

**PREDICTION OF GROUNDWATER QUALITY
USING TRANSFER FUNCTIONS
–
AN APPROACH TO LINK
HISTORICAL DATA TO FUTURE CONCENTRATIONS**

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Prediction of groundwater quality using transfer functions – An approach to link historical data to future concentrations

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*« Je sers la Science
et c'est ma joie »
Basile, discipulus simplex*

ABSTRACT

Groundwater quality has been degraded by anthropogenic activities at many locations. In order to reverse upward concentration trends, environmental programs such as land use changes are frequently implemented. To evaluate the efficiency of such measures, methods linking the evolution of the groundwater quality at public-supply wells to the history of pollutant inputs in their capture zones are required. The use of numerical flow and transport model is the most comprehensive approach to evaluate and predict pollutant concentration trends. However, the application of this approach is frequently restricted by financial constraints or lack of sufficient data to reliably calibrate such models. Furthermore, the development of a sophisticated numerical model may be disproportionate for an initial estimation of the time-scale of groundwater remediation.

Therefore, this thesis proposes an alternative, simpler approach to evaluate the effect of pollution pressures or remediation programs on the evolution of pollutant concentrations at aquifer outlets. This alternative is based on the transfer function approach which has been commonly applied to the transfer of environmental tracers through aquifers. The method consists of a combination of input concentration trend and travel time distribution represented by a transfer function, using a convolution integral.

While the classical transfer method approach is appealing due to its simplicity, it relies on several assumptions such steady-state hydrodynamic conditions, a homogeneous solute input and a single compartment of solute transfer in the aquifer system. These assumptions limit its use for common scenarios of diffuse pollutions, which often show a spatially distributed input on the catchment and several compartments of transfer within the aquifer, typically the unsaturated and saturated zones. Moreover, steady state conditions are rarely observed.

In an initial part of this thesis, the different methods that can be applied to characterize the transfer functions are reviewed. The analytical models of transfer functions are detailed and new formulations of the exponential model are developed to be applied for input and output zones of limited extent. Furthermore, it is demonstrated that the steady state approximation can be applied when characteristic periods of hydrodynamic fluctuations are smaller than the mean travel time of solute in the system. In a next step, the convolution integral is modified to incorporate spatially varying concentration inputs of diffuse contamination from agriculture. It is demonstrated that the transfer function only needs to be characterized for the section of the catchment in which the contaminant input is modified. Finally, the equation is extended to include distinct transfer compartments of the aquifer system, such as the unsaturated and saturated zone.

The modified transfer function approach is then applied to the Wohlenschwil site, where land use changes have been implemented since 1997. This site is well suited for testing the approach because the land use history is well known and the full cycle of upward concentration trend followed by trend reversal is documented. For this site, analytical and numerical methods are applied to characterize the transfer functions of nitrate. Separate numerical models are established for the unsaturated (HYDRUS) and saturated (FEFLOW) zones, respectively. The analytical method consists in determining the mean transit time of water in the unsaturated and saturated zones of the aquifer, using respectively a water balance approach and the results of artificial tracing, for the parameterization of analytical dispersion models of transfer functions. The nitrate concentration input is reconstructed on the basis of land use history and the recharge rate. Two different recharge scenarios are compared: an average recharge rate and annually varying recharge rate.

Both analytical and numerical methods well reproduce the observed concentration trend. The contribution of each step of land use changes to the water quality improvement is established. A better agreement is found when using annually varying recharge rates. This approach allows reproducing an increasing nitrate concentration trend following a period of low recharge rate.

To summarize, this thesis redefines the framework of application of the transfer function approach. The study demonstrates that the transfer function approach can be applied in most cases of diffuse pollutions affecting groundwater and is particularly suited for remediation programs. The advantages of the transfer function approach are its simplicity and its flexibility, even if it requires a good understanding of the aquifer functioning, in particular the delimitation of the capture zone. The limits of the approach depend on the conditions in which steady-state hydrodynamic conditions can be assumed. Furthermore, the accuracy of the transfer function approach depends on a good quantification of the functions describing inputs and transfers of pollutants in the aquifer system. This study suggests that the choice of one or the other method for the characterization of the transfer functions mainly depends on the availability of data relevant for their implementation. A combination of different methods is also possible, such as the use of analytical models for the unsaturated zone and numerical models in the saturated zone.

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KEY WORDS

groundwater quality trend
contaminant concentrations
travel time distribution
transfer function
lumped parameter model
nitrate
nonpoint source pollution
Wohlenschwil aquifer

Chapter 1

Introduction

Groundwater pollution has been significantly increasing since the second half of the 20th century. This has been first observed in developed countries [Strebel *et al.*, 1989] but more recently recognized over the whole world [World Water Assessment Programme, 2009]. In light of those observations, environmental programs were implemented in the last decades for the protection and the restoration of groundwater quality, especially where this resource is crucial for human water supply.

Against agricultural contaminants, for instance, some specific measures have been introduced since the 1990's. In the USA, for example, the concept of the Best Management Practices defines agricultural practices that are suitable for minimizing water quality impacts [Spalding *et al.*, 2001; Owens and Bonta, 2004; Wassenaar *et al.*, 2006; Owens *et al.*, 2008]. In Switzerland, environmental projects have been introduced under Article 62a of the Water Protection Act [Confédération Suisse, 1991] to reduce persistent contaminants in groundwater. In this last framework, most of the environmental actions took the form of "nitrate projects", aiming to reduce nitrate concentration in public pumping wells supplying drinking water. More recently the European Water Framework Directive [European Union, 2000] has introduced a comprehensive approach to groundwater quality protection: to inverse the deterioration of water quality in all the European water bodies (including aquifers) and so as to tend to a good quality status of waters by 2015.

The examples of the "nitrate projects" of Switzerland provide a lot of insight on how groundwater quality reacts to such environmental measures under various hydrogeological situations. These measures, encouraged by financial support of the Swiss Confederation, consist of local and targeted land use changes to reduce the concentration of nitrate in groundwater that, after having been subjected to agricultural pollution, no longer meets the environmental requirements for groundwater quality [OFEV, 2002]. A few years after their implementation, generally in the mid-2000s, it was noticed that only part of the nitrate projects responded favorably to the implemented measures and showed a decrease in nitrate concentrations [DSE and DEC, 2009; OFEV, 2009a; Niederhäusern *et al.*, 2010]. Other aquifer systems experienced a lag time long enough to put in question the efficiency of the nitrate project itself, particularly in relation to the financial compensation granted to stakeholders over time. Of course it cannot be excluded that, for some projects, the implemented measures did not sufficiently reduce the nitrate input, but it appeared that the time required for flushing out contaminants present in the aquifer was not sufficiently taken into account, which could lead to underestimate the long term efficiency of the remediation project.

