
<td>Kb 14</td>
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<td>1.4</td>
<td>9.61</td>
<td>0.42</td>
</tr>
<tr>
<td>Kb 14</td>
<td>09/05/2006</td>
<td>40.0</td>
<td>1.9</td>
<td>10.25</td>
<td>0.30</td>
</tr>
<tr>
<td>Kb 14</td>
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<td>41.6</td>
<td>2.4</td>
<td>9.83</td>
<td>0.49</td>
</tr>
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<td>Kb 85-1</td>
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<td>38.0</td>
<td>2.7</td>
<td>10.27</td>
<td>0.31</td>
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<td>Kb 85-1</td>
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<td>1.4</td>
<td>11.88</td>
<td>0.31</td>
</tr>
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<td>4.3</td>
<td>8.38</td>
<td>0.59</td>
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<tr>
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<td>1.6</td>
<td>8.41</td>
<td>0.34</td>
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<td>1.6</td>
<td>10.21</td>
<td>0.19</td>
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<tr>
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<td>1.3</td>
<td>7.89</td>
<td>0.17</td>
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<td>2.3</td>
<td>7.90</td>
<td>0.47</td>
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<td>29/04/2004</td>
<td>68.2</td>
<td>2.7</td>
<td>3.02</td>
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<tr>
<td>PW Bruttisellen</td>
<td>29/06/2005</td>
<td>65.6</td>
<td>2.8</td>
<td>3.77</td>
<td>0.46</td>
</tr>
<tr>
<td>PW Buel</td>
<td>29/04/2004</td>
<td>30.0</td>
<td>1.6</td>
<td>11.96</td>
<td>0.34</td>
</tr>
<tr>
<td>PW Buel</td>
<td>30/06/2005</td>
<td>38.9</td>
<td>1.1</td>
<td>10.16</td>
<td>0.13</td>
</tr>
<tr>
<td>PW Girhalden 1</td>
<td>08/09/2004</td>
<td>37.8</td>
<td>1.3</td>
<td>10.37</td>
<td>0.15</td>
</tr>
<tr>
<td>PW Girhalden 2</td>
<td>08/09/2004</td>
<td>36.5</td>
<td>1.8</td>
<td>10.52</td>
<td>0.21</td>
</tr>
<tr>
<td>PW Girhalden 2</td>
<td>29/06/2005</td>
<td>33.8</td>
<td>2.0</td>
<td>11.36</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The trend at PW Büel is decreasing while it is the opposite at Kb 85-1. These oscillations are not observable elsewhere probably because of scarcity of data. At Kb 14 an almost constant trend in the measured concentrations is recorded. A constant trend of data is also recorded at PW Bruttisellen, PW Girhalden-II, Kb 94-2 Kb 84-1 and Kb 84-4. At PW Girhalden-I and Kb 84-3 only one measurement is available. The values recorded at PW Bruttisellen are the highest in the domain and double with respect to all the other observation locations. This pumping station, located very close to the Western boundary of the modeled domain, is thus fed with very young water (about three years old).
The interpretation of such heterogeneous Krypton-85 concentration data is not straightforward in terms of residence times. The calculated Piston-Flow ages reflect the variability observed in the concentration data and range between 7 and 12 years, even at the same observation location (e.g. PW Baltenswil), except the PW Bruttisellen ‘anomaly’. The Krypton-85 data indicate that mixing effects are not important in the modeled domain. Instead, and especially at PW Baltenswil, there is a clear indication that water with distinctly different ages is collected at the well at different times, according to the different actual conditions of the groundwater flow.

Tritium and Helium-3 data are shown in Tab. 5.2. The abundant data at the PW Baltenswil, Kb 94-1 and Kb 14 show that the concentration trend in the groundwater is strictly following the monotonically decreasing atmospheric input function recorded in the last 20 years. The few measurements at other observation locations confirm this trend. Helium-3 data show smoothly variable concentration values at all locations. In contrast to what is observed in the Krypton-85 data, oscillations in the concentration are not apparent in the case of Tritium and Helium-3. The resulting \(^3\)H/\(^3\)He ages do thus not display significant variations of the groundwater age. They are almost constant across the domain and range between one and four years. The discrepancy between Tritium/Helium-3 and Krypton-85 derived groundwater ages may be explained by the passage in the unsaturated zone. While the \(^3\)H/\(^3\)He clock starts at the groundwater table, the Krypton-85 ages will include the transport in both the saturated and vadose zone.

The transport model is based on the velocity field obtained by the stochastic modeling of groundwater flow. The transport simulations of the environmental tracers Krypton-85, Tritium and Helium-3 are run deterministically for each transmissivity realization of the ensemble and, thus, for a different velocity field but the same recharge field each time. This will allow to investigate the impact of stochastic transmissivity on the environmental tracers' transport.

The tracer input at the groundwater table is reconstructed by solving, for each cell of the domain, the transport equation in the unsaturated zone for a 1-D column with lower boundary set at a depth equal to the groundwater table depth at that cell. The reconstructed concentration history at the bottom of the unsaturated zone is then used as concentration input flux for transport modeling in the saturated zone. As for the flow model, the simulation time for transport is 1991-2006. Initial concentration
Concentration and age errors are expressed as one standard-deviation errors derived groundwater apparent ages, calculated for Piston Flow conditions according to equation 4.2.

Table 5.2: Tritium and Helium-3 data collected in the Baltenswil aquifer for the period 2003-2006 and derived groundwater apparent ages, calculated for Piston Flow conditions according to equation 4.2. Concentration and age errors are expressed as one standard-deviation errors

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>Sampling date</th>
<th>$^{3}H$ [TU]</th>
<th>$^{3}H$-error [TU]</th>
<th>$^{3}He$ [TU]</th>
<th>$^{3}He$-error [TU]</th>
<th>$^{3}H$-$^{3}He$ age [yrs]</th>
<th>$^{3}H$-$^{3}He$ error [yrs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW Baltenswil</td>
<td>15/02/2000</td>
<td>17.8</td>
<td>1.2</td>
<td>1.42</td>
<td>0.37</td>
<td>1.4</td>
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Table 5.2: Tritium and Helium-3 data collected in the Baltenswil aquifer for the period 2003-2006 and derived groundwater apparent ages, calculated for Piston Flow conditions according to equation 4.2. Concentration and age errors are expressed as one standard-deviation errors.
values for year 1991 are derived from a separate transport model simulating the tracer concentrations for the three decades 1961-1990.

5.2 Krypton-85 modeling

The Krypton-85 transport in the saturated zone is modeled with the module MT3DMS (Zheng and Wang, 1999a) in Processing Modflow (Chiang and Kinzelbach, 2001). The numerical solution scheme is the Method of Characteristics (MOC) (Zheng, 1990).

The transport model is two dimensional as the flow model. Therefore the (time-varying) reconstructed tracer input history at the groundwater table is regarded as source term, as well as the wells and the drains are sink terms. No-flow boundary conditions are established along the impermeable lateral domain boundaries (see Section 2.2). The Krypton-85 initial concentration (year 1991) is determined from an independent flow and tracer transport model for the years 1961-1991.

The transport simulations are performed for each transmissivity realization of the ensemble. A set of optimal homogeneous parameter values could be estimated by calibration of the parameter set - with regard to transport in both the unsaturated and saturated zones - to the concentration data (Tab. 5.3). These parameter values are chosen as default set for later comparison within the sensitivity analysis.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Description</th>
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</tr>
<tr>
<td>$\epsilon_a$</td>
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<td>gas-filled porosity - uns. zone</td>
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<tr>
<td>$\tau_g$</td>
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<td>gas-phase tortuosity - uns. zone</td>
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<td>longitudinal dispersivity</td>
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<td>transverse horizontal dispersivity</td>
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<td>$\alpha_{TV}$</td>
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<td>transverse vertical dispersivity</td>
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<td>$D_0$</td>
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<td>molecular diffusion coefficient in free water</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>0.0644 yr$^{-1}$</td>
<td>decay constant</td>
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</tbody>
</table>

Table 5.3: Default parameter set of values for stochastic transport of Krypton-85
Stochastic transport simulations are performed for the three transmissivity realization ensembles characterized by $\sigma_{\log T}^2 = 0.25$, $\sigma_{\log T}^2 = 0.5$ and $\sigma_{\log T}^2 = 1$ (see chapter 3) for years 1991-2006, making use of the default parameter set in Tab. 5.3. At none of the observation locations, simulated concentration time-series displayed any significant difference for the three different ensembles. Transport simulations based on the ensemble with variance $\sigma_{\log T}^2 = 1$ will be shown and used for later analysis.

5.2.1 Concentration oscillations at PW Baltenswil

The stochastic simulation results at the pumping station Baltenswil, are shown in Fig. 5.1 - left.

The simulated concentrations show significantly lower concentration values and smoother increasing trend when compared to the atmospheric and water table input (Fig. 5.1 - right). The initial concentration in the groundwater in 1991 is about 30 dpm/ccKr, while the atmospheric input is about 60 dpm/ccKr in that year. Between 1991 and 2006 simulated concentrations in the groundwater rise and display a different temporal variability if compared to the Krypton-85 time series at depth in the unsaturated zone (Fig. 5.1 - right). During the years 2000-2006 the atmospheric concentrations reached a constant value of about 90 dpm/ccKr (Fig. 5.1, right). The calculated concentrations at depth in the saturated zone reflect instead the steadily
increasing trend of the input function in the past years (1990-2000).

The appearance of concentration oscillations in the Krypton-85 data at the PW Baltenswil observation location and not elsewhere can be due to the rather shallow groundwater table in this area, to the relatively small size of its catchment and to the presence of groundwater boundary inflow (and thus lateral tracer input to the saturated zone) coming from the moraine hills in the North and North-East (unsaturated overburden with spatially variable thickness). These peculiar conditions in the neighborhood of the PW Baltenswil make mixing effects negligible in its catchment, where the well is apparently collecting water with distinctly different ages at different times. In particular, most of the measured Krypton-85 data at PW Baltenswil are smaller than the simulated values. Older water of unknown origin must thus be accounted for.

The high frequency oscillations in the measured concentrations at the Baltenswil well show that water of different origin can be collected on a short time-scale, from areas with shallow and relatively thin groundwater (less than 10 m deep and thick) and from areas with deep groundwater tables (Fig. 5.4). The conceptual model does not incorporate the mechanism able to explain the high frequency variations. The interplay of different phenomena may contribute in explaining and allowing a correct quantitative reproduction of the observed concentration oscillations. Different model conceptualizations can be implemented in the transport model to explain such oscillations.

**Effect of the pumping rate on Krypton-85 samples and simulated concentrations**

Local pumping stress may influence the measured concentrations in the sampled water. The group at IPB Bern performed a sampling experiment to assess the effect of pumping conditions on the sampled concentrations. Three samples have been taken at PW Baltenswil during an eight-hours pumping experiment. A decrease in measured concentrations of about 10% is observed due to pumping (Fig. 5.2), whereas the observed oscillations at PW Baltenswil are maximally 25% if compared to the Krypton-85 measurements average (Fig. 5.1, left).

Pumping conditions may thus have some influence on the measured Krypton-85 concentrations. An increased pumping rate results in older water (i.e. with smaller Krypton-85 concentration) collected at the pumping station. By comparison of measured Krypton-85 concentration and pumping rates over different time intervals
5.2. Krypton-85 modeling

Fig. 5.2: One day experiment at PW Baltenswil performed on July, 18th 2007

Fig. 5.3: Correlation analysis between measured Krypton-85 concentrations and different averaged pumping rates at PW Baltenswil. The temporal trends of measured concentrations and pumping rates averaged over different time intervals preceding the sampling day are shown (top), together with the correlation diagram between the measured concentrations and the best-correlated average ('1-week-before' average, bottom)
preceding the sampling day, anti-correlation of the two quantities becomes apparent at least in a first period of time (May 2003 to Sep 2004, Fig. 5.3).

The time period over which the pumping rate is averaged is important because it relates the intensity of the pumping to the timescales of Krypton-85 transport. For this reason, averages over different time intervals are used for comparison. At least in a first period (e.g. including the first four Krypton-85 measurements, from May 2003 to Sep 2004), the measured concentrations show a clear anti-correlation with the pumping rates averaged over different times (Fig. 5.3, top). However, the anti-correlation of the two quantities loses robustness in the next period (including the last three concentrations measurements, September 2005 to August 2006), finally resulting in a poorer overall (e.g. considering all Krypton-85 data) anti-correlation (Fig. 5.3, bottom). This result partially confirms that young water can be typically collected at the Baltenswil well in low pumping conditions, while in the opposite case the well will collect older water.

**Effect of the recharge to groundwater on simulated Krypton-85 concentrations**

The strong oscillations in the measured concentrations could not be properly reproduced by the simulated concentrations in the groundwater, with the exception of two distinct peaks during winter 2001/2002 and 2002/2003 and two local minima during the following two summers. The simulated concentration drop is especially relevant during the hot summer 2003. The behavior of the simulated oscillations strictly resembles the high recharge conditions during winter 2002/2003 and the following dry summer which took place during the year 2003 (see chap. 3, Fig. 3.8).

The peak-to-peak amplitude of the simulated oscillations is of the order of 5 dpm/ccKr, which lies within the concentration measurement (one standard-deviation) error. Correspondingly, the observed concentrations at PW Baltenswil show a minimum during summer 2003 (27.9 dpm/ccKr, see Tab. 5.1) and rising values during winter 2003-2004 (up to 47.7 dpm/ccKr). Although the simulated concentrations show smaller variations than the measured ones, the former are in phase with the latter.

Both the measured and simulated concentrations vary on a seasonal time-scale as recharge does. A partial explanation to the mechanism driving this temporal variability is thus likely to be the seasonal variations in recharge to groundwater, although the
transport model cannot fully reproduce their amplitude. The largest reproduced oscillations take place in the year 2003, when recharge to groundwater was very small especially during the hot summer months. This hypothesis is confirmed by further simulation runs, where the recharge rate during spring and summer 2003 was artificially raised, resulting in the disappearance of the above-mentioned oscillations in the simulated results. The model can only account for limited variations in the concentrations, about 10% (Fig. 5.4).

Fig. 5.4: Simulated concentration time-series for one single realization. The effect of artificially raising recharge in spring and summer 2003 is apparent in the discrepancy between the blue (standard simulation) and the green line (with modified recharge)

The concentration oscillations, which take place on a quite short time scale (seasonal rather than yearly), could be reproduced in their amplitude only partially by the transport model. It is thus likely that recharge variations alone cannot be accountable for these concentration fluctuations.

**Effect of the spatial boundary conditions on Krypton-85 concentrations**

Incorrect spatial boundary conditions may also contribute to high frequency transient mixing of different water ages. By inclusion of new parts of the larger Aathal aquifer into the modeled aquifer domain, water of different origins and thus ages can be accounted for. In particular, the shallow and thin groundwater layer lying West of the modeled domain (see the hydro-geological map in chapter 2, Fig. 2.6), although thin and with
limited spatial extension, is likely to bring very young water to the well. On the other hand, older water components may instead come from the aquifer part lying beyond the original Eastern boundary (Fig. 2.6). In this way, a larger part of the water originating from the moraine hills on the North-East may be collected at the PW Baltenswil, thus bringing more older water to the PW Baltenswil. These hypotheses are tested by means of the numerical model with differently modified spatial boundaries and compared with the original model results (Fig. 5.5):

1. Modified boundary West of Drain #1, PW Baltenswil catchment (Fig. 5.5, top right). The new young water cannot reach the PW Baltenswil because of the drainage action of the drain Nr.1 located to the West of the pumping station. Due to the drain configuration chosen to model the groundwater flow, this drain 'screens' the PW Baltenswil hampering the younger water to reach the pumping station. No modifications are found in the Krypton-85 concentration time-series at

![Fig. 5.5: Quasi steady-state extension of the five pumping stations’ catchments in March 2003 with original boundaries (top left) and with: 1. Modified Western boundaries close to Drain Nr.1 (top right); 2. Modified Western boundaries close to PW Bruttisellen (bottom left); 3. Modified Eastern boundaries (bottom right)](image-url)
5.2. Krypton-85 modeling

PW Baltenswil.

2. Modified boundary West of PW Bruttisellen catchment (Fig. 5.5, bottom left). The new young water is collected at PW Bruttisellen in significant amounts. The discrepancy between simulated and observed Krypton-85 concentrations is reduced from 50% (original model) to 30% (Fig. 5.6).

![Krypton-85 concentration-time series at PW Bruttisellen.](image)

Fig. 5.6: Krypton-85 concentration-time series at PW Bruttisellen. Comparison of the original model results with the extended boundaries model (Fig. 5.5 - bottom-left). Significant amount of water enriched in Krypton-85 is collected at the pumping station.

3. Modified Eastern boundary (Fig. 5.5, bottom right). The older water coming from the Western part of the domain is mostly collected at other pumping stations than PW Baltenswil. Its catchment is not significantly modified with respect to the model with original boundaries (Fig. 5.5, top left). This alternative model does not provide an explanation neither for the Krypton-85 concentration oscillations nor for the older water which Krypton-85 data show is collected at PW Baltenswil.

Effect of the nearby-drain on Krypton-85 concentrations

A possible alternative explanation to the observed concentration oscillations may also be found in the drain configuration (position and discharge rate of the springs in the model domain) chosen for the hydraulic system. One drain (Drain Nr.1) with relatively
large equivalent hydraulic conductance is located very close to PW Baltenswil (see chapter 3). This drain may collect large amounts of water, especially in case of high groundwater tables and low pumping regimes (see Fig. 4.26 and Fig. 4.27) and thus give rise to different transient mixing rates of high and low Krypton-85 concentration water. The simulated concentrations show that younger water is collected at this location if compared with the concentration time-series at PW Baltenswil (Fig. 5.7).

![Graph showing Krypton-85 concentration time-series at PW Baltenswil and Drain Nr.1](image)

Fig. 5.7: Comparison of Krypton-85 concentration time-series at PW Baltenswil and at Drain Nr.1. Younger water is collected at the drain location

**Effect of the water inflow from the moraine hills**

A possible candidate to explain the older water (e.g. poorer in Krypton-85) collected at the PW Baltenswil is also the water originating from the thick hilly moraines in the North and North-East part of the domain (see the hydro-geological map in chapter 2, Fig. 2.6 and unsaturated zone thickness spatial distribution in Fig. 5.8).

This part of the model domain provides the tracer input to the groundwater in two different ways. The first is via the lateral inflow into the aquifer proper from the 'virtual groundwater' layer (see chapter 3), i.e. from the thin saturated layer of 0.1 m. thickness in the North-East. The second one is water from the hilly moraines which lie above the aquifer in the PW Baltenswil catchment (Fig. 5.8). Being overlaid by a thick (up to 40 m.) unsaturated overburden if compared to the rest of the modeled aquifer, this area
5.2. Krypton-85 modeling

Fig. 5.8: Unsaturated zone thickness (left) and modeled moraine area (right). In this area, perched aquifer and natural springs are particularly numerous. The brown area is used for simulation with $\tau_g = 0.01$ (violet line in Fig. 5.9), while the green one refers to the simulation where the hilly moraine area is closer to the PW Baltenswil ('larger area', green line in Fig. 5.9).

may contribute with significant amounts of older water.

The impact of this area on the Krypton-85 concentration time-series at PW Baltenswil is tested by means of different simulation runs by varying the transport parameters in this area only. By choosing a very small value of the gas-phase tortuosity ($\tau_g = 0.01$) in the unsaturated zone in the moraine area, 'artificially' older water coming from this area could be simulated. With this hypothesis the gas-phase Krypton-85 will diffuse with a very small effective diffusion coefficient $D_g$ in the unsaturated hilly moraines. The effect will be enhanced by making the hilly moraines area larger and closer to the PW Baltenswil (green area, Fig. 5.8, right). Results are shown in Fig. 5.9.

By assuming a slower tracer dynamics in thick unsaturated zones, the discrepancy between simulated and measured Krypton-85 concentrations is reduced. In particular, a reduction of one-tenth of the effective diffusion coefficient allowed to fit multiple time-distributed data. Besides, the spatial concentration gradient between the hilly and flat parts of the aquifer (see Fig. 5.8, left) is increased, providing the necessary (according to data) older water component (Fig. 5.10).

This can be explained by geological considerations. The less pervious lenses present in the unsaturated zone are probably more numerous in areas with a thick unsaturated
Chapter 5. Transport simulations

Fig. 5.9: Krypton-85 concentration-time series at PW Baltenswil. Comparison of the original model results ($\tau_g = 0.1$) and the model with artificially older water from the moraine ($\tau_g = 0.01$)

Krypton-85 simulated groundwater concentration
- August 2002 -

Original model - constant $\tau_g = 0.1$
Modified model - constant $\tau_g = 0.01$ in the moraine area

Fig. 5.10: Calculated Krypton-85 input at the groundwater table in August 2002 for the original model (left) and for the modified model (right), where the tracers dynamics in the thick unsaturated moraines was artificially slowed by a factor 10. Significant modification of the concentration gradient is apparent in the Northern part of the domain. The blue cells show the preferential flow paths (with LogT=0.1) simulation.
5.2. Krypton-85 modeling

These lenses typically provide local perched aquifer which - although not exactly localized - are well known from geological investigations and from the presence of natural springs in the Northern part of the domain. The gas-phase Krypton-85 cannot pass through these lenses and must thus circumvent them. This in turn coincides with the reduction of the gas-phase tortuosity value, e.g. with the increased of the tortuosity of the path the gas tracer must follow in thick unsaturated zones. In some places, these lenses may also completely impair the Krypton-85 input to the groundwater.

By varying the other transport parameters such as transmissivity and porosity in the above-mentioned area, no significantly different concentration time-series could be obtained. Simulations with smaller variogram correlation length in this zone ($r = 300$ m.; original: $r = 10^9$ m.) did not bring to different concentration patterns in the subsurface. In particular, the simulation of preferential flow paths (high transmissivity conduits) connecting the hilly moraines with the PW Baltenswil did not lead to a better match (Fig. 5.10, right).

5.2.2 Simulations results at the other observation locations

The stochastic simulation results at all the observation locations are shown in Fig. 5.11. The concentration time-series trend is increasing at all locations through the simulation time. Oscillations in the simulated concentration time series are still apparent at observation locations where the groundwater is shallow and relatively thin (less than ten meters - Fig. 5.12) and the travel paths in the groundwater are comparatively short (see chapter 4, Fig. 4.26 and 4.27): Kb 94-2, Kb 85-1, Kb 84-1, Kb 84-3 and Kb 84-4. Yet, there is little experimental evidence of such oscillation at these locations due to lack of data. At the observation locations further downstream, i.e. with larger groundwater residence times and where the groundwater thickness is in general larger (between 10 and 20 m, Fig 5.12), the oscillations due to the 2002-2003 recharge and tracer input conditions are very limited.

The obtained match between simulated and measured concentrations is fairly satisfactory at all locations except at PW Baltenswil, PW Bruttisellen, Kb 94-2, Kb 14 and Kb 84-3. The simulated concentrations at PW Bruttisellen, Kb 94-2 and Kb 14 are significantly lower than the measured ones, indicating that the water intercepted at these three locations is younger in reality than expected by the simulated results. The
Fig. 5.11: Krypton-85 concentration-time series for 100 transmissivity realizations. Default parameter set (see Tab. 5.3)
opposite happens at Kb 84-3, where simulated concentrations are in general higher than the measured ones.

The impact of the different transmissivity realizations is apparent in the bandwidth of the simulated concentrations. The transmissivity-induced variability is of the order of magnitude of the measurement error on Krypton-85 concentrations. Its impact on the simulated concentrations is in general a regular displacement of the complete time-series along the \( y \)-axis. The largest effect is observed at Kb 84-3, where the streamlines come from zones with high transmissivity variance (see chapter 3, Fig. 3.18). Also Kb 84-4, close to Kb 84-3, displays a larger spread compared to other observation locations. The spread is on the other hand particularly limited at locations where short streamlines are intercepted (e.g. Kb 94-2, Fig. 4.26 and Fig. 4.27).

The resulting spread in the simulated Krypton-85 concentration time-series induced from the different transmissivity realizations does not in general allow to ‘sieve’ among the different realizations according to the observed/simulated concentration match. The uncertainty bandwidth is at most locations of the order of magnitude of the Krypton-85 measurement error, with the two exceptions of Kb 84-3 and Kb 84-4. Moreover, at several observation locations the simulated time-series cannot honor all the available Krypton-85 measurements, but only one or a few in a row (e.g. PW Baltenswil, PW Buei, PW Girhalden-II, Kb 94-1, Kb 85-1). Nonetheless, at some locations sieving the transmissivity realizations by the honoring or not-honoring of the data would in principle still be possible (e.g. PW Girhalden-I, Kb 84-1, Kb 84-3 and Kb 84-4).
At locations where the time-variability of the concentration measurements is large (oscillations), different transmissivity realizations may allow to honor alternatively only a few of them. In general, where more than one measurement is available, it is difficult to match all the points at the same observation location, due to the often large difference between measurements at different times at the same location. This is the case at PW Baltenswil, PW Buel, PW Girhalden-II, Kb 94-1 and Kb 85-1.

The impact of transmissivity realizations is smaller than expected, being of the order of magnitude of the tracer measurement error. This can be explained by comparison of the average travel times in the unsaturated zone and the residence times in the groundwater (Fig. 4.22, Fig. 4.24 and Fig. 4.25). The time spent in the groundwater is on average ten times smaller than in the unsaturated zone. The effect of transmissivity on the tracer transport will thus be limited.

The limited impact of the different transmissivity realizations does not mean that the tracer transport in the saturated zone is of minor importance. Figure 5.13 shows a comparison of the spatially distributed tracer input at the groundwater table (left)
and the tracer concentration in the groundwater (right) at the same simulation time (e.g. January 2003). Both differences in the absolute concentration values and in the spatial distribution are apparent. The simulated concentrations in the groundwater are sensibly lower and show less marked spatial patterns. Since the exchange at the groundwater table is assumed instantaneous, this fact indicates that mixing is a more prevalent phenomenon taking place in the groundwater. The mixing of the different streamlines in the groundwater modifies the tracer concentration in the groundwater body (both in its absolute value and spatial distribution), resulting in concentrations in the saturated zone lower than the input at the groundwater table at the same time.

5.2.3 Sensitivity analysis

Sensitivity analysis is performed to assess the most important simulation parameters controlling the transport process both in the unsaturated and saturated zones.

Porosity. Sensitivity of the simulated concentrations to porosity is relevant. Simulation results with a porosity of $n = 0.15$ are shown in Fig. 5.14. The effect of lower porosity is to increase flow velocities and thus the transmission-velocity of the input function signal from the groundwater table to the observation locations. Lower porosity in the saturated zone results in a steeper increase of the concentration time-series before the year 2000 and thus sensibly higher concentration values at observation locations during the following period of interest (2003-2006), where Krypton-85 measurements are available.

As a further consequence, the impact of the heterogeneity of the velocity field increases, resulting in increased variance of the simulated concentration values. The effect of heterogeneity becomes more apparent at the pumping stations downstream, as the residence time in the groundwater increases, i.e. when the streamlines intercepted at the different observation locations become longer. At the borehole locations, which intercept shorter streamlines compared to the pumping stations, this effect is instead limited.

Where oscillations in the simulated concentrations are apparent (e.g. PW Baltenswil, Kb 94-2, Kb 84-3) lower porosity also implies slightly larger oscillations. At locations where residence times in the groundwater are small, the impact of lower porosity is
Fig. 5.14: Krypton-85 concentration-time series for 100 transmissivity realizations with constant porosity value $n = 0.15$. Due to space reasons, the legend is omitted: see Fig. 5.11 for explanations.
Fig. 5.15: Krypton-85 concentration-time series for 100 transmissivity realizations with constant gas-phase tortuosity value $\tau_g = 0.2$
limited and a reasonable fit is still obtained with \( n = 0.15 \) (e.g. Kb 94-1).