Actually, the problem of the lag time observed between the implementation of remedial measures and the effective improvement of groundwater quality or, more generally, the problem of the time required for a pollution event to effect changes in groundwater quality was reported in many studies [Bohlke and Denver, 1995; Zoellmann et al., 2001; Tomer and Burkart, 2003; McMahon et al., 2006; Osenbrück et al., 2006; Owens et al., 2008; Gutierrez and Baran, 2009; Meals et al., 2010]. The knowledge of this lag time appears to be a prerequisite for the implementation of remediation programs, because it permits to know when the expected results are produced and thus avoiding a wrong interpretation about the efficiency of these programs. More generally this factor can also be of utmost importance for the interpretation of groundwater quality trends, trends that are for example followed in the NAQUA National Groundwater Monitoring [OFEV, 2009b], in Switzerland.

In published literature, the consideration of lag time is quasi specifically carried out through numerical simulations of flow and transport in aquifers [Zoellmann et al., 2001; Molenat and Gascuel-Oudou, 2002; McMahon et al., 2008; Orban et al., 2010; Bonton et al., 2011]. However these numerical simulations, widely used in research, are currently not accessible for most environmental projects, for mainly technical and financial reasons. That is the reason the lag time was not systematically, and even rarely, taken into account in the management of remediation projects.

The main aim of the research outlined in this thesis was to develop a methodology to quantify over time the response of an aquifer system to contaminant input, the idea being to introduce a method that is sufficiently simple to be applicable for most remediation projects, all the while being verified as much as possible by field data.

This thesis develops the theoretical background supporting the choice of the transfer function approach to quantify the evolution of groundwater quality at the outlet of aquifers, as an alternative or a complement to numerical simulations of flow and transport in aquifers.

Chapter 2 describes with a simple conceptual aquifer model how the travel time distribution controls the lag time, observed between the implementation of the environmental actions and the response of groundwater quality trends at the outlet. The distribution of travel time can be described by transfer functions, whose methods of determination are various. In this section, the thesis summaries the current states of these methods. Then, the bases of the transfer function approach are established through the principle of convolution, initially described in hydrogeology for the study of the transfer of environmental tracers in aquifers, and the convolution integral emerges as the key element of the approach. Nevertheless, the transfer function, thus expressed, is more suitable for studying the transfer of environmental tracers than for studying the transfer of contaminants, usually heterogeneously introduced in the watershed. This explains why the transfer function approach is rarely used in remediation projects.

These limits are partially overcome in Chapter 3, in particular by a reformulation of the convolution integral. By these new developments, the thesis opens the field of application of the transfer function approach to most environmental projects applied to unconsolidated shallow aquifers affected by diffuse pollution spatially and temporally heterogeneous. The analytical descriptions of transfer functions, discussed in this chapter, also allow the application of the method for projects where the available data and investigation resources are limited, which is a fairly common situation. Among the analytical model, this thesis introduces new formulations of the exponential model for more realistic configurations of pollutant inputs and outputs.

Chapter 4 finally outlines the case study of the aquifer Wohlenschwil, subject to a “nitrate project,” since 1997. The study is focused on the nitrate because this is an excellent test case because changes of the input function are known (which is not the case for other contaminants) and since the compound shows a conservative behavior. The comparison between the observed and calculated data gives the possibility to test the proposed approach.

Chapter 5 contains concluding comments and perspectives.

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Chapter 2

Quantification of groundwater quality trends at pumping wells using a transfer function approach

ABSTRACT

This chapter highlights the importance of the travel time distribution of solutes in aquifers, in order to evaluate the evolution of solutes at pumping wells. This evaluation is important when the solute is a contaminant and when measures are introduced in the groundwater catchment area in order to reduce the solute concentration at a pumping well. When flow and solute transport in the aquifer cannot be easily characterized by deterministic numerical simulations, the evolution of the solute at the pumping well can be evaluated with a transfer function approach.

The principle of the transfer function approach is to solve the convolution integral, which links the solute concentration at the pumping well to history of solute input in the recharge zone of the aquifer via a transfer function. The transfer function describes the travel time distribution of the solute from the input zone to the pumping well. It can be determined by numerical, analytical or experimental methods, or a combination of them. These methods are compared and their advantages and drawbacks are analyzed.

Since the analytical description of the transfer function is one of the most common approaches, the main analytical formulations in the published literature are reviewed. Decay and retardation factors affecting the transfer of nonconservative and reactive solutes are included in these analytical formulations. Strength and weakness of the transfer function approach are highlighted in the conclusion and the areas that would benefit from further development are pointed out.

2.1. INTRODUCTION

In recent decades, changes in environmental policies have been carried out by governments in order to limit the deterioration of groundwater quality, which is observed in many parts of the world [*World Water Assessment Programme*, 2009]. The remediation measures usually consist of limiting pollutant input in the catchment area of the aquifer with the aim of decreasing pollutant concentration at pumping wells. In Switzerland, for instance, such an approach is developed through the "Nitrate projects", whereby farmers receive compensation for implementing land use changes that results in lower pollutant leaching [*OFEV*, 2002]. As highlighted in several studies [*Bohlke and Denver*, 1995; *Zoellmann et al.*, 2001; *Tomer and Burkart*, 2003; *McMahon et al.*, 2006; *Osenbrück et al.*, 2006; *Owens et al.*, 2008; *Gutierrez and Baran*, 2009; *Meals et al.*, 2010], the improvement of groundwater quality at the pumping wells only occurs with a delay which can be highly variable.

When implementing such measures, two questions are usually of main interest: To what level will the contaminant concentration be reduced? In which time frame will the reduction be achieved? Uncertainty about the time period required to reach water quality objectives can have financial implications and can put in doubt the efficacy of the remediation measures. Consequently, it is important for authorities to know how rapidly groundwater quality will improve, prior to applying their environmental policies.

Visser et al. [2009b] identify and compare four main methods for the evaluation of groundwater quality evolution: (1) statistical trend analysis, (2) groundwater dating, (3) transfer function approaches and (4) deterministic models. The authors demonstrate that a simple statistical approach does not give sufficiently robust results for a long term prediction, mainly because the extrapolations derived from statistical analyses do not consider present and future changes in pollutant input. Although groundwater dating gives valuable information to interpret groundwater quality trends and to evaluate the tendency of the system to react to a change on pollution input [*Bohlke*, 2002; *MacDonald et al.*, 2003; *Tomer and Burkart*, 2003; *Visser et al.*, 2007; *Rupert*, 2008; *Visser et al.*, 2009a], this method does not permit to quantitatively predict the groundwater quality evolution. Furthermore, the environmental tracers used for age dating are representative for the recharge in the entire groundwater catchment and do not represent the travel time of pollutants from a specific part of the recharge zone.