**Gas-phase tortuosity.** A lower porosity alone would not suffice to fit the measured data at locations such as PW Bruttisellen, Kb 94-2 and Kb 14, where faster dynamics is apparent from the Krypton-85 data. A way out is to make the dynamics faster also in the unsaturated zone. In the case of Krypton-85, this can be done by increasing the gas-phase tortuosity value, i.e. the effective gas diffusion coefficient \( D_g \). Stochastic simulation results for \( \tau_g = 0.2 \) are shown in Fig. 5.15.

Simulated concentrations increase significantly at all observation locations. The impact of a larger diffusion coefficient will be larger where thicker unsaturated overburden overlays the saturated zone. This is exactly the case at Kb 94-2 and Kb 14, where the intercepted streamlines come from the hilly North-east inflow area. As a matter of fact, at these two locations a larger tortuosity allows to match the measured Krypton-85 concentrations. At other locations, larger tortuosity values also result in higher concentrations and a worse match between simulated and measured concentrations.

The sensitivity of the concentration time-series to the dispersion coefficient was found to be negligible.

**Effect of spatially variable transport parameters**

The sensitivity analysis shows that by an *ad-hoc, local* choice of the values for gas-phase tortuosity in the unsaturated zone and porosity in the saturated zone, a simultaneous match at all locations can be obtained. As example, a fair match at the boreholes Kb 94-2 and Kb 14 could be obtained by assuming gas-phase tortuosity \( \tau_g = 0.2 \) (Fig. 5.15).

Yet, the measured tracer concentration at two observation locations (PW Bruttisellen and Kb 84-3) could not be fitted by varying the parameter values as done in the sensitivity analysis. Simulated concentrations at PW Bruttisellen are lower than the measured values for all simulation runs. A very small porosity value \( (n = 0.05) \) or combination of a small porosity value and a large value of gas-phase tortuosity (e.g. \( n = 0.1 \) and \( \tau_g = 0.35 \)) would allow to match the data (Fig. 5.16, left).
5.2. Krypton-85 modeling

At the observation borehole Kb 84-3, large values of porosity \((n = 0.35\) or higher) and/or small values of gas-phase tortuosity \((\tau_g = 0.05\) or smaller) would be needed to obtain a fair match (Fig. 5.16, right).

![Krypton-85 concentration-time series](image_url)

**Fig. 5.16:** Krypton-85 concentration-time series with different local porosity and gas-phase tortuosity values porosity at PW Bruttisellen (left) and at Kb 84-3 (right). Original simulation results, using the default parameter values in Tab. 5.3 are shown (in blue) for comparison.

With regard to the non-homogeneity hypothesis of the porosity parameter across the domain, it can be supported by experimental evidence derivable from geological profiles available at the boreholes and well locations. In the South-Western part of the domain, where the groundwater thickness is larger than 10 m, soil profiles reveal the existence of cemented conglomerate layers of a few meters thickness at different depths (PW Bruttisellen, PW Girhalden-I and -II, Kb 84-1, Kb 84-4). Such a layers become relevant at PW Bruttisellen, where the conglomerate layer thickness is 13 m. (out of 20 m. total saturated thickness). This geological formation is known to have very small porosity values \((n = 0.1\) or smaller).

Although realistic, these combined values of porosity and gas-phase tortuosity would introduce an important local heterogeneity in the description of the porous media, restricted to the PW Bruttisellen and Kb 84-3 neighborhood. In absence of local tortuosity and porosity measurements, only an ad-hoc choice of spatially variable parameter values - although justified by geological drilling profiles - allows to obtain a satisfactory simultaneous match at all locations.
5.2.4 Comments

The Krypton-85 data collected in the Baltenswil domain do not allow a straightforward interpretation. Where multiple measurements are available at the same location, important variations take place on a very short timescale, less than yearly. In particular at PW Baltenswil and Kb 94-1 they show an oscillating character. In general, at the other locations such oscillations were not observed. This may also be due to the small number of measured data at some observation locations. The oscillations in the simulated concentrations time-series could be obtained by the transport model only at some locations (PW Baltenswil, Kb 94-1, Kb 94-2, Kb 85-1, Kb 84-3, Kb 84-4). The simulated amplitudes of the oscillations are nonetheless smaller than the observed.

In most cases it is thus not possible to assign a unique age to the groundwater by direct comparison between tracer concentrations at sampling locations and the atmospheric input function, even by accounting for the important impact of the unsaturated zone on the subsurface tracer concentrations. To our knowledge, such abrupt variations in measured Krypton-85 concentrations were not reported in any other study.

The presence of water with different ages at the Baltenswil well could be partially explained by the pumping action of the well and by the time-varying recharge to groundwater. Different spatial boundary conditions do not play a major role at this observation location. In particular, the older water component collected at the well could be found in the hilly moraines in the North and North-East of the modeled domain.

With regard to the other observation locations, sensitivity analysis indicates that spatially-homogeneous values of the most consequential transport parameters (e.g. gas-phase tortuosity in the unsaturated zone and porosity in the saturated zone) are not suited to obtain a simultaneous match at all locations. Ad-hoc spatially variable parameters will instead better account for concentration variations as observed from measurements across the domain.

Alternatively, different spatial boundary conditions were also shown to play a role at one observation location (PW Bruttisellen). Here, the young water (rich in Krypton-85) collected at PW Bruttisellen originated in a shallow and thin (less than 2 m) groundwater layer adjacent to the original modeled domain, West of the Bruttisellen well (see the hydro-geological map in chapter 2, Fig. 2.6). Although very thin and with limited
5.2. Krypton-85 modeling

spatial extension, this groundwater layer external to the original modeled domain provides the very young water component which will mix with the older water coming from the PW Bruttisellen catchment within the original modeled domain. This younger water component raises the Krypton-85 concentration at the well and thus reduces the discrepancy between simulated values and data.

The explanation of the Krypton-85 data required the introduction of spatially variable gas-phase tortuosity and porosity in order to achieve a simultaneous match at all observation locations. The interplay of both parameters will determine the fast/slow dynamics zones of transport and consequentially its velocity, which could be different across the domain. In other words, the older and younger water components of the groundwater flow can be correctly described by the identification of different zones where the tracer dynamics is faster/slower than in the rest of the aquifer (Fig. 5.17). The zonation of the above-mentioned parameters allows to reduce the discrepancy between observed and simulated concentration values:

- In zone A faster dynamics can be obtained either by raising the gas-phase tortuosity to \( \tau_g = 0.2 \) on the hilly unsaturated moraine upstream of the two boreholes (see Fig. 5.15 and Fig. 5.12 - left) or by decreasing porosity to \( n = 0.1 \). Alternatively, intermediate values of both tortuosity and porosity can also be successfully used. The lack of specific local data hampers any distinction between the above-mentioned possible parameter configurations.

- In zone B, even a strong reduction of the porosity value (e.g. \( n = 0.05 \)) would not suffice to reproduce the very high Krypton-85 concentrations at PW Bruttisellen, the highest measured concentrations in the whole domain. This low value of porosity for the whole well catchment would be expected only in the vicinity of the well, since the concentration measurements at the borehole Kb 84-1 - which in several flow scenarios (see Fig. 4.26 and Fig. 4.27) was found to belong to PW Bruttisellen catchment - could be fitted with a constant porosity \( n = 0.25 \). Indeed, the geological profile at PW Bruttisellen reveals the presence of a thick cemented conglomerate layer which would justify a very small local value of porosity (\( n = 0.05 \) or smaller) around the well.

By assuming a very fast transport both in the unsaturated zone (i.e. \( \tau_g = 0.35 \)) and in the saturated zone (i.e. \( n = 0.1 \)), the very-high Krypton-85 data can be reproduced. Yet, such a strong parameter heterogeneity in both zones is hard to
Fig. 5.17: Zones with different dynamics within the modeled domain, as indicated by Krypton-85 modeling. Zone A: upstream boreholes Kb 94-2 and Kb 14. Zone B: PW Bruttisellen catchment. Zone C: upstream PW Baltenswil, in the direction of the hilly moraines in the North, providing the lateral inflow to the well catchment. Zone D: upstream borehole Kb 84-3. Blue zones indicate faster dynamics compared to the rest of the domain, whereas red zones indicate where slower dynamics is needed. The green zone at the Western boundary indicates where a boundary re-definition is needed. The average discrepancy between simulated and measured data at each location is also indicated as $\Delta c = c_{\text{sim}} - c_{\text{meas}}$ in the case of the simulation run with default transport parameter set (see Fig. 5.11).

expect in the relatively small PW Bruttisellen catchment, especially in the light of the lack of measurements.

As a matter of fact, the Krypton-85 input values at the groundwater table in recent years, due to the thin unsaturated zone overlying the aquifer around the well location, are of the order of the measured concentrations at the well (Fig. 5.13) and would in principle allow to reproduce the data at PW Bruttisellen. It is thus likely that younger water (richer in Krypton-85) coming from outside the modeled domain is collected at the well. By a re-definition of the Western boundary and the inclusion of the adjacent groundwater layer to the West, it was shown that the younger water can also come from this part of the aquifer (green zone in Fig. 5.17).
The zone C calls instead for a slower Krypton-85 dynamics. It was found that a consistent part of old water collected at the Baltenswil well must originate in the North and North-Eastern hilly moraines which provide the boundary inflow to the well catchment. A satisfactory Krypton-85 data fit could be achieved on average by making the unsaturated zone transport in this area very slow (i.e. $\tau_g = 0.01$). Such a small value of gas-phase tortuosity, i.e. the fact that the tracer must follow a more tortuous path to get to the groundwater table, can be justified by the presence of less pervious lenses in the thick unsaturated overburden. These lenses give locally rise to perched aquifers which at some locations appear as localized natural surface springs. The gas-tracer cannot go through these lenses and must necessarily by-pass them. The lenses isolate locally the gas tracer and will retard it in its way to the groundwater table.

Also the zone D requires slower dynamics. This could be partially accomplished by smaller values of tortuosity ($\tau_g = 0.05$) in the unsaturated zone or by higher values of porosity ($n = 0.35$). According to geological conditions as derivable from the borehole profile, this extreme value of porosity would not be justified.
Fig. 5.18: Tritium concentration time series for 100 transmissivity realizations. Default parameter set (see Tab. 5.3)
5.3 Tritium and Helium-3 modeling

Tritium and Helium-3 transport simulations in the saturated zone are modeled in Processing Modflow (Chiang and Kinzelbach, 2001) with the module MT3D99 (Zheng and Wang, 1999a), which allows the simulation of first-order parent/daughter chain reactions. Boundary conditions and source/sink terms are defined as in the Krypton-85 simulations (see section 5.2).

Transport simulations are performed for each transmissivity realization of the ensemble with variance $\sigma_{\text{LogT}}^2 = 1$. The optimal parameter set used for Krypton-85 simulation is used also for Tritium and Helium-3 transport simulations. The aim is to evaluate whether the scenario depicted by means of Krypton-85 simulations is also consistent with the Tritium and Helium-3 concentration data or some modifications to parameters or to the conceptual model will be necessary to get a more realistic picture of reality.

The Tritium input function at the groundwater table is reconstructed by solution of the tracer transport equation for the unsaturated zone (presented in chapter 4), according to the spatially variable groundwater table depth. Only the Tritium input at the groundwater table is considered and not the Helium-3 contribution (see chapter 4). Helium-3 will thus enter the system only as decay-product of Tritium in the saturated zone.

The stochastic simulation results for Tritium at the different observation locations with the default parameter set (Tab. 5.3) are shown in Fig. 5.18. The monotonically decreasing trend of the input function (see Fig. 5.19) is reflected in the Tritium concentration time-series at the observation locations and matches the decreasing trend of the data (apparent at e.g. PW Baltenswil, Kb 94-1 and Kb 14). In general, a fairly satisfactory match is achieved at all locations.

The bandwidth of the concentration time-series is smaller than in the case of Krypton-85, indicating that the impact of the transmissivity realization on the Tritium concentrations in the saturated zone is limited. This is most probably due to the almost spatially smooth values of the input function at the groundwater table in the last 5 years (see Fig. 5.20 - left). As in the case of Krypton-85, the most relevant mixing effects take place in the saturated zone. Besides, the nearly steady-state concentrations at the groundwater table at all depths (Fig. 5.19) result in a smoother spatial concentration distribution in the groundwater, if compared to the reconstructed
Chapter 5. Transport simulations

Fig. 5.19: Tritium concentration time series at different unsaturated zone column depths for years 1991-2006

Fig. 5.20: Calculated Tritium input at the groundwater table (left) and simulated concentration in the groundwater (right) in March 2001 and in March 2005
input at the groundwater table (Fig. 5.20 - right).

The stochastic simulation results at the different observation locations for Helium-3 are shown in Fig. 5.21, with the default parameter set given in Tab. 5.3. The simulated concentrations are higher than the observed ones at almost all locations. This fact may indicate a too slow dynamics in the saturated zone (see next section).

Two typical simulated spatial concentration distributions of Helium-3 across the domain are shown in Fig. 5.22. In contrast to Tritium and Krypton-85, the Helium-3 spatial distribution is a direct consequence of the groundwater flow, accumulating downstream at all simulation times.
Fig. 5.21: Helium-3 concentration time series for 100 transmissivity realizations. Default parameter set (see Tab. 5.3)
5.3. Tritium and Helium-3 modeling

5.3.1 Sensitivity analysis

Fig. 5.22: Simulated Helium-3 concentration in the groundwater in March 2001 and in March 2005. The high concentrations at the Southern boundary are numerical artifacts. Despite the presence of two drains at the Southern boundary, Helium-3 accumulates at the Southern end of the domain (no-flow boundary).

The Tritium concentrations time-series display almost no sensitivity to water content $\theta$, gas-filled porosity $\epsilon_a$, liquid-phase tortuosity $\tau_l$ and dispersion coefficient $\alpha_L$. Only a change in the porosity value (e.g. $n = 0.15$) will modify to some extent the time-series at all locations (Fig. 5.23). Assuming faster dynamics in the saturated zone will result in slightly lower concentration time-series at all locations.

The smoothly decreasing trend recorded in the last fifteen years in the Tritium atmospheric input function and its spatially almost constant values in the last five years are most probably responsible for the negligible sensitivity of Tritium time-series in the groundwater to most soil and transport parameters involved in the transport simulations.

Sensitivity of Helium-3 to all subsurface transport parameters is negligible. Only porosity - which governs the residence time - plays a key role in determining the tracer concentration time-series in the groundwater (Fig. 5.24).
Fig. 5.23: Tritium concentration time series for 100 transmissivity realizations with constant porosity value $n = 0.15$. 
5.3. Tritium and Helium-3 modeling

Ensemble 3He Conc. at PW Baltenswil - n = 0.15

Fig. 5.24: Helium-3 concentration time series for 100 transmissivity realizations with constant porosity value $n = 0.15$
5.3.2 Comments

Tritium data offer a straightforward interpretation, although not a very robust one. The smoothly decreasing input function at the groundwater table results in almost constant concentrations propagated across the domain at least in the last ten years. Sensitivity to all transport parameters in both the unsaturated and saturated zones (with the exception of a small sensitivity to porosity) is very limited. Nonetheless, a fair agreement between simulated and measured Tritium concentrations could be obtained at all locations. Although its 'flat' atmospheric input function smoothes out the dependence on any model parameter, correct Tritium modeling (i.e. not in contradiction with the data) provides a necessary basis to model the Helium-3 concentrations in the groundwater.

As all the Helium-3 produced before recharge enters the saturated zone is assumed to be in equilibrium with the atmospheric concentrations and thus not providing any input at the groundwater table, Helium-3 produced by Tritium decay in the saturated zone only is modeled. Helium-3 simulation will thus account for transport in the saturated zone only. Helium-3 modeling is thus valuable to gain specific information on groundwater flow only.

As Tritium moves along the streamlines, the amount of Helium-3 in the groundwater increases and is transported downstream. The result will be an increasing Helium-3 accumulation as water moves downstream. This fact is confirmed by the higher Helium-3 concentration measurements at the downstream observation locations (PW Buel, PW Girhalden-I and -II, see Tab. 5.2). Increasing Helium-3 concentrations downstream are also obtained by simulations.

The simulated Helium-3 concentrations with porosity $n = 0.25$ considerably overestimate the observed concentrations at all observation locations. Simulations performed with porosity $n = 0.15$ allow instead to match the Helium-3 observed concentrations at most observation locations (Fig. 5.24). This indicates that at these locations either a faster dynamics, or younger water, is needed to match the observations or some Helium-3 loss mechanism must be accounted for in the conceptual model.
5.4 Discussion

A correct reproduction of environmental tracer measurements could in principle be achieved with realistic parameter values for both the unsaturated and saturated zones. However, the issue of simultaneously honoring all the tracer data at all locations could not be completely resolved within the proposed conceptual model and with spatially constant parameter values, most notably gas-phase tortuosity for Krypton-85 transport in the unsaturated zone and porosity for both Krypton-85 and Helium-3 transport in the saturated zone.

Krypton-85 unveiled the presence of older and younger water components across the domain. Heterogeneity of the transport parameter in both the saturated and unsaturated zones together with the redefinition of the spatial boundary conditions allowed to define a clear picture of these components, according to the match between observed and simulated Krypton-85 concentrations. By suitable combination of gas-phase tortuosity and porosity values, the domain can be divided in zones with higher or slower dynamics according to the measured tracer concentrations. Krypton-85 modeling provides valuable information on the origin of water with different ages.

Within the proposed model set-up, Tritium data could be rather easily modeled, reproduced and interpreted due to the smoothly decreasing trend of its input function in the last fifteen years. Tritium modeling alone is today not very useful in shallow groundwater with short residence times (less than ten years) because of its almost constant input in recent years. Its modeling remains nevertheless fundamental to the modeling of Helium-3 transport, which instead can provide detailed information on the water movement in the saturated zone.

Helium-3 data allow to focus only on the saturated zone transport. In contrast to Krypton-85, Helium-3 data could be simultaneously reproduced at all locations with a constant porosity $n = 0.15$, while models for Krypton-85 and Tritium indicate a better fit with a constant porosity $n = 0.25$. It is noticeable that Helium-3 is sensitive only to the porosity parameter. Due to the geological conditions known (unconsolidated material) within the aquifer under study, porosity is not expected to vary much across the aquifer, although local variations can be expected due to different geological conditions as revealed by borehole profiles. Local porosity measurements at the specific locations where tracer
data are collected would anyway prove very useful. Helium-3 simulation runs with the porosity value calibrated by Krypton-85 and Tritium simulations \( n = 0.25 \) considerably overestimate the Helium-3 measured data at all locations. Since the porosity value \( n = 0.25 \) was successfully used in the Krypton-85 and tritium simulations, it is unlikely that the systematic overestimation at all locations of the simulated vs. measured Helium-3 concentrations can be explained by a lower porosity value \( n = 0.15 \) across the whole domain. This basic, apparent contradiction between Krypton-85 and Helium-3 data interpretation may instead be clarified by accounting for Helium-3 loss in the subsurface. This argument will be investigated in chapter 6.

Tritium simulations could be easily accommodated to honor the measured data, and the following Helium-3 simulations were essentially sensitive to the porosity parameter only. While Tritium and Helium-3 could provide a clear picture of the transport dynamics in the subsurface (neglecting for the moment the systematic overestimation of Helium-3 simulated concentrations, which will be tackled in Chapter 6), Krypton-85 simulations allowed a deeper insight into the separation of the tracer dynamics in their unsaturated and saturated part and, most importantly, into the ages of the different water components collected at the observation locations across the domain. In particular, at one observation location, older and younger water is collected in different amounts at different times. At this location, the measured data showed oscillations in the concentration value.

5.4.1 Krypton-85 oscillations

The oscillations of concentration measurements essentially concern the Krypton-85 measurements, most notably at the PW Baltenswil, where enough measurements are available. Small oscillations both in Tritium and Helium-3 measured concentrations are recorded at some locations, although their magnitude is often comparable to the concentration measurement error.

At PW Baltenswil, the model can reproduce the measured data and the oscillations only on average, i.e. not accounting for their complete amplitude. Nonetheless, these oscillations could be partially explained by a variety of causes. At PW Baltenswil and within its catchment, or where the groundwater table is shallow and relatively thin (less
than 10 m), variable recharge conditions can lead to time-varying tracer input into the groundwater, and then to mixing of water which will be variable in time. Typically, the major phase of recharge takes place during winter, becoming smaller or even zero during the summer months.

Pumping was proven to affect the measured Krypton-85 in the samples. During pumping, a decrease in the measured concentration was observed. Older water is collected at the well in this case. Moreover, the presence of a drain to the West of PW Baltenswil may hamper the younger water components to reach the Baltenswil pumping station, especially in case of low pumping and high water table, e.g. when the drain catchment is particularly wide (Fig. 4.26).

The assumption of different spatial boundary conditions did not allow to explain the presence of older water at PW Baltenswil. On the other hand, the origin of an older water component at the well could be identified in the hilly unsaturated moraines in the North and North-East, providing the lateral inflow to the groundwater. This could be achieved by a low gas-phase tortuosity value (and, thus, low effective diffusion coefficient) for the thick unsaturated moraines, and justified by the presence of local lenses which are likely to delay/hamper the Krypton-85 diffusion in soil air.

The presence of real Krypton-85 concentration oscillations at the Baltenswil well show that box model are limited tools for tracer modeling in the Baltenswil aquifer. Yet, the proposed distributed model does also not fully describe the behavior seen in the experimental evidence. It can reproduce the data and their oscillations on average, but cannot account for their whole amplitude, i.e. for the oldest and youngest water components. Some conceptual uncertainty may still exist. Data availability at this location is anyway too low to draw hard conclusions.

5.4.2 Impact of transmissivity

The bandwidth of the concentration time-series indicates a small impact of the transmissivity realization on the transport in groundwater for all tracers. The results show that the different transmissivity realizations result in concentration variations in the subsurface comparable to the tracer concentration measurement errors. These variations concern only the absolute concentration values and not the trend of the
simulated time-series. Transmissivity is usually the most uncertain parameter in groundwater modeling, but in our case study it is not the most consequential parameter to the fate of environmental tracers. What is more important are all storage and residence time related parameters. A possible and also likely explanation is found in the relatively small residence times in the saturated zone compared to the much larger time spent by the tracer in crossing the unsaturated zone (about ten times, see Fig. 4.22 and Fig. 4.22). As for the flow model (see chapter 3), it is also possible that the choice of a Multi-Gaussian Random Function model, being not suited to account for preferential flow paths (i.e. channels with extreme values of transmissivity), hampered the reproduction of low and high velocity channels thus reducing the impact of transmissivity on tracer transport.

The origin of the older and younger water components may also be due to 3-Dimensional effects, such as layers and/or lenses with different hydraulic conductivities and porosities giving rise to preferential flow paths. The description of the transmissivity field by means of a two dimensional model can be limiting. Even in the relatively small Baltenswil aquifer, local less pervious lenses distributed within the unsaturated and saturated medium may significantly modify both the tracer input at the groundwater table as well as the tracer transport through the saturated zone. There is geological evidence of lenses in the modeled domain (e.g. clays and silt), but the data availability in this regard is too small to implement them into a 3-Dimensional model. Besides, different degrees of cemented gravel, as apparent from geological drilling profiles at some locations across the domain, will result in different porosities in the vertical dimension.

All the above-mentioned causes may have resulted in a too small spatial variability of the different transmissivity realizations and thus a smaller-than-expected impact on the tracer transport in the saturated zone. The observed small impact of the transmissivity realization on the tracer transport is likely to be shared by the above-mentioned causes.

### 5.4.3 Impact of other transport parameters

The impact of other transport relevant parameters is larger than that of transmissivity. By varying the gas-phase tortuosity in the unsaturated zone within the range of the reasonable values (e.g. \( \tau_g = 0.05 \) up to \( \tau_g = 0.35 \)), the Krypton-85 concentration time
Fig. 5.25: Uncertainty bandwidth associated with the gas-phase tortuosity ($\tau_g$) parameter (unsaturated zone) for Krypton-85 simulations at all observation locations
Chapter 5. Transport simulations

Fig. 5.26: Uncertainty bandwidth associated with the porosity (n) parameter (saturated zone) for Krypton-85 simulations at all observation locations
5.4. Discussion

Fig. 5.27: Uncertainty bandwidth associated with the porosity parameter for Helium-3 simulations at all observation locations
series can vary from 20% up to 60% according to the observation location if compared to the 'standard' simulation run (‘Default set’, $\tau_g = 0.1$, see Tab. 5.3). The different variability at the different locations is due to the spatially variable unsaturated zone thickness, the impact being larger in presence of thicker unsaturated overburden (Fig. 5.25).

In the case of porosities, a variation within the range of the reasonable values (e.g. $n = 0.1$ up to $n = 0.35$) will cause a variation in the concentration time series from 10% up to 25% for Krypton-85 (Fig. 5.25) and 20% up to 70% for Helium-3 (Fig. 5.27) if compared to the 'standard' simulation run (‘Default set’, $n = 0.25$, see Tab. 5.3). The impact of porosity at the different observation locations stems from the residence time along a travel path before reaching the observation locations.

The uncertainty associated with these two parameters is by far larger than that associated with the transmissivity parameters which ranges between 5% and 20% (see Figs. 5.11, 5.18, 5.21).

The use of additional environmental tracers in groundwater investigations is thus unescapably correlated with the introduction of new sources of parameter uncertainty. Although the use of tracers can provide access to information which cannot be derived by other means, the problem of the new uncertainty on the parameter regulating the transport of a particular tracer in the subsurface must not be underestimated.

### 5.5 Conclusions

The apparent discrepancy between Krypton-85 and Tritium/Helium-3 -derived groundwater ages (see Tab. 5.1 and Tab. 5.2) could be explained considering Krypton-85 transport in the unsaturated zone. This allowed to properly account for the time-lag in the vadose zone and thus to reproduce correctly the observed concentrations at most observation locations. The groundwater residence times derived by the Tritium/Helium-3 method are consistent. They coincide with the residence times calculated by advective transport with PMPATH (from 1 to 4 years). By accounting also for the unsaturated zone transport, the Krypton-85 derived groundwater ages become consistent with the Tritium/Helium-3 ages.
5.5. Conclusions

In general, Tritium could be rather easily modeled, providing a sound basis for Helium-3 modeling. It may be argued that today Tritium is not useful as tracer for shallow groundwater investigations due to its ‘flat’ atmospheric input. It provides instead a necessary basis and cross-check for Helium-3 modeling.

The modeling of gas-phase tracers Krypton-85 and Helium-3 appear instead more complicated. The discrepancy between simulated results and experimental evidence for the gas tracers Krypton-85 and Helium-3 show that we either have conceptual uncertainties or unresolved heterogeneity.

The Krypton-85 modeling indicates, especially at the PW Baltenswil, that both young and old water can be collected at the well in different amounts at different times. The mechanisms driving this phenomenon, and leading to the observed experimental fluctuations of the tracer concentration, have been identified and are mainly related to the uncertainty of the spatially distributed parameters (recharge to groundwater, un-localized preferential flow paths and spatial model boundaries) and of the external stresses (e.g. pumping action). Unresolved spatial heterogeneity of soil and transport parameters (e.g transmissivity, recharge to groundwater, porosity, tracer atmospheric input function, gas-phase tortuosity and water content) as well as conceptual uncertainty (e.g. model boundaries, Random Function Model choice for transmissivity and three dimensional effects) will strongly affect the tracer transport in the groundwater and thus the subsurface tracer concentrations.

Krypton-85 modeling will prove useful in aquifers where the groundwater residence time is much larger than the residence time in the unsaturated zone. Yet, if the opposite is the case, as in the Baltenswil case study, Krypton-85 can provide valuable information on the water originated in zones with thick unsaturated overburden. As the unsaturated zone gains in importance, environmental gaseous tracer modeling need the estimation of additional transport parameters. These are usually not available (e.g. local measurements of gas-phase tortuosity, saturation conditions, etc.). In particular, the spatial variability of the gas-phase effective diffusion coefficient will be fundamental to the fate of the gaseous tracer movement in the vadose zone. Box models are thus not suited for case studies like Baltenswil. Distributed models only can instead lead to successful modeling. In other words, gas tracer modeling in aquifers with large and spatially variable unsaturated zones thickness will not necessarily provide additional (better) information on the system under study, unless detailed knowledge of the
unsaturated zone is available.