On the contrary, Visser et al. [2009b] demonstrate that numerical modeling of subsurface flows and transports and transfer function approach can be well suited methods. To date, numerical simulation of solute transport is the most common approach to calculate the evolution of a contaminant concentration [*Zoellmann et al.*, 2001; *Molénat and Gascuel-Oudoux*, 2002; *McMahon et al.*, 2008; *Orban et al.*, 2010].

Nevertheless, numerical modeling is a complex and time consuming method requiring good knowledge of parameters controlling flow and transport in the aquifer system. Hence, the calibration of deterministic models requires detailed hydrogeological investigations, such as the characterization of aquifer geometry, measurement of hydraulic heads and use of environmental or artificial tracers to calibrate transport parameters [Zoellmann *et al.*, 2001; Zuber *et al.*, 2011]. The deterministic numerical simulation is also not easily computable for complex aquifer systems. It is for example the case of groundwater flow processes within karst aquifers for which numerical modeling is still at the development stage [Sauter *et al.*, 2006]. Consequently, its applicability is not always feasible or requires a degree of investigation and computation too high for simple environmental projects.

An alternative approach to quantify the evolution of a contaminant at pumping wells is the use of transfer functions [Bohlke, 2002; Osenbrück *et al.*, 2006; Eberts *et al.*, 2012]. This approach is based on the convolution integral, that has been introduced in hydrogeology to describe the transfer of environmental tracers in aquifers [Maloszewski and Zuber, 1982] or of solutes in the vadose zone [Jury, 1982]. The convolution integral mathematically links the evolution of a solute concentration at a given outlet to the input function of solute concentration by the transfer function of the solute in the aquifer system, which will be defined in more detail in this chapter.

The transfer function approach was applied, for example, by Osenbrück *et al.* [2006] in order to estimate the future evolution of nitrate concentration in several pumping wells of a porous aquifer in Saxony, Germany. According to the authors, the choice of using a transfer function approach, instead of a numerical simulation method, was governed by the lack of data available on the aquifer characteristics, which is a common situation for most drinking water catchments. The characteristics of the transfer function describing the transfer of nitrate in the aquifer were determined by a lumped parameter model calibrated with environmental tracers. The evolution of nitrate concentration at the pumping wells was calculated under various scenarios of land use. While the transfer function approach provided promising results, the study also highlighted some limitations to its application. The main limit is induced by the fact that the transfer function is characterized by a lumped parameter model calibrated by input-output times-series of environmental tracer data. First, this requires that the nitrate has a conservative and non-retarded behavior in the aquifer system, in accordance with the behavior of the environmental tracers. While nitrate movement is usually not retarded, nitrate may not be conserved due to denitrification under reducing conditions. Second, the environmental tracer input is quasi homogeneous throughout the recharge area of the aquifer, whereas the nitrate input is, in most cases, spatially varying.

Compared to the numerical method, the use of the transfer function approach requires fewer field investigations and computational tools, even if calibration of transfer functions

parameters requires long time series of data or knowledge of the main factors governing flow and transport in the aquifer. Nevertheless, the transfer function approach, as it is usually carried out, is based on some assumptions that limit its suitability for many cases.

This chapter introduces the transfer function approach, as an alternative to numerical simulations, for the quantification of contaminant concentration evolution at pumping wells. Strengths and weakness of such a method are pointed out in order to emphasize the need for further developments.

First, the importance of the travel time distribution for the concentration evolution at a pumping well is illustrated based on a conceptual example. The influence of aquifer and input zone characteristics on the travel time distribution of contaminants in aquifers is analyzed. Second, the transfer function, a key element of the approach, is explained in more detail. And third, a short review of the available methods to characterize the transfer function is provided. Advantages and disadvantages of each of these methods are discussed.

2.2. EFFECT OF TRAVEL TIME DISTRIBUTION ON CONCENTRATION TRENDS

2.2.1. INTRODUCTION

Several studies have documented a time lag between the implementation of agricultural measures and the improvement of groundwater quality [Bohlke, 2002; Tomer and Burkart, 2003; Osenbrück *et al.*, 2006; Hund-Goschel *et al.*, 2007; McMahon *et al.*, 2008; Visser *et al.*, 2009a; Meals *et al.*, 2010]. For a conservative solute, the time lag corresponds to the time required by water to travel from the recharge zone, where pollution is reduced, to the pumping well, where an improvement of groundwater quality is expected.

Contaminants arriving at a pumping well do not have a unique travel time, but reach the pumping well according to a distribution of travel times, which reflects the diverse pathways that the solute can take, depending on the location of the contaminant input in the capture zone and the hydrodynamics and transport conditions within the aquifer. In this context, it is important to better understand how the distribution of the travel time affects the evolution of contaminant concentration at a pumping well and the time lag after implementation of agricultural measures.

2.2.2. OBJECTIVE

In this section, the effect of the travel time distribution on the evolution of contaminant concentration at a pumping well is explored using simplified conceptual models of an aquifer. The objectives are (1) to test the influence of aquifer characteristics and mass input location on the travel time distribution of contaminants and (2) to test the influence of the travel time distribution on the evolution of contaminant concentration at the pumping well.

2.2.3. METHOD

The demonstration is based on the simulation of flow and solute transport across a conceptual aquifer with a contaminant input on its recharge area and an outlet representing a pumping well. Five scenarios are simulated with either a different distribution of the hydraulic conductivity or different distributions of zone of contaminant input, while maintaining the same recharge rate. For each scenario, flow and transport is simulated using FEFLOW [Diersch, 2009] to calculate the evolution of contaminant arrival rate in the pumping well and the probability distribution of contaminant travel time. Finally the travel time distributions of the contaminant in the aquifer are compared and their effect on the evolution of the contaminant concentration at the pumping well is analyzed.

The simulated scenarios are illustrated in Figure 2.1: dimension of the system are 20 x 1000 m (2D vertical section), the recharge rate on the surface is of 2 mm/day (corresponding to a total input flow rate of 2 m³/day), the hydraulic conductivity varies between 10⁻⁵ m/s and 10⁻³ m/s, the fully-penetrating pumping well is simulated by an outlet with a constant head (H = 100 m) and the mass input zone corresponds to the first 0.4 m from the top. The porosity is 0.2, the longitudinal dispersivity is 5 m and the transverse dispersivity is 0.5 m. The simulated contaminant is an ideal tracer, which means that it is not retarded and not degraded during the transport.