The spatial and temporal heterogeneity of the effective gas-phase diffusion coefficient leads to the largest variations in the simulated concentration time series. The lack of detailed knowledge (i.e. conditioning information) on the gas-phase tortuosity in the unsaturated zone impairs any meaningful stochastic modeling of this very consequential parameter. Where these measurements may become available, they may allow to better determine the tracer input function at the groundwater table.

In the case of Helium-3, which allows to focus on the saturated zone transport only, the modeling shows instead that the simulated values systematically overestimate the measured concentrations when using the transport parameter set which well calibrates both Krypton-85 and Tritium models. This is more likely due to conceptual uncertainty rather than unresolved heterogeneity of the transport parameters. The fact that Helium-3 data could not be honored by making use of the same soil and transport parameter set used for Krypton-85 cannot be explained within our conceptual model. A possible solution is to account for Helium-3 degassing from the groundwater table. This model enhancement will be discussed in chapter 6.
Chapter 6

Helium loss and differential diffusion

Tritium and Helium-3 are commonly regarded as ideal tracers in groundwater modeling applications, since they move at the same velocity of the water containing them and are geo-chemically inert. In absence of dispersion, their sum is a conservative quantity, meaning that no sources or sinks are present in the subsurface after Tritium has entered the saturated zone. In the above mentioned conditions (piston-flow conditions), the true groundwater age is equal to the apparent age, i.e. the tracer-derived age (see equation 4.2). The true groundwater age is instead determined as the time elapsed since the water particle is isolated from the atmosphere until it is collected at some observation location. The presence of Helium-3 sources other than Tritium decay, Helium-3 sinks or mixing of waters with different Tritium/Helium-3 concentrations may lead to significant discrepancies between true and apparent groundwater ages.

Two processes contribute to hydro-dynamic dispersion in groundwater: mechanical mixing (macro-dispersion) caused by spatial variability of groundwater flow velocities and molecular diffusion (Solomon and Sudicky, 1991; Solomon et al., 1993b). Molecular diffusion may become a dominant process in zones with low groundwater flow velocities. Due to the different molecular diffusion coefficient and solubilities in water of Krypton-85 and Helium-3, the role of molecular diffusion deserves particular attention in heterogeneous aquifers and may provide an explanation to the basic discrepancy between Krypton-85 and Tritium/Helium-3 transport simulation results.

We observed that Krypton-85 and Tritium concentration data could be reasonably well matched with a constant porosity value \( n = 0.25 \), while such a value resulted instead in a significant overestimation of the simulated vs. measured Helium-3 concentrations at all observation locations (see chapter 5). This basic contradiction may be explained
if some un-accounted for Helium-3 loss mechanisms ruled by molecular diffusion are considered in the transport modeling.

In the present chapter, we discuss two possible diffusion-dominated mechanisms that will work as Helium-3 store/sink within the aquifer system. Because of its low water-gas partitioning coefficient, Helium-3 is likely to back-diffuse from the groundwater table into the unsaturated zone and then migrate upwards through soil air into the atmosphere due to its large diffusion coefficient in the air phase. Helium-3 back-diffusion through the unsaturated zone into the atmosphere (Helium-loss) is presented in section 6.1. Another mechanism which is likely to affect the Helium-3 concentration in the groundwater is Helium-3 preferential diffusion into little permeable lenses relative to Tritium and Krypton-85. Since the molecular diffusion coefficient of Helium-3 in the water phase is four times larger than that of Tritium, it is likely that Helium-3 is stored to a larger extent than tritium in little pervious lenses. This phenomenon is called “differential diffusion” and is discussed in section 6.2.

6.1 Helium-3 loss

Helium-3 produced in the saturated zone by Tritium decay can be assumed to be confined in case of relatively large vertical groundwater flow velocities in the vicinity of the groundwater table, e.g. in case of high recharge conditions. When recharge becomes either small or zero, back-diffusion of Helium-3 to the atmosphere across the water table may take place in significant amounts. This is more likely to happen where the vadose zone overlying the groundwater is thin and the (atmospheric) zero-concentration boundary condition can be assumed at the groundwater table depth. Under the above-mentioned conditions, due to the large diffusion coefficient of Helium-3 in free air (Tab. 6.1), the usual assumption of Helium-3 confinement in the groundwater may not hold.

Due to Helium-3 upward loss, the sum of Tritium and Helium-3 may not behave as a conservative tracer in all conditions. Two studies have pointed out that although a 15% Helium-3 upward loss is good enough to consider Tritium and Helium-3 as conservative tracers, larger losses may take place in a shallow groundwater system, thus affecting the reliability of Tritium/Helium-3 apparent ages. It was also shown that
6.1. Helium-3 loss

<table>
<thead>
<tr>
<th></th>
<th>$^3$H</th>
<th>$^3$He</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_i^0$</td>
<td>0.0495 m$^2$·yr$^{-1}$</td>
<td>0.207 m$^2$·yr$^{-1}$</td>
</tr>
<tr>
<td>$D_g^0$</td>
<td>-</td>
<td>2179 m$^2$·yr$^{-1}$</td>
</tr>
</tbody>
</table>

Table 6.1: Liquid- and gas-phase diffusion coefficient in free water/air for Tritium and Helium-3

Helium-3 confinement increases with increasing recharge and decreasing dispersivity in the saturated zone (Schlosser et al., 1988, 1989).

In the Baltenswil aquifer modeled domain, 65% of the cells have a saturated zone thickness smaller than 25 meters (see chapter 3, Fig. 5.12). The Helium-3 concentrations in the vadose zone were shown to be negligible in the first 20-25 meters, becoming relevant only below 30 m. The calculated recharge in the last 30 years shows a seasonal trend, with low recharge conditions during most summers (see chapter 3, Fig. 3.8). Under such conditions Helium-3 loss is likely to be enhanced. We will investigate the potential for Helium-3 back diffusion into soil-air by means of two different conceptual models:

1. Solution of the advection-diffusion equation in a unsaturated/saturated one dimensional soil column
2. Transport modeling of the aquifer system with a two layer structure with one layer working as constant zero-concentration boundary, mimicking the atmospheric boundary condition

6.1.1 Solution to the advection-diffusion equation in a one dimensional soil column

The Helium-3 confinement, i.e. the extent to which Helium-3 produced by Tritium decay is retained in the aquifer and thus prevented to escape across the water table, is a simple advection-diffusion problem. We want to estimate the Helium-3 diffusive loss from the groundwater to the atmosphere in conditions similar to what could be observed in the Baltenswil domain.

The conceptual model is set up as follows. A 1-Dimensional soil-column, representing a vertical section of the subsurface, is split into two equal parts: one unsaturated and
one saturated. Helium-3 in the saturated part is assumed at constant concentration, as indicated by the simulated Helium-3 concentrations in the Baltenswil domain (simulated Helium-3 concentrations are almost constant during the last five years, see chapter 5, Fig. 5.21). We assume that the lowest cells of the saturated part of the column are maintained at constant Helium-3 concentration due to the constant Helium-3 input from Tritium decay, ideally coming from the saturated part of neighboring 1-D soil columns via groundwater flow. We also assume that only the saturated boundary cell can exchange Helium-3 via molecular diffusion with the overlying unsaturated cell which then escapes to the atmosphere (set as constant zero-concentration boundary).

We investigate the potential Helium-3 loss by the numerical solution of the advection-diffusion equation (4.3) in a 1-Dimensional soil column divided in two parts of equal thickness, one unsaturated and one saturated. The following assumptions are made:

- Homogeneous porous medium with physical parameters

<table>
<thead>
<tr>
<th></th>
<th>uns. zone</th>
<th>sat. zone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(upper part)</td>
<td>(lower part)</td>
</tr>
<tr>
<td>$\epsilon_a$</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>$\theta$</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>$\tau_g$</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>$\tau_l$</td>
<td>0.25</td>
<td>1</td>
</tr>
<tr>
<td>$n$</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>$D^*$</td>
<td>$D^0_g \tau_g \epsilon_a$</td>
<td>$D^0_l \tau_l \theta$</td>
</tr>
</tbody>
</table>

where $D^*$ is the effective molecular diffusion coefficient

- **Solubility equilibrium** at the unsaturated/saturated zone boundary: water/air partitioning coefficient is $K_{3He}w = 0.0093$ (Weiss, 1971).

- **Negligible sorption**: solid/water partitioning coefficient: $K_d = 0$

- Helium-3 transport is **diffusion-dominated** in both parts of the soil column: advection in the liquid- and gas-phase are neglected: $q_l = q_g = 0$

Equation (4.3) thus becomes

$$\frac{\partial \theta c_{3He}}{\partial t} = D^* \frac{\partial^2 c_{3He}}{\partial z^2}$$
The 1-Dimensional soil column is divided in $N$ cells with spatial discretization $\Delta z = 1$ m (Fig. 6.1), half of them unsaturated and half saturated (see Tab. 6.1). The first cell ($i = 1$) is set as upper boundary condition equal to the Helium-3 constant atmospheric concentration. The cells in the saturated lower part are all set at constant concentration at all simulation times, except the cell at the unsaturated/saturated boundary. The cells above ($i = N/2 - 1$) and below ($i = N/2$) the unsaturated/saturated zone boundary are used to calculate the Helium-3 exchange. Helium-3 can be exchanged from the saturated cell at constant concentration ($i = N/2 + 1$) via the effective molecular diffusion coefficient in water $D_l$ to the cell $i = N/2$, and from this cell to the lowest cell of the unsaturated zone $i = N/2 - 1$ via the effective molecular diffusion coefficient in air $D_g$. Formally, the boundary conditions are

- Upper boundary condition: soil surface

$$c_{3He}(i, t)|_{i=1} = 0 \quad \forall t$$
Chapter 6. Helium loss and differential diffusion

- Lower boundary condition: constant concentration in the groundwater

\[ c_{3He}(i, t)_{|i=N/2+1...N} = 1 \quad \forall t \]

- Initial condition in the soil column at time \( t = 0 \)

\[ c_{3He}(i, t)_{|t=0} = 0 \quad \forall i \]

The simulation time is one year, divided in 1200 time-steps. The results are shown in Figure 6.2. This simple model shows that, starting from a constant concentration arbitrarily assumed equal to 1 TU in the groundwater, the diffusive loss from the groundwater can be 20% to 45% in case of very shallow groundwater (up to 4 m) and about 10% for deeper ones (up to 20 m depth). Qualitatively speaking, since the unsaturated zone thickness across the modeled domain is 13% below 10 m and 23% between 10 and 20 m thick, this simple calculation shows that a significant reduction of Helium-3 concentrations in the groundwater can be achieved by considering Helium-3 loss.

However, the discrepancies between observed and simulated Helium-3 concentrations (see chapter 5, Fig. 5.21) are of the order of 50% to 70% for PW Baltenswil, PW Buel, PW Girhalden I and II, Kb 94-1, Kb 94-2, Kb 14 and of 30% to 40% for PW Bruttisellen,

![Fig. 6.2: Helium-3 loss at different groundwater table depths](image-url)
6.1. Helium-3 loss

Kb 85-1, Kb 84-1, Kb 84-3 and Kb 84-4. The rates at which Helium-3 back-diffusion to the atmosphere will take place will be depending on the unsaturated thickness overlying the streamlines intercepted at these locations. Helium-3 loss should then be calculated following each streamline to obtain a better quantitative estimation of its effects on the Helium-3 concentrations in the groundwater. This can be done by a simple groundwater flow and transport model refinement.

6.1.2 Groundwater modeling

The Helium-3 loss can be also directly modeled in the tracer transport for the Baltenswil aquifer by superimposing to the two-dimensional one-layer model a second layer (Fig. 6.3).

![Fig. 6.3: Vertical profile along the North-South axis for the refined two-layers model. The thin lower layer is set at constant zero-concentration and will work as permanent Helium-3 sink.](image)

The lower layer is set at constant zero Helium-3 concentration and will act as boundary layer representing the constant Helium-3 concentration in the atmosphere. The layer thickness is spatially variable and proportional to the unsaturated zone thickness. In this way, the calculated Helium-3 effective diffusion coefficient is larger for shallow groundwater tables and smaller for deeper ones (see section 6.2.2). This layer is
endowed with very small transmissivity ($T = 10^{-10} \text{ m}^2/\text{s}$) and storativity ($S = 10^{-4}$) to avoid modifying the groundwater flow conditions. The porosity value for the second layer is the same ($n = 0.25$) as for the upper layer.

The simulation results are shown in Fig. 6.4. The simulated concentration time-series show relevant reduction at all observation locations. In particular, at locations within the PW Baltenswil catchment (PW Baltenswil, Kb 94-1, Kb 94-2 and Kb 14) a strong reduction is obtained (up to 70%), allowing a satisfactory match between observed and simulated concentrations. At locations PW Girhalden-I and -II the reduction is more limited (about 20%), but the simulated Helium-3 concentrations are close enough to the observed data.

The observation boreholes Kb 85-1, Kb 84-3 and Kb 84-4 - located in the central part of the modeled domain - in many transmissivity scenarios belong to the catchment of PW Buel (see chapter 4, Fig. 4.26 and 4.27). At these locations, a significant reduction is obtained (up to 40%) and a better, although not yet completely satisfactory match between observed and simulated concentrations is achieved.

Only at three (out of twelve) observation locations the reduction in Helium-3 concentrations due to degassing is not sufficient to match the observed data. At PW Bruttisellen and Kb 84-1 within its catchment the reduction is limited to about 10% and the resulting simulated concentrations are still far from honoring the measured ones. The discrepancy between simulated and measured Helium-3 data may at the latter locations instead be explained by locally smaller porosity values or different spatial model boundaries, as argued for the Krypton-85 transport simulations in chapter 5. Results for the borehole Kb 84-3 also remain unclear. The reduction due to Helium-3 loss is relevant (about 30%), but still far from matching the observed data. Either a faster dynamics (e.g. locally smaller porosity value) or increased Helium-3 loss rate are needed at this location to match the data. On the contrary, Krypton-85 transport simulations showed that at this locations a slower dynamics (e.g. locally higher porosity value) is needed to match the Krypton-85 data. Data interpretation remains weak at this observation location. The Krypton-85 and Helium-3 simulation results may not necessarily be in contradiction, since slower Krypton-85 dynamics can be obtained also by local reduction of tortuosity value in the unsaturated zone.

We can conclude that the implementation of the modeling of Helium-3 loss into the
6.1. Helium-3 loss

Fig. 6.4: Helium-3 concentration-time series for the original one-layer model and the modified two-layer model including Helium-3 loss.
original conceptual model proves to be a significant improvement in the interpretation of Helium-3 data in the aim to integrate the information coming from Tritium/Helium-3 and Krypton-85 tracers.

## 6.2 Differential Diffusion

In a recent study by Labolle et al. (2006) it is argued that differential diffusion rates of Tritium and Helium-3 can, under common hydro-geological conditions, significantly alter the apparent $^3\text{H}/^3\text{He}$ groundwater ages. Where groundwater velocities become small, e.g. in low permeability lenses, the effect of molecular diffusion may override that of mechanical dispersion (Solomon et al., 1993b; Solomon and Sudicky, 1991). In addition, the large molecular diffusion coefficient in water of Helium-3 (about four times larger than Tritium, see Tab. 6.1) may lead to enhanced migration of Helium-3 relative to Tritium in low permeability lenses. This effect (called *differential diffusion* or *diffusive fractionation*) was shown to have considerable effects on Helium-3 transport in alluvial, heterogeneous aquifers leading to deceptively young/old groundwater ages for pre-bomb and post bomb-peak respectively (Labolle and Fogg, 2001; Labolle et al., 2006).

Labolle et al. (2006) found out that the potential for diffusive fractionation will strongly depend on the subsurface heterogeneity (larger transmissivity contrasts resulting in a larger effect), the flow field and the tritium input source. They studied Tritium and Helium-3 transport during the time interval between 1950, through the early-sixties bomb fallout and present-day in both artificial and real case studies. They found out that preferential migration of Helium-3 relative to Tritium in adjacent aquitards will lead to an overestimation of Tritium/Helium-3 groundwater apparent ages for post 1950, pre-bomb-peak waters (increasing Tritium input function) and to an underestimation of groundwater ages for post-bomb-peak waters (subsequent to the Tritium bomb-peak leading edge). Another issue identified in the study refers to the possibility that the long-term exponentially decaying Tritium atmospheric input function (post 1963) combined with transverse dispersion establishes near equilibrium conditions between aquifers and adjacent low permeability lenses (or aquitards) that would curtail significant diffusive fractionation. In this latter case, little effect of diffusive fractionation is found for young (post bomb-peak) waters.
The dispersion tensor in the transport equation (see chapter 1, Eq. (1.2)) can be written in its components (assuming that the flow direction is aligned with the $x$-axis)

$$
D_{xx} = \alpha_L |v| + D_m \\
D_{yy} = \alpha_{TH} |v| + D_m \\
D_{zz} = \alpha_{TV} |v| + D_m
$$

where $\alpha_L$, $\alpha_{TH}$ and $\alpha_{TV}$ are the longitudinal, transverse horizontal and transverse vertical dispersivities [m], $|v|$ is the pore velocity [m/s] and $D_m$ is the effective molecular diffusion coefficient [m$^2$/s]. The dispersion coefficient is mechanical dispersion dominated in case of high velocities, but will become diffusion dominated as the velocities decrease such that the terms $\alpha |v|$ and $D_m$ become comparable.

Differential diffusion of Helium-3 can thus be expected for heterogeneous transmissivity fields, with a special relevance in zones with very low groundwater velocities. In the vicinity of small lenses with significantly lower than average transmissivity (e.g. clays), Helium-3 diffusion may be enhanced.

### 6.2.1 Modeling

In the Baltenswil aquifer, geological evidence from borehole drillings shows the presence of smaller, less pervious clayey, silty-sandy lenses distributed in the vertical direction, with longitudinal sizes in the range of a few meters. These lenses with smaller hydraulic conductivity may work as small scale aquitards and thus as store-buffer zone for the immobile groundwater that will exchange Helium-3 by molecular diffusion with the mobile groundwater in the surroundings.

It becomes thus essential to model the groundwater in both its mobile and immobile phases. This is usually done by means of Dual Porosity models. Here, we do not tackle a 3-dimensional modeling, but look instead for a 2-dimensional conceptualization of the problem. We model the (real) 3-dimensional distribution of these lenses in the unsaturated medium by assuming that they can be described by a single layer set below the original layer in which the groundwater flow is simulated. This can be done by giving to the second layer the specific equivalent properties (Fig. 6.5).
The second layer is aimed at the modeling of the immobile phase component of the groundwater, entraped in clayey aquitards. We thus assign very low values to its transmissivity and storativity ($T = 10^{-10} \text{ m}^2/\text{s}$ and $S = 10^{-10}$). In this way, the immobile phase can be modeled without disturbing the groundwater flow. We also set the vertical hydraulic conductivity between the two layers to a very small value ($K_v = 10^{-8}\text{ m/s}$) to ensure two distinct water components in the saturated zone (mobile and immobile phase).

Supported by geological evidence, the thickness of the lenses is assumed to be $1/10$ of the saturated thickness: $\Delta z_2 = \Delta z_1/10$. Porosity is $n = 0.25$ for both layers. The longitudinal dispersivity is $\alpha_L = 25 \text{ m}$, while transverse vertical and horizontal dispersivities are $\alpha_{TH} = \alpha_{TV} = 0$. Preferential diffusion of Helium-3 relative to Tritium may take place at the layers' boundary.

With regard to the tracer initial conditions on concentrations in the lower layer, we assume that Helium-3 only could significantly diffuse into the less permeable lenses from the beginning of tritium emissions to the atmosphere prior to the beginning of the emission process.

---

**Fig. 6.5**: Vertical sections of the modeled domain along the $z$-axis. The less pervious lenses, containing water in the immobile phase, are vertically distributed across the saturated medium and exchange Helium-3 by molecular diffusion with the mobile phase in the groundwater (left). On the right, the 2D conceptualization of the 3D problem is shown: a layer with extremely small transmissivity and storativity but usual porosity is put below the original one-layer model. Diffusive exchange between the two phases is modeled at this boundary. Black dots indicate the central nodes of the cells. $A_{im}$ and $V_{im}$ indicate the upper surface and the volume respectively of the cell containing the immobile phase.
6.2. Differential Diffusion

the simulation time (1991). Due to the small diffusion coefficient of tritium in water, we assume that the tritium concentration in the lower layer can be neglected and set its initial concentration to zero. The Helium-3 initial concentration, due to the high Helium-3 groundwater concentrations in the past-1991, is instead slightly larger than in the upper layer (e.g. the groundwater mobile phase).

6.2.2 Effective molecular diffusion coefficient

Molecular diffusion of Helium-3 between the mobile and the immobile phase will depend on the concentration gradient between two adjacent cells in the first and second layer expressed in the diffusive term of the transport equation

\[
D_m \frac{\Delta c}{\Delta z}
\]

where \( D_m \) is the molecular diffusion coefficient and \( \Delta z \) is the separation distance between the central nodes of the cells. In a full 3-dimensional model, Helium-3 exchange will take place on a scale equal to half the vertical size of the lenses \( \Delta z = \frac{\Delta z_2}{2} \) (see Fig. 6.5, left), where \( \Delta z_2 \) is the vertical thickness of the clay lenses. In the 2-dimensional conceptual model, the gradient will instead be calculated over a larger distance, e.g. over the separation distance between the two central nodes of adjacent cells in the first and second layer \( \Delta z = \frac{\Delta z_1}{2} + \frac{\Delta z_2}{2} \) (Fig. 6.5, right). The calculated concentration gradient between the two layers will thus be underestimated by the 2-dimensional model.

A scaling factor must be introduced in the calculation of the effective molecular diffusion coefficient to calculate correct diffusive fluxes also in the 2-dimensional conceptualization:

\[
D_{eff} = K \cdot D_m
\]

To calculate the factor \( K \), we first consider the concentration variation within the immobile phase \( \Delta c_{im} \) in a time \( \Delta t \) due to exchange between the mobile and immobile groundwater in the (real) 3-dimensional case (Fig. 6.5, left)
Chapter 6. Helium loss and differential diffusion

\[
\frac{\Delta c_{im}}{\Delta t} = \frac{\alpha}{n_{im}} (c_m - c_{im}) \tag{6.1}
\]

where \( \alpha = D_m/A_z \), \( D_m \) being the diffusion coefficient of Helium-3 and \( A_z \) the vertical section over which diffusion takes place, \( n_{im} \) is the porosity of the clay lense, \( c_m \) and \( c_{im} \) are the Helium-3 concentrations in the mobile and immobile phase. In a 3-dimensional set-up, the diffusive exchange takes place on a scale \( \Delta z = \Delta z_2/2 \). The area \( A_z \) is thus equal to \( A_z = (\Delta z_2/2)^2 \).

On the other hand, we consider the mass conservation between the upper and lower cells in the 2-dimensional set-up (Fig. 6.5, right) during a time step \( \Delta t \)

\[
j_{\text{exch}} \cdot A_{im} \cdot n_{im} \cdot \Delta t = \Delta c_{im} \cdot V_{im} \cdot n_{im} \tag{6.2}
\]

where

\[
j_{\text{exch}} = \frac{c_m - c_{im}}{\Delta z_1^2 + \Delta z_2^2} D_{eff}
\]

is the exchange flux between the two adjacent cells (mobile and immobile phases) in the upper and lower layers, \( A_{im} \) and \( V_{im} \) are the area of the upper surface and the volume of the lower cell containing the immobile phase respectively (see Fig. 6.5, right) and \( D_{eff} \) is the (scaled) effective diffusion coefficient for the 2-dimensional model.

By comparison of equations (6.1) and (6.2) two different expressions for the concentration variation \( \Delta c_{im} \) referred to a time interval \( \Delta t \) can be derived for the 3-dimensional and 2-dimensional models respectively

\[
\Delta c_{im} = \frac{D_m}{(\Delta z_2^2/2) n_{im}} \cdot (c_m - c_{im}) \cdot \Delta t
\]

\[
\Delta c_{im} = \frac{D_{eff}}{\Delta z_1^2 + \Delta z_2^2} \cdot \frac{A_{im}}{V_{im} n_{im}} \cdot (c_m - c_{im}) \cdot \Delta t
\]

Given that \( V_{im}/A_{im} = \Delta z_2 \), by equating the two expressions the effective diffusion coefficient is obtained
6.2. Differential Diffusion

\[ D_{\text{eff}} = D_m \frac{2(\Delta z_1 + \Delta z_2)}{\Delta z_2} \]

and, given that \( \Delta z_2 = \Delta z_1 / 10 \), the scaling factor can be calculated: \( K = 22 \).

In addition, while in the (real) 3-dimensional problem the clay lenses can exchange Helium-3 with the mobile parte through both their upper and lower surfaces (see Fig. 6.5, left), the 2-dimensional conceptualization allows the exchange between the mobile and immobile phases only in one direction (e.g. upwards \( z \)-axis, see Fig. 6.5, right). This results in an additional factor of two to be included in the effective molecular diffusion coefficient calculation. In conclusion, the ‘effective’ diffusion coefficient to be used in the 2-dimensional model is thus

\[ D_{\text{eff}} = 44 \, D_m \]

6.2.3 Results

Transport simulations are performed with the module MT3D99 (Zheng and Wang, 1999a) in a modified version that allows the modeling of Tritium and Helium-3 transport with different molecular diffusion coefficients (personal courtesy of Prof. Chunmiao Zheng, University of Alabama). Five different transport simulation runs are performed for the layered model set-up to estimate the potential of tracer diffusion into the little pervious lower layer, where the correction factor \( K \) is included in the effective molecular diffusion coefficient for both Tritium and Helium-3:

1. Simulation with all transverse dispersion and diffusion parameters set to zero. This run will be taken as standard for comparison, since it is equivalent to the original model with only one layer

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3. Simulation with pure molecular diffusion and different molecular diffusion coefficients for Tritium and Helium-3

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4. Simulation with pure molecular diffusion, different molecular diffusion coefficients for Tritium and Helium-3 and porosity of the second lower layer $n = 0.05$

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5. Simulation with pure molecular diffusion, different molecular diffusion coefficients for Tritium and Helium-3 and porosity of the second lower layer $n = 0.4$

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Transport simulation results for Tritium are shown in Fig. 6.6. Tritium is not affected by any of the four different parameterizations of the transport simulation. Molecular diffusion in the lower layer does not sensibly affect the Tritium concentration in the groundwater. The match between observed and simulated Tritium concentrations remains undisturbed.

Transport simulation results for Helium-3 are shown in Fig. 6.7. In the case Helium-3 only (simulation #2) is allowed to diffuse in the lower layer (immobile phase), due to
Fig. 6.6: Tritium concentration-time series for the original one-layer model and the modified two-layer model including differential diffusion.
Fig. 6.7: Helium-3 concentration-time series for the original one-layer model and the modified two-layer model including differential diffusion.
6.2. Differential Diffusion

its large production from the 1963 bomb-peak, Helium-3 concentrations in the lower layer are always (i.e. at all simulation time-steps) slightly larger than in the upper layer. As a consequence, a very small Helium-3 concentration gradient is established from the lower to the upper layer. The Helium-3 release from the lower to the upper layer is negligible and makes the simulated concentrations for the layered model equal to the original one-layer model (Fig. 6.7).

No effect of preferential Helium-3 diffusion relative to Tritium was found. Simulations #2 and #3 do not show any significant difference (Fig. 6.7). As confirmed by the study of Labolle and Fogg (2001), large effects can be expected in the proximity of large peaks of the input function, such as the 1963 Tritium spike. Due to the decreasing trend of the tritium input function at the groundwater table and the consequent nearly steady-state conditions for concentration established in the groundwater for both tritium and Helium-3, the resulting concentration gradient between the two phases is very small. For the actual values of the Tritium input function, and consequently of the production rate of Helium-3 in the saturated zone, no evidence of differential diffusion effects can be found in our case study.