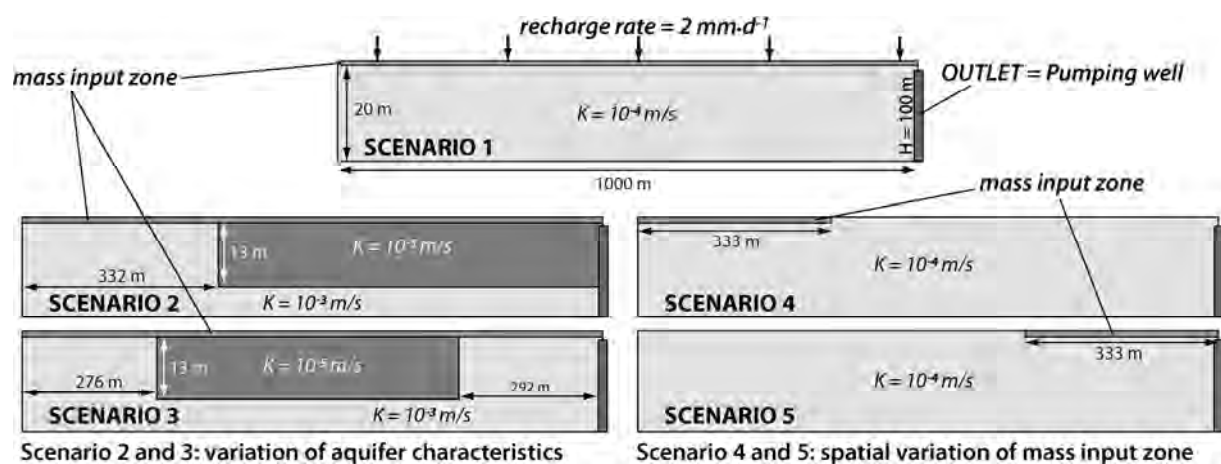


Figure 2.1 Main parameters for the five scenarios of the conceptual model of aquifer affected by contamination, where scenario 1 is the reference, scenarios 2 and 3 have a particular distribution of hydraulic conductivity and scenarios 4 and 5 have a particular spatial distribution of the mass input rate.

Scenario 1 is the reference: the hydraulic conductivity is homogeneous (10⁻⁴ m/s) and the mass input is homogeneously distributed over the recharge zone. Scenarios 2 and 3 also have a homogeneous contaminant input but the hydraulic conductivity varies spatially (10⁻³ and 10⁻⁵ m/s). Scenarios 4 and 5 have a homogeneous distribution of the hydraulic conductivity but the contaminant input zone varies spatially (in the first third or the last third of the surface). All scenarios are identical in term of mean transit time t_w of water, that is equal to 2000 days, according to [Maloszewski and Zuber, 1982]:

$$t_w = \frac{V_m}{Q} \quad \text{Equation 2.1}$$

where V_m is the mobile water volume (4000 m³) and Q is the flow rate through the system (2 m³/day).

Simulations are carried out for fully saturated conditions. The travel time distribution of the contaminant from the input zone to the pumping well is represented by a probability density function of travel time (travel time pdf). According to a number of authors [*Maloszewski and Zuber, 1982; Jury and Roth, 1990*] the travel time pdf corresponds to the normalized outflow concentration resulting from an instantaneous injection of mass in the recharge flow. Consequently, the application of an initial unit mass of solute in the recharge zone is simulated with a zero background concentration and the normalized breakthrough of mass solute at the pumping well corresponds to the travel time pdf [*Zoellmann et al., 2001*].

In the first step, the travel time pdfs of contaminant are simulated for each scenario to study the effect of the different configurations on the travel time distribution of contaminant. In the second step, the evolution of contaminant concentration at the pumping well is simulated for each scenario from the year 1950 to the year 2050, assuming that contaminant input rate is 20 g/d in the period 1950 – 2010 and 3 g/day in the period 2011 – 2050.

2.2.4. RESULTS

Figure 2.2 shows the probability density function (pdf) of travel time calculated using a daily time step and Figure 2.3 shows the evolution of contaminant concentration at the pumping well for the period 2010 – 2040. Table 2.1 reports some characteristic properties of the calculated travel time pdfs: the 5% and 95% quantiles [days], the mean travel time of contaminants [days], the time of maximum travel time probability [days] and the shape of the distribution (unimodal or bimodal).

A first observation in Figure 2.2 is that the travel time distribution is mainly spread over a range of time from 0 to about 10000 days, with likely a very long tailing beyond 10000 days that is insignificant.

The second observation is that the shape of the travel time pdfs varies significantly, according to the various scenarios. Travel time pdfs of scenario 1 and 5 show the highest travel time density at time 0 days followed by a monotonous decrease with time. Pdfs of scenario 2 and 4 show low probability of travel time at time 0 day and a high probability centered on 1100 and 2250 days, respectively (Table 2.1). Scenario 3 shows a bi-modal distribution of the travel time probability centered on the times 0 and 1750 days. Mean travel time is equal to 2000 days for scenario 1, 2 and 3. It is equal to 4000 and 400 days for scenario 4 and 5, respectively. All these results are summarized in Table 2.1.

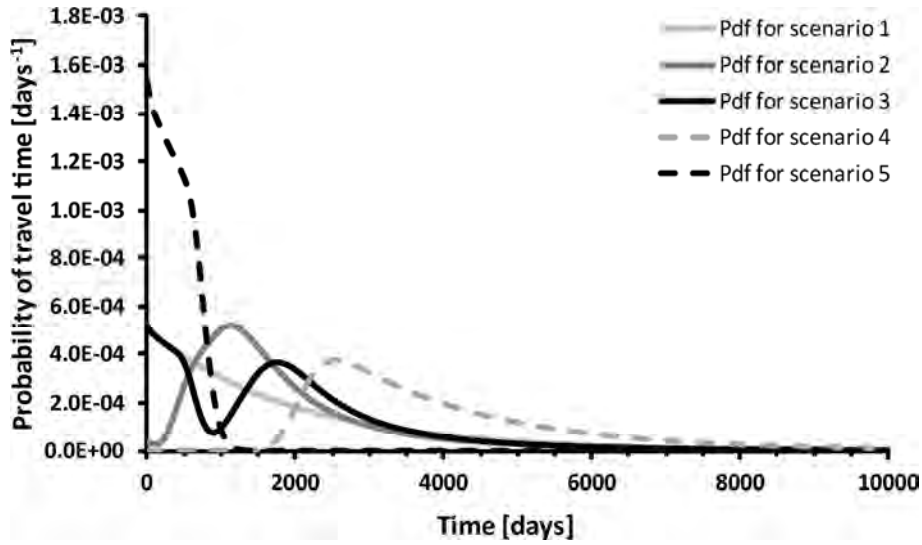


Figure 2.2 Travel time pdf of the contaminant for the various hydrogeological and mass input configurations