The sandy/silty-clay lenses represented by the second layer are also likely to have a different porosity value than the rest of the aquifer matrix where mobile groundwater flows. This scenario is investigated in simulations #4 and #5, where the porosity value is $n = 0.05$ and $n = 0.4$ respectively. Simulated Helium-3 concentrations do not change with respect to the simulation runs #2 and #3 and are not reported here.

Different transmissivity realizations show different patterns of spatial variability of the transmissivity parameter which can in turn result in different migration of the tracers between the mobile and the immobile groundwater. The impact of the transmissivity realization on the simulated concentration time series is also assessed by running simulation #3 for four different realizations randomly chosen from the ensemble (see chapter 3). The impact of the different realizations on transport simulation results is negligible, smaller than the measurement errors on Helium-3 concentrations (Fig. 6.8).
Chapter 6. Helium loss and differential diffusion

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Fig. 6.8: Sensitivity to Transmissivity realizations of Helium-3 concentration-time series for the two-layer model including differential diffusion. Different T-patterns show negligible impact on the potential differential diffusion effect.
Krypton-85

The differential diffusion was also explored for completeness in the case of Krypton-85. Due to the steadily increasing trend in time of Krypton-85 concentrations in the groundwater, its initial concentration in the lower layer (immobile phase) at the beginning of the simulation time is non-negligible as for the case of Helium-3. This contributed to the establishment of a small concentration gradient between the two phases and thus to a small Krypton-85 exchange between the two, also due to the small diffusion coefficient of Krypton-85 in water (comparable to that of tritium). Because of the above-mentioned reasons, Krypton-85 simulations did not show any relevant differential diffusion effect on the simulated concentration time-series. The results are therefore here omitted.

6.3 Discussion and comments

With the simple introduction in the flow and transport models of a second layer below the original one-layer, two interesting phenomena could be analyzed for the Baltenswil case-study.

As the added second layer is set to constant zero Helium-3 concentration, it acts as a constant concentration boundary representing the atmosphere and allows to study the Helium-3 back-diffusion into the atmosphere from the groundwater table through the unsaturated zone. Because of its low solubility in water (small water/air partitioning coefficient), Helium-3 is prone to escape the water phase and join the air phase (soil air) above the groundwater table. This effect will be enhanced in case of low recharge conditions and where the groundwater table is closer to the soil surface (shallow groundwater). The hypothesis of Helium-3 loss in the Baltenswil aquifer proved decisive in curtailing the Helium-3 concentration in the groundwater of 20% up to 70%, depending on the observation location. While Krypton-85 is a monotonically increasing tracer and thus gains from the input at the groundwater table, Helium-3 is instead lost by gassing-out due to its higher diffusion coefficient and lower solubility in water. This mechanism can be regarded as the most effective candidate in explaining the contradiction that the Tritium/Helium-3 ages obtained with a box model at the Baltenswil well are smaller than the Krypton-85 derived ages.

Alternatively, the endowment of the added second layer with extremely small transmis-
sivity and storativity but usual porosity makes it a buffer zone where Helium-3 only can be exchanged with the overlying mobile groundwater by pure molecular diffusion. Yet, the large Helium-3 concentrations from the past (pre-1991) could diffuse in the lower layer (e.g. the immobile phase). The Helium-3 stored in the lower layer from the past years (from the 1963 bomb-peak) is thus slightly larger than Helium-3 in the upper layer (e.g. mobile phase). The concentrations in the two layers differ too little to establish a significant gradient between the two. Due to the nearly steady-state conditions of the tritium input function at the groundwater table and consequently of the groundwater concentrations of both tritium and Helium-3 in the last five and more years, no effect of differential diffusion could be observed in the simulation runs.

Within the latter framework, the second layer only provides a buffer zone for the tracer exchange between the groundwater mobile and immobile phase. Although the transmissivity contrast reproduced by the two-layer set-up would in principle be enough to simulate low velocity conditions and thus enhanced diffusive fractionation, the concentration gradient between the two layers is too small to trigger any effective different diffusive behavior of Helium-3 relative to Tritium in the actual conditions.

In conclusion, the inclusion of differential diffusion into the conceptual model is not of help in achieving the goal of reducing the simulated Helium-3 concentrations, towards a better match with the measured ones. This conclusion is in agreement with the work of Labolle and Fogg (2001), who found out that long after the 1963 Tritium fallout the effects of diffusive fractionation (e.g. with regard to young groundwater) may often be negligible.
Chapter 7

Conclusions and recommendations for further studies

The aim of the present thesis is to establish to which extent environmental tracer data can be used to improve groundwater model accuracy and reliability. Three different environmental tracers (Krypton-85, Tritium and its decay product Helium-3) were used for groundwater investigations in an aquifer in Northern Switzerland. The use of different tracers allowed a thorough investigation of the subsurface through the different transport mechanisms affecting gas-phase (i.e. Krypton-85 and Helium-3) and water-bound (Tritium) tracers and their different atmospheric input functions (monotonically increasing for Krypton-85 and monotonically decreasing for Tritium, zero for Helium-3) as well as their different behavior in the unsaturated and saturated zones (Krypton-85 and Tritium joining the saturated zone after their passage through the unsaturated one, Helium-3 being instead produced directly in the groundwater).

7.1 Stochastic inverse modeling

The major task was to determine the role of the transmissivity field in modifying the environmental tracer concentration spatial and temporal distribution in the subsurface across the domain. A stochastic groundwater flow model was regarded as a necessary basis for this purpose to account for a realistic spatial variability of the transmissivity parameter. The heterogeneity of the transmissivity field and its spatial variability at the field scale were reproduced by means of Stochastic Inverse Modeling within the framework of the Sequential Self-Calibrated Method (Gomez-Hernandez et al., 1997;
Capilla et al., 1997) as implemented in the code INVERTO (Hendricks-Franssen, 2001). For the specific case study considered in the present thesis, groundwater discharge by drains had to be implemented in the original code.

In the proposed stochastic approach, a large ensemble of realistic spatial realizations of the transmissivity parameter that do not contradict the observed transmissivity and head data was generated. Each realization was regarded as a possible representation of the real heterogeneous transmissivity field displaying the same spatial variability as observed by field measurements. Particular care was devoted to the correct reproduction of measured transient heads.

While the conditioning to the 17 transmissivity measurements resulted in a distinct spatial variability of the transmissivity field, the appearance of global transmissivity patterns (i.e., zones with similar transmissivity values) could instead be achieved only by conditioning to hydraulic head data at different locations across the domain. A total of 960 available transient head data were used for conditioning: 120 head measurements at each of the 4 borehole locations and 96 at each of the 5 pumping stations. The reproduction of the observed water table variations could be achieved to a satisfactory extent, although results show that fast water table fluctuations could not be fully honored by the simulated head time series. This fact may reflect additional uncertainties in the conceptual flow model, such as for example too little resolution (e.g. monthly) of the recharge events.

A careful determination of the water balance proved a key issue towards the full reproduction - i.e. in amplitude and phase - of the observed groundwater table fluctuations. In particular, time-varying recharge to groundwater - assessed by means of a physically-based independent model (Soil-Water Budget method (Blau et al., 1983)) - and the aquifer discharge rate - modeled by drain locations representing natural springs at the aquifer boundaries - were manually calibrated by relying on the available little information and poor knowledge of some hydrologic parameters (Evapotranspiration and drain discharge rate above all). Recharge to groundwater, discharge via drains and storage capacity of the aquifer are simultaneously subject to the constraints imposed by transient head data. The uncertainties in the water balance parameters are most probably the reason for partial discrepancies in the achieved simulated vs. observed heads match.
7.2. Unsaturated zone modeling

The stochastic modeling of transmissivity conditioned to transient piezometric heads showed a clear tendency of the transmissivity realizations to similar transmissivity patterns. In particular, the conditioned realizations show the presence of a zone with low transmissivity in the middle of the modeled area, acting as a 'dam' between the Northern and the Southern halves of the domain. The worth of a large number of transient head data was also confirmed, although the proposed stochastic flow model could not fully describe the observed water table variations. Recharge to groundwater reconstruction looks reasonable in that it correlates - with a small delay - extremely well with the observed piezometric fluctuations in time. The model discrepancies indicate that there is still some uncertainty in the conceptual model regarding most probably the recharge input to groundwater and the discharge via drains.

The conditioning to transient head data allowed to obtain a large number of plausible transmissivity realizations on the one hand, and to exclude transmissivity realizations not honoring the data on the other. In other words, conditioning to data allowed to sieve from the larger ensemble of non-conditional realizations the smaller set of conditional realizations. The analysis of ensemble results allowed to set the problem in a probabilistic framework, thus allowing to quantify the uncertainties of the model results. Conditioning and calibrating the $T$-realizations to the transient hydraulic heads allowed to reduce the uncertainty on the simulated head time series by a significant reduction of the penalty function $J$.

7.2 Unsaturated zone modeling

The importance of the impact of thick unsaturated zones on the gaseous tracers' input function at the groundwater table is considered and accounted for before modeling the tracer transport in the saturated zone, as suggested by Cook and Solomon (1995). Especially when investigating aquifers with spatially variable depth-to-groundwater, the input function in the atmosphere cannot be considered as realistic input for tracer transport modeling in the groundwater. The different transport mechanisms driving the three tracers in the vadose zone allowed to investigate the subsurface dynamics from different points of view. Krypton-85 and Helium-3 are gas tracers and their transport in the vadose zone takes place most importantly in the soil air and is thus diffusion-dominated. Tritium is instead physically bound to the water molecule and its transport is thus advection-dominated.
For thick unsaturated zones, the atmospheric input function must be corrected by a diffusion model for Krypton-85 and Helium-3 and by an advective model for tritium. This consideration was accounted for and implemented in the model framework by the development of a one-dimensional numerical code that solves the advection-diffusion transport equation in the unsaturated zone for the three tracers starting from their more or less known atmospheric input function. In absence of local measurements, homogeneous soil parameters were considered.

The Krypton-85 concentration time series at depth in the vadose zone show relevant differences compared to its atmospheric input function. Owing to its fast transport in the soil air, Krypton-85 concentrations time series at depth were found to be smoother and of lower concentrations compared to the atmospheric input function values. Sensitivity analysis showed that the effective diffusion coefficient is the key factor controlling the fate of Krypton-85. In particular, a small-scale property of the unsaturated medium - gas-phase tortuosity - will be decisive in determining the spatially-varying and time-varying value of the effective diffusion coefficient. Although the variability for gas-phase tortuosity - depending on the saturation conditions across the vadose zone - is not as large as for transmissivity, its impact on transport in the case of the shallow Baltenswil aquifer needs to be considered.

Tritium concentration time series at depth on the other hand, were just shifted (delayed) in time compared to the atmospheric input. Due to the advective character of its transport, time series at depth are found to be less smoothed compared to Krypton-85 time-series at depth. On the other hand, Tritium is less sensitive to soil parameters due to the smoothly decreasing trend of its atmospheric input in the last two decades.

Both Tritium and Krypton-85 are sensitive to the respective atmospheric input functions only in case of strong concentration variations in time. This parameter shows a relevant spatial and temporal variability and thus the reliability of the input function is also key issue for successful tracer transport modeling.

Tritium decay-product Helium-3 does not take part in the input to the saturated zone, owing to its large diffusion coefficient in the gas-phase and to its low water-air partitioning coefficient, which both enhance its direct loss from the soil to the atmosphere.

No reasonable fit of the simulated vs. observed tracer concentrations could be achieved
without considering the Krypton-85 transport in the unsaturated zone. Neglecting the vadose zone would have brought an overestimation of the simulated concentrations in the groundwater and thus an underestimation of Krypton-85 derived water-age. Owing instead to the nearly steady-state conditions established in the last decade by Tritium in the atmosphere-subsurface system, its passage through the unsaturated zone was shown to have smaller impact on final simulated concentrations in the groundwater in the case of the shallow Baltenswil aquifer where groundwater is very young (< 5 yrs. as estimated by tracer-derived water ages). By accounting also for the unsaturated zone transport, the Krypton-85 derived groundwater ages could be made consistent with the Tritium/Helium-3 derived ages.

### 7.3 Tracer transport in the saturated zone

The modeling of the environmental tracers' Krypton-85, Tritium and Helium-3 transport in the subsurface was performed with the module MT3DMS (Zheng and Wang, 1999a) in Processing Modflow (Chiang and Kinzelbach, 2001). Krypton-85 simulations provided the most challenging scenario for interpretation of both data and transport simulation results. At most observation locations, a satisfactory agreement of simulated vs. measured tracer concentrations could be achieved with selected homogeneous transport parameters. The unsaturated zone thickness will be decisive in determining the absolute value of the input concentrations to groundwater.

At one observation location (Baltenswil pumping station), where multiple measurements were available, unusual short-term oscillations in Krypton-85 concentration measurements were recorded and reproduced by the transport simulations only to a limited extent (only 20% of the total amplitude). These concentration oscillations could not be fully reproduced by the model. The range of measured concentrations indicates that this well can collect water of different ages. A possible driving mechanism was found to be seasonality of the groundwater recharge rate which, especially in shallow and thin aquifer zones such as PW Baltenswil catchment, can account for concentration variations on a seasonal scale. About three times larger recharge rates resulted in 10% larger simulated concentrations. The concentration time-series may also be over-smoothed and thus not able to completely catch the concentration oscillations because of the monthly averaging of the recharge rate parameter.
It was also found by a one-day sampling experiment that the measured Krypton-85 concentrations can be reduced up to about 10% during eight hours of pumping. By comparison of the measured concentrations with the average pumping rate during the period prior to the sampling it was found that these two quantities show a clear anti-correlation, at least in a first period. This fact indicates that younger water can be collected at the Baltenswil well in low pumping conditions, and older water in the opposite case.

The measured concentration oscillations show that waters of different origins are mixed over a short time scale at the pumping station. It is thus not possible to define a unique water age at the Baltenswil well. Instead, the model must be capable of reproducing a distribution of ages or better the observed concentrations. Older water is needed to reproduce the observed oscillations. The origin of such older water cannot be accounted for by including the shallow and thin groundwater body lying West of the modeled Baltenswil catchment, since this groundwater body would feed the pumping station with very young water. On the other hand, it also cannot come from other parts of the aquifer lying East of the modeled domain, since this water would be intercepted by other pumping stations. The only possibility left is older water coming from the hilly moraines in the North and North-East. This area, which provides the lateral inflow to the modeled aquifer, was shown to provide older water in different amounts and with different ages due to its spatially variable thick unsaturated overburden.

Krypton-85 transport simulations in the saturated zone showed relevant sensitivity to the porosity value and to the input function at the groundwater table, which in turn is controlled by the gas-phase tortuosity in the unsaturated zone. By making these two parameters spatially variable (e.g. by zoning), a simultaneous fit of simulated vs measured concentration values at all observation locations could be achieved.

In particular, the effective diffusion coefficient in the unsaturated zone was found to be crucial for the Krypton-85 transport. Its spatial and temporal variability can be up to two orders of magnitude, and is controlled by gas-phase tortuosity. In areas where a thick unsaturated overburden is present, as is the case in the Northern part of the Baltenswil aquifer, it was shown that a smaller value of tortuosity, i.e. assuming a longer travel path for the tracer before reaching the groundwater table, can partially explain the different tracer concentrations sampled at the Baltenswil well in such a short time scale (variations of 20 dpm/ccKr in less than one year). The importance of
tortuosity should not be underestimated, especially in highly heterogeneous moraines. Here, the presence of less pervious lenses or even perched aquifers may indeed force the gas-phase tracers to follow a longer path or even hinder them from reaching the groundwater table. In case of availability of local measurements, this effect can be accounted for by stochastic modeling of the gas-phase tortuosity.

Krypton-85 simulations and data indicate that significant mixing effects on both the spatial and temporal scale may take place in the heterogeneous Baltenswil aquifer. Mixing phenomena may have a range of origins: variable recharge conditions leading to time-varying tracer input to groundwater (which may have a larger impact than in our model simulations), water originating outside the modeled domain (re-definition of the model spatial boundaries), unresolved spatial heterogeneity of several parameters affecting subsurface transport (transmissivity, recharge to groundwater, porosity, gas-phase tortuosity above all). As example, at one location (PW Bruttisellen) the use of different spatial boundary conditions allowed the reduction of the discrepancy between simulated and measured Krypton-85 data. Yet, although accounted for in the conceptual model, the above-mentioned factors may have a larger impact than the model results are able to reproduce. Despite the number of possible candidates to the explanation of such (measured) oscillations, their origin remains unclear and deserves more investigation and validation studies.

In contrast to Krypton-85, Tritium transport simulations offer a more straightforward, although less robust, interpretation. The nearly steady-state conditions established by the smoothly decreasing Tritium atmospheric input function considerably diminishes the dependence of the concentration time series at depth on almost any model parameter. Using realistic regional transport parameter values, a satisfactory fit between simulated and measured concentrations was easily achieved at all locations. Although Tritium alone may for the above argument seem not appropriate for groundwater investigations, it nevertheless provided a necessary validation basis - through the simulated concentrations’ match to data - for Helium-3 modeling.

Helium-3 was found to be the more effective investigation tool since in the examined case study its input can be considered to take place directly in the groundwater. The Helium-3 input to the groundwater takes place along the streamlines, thus providing detailed information on the water movement with focus on the saturated zone alone. Simulations showed that Helium-3 data were considerably overestimated by the model
results when using the porosity value which allowed to fit both the Krypton-85 and Tritium data. To solve this basic inconsistency of the proposed model, *ad-hoc* zonation of the porosity parameter was not justifiable in the light of the lack of local porosity measurements.

It was argued that Helium-3 subsurface dynamics might be affected by diffusion phenomena not yet accounted for in the conceptual model and capable of explaining the Helium-3 results' discrepancy with indications coming from Krypton-85 and Tritium tracers. Accounting for Helium-3 back-diffusion from the groundwater table to the atmosphere allowed to account for a decrease of 20% up to 70% in the simulated concentrations time-series at the different observation locations. The implementation of the mechanism of differential molecular diffusion of Helium-3 relative to Tritium did not help to reduce the Helium-3 concentration in the groundwater (mobile phase) and thus to achieve a better match for Helium-3.

### 7.4 Impact of transmissivity on tracer transport

Each realization with its own spatial transmissivity variability and transmissivity contrast was tested to see the effect on tracer migration in groundwater. For all tracers, the role played by the transmissivity field heterogeneity was found to be less important than expected. The effect of different transmissivity realizations on the simulated tracer concentration time series at the various observation locations was limited to a vertical shift of the concentration time series through the whole simulation time and not to a substantially different shape of the time series. The variations in concentrations were comparable to the measurement error in data. Although each conditional realization displays its own spatial transmissivity pattern and contrast zones, no significantly different shapes of the concentration time series could be obtained by changing the transmissivity realization.

Neglected three dimensional effects and the choice of a Multi-Gaussian Random Function model for transmissivity fields may also contribute to conceptual uncertainty. The presence of low conductivity lenses, in both the unsaturated and saturated zone, can play a significant role. Local less pervious lenses in the unsaturated zone will slow Krypton-85 transport and thus result in a lower tracer input to the groundwater table. In
the saturated zone, such lenses will also affect the transport of dissolved Krypton-85 and Helium-3 and contribute to the mixing.

On the other hand, transmissivity was less consequential than expected with respect to the concentration distribution in the subsurface also owing to the much larger (about 10 times) travel times spent in the unsaturated zone compared to the residence time in the saturated zone, as could be derived by particle tracking with PMPATH (Chiang and Kinzelbach, 1994). A much larger impact on the tracer concentration time-series is instead found in the spatial variability of two tracer transport parameters: gas-phase tortuosity for Krypton-85 transport in the unsaturated zone (affecting its effective diffusion coefficient in soil-air) and porosity for both Krypton-85 and Helium-3 in the saturated zone. While the uncertainty associated with the spatial variability of transmissivity was found to be between 5% and 20%, the uncertainty associated with the gas-phase tortuosity ranges from 20% up to 60% according to the observation location (Krypton-85). In the case of porosities, the uncertainty can vary from 10% up to 25% for Krypton-85 and 20% up to 70% for Helium-3. Helium-3 shows larger sensitivity to saturated-porosity since its production and transport take place in the saturated zone only, while Krypton-85 constantly receives input concentrations from the unsaturated zone.

7.5 Information derivable from the three tracers and final remarks

The combined use of three different tracers in the Baltenswil study allowed a deeper insight into the subsurface physical system. Two gas tracers - Krypton-85 and Helium-3 - and one water-bound tracer - Tritium - were used in the investigations. The different behaviors in the subsurface - e.g. in the unsaturated and saturated zones - and the different input function at the groundwater table allowed to separate the focus on different physical phenomena affecting the system dynamics and provided different information on the spatial and temporal scale of the physical processes.

The gas tracers behave differently in the unsaturated zone. Krypton-85 diffuses via soil-air from the atmosphere to the groundwater table. It provides a monotonically increasing input function. Helium-3 is instead produced in the unsaturated zone by
Tritium decay, but it is shown to provide negligible input to the groundwater. In case of thick unsaturated zones, the input function of gas tracers into groundwater must be necessarily corrected by a diffusion model.

The gas tracers behave also differently in the saturated zone. Krypton-85 joins the saturated zone via its input at the groundwater table and is transported by the groundwater flow. Helium-3 is instead significantly lost by gassing-out back to the unsaturated zone and finally to the atmosphere especially in zones where the groundwater is shallow, due to its high diffusion coefficient in water and to its small partitioning coefficient. The latter fact could be used to explain the discrepancy between the Helium-3 derived water ages and the Krypton-85 derived ages at the Baltenswil pumping station.

In particular, the data show that older water than the model can reproduce is collected at the Baltenswil well. Different hypotheses could be tested to explain this discrepancy. The large action of the drain located close to the well and the contribution from water coming from beyond the drain location could be excluded since the concentrations at the drain location indicated that water of almost the same age is collected at the drain. Older water coming from beyond the model Western boundary could also be excluded in the light of particle tracking, since this water was collected at other pumping stations. The most likely explanation was then found in the older water coming from the hilly moraines in the North and North-East constituting the lateral inflow area to the groundwater body. The latter hypothesis could be successfully tested by the model. By allowing older water coming from the hilly moraine area in the North and North-East amounts of significantly older water (e.g. poorer in Krypton-85) could be collected at the PW Baltenswil.

Nonetheless, environmental tracer data availability in Baltenswil is too low for drawing hard conclusions. This lack can be compensated by stochastic modeling of spatially variable parameters, transmissivity for the groundwater flow model and the effective gas diffusion coefficient for the transport model. Due to lack of effective diffusion coefficients data (or physically-related quantities such as gas-phase tortuosity and saturation conditions), in the present work only the stochastic modeling of transmissivity conditioned to transient hydraulic heads has been performed.

It must be pointed out that nowadays water bound Tritium is no longer a useful environmental tracer in studying shallow heterogeneous aquifers - such as Baltenswil - where
the travel times in the subsurface are small (< 10 years) because the atmospheric and groundwater input are too flat. Nevertheless, Tritium is indirectly an indispensable environmental tracer also in shallow aquifers since it allows to model the Helium-3 concentrations in the saturated zone. Besides, Tritium itself can provide an important cross-check tool for Helium-3 modeling, by the correct reproduction of measured Tritium concentrations in the groundwater.

The gas tracer Krypton-85 is in turn useful only in aquifers where the groundwater residence time is much larger than the travel time in the unsaturated zone. In the opposite case - i.e. as in the Baltenswil case-study - the gas tracers can indicate older water components coming from aquifer zones with large unsaturated overburden. In aquifers where the importance (e.g. thickness and travel time) of the unsaturated zone is comparable or higher than the saturated zone, the use of environmental tracers may not necessarily bring further and better information since their modeling in the vadose zone will require the knowledge of additional spatially distributed parameters (e.g. the effective diffusion coefficients).

The combined use of the three different environmental tracers’ data - each with its own transport properties and input function - allowed significant cross-check of different hypotheses regarding the conceptual model. They allowed the discussion and provided a verification tool for

- the definition of the spatial domain boundaries
- homogeneity/heterogeneity of the different parameters involved in the tracer transport
- the separation of subsurface dynamics in the unsaturated and saturated part
- the mixing phenomena in the groundwater
- the possible origin of water sampled at the observation locations
- the reduction of conceptual uncertainty by the inclusion of additional physical phenomena taking place in the subsurface, such as Helium-3 back-diffusion and diffusive-fractionation

In conclusion, the information coming from different tracers can help in mitigating some sources of uncertainty in the conceptual groundwater flow and tracer transport models.
In the present work, the indications which could be derived from tracer modeling helped in the discussion about the possible location of the model boundaries, in the calibration of the tracer transport parameters both in the unsaturated and saturated zone and their spatial variability, in the mapping of the groundwater age spatial distribution (zones with older, resp. younger water). In particular, at PW Baltenswil, they provided evidence of a complicated age structure of the water sampled at the well, and thus of the consequences on the conceptual flow and transport model in the well catchment. Krypton-85 data oscillations allowed to focus on a relatively small portion of the aquifer under study and to try different interpretations of the measured data by updating the conceptual flow and transport models following the experimental evidence.

Yet, to be fully exploited, environmental tracer modeling calls for the estimation of additional parameters, which are usually also uncertain and difficult to quantify. Without a confident knowledge of these transport parameters (gas-phase tortuosity and porosity above all), the uncertainty of results may still remain large. Nonetheless, the mismatch of model results and experimental data allowed the refinement of the conceptual model by including additional physical processes not considered in a first-stage modeling. The discrepancy between the Krypton-85 and Tritium modeling and Helium-3 results, allowed to argue the possibility of significant Helium-3 loss from the groundwater table. This hypothesis could be successfully tested by a simple refinement of the transport model.

The environmental tracers allow to restrict the range of possible hypotheses which could explain the observed reality, at the price of new sources of uncertainty related to the transport parameters necessary to model the tracer movement in the subsurface. In this regard, local knowledge of such parameter values can be of utmost importance. In the present case-study, they could also suggest improvements in the conceptual model by the identification of new phenomena affecting subsurface transport. Environmental tracers were found valuable in giving indications on the system under study over large timescales (decades in our case) as well as over smaller ones (e.g. seasonal). Environmental tracers provide a preferential tool which can potentially largely improve the effectiveness of groundwater investigations. Assembling the information from different tracers may still leave the modeler with a multiplicity of solutions and interpretation, but may definitely allow a clearer, refined picture of the unknown subsurface reality.
7.6 Recommendations for further studies

A key issue to fruitfully exploit the environmental tracers as groundwater investigation tool is the planning of a sampling campaign both pre- and post- modeling effort. This is important since environmental tracers help in calibrating the model set-up in terms of the reproduction of acquired data and can give valuable indications for forecasting the future development. The timetable of the sampling campaign should be planned according to the specific needs of the investigation. In our case study, samples were planned to observe both the spatial and temporal variability of the tracers concentrations over a time interval of 4 years. This allowed to investigate in particular the aquifer system conditions during the particular conditions of year 2003, where a dramatic decrease of precipitation lead to almost zero recharge to groundwater during the summer months.

According to the investigation goals, sampling should be consistently planned and eventually older tracer measurements should be recovered. The effectiveness of environmental tracer modeling may in many cases suffer from a consistent lack of measurements from the past. This would provide a very important model calibration tool, as in our case the simulation time under study was running from 1991 to 2007, and the first available measurement dated 2000. In particular, tracer concentration time-series will provide useful information on the system dynamics over the short and long term. The timing of the sampling should be planned according to the typical time-scales of the system. In the present case-study, where groundwater residence times are on the order of a few years and the unsaturated thickness variability gives rise to both small and large depths to groundwater, a seasonal sampling (every 3-4 months) is highly recommended. Also, the location of the sampling should be chosen according to the different areas of the aquifer (e.g. small/large unsaturated overburden).

Additional measurements of soil parameters which more than others affect the tracer concentration distribution in both the unsaturated and saturated zone would constitute an advantage for successful transport modeling. Measurements of gas-phase tortuosity in different saturation conditions may help in the calibration of a correct input function at the groundwater table. Local porosity data may help in the interpretation of tracer data. Available environmental tracer data themselves may also indicate where these measurements are needed.
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