Characteristics of contaminant travel time pdfs				
	5%- and 95%-quantile [days]	Mean travel time [days]	Maximum of the travel time pdf [days]	Distribution of probability
Scenario 1	100 - 6000	2000	0	unimodal
Scenario 2	150 - 5200	2000	1100	unimodal
Scenario 3	100 - 5450	2000	0 and 1750	bimodal
Scenario 4	2100 - 8125	4000	2550	unimodal
Scenario 5	30 - 950	400	0	unimodal

Table 2.1 Characteristics of travel time pdf for each simulated scenario

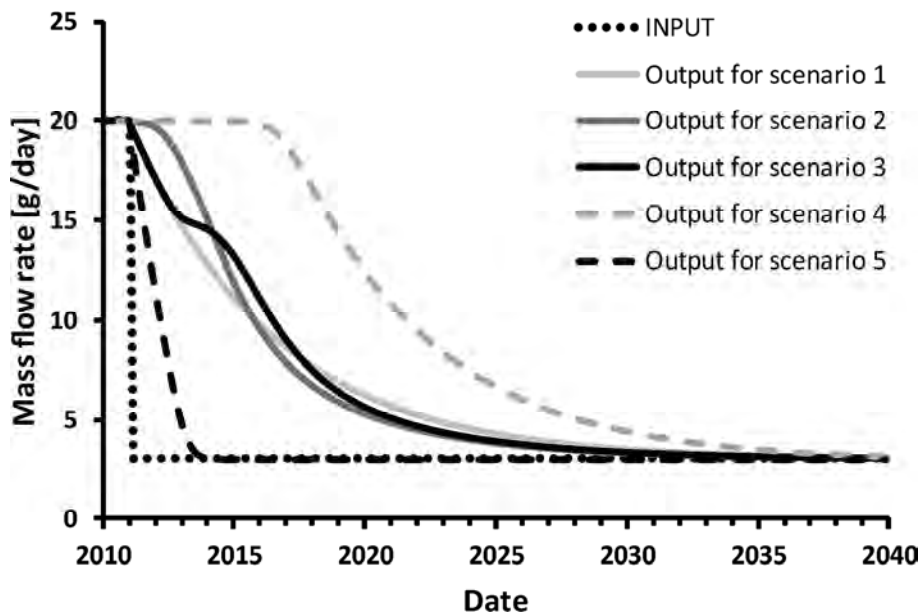


Figure 2.3 Period 2010 – 2040: mass flow rate applied on the input zone (black dashed line) and calculated mass flux rate at the pumping well (gray scale lines and grey dashed line) according to each scenario of Figure 2.1.

Figure 2.3 shows a large difference of the contaminant concentration evolution between the various scenarios when the input mass flux decreases instantaneously from 20 g/d to 3 g/d at the year 2011. On a large time scale (i.e. a decadal scale), scenarios 1, 2 and 3 show a comparable decrease in mass arrival rate from the year 2011, reaching the 3g/d level after around 20 years. The decrease is much more rapid for scenario 5 and the mass flux reaches the 3 g/d level after 3 years. Scenario 4 contrasts with the other scenarios with a delayed decrease: the decrease is only visible after 2017. On a shorter time scale (i.e. yearly scale), the evolution of mass flux rate at the pumping well is significantly different for scenario 1 to 3: the decrease of mass arrival rate is the same for scenario 1 and 3 during the first two years (period 2011 – 2013) but differs significantly from the third year on. For scenario 2, the decrease of the mass arrival rate is delayed by 1-2 years, but the reduction rate is very high after the year 2013.

2.2.5. INTERPRETATION

The evolution of mass flux at pumping well for each scenario (Figure 2.3) must be interpreted according to the travel time distribution of the contaminant, which is in relation to the hydrogeological configuration of each scenario and the spatial distribution of mass input.

Scenario 1 is the simplest configuration: the hydraulic conductivity is homogeneous and mass input flux is homogeneously distributed on the recharge zone (Figure 2.1). The travel time distribution tends to follow an exponential model (Figure 2.2). This is in accordance with previous studies [Haitjema, 1995; Luther and Haitjema, 1998; Etcheverry and Perrochet, 1999; Kazemi et al., 2006] showing that the travel time distribution in aquifers of constant thickness and porosity follows such an exponential model. In the unconfined homogenous system, an immediate improvement of the water quality occurs due to the arrival of less polluted water that has infiltrated close to the well (Figure 2.3). Due to the accumulation of recharge water along the flow system, the flow velocity increases linearly towards the well. As a result, contaminated water close to the well is flushed out most rapidly leading to a steep concentration decrease after implementing measures (period 2011 – 2015) that then slowly levels out (period 2020 – 2040).

Scenario 2 includes a low hydraulic conductivity zone for the part of the aquifer near the pumping well. The change of input mass flux from the year 2011 affects the pumping well with a certain delay, compared to scenario 1. This configuration is well represented by the travel time distribution (Figure 2.2), where travel time pdf is low for times < 500 days. These aspects can be explained by the two layer system of the aquifer configuration. Under a homogeneous recharge rate, which is enforced in the simulations, the velocity of water is higher in the deeper layer than in the shallow layer, due to the contrast of hydraulic conductivity (10^{-3} and 10^{-5} m/s). As consequence, a part of the mass input located in the

lower conductivity zone tend to be transported toward the deeper layer. Hence, the travel time from the input zone to the pumping well is slightly increasing, compared to the homogeneous configuration of scenario 1.

Scenario 3 shows a zone of low hydraulic conductivity at the center of the recharge zone (Figure 2.1). By reasoning analogous to the previous section (Scenario 2), the arrival of contaminants coming from this recharge area is delayed compared to the general contaminant flux in the aquifer. This aspect is well represented by the bimodal distribution of the travel time, with a decrease of travel time pdf around 1000 days (Figure 2.2). As a consequence, the reduction of mass flux tends to slow down around year 2014 before to quicken again.

Scenario 4 includes a mass input zone located at a certain distance from the well (Figure 2.1). In this case, the contaminant arrives at the pumping well only after some time (the necessary time for the contaminant travel from the input zone to the well). Consequently, the travel time pdf is zero for an initial period (0 to 1500 days) and is maximal at around 2550 days (Figure 2.2 and Table 2.1). With this configuration of mass input, the reduction of mass flux at the well is delayed in comparison with the other hydrogeological scenarios (Figure 2.3).

Scenario 5 shows a mass input zone located close to pumping well (Figure 2.1). In this part, the accumulation of recharge along the flow leads to a high velocity flow. Consequently, most of the contaminants directly reach the pumping well with a very small travel time and the maximum of the travel time pdf is close to 0 days (Figure 2.2 and Table 2.1). This aspect explains the strong and quick reduction of mass flux at the pumping well (Figure 2.3).

2.2.6. DISCUSSION

Based on five variants of hydraulic conductivity configurations (scenario 1, 2 and 3) and of mass input distributions (scenarios 4 and 5), this study presents five distributions of contaminant travel time distinct from each other and five distinct evolutions of mass flux rate at the pumping well. These results lead to the following conclusions.

First, the aquifer characteristics, like the hydraulic conductivity distribution, can have a significant impact on the travel time distribution of a contaminant in the aquifer (Scenario 2 and 3). Consequently, even if the mean travel time of contaminant is the same (2000 days for scenario 1, 2 and 3 in Table 2.1), the travel time distribution can be significantly different (Figure 2.2). Second, the travel time distribution of the contaminant controls the mass flux evolution at the pumping well, in relation with the mass flux history at the input zone. Different travel time distributions (Figure 2.2) lead to a different evolution of contaminant flux at the pumping well (Figure 2.3). Third, the delay of the reaction in pumping well (Figure 2.3) is well correlated with the mean travel time of contaminants reported in Table 2.1 (400

days for scenario 5; 2000 days for scenario 1, 2 and 3; 4000 days for scenario 4). The mean travel time of contaminant could consequently give a first idea on the reaction time of the system to variation of input mass flux. Finally, it highlights that the mean transit time of water (2000 days according to Equation 2.1) does not necessarily correspond to the mean travel time of contaminant (for example 400 and 4000 days for scenario 4 and 5 in Table 2.1). Mean transit time of water in the aquifer and mean travel time of contaminant are independent if the recharge zone does not correspond to the input zone (Figure 2.1). In this case, the knowledge of the mean transit time of water in the aquifer system is not sufficient to interpret observed evolution of mass flux at the pumping well.

In conclusion, when a variation of mass input occurs in the capture zone, the evolution of the mass flux at the pumping well is mainly controlled by the travel time distribution of the mass, from the input zone to the well. As expressed in Fiori and Russo [2008], "*the travel time distribution $f(t)$ is a global descriptor of the system response to a contamination event*". The knowledge of the mean travel time of contaminants is not sufficient to characterize this distribution but it can give a first idea about the reaction time of the system. Hence, the characterization of the reaction time of the system to contamination events using the mean transit time of groundwater should be avoided or carried out carefully.

2.3. THE TRANSFER FUNCTION APPROACH FOR THE QUANTIFICATION OF THE EVOLUTION OF CONTAMINANT CONCENTRATION AT PUMPING WELLS

2.3.1. INTRODUCTION

The transfer function approach was introduced in hydrogeology for the interpretation of groundwater age, based on the study of environmental tracers [Maloszewski and Zuber, 1982; Zuber, 1986a]. Although this approach is poorly documented for groundwater pollution studies, it has recently been used for the quantification of nitrate evolution at pumping wells [Osenbrück *et al.*, 2006] and at springs or for the characterization of the transfer of pesticides through the vadose zone [Stewart and Loague, 2004]. The approach is based on two key elements, the convolution integral and the transfer function, which are defined in more details in the first part of this section. In a second step, the application of the approach for the quantification of contaminant evolution at the pumping well is demonstrated in a conceptual example. The conditions of its application are introduced in the final part.

2.3.2. DEFINITION OF THE TRANSFER FUNCTION

The notion of transfer function, in the framework of the present study, refers to a mathematical description of the transfer of a solute through an aquifer system, which means from an input zone to an outlet defined in the aquifer system. This involves first a definition of the outlet, which can be for example a pumping well, a spring, a stream or the surface of

the water table, if the study is focused on the transfer through the unsaturated zone. Second, this involves a definition of the input zone, which has to correspond to the capture zone of the outlet considered. Indeed the transfer function approach assumes that the system aquifer is closed between the inlet and the outlet. A typical example, which is the standard case of this study, is the definition of a pumping well as the outlet and of its capture zone as the input zone.

The transfer function of a solute describes the probability that the solute, coming from the input zone, reaches the outlet after a certain time of travel. Mathematically, the transfer function corresponds to a probability density function of travel time (travel time pdf), that can be illustrated by the examples of Figure 2.2. More precisely, the integral of the transfer function $g(\tau)$, between the instant t_1 and the instant t_2 , corresponds to the probability that the travel time τ takes place between time t_1 and time t_2 , which is formulated in Equation 2.2.

$$\Pr(t_1 \leq \tau \leq t_2) = \int_{t_1}^{t_2} g(\tau) d\tau; \quad \text{Equation 2.2}$$

with $\Pr(t_1 \leq \tau \leq t_2) \in [0; 1]$. For a conservative transport, there is no loss of mass between the input zone and the outlet, which means that $\Pr(0 \leq \tau \leq +\infty) = 1$. If a part of the input mass is degraded before reaching the pumping well, due to bio-geochemical processes within the aquifer, then $\Pr(0 \leq \tau \leq +\infty) < 1$.

Hence, the transfer function $g(\tau)$ describes three aspects of the transfer: (1) the spatial distribution of the contaminant source in the input zone; (2) the dispersion and retardation processes affecting the transported contaminant in the aquifer; (3) the loss of mass in the aquifer system.

2.3.3. THE CONVOLUTION INTEGRAL EQUATION AND ITS VARIANTS

The convolution integral equation describes the relation between an input and an output concentration of a tracer, in a steady state flow aquifer system. The definition of the convolution integral equation is (Equation 2.3) [Zuber and Maloszewski, 2001; Osenbrück et al., 2006; Leibundgut et al., 2009]:

$$C_{\text{OUT}}(t) = \int_0^t C_{\text{IN}}(t - \tau) f(\tau) \exp(-\lambda\tau) d\tau \quad \text{Equation 2.3}$$

The observed concentration of tracer $C_{\text{OUT}}(t)$ at the outlet is related to the known input function $C_{\text{IN}}(t)$ of tracer on the capture zone of the outlet, through a transfer function $f(\tau)$ describing the travel time distribution of a conservative tracer from the input zone to the outlet, which means through both unsaturated and saturated zones. t is the observation

time and τ is the travel time. As it has been mainly introduced in hydrogeology for the study of environmental radioisotopes [Maloszewski and Zuber, 1982; Zuber, 1986a], this expression of the convolution integral equation includes a decay constant λ in the case of a first-order exponential decay of the tracer.

For the study of the relation between the input concentration and output concentration of a solute, a variant of Equation 2.3 can be introduced (Equation 2.4) [Jury and Roth, 1990; Zoellmann et al., 2001] :

$$C_{\text{OUT}}(t) = \int_0^t C_{\text{IN}}(t - \tau)g(\tau)d\tau \quad \text{Equation 2.4}$$

where $g(\tau)$ directly integrates the degradation of the studied chemical element during its travel in the aquifer system. The difference here is that the compound can be subject to any degradation mechanism and not only a first-order exponential decay as expressed in Equation 2.3. This implies that, in Equation 2.4, the integral of $g(\tau)$ from 0 to $+\infty$ (as formulated in Equation 2.2) can be lower than 1.

The convolution integral equation can also refer to the relation between the mass flux rate $M_{\text{IN}}(t)$ at the input zone and the mass flux rate $M_{\text{OUT}}(t)$ at the outlet of the aquifer system, as reported in Fiori and Russo [2008]. The integral equation becomes (Equation 2.5):

$$M_{\text{OUT}}(t) = \int_0^t M_{\text{IN}}(t - \tau) \cdot g(\tau) \cdot d\tau \quad \text{Equation 2.5}$$

where $M_{\text{OUT}}(t) = Q_{\text{W}}C_{\text{OUT}}(t)$ and $M_{\text{IN}}(t) = Q_{\text{W}}C_{\text{IN}}(t)$, with Q_{W} the constant recharge/discharge rate of water.

It must be emphasized that the use of Equation 2.3, Equation 2.4 and Equation 2.5 involves a steady state flow in the aquifer system. In the next part of this study, Equation 2.4 will be called the convolution integral.

2.3.4. ILLUSTRATION BY A CONCEPTUAL EXAMPLE

Figure 2.4 illustrates the various terms of Equation 2.4, in the context of the transfer of a solute in a schematic aquifer system, delimiting the capture zone of a pumping well. Existing approaches to characterize the transfer function are presented further, in Section 2.4.

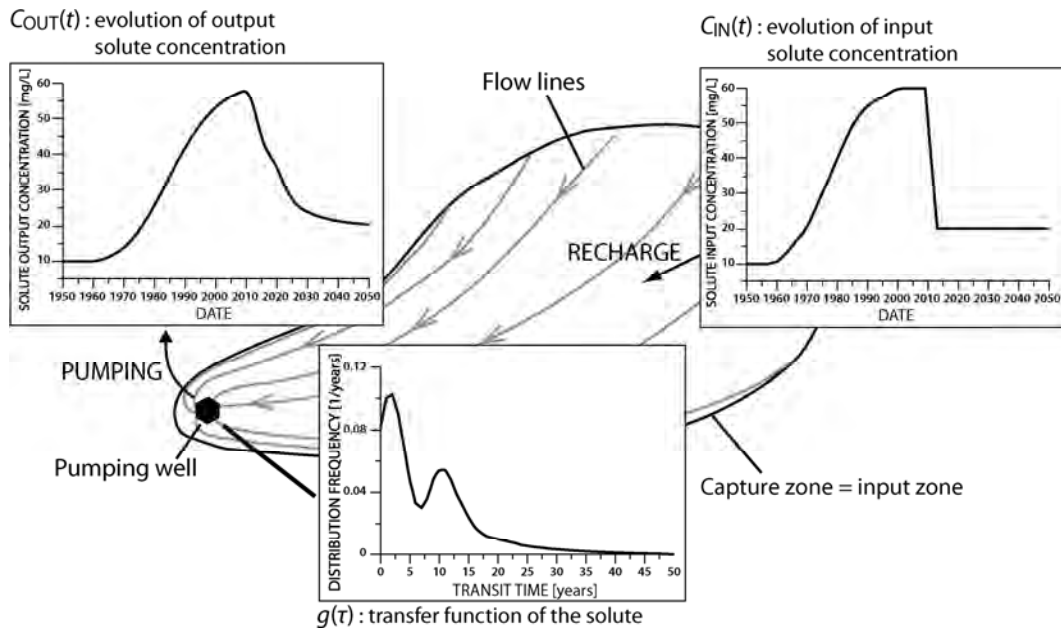


Figure 2.4 Conceptual model of an aquifer system and illustration of the three terms of the convolution integral (Equation 2.4), which are: $C_{IN}(t)$ the input function of contaminant concentration on recharge flows; $g(\tau)$ the transfer function of the contaminant from the recharge zone to the pumping well; $C_{OUT}(t)$ the contaminant concentration in pumping flow of the well.

The solute is uniformly applied on the capture zone following a history of recharge concentration, represented by the function $C_{IN}(t)$. The solute is transported through the aquifer towards the pumping well according to a travel time distribution represented by the transfer function $g(\tau)$. The solute concentration in the pumped water follows the output concentration function $C_{OUT}(t)$. The pumping rate is constant and equal to the recharge rate.

As it is demonstrated in the previous section, the transfer function depends (1) on the diversity of flow lines followed by the solute, themselves dependent on the location of recharge point and the hydrogeological characteristics, controlling flow pathways and dispersion within the aquifer, and (2) on the velocity of travel along these flow lines, themselves dependent on the hydrodynamic conditions and the retardation processes affecting the solute transport.

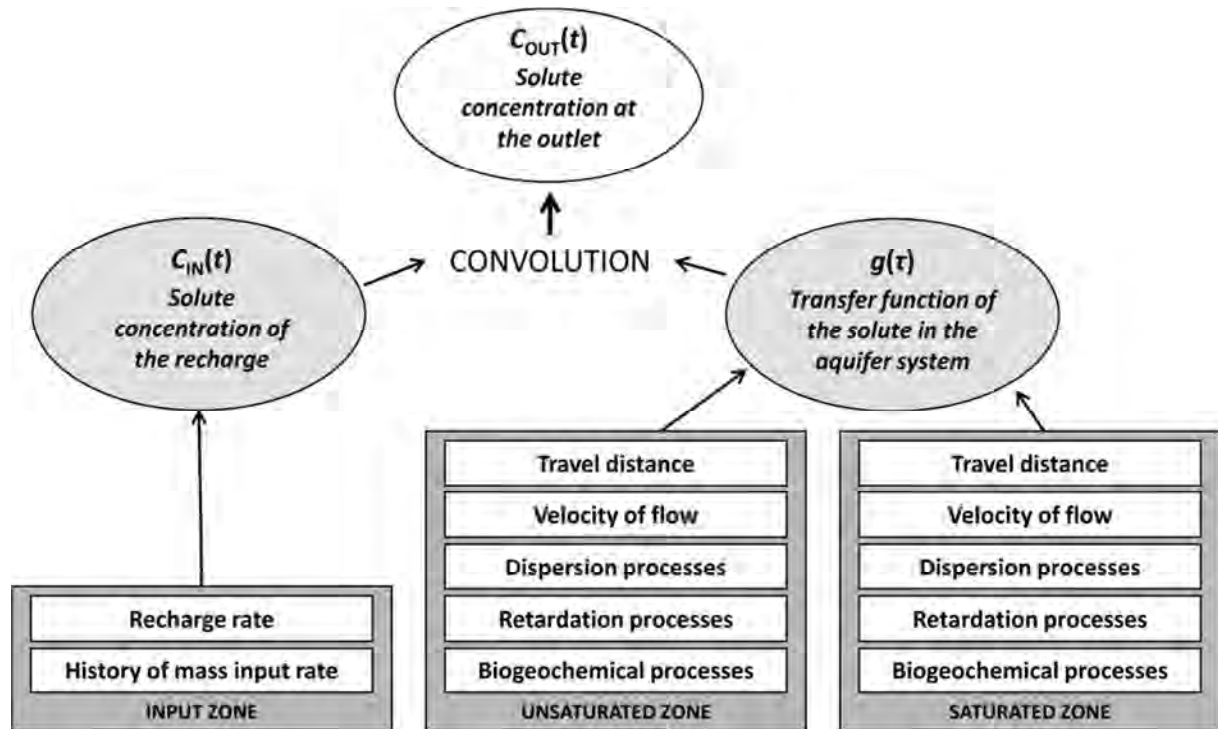


Figure 2.5 Using the convolution integral equation in the context of aquifer contamination, the evolution of contaminant concentration at a pumping well $C_{OUT}(t)$ is calculated with the function of contaminant concentration $C_{IN}(t)$ in the recharge and the transfer function $g(\tau)$ of contaminant into the system (including the saturated and unsaturated zone). $C_{IN}(t)$ is controlled by the history of mass input and the recharge flow. $g(\tau)$ is controlled by the travel distance of solute, the flows velocity into the system and the dispersion, retardation and biogeochemical processes.

Figure 2.5 summarizes the links between the three functions of the convolution integral (Equation 2.4) and shows the various parameters controlling these functions in different compartments of the system: the input zone, the unsaturated zone and the saturated zone. The history of the input solute concentration $C_{IN}(t)$ is controlled by the ratio between mass application rate and the recharge rate. The transfer function $g(\tau)$ is assumed to represent the travel times of solute both in the unsaturated and saturated zone. The transfer function is controlled by these various parameters: travel distance of the solute, flow velocity, retardation processes, dispersion processes and biogeochemical processes in the system. All these parameters are controlled by the characteristics of the aquifer and of the studied solute.

2.3.5. CONDITIONS OF USE

The use of the convolution integral (Equation 2.4) relies on several assumptions: (1) steady-state flow in the aquifer system, (2) homogeneity of the distribution of mass flux rate in the input zone and (3) a closed aquifer system between the input zone and the outlet.

The first assumption is the time-independence of the transfer function, which is valid for steady state flow in the aquifer system. In reality, steady state is unlikely to occur in most cases, particularly because recharge rates, and more generally boundary conditions, are

transient. As a consequence, solutes entering in different periods of the year might experience a different travel time distribution, depending on the initial hydrodynamic conditions and the evolution of the boundaries conditions like recharge and pumping rates [Fiori and Russo, 2008; Van der Velde et al., 2010]. Nevertheless some authors pointed out that hydrodynamic condition in steady-state can be assumed in aquifer systems in which the variation of the volume is sufficiently small compared to the total volume of the system [Zuber, 1986b; Maloszewski and Zuber, 1996]. More precisely, if the characteristic period of hydrodynamic fluctuations is smaller than the mean travel time of solutes in the aquifer system, some authors consider that the system is sufficiently buffered to reduce the variations of the travel time distribution [Zuber et al., 1986; Osenbrück et al., 2006; Badoux, 2007; Zuber et al., 2011]. In this case, the transfer function tends to become time-independent, in other words invariant with the observation time.

The second assumption is the homogeneity of solute flux in the input zone. This assumption is valid for environmental tracers, which are generally of an atmospheric origin and hence very homogeneous at the scale of the groundwater catchments.

In the case of diffuse contaminants, the land use distribution leads to a mass input not necessarily homogeneously distributed in the recharge zone. One approach to deal with this variability is to spatially average the solute input rate in the whole capture zone of the pumping well, as was done for example by Osenbrück et al. [2006]. However, as demonstrated in the previous section, the location of mass input can have a strong impact on the travel time distribution of the solute through the aquifer system. Consequently averaging the mass input on the entire input zone can lead to a strong discrepancy between real and calculated concentration evolution at the pumping well.

The third assumption is an aquifer system closed between the input zone and the outlet, at least regarding the transfer of mass. Indeed, aside from the loss of mass due to potential degradation within the aquifer system, the transfer function approach is based on the principle that the mass input reaches the outlet. Hence, the definition of the input zone should strictly correspond to the capture zone of the outlet.

2.3.6. DISCUSSION

The convolution integral (Equation 2.4) provides the mathematical relation between the input and the output solute concentration in an aquifer system. The input solute concentration function $C_{IN}(t)$ and the transfer function of solute $g(\tau)$ are the two necessary elements that are required to resolve the equation. The transfer function depends on the intrinsic characteristics of the aquifer and on the spatial distribution of input, but is also specific to the nature of the solute and its interactions with the media. The transfer function must particularly account for the retardation and degradation processes during the transport of the solute in the aquifer. This is for example the case for nitrate that can be subject to bio-

degradation by denitrification or the case for pesticides strongly subject to retardation by sorption processes.

The transfer function approach is based on the following assumptions:

- a steady state condition in the aquifer system
- a homogenous historical change in recharge concentrations in the capture zone
- an input zone that corresponds to the capture zone of the outlet

Hence, the use of such an approach requires controlling if these three conditions can be assumed in the studied aquifer system.

2.4. REVIEW OF METHODS TO QUANTIFY TRANSFER FUNCTIONS OF SOLUTE IN AQUIFERS

2.4.1. INTRODUCTION

The previous section shows, under some conditions, the links between the characteristics of the transfer function and the response of groundwater quality at the pumping well to a contamination event. Consequently, the application of the transfer function approach requires mathematical description of the transfer function. This chapter gives a short review of the main existing methods for the characterization of the transfer function for aquifer systems.

Based on the scientific literature, such approaches can be classified as follow: (1) numerical approaches, (2) analytical approaches and (3) tracers methods. The main characteristics, advantages and drawbacks of each method and the possible combinations are discussed in this section and are reviewed in Table 2.3.

At first, the approaches for the saturated zone of the aquifer are reviewed. Nevertheless, almost all of these approaches are also valuable for the unsaturated zone, as it will be reported later.

2.4.2. NUMERICAL APPROACHES

Numerical approaches are based on a mathematical model of flow and transport in aquifers, using computing tools such as: MODFLOW, FEFLOW [Diersch, 2009] or HYDROGEOSPHERE [Therrien *et al.*, 2007].

A usual numerical tool for the determination of the transfer function is the particle-tracking analysis. In this case particles are uniformly distributed on the inflow limits of the model and forward flow is simulated [McMahon *et al.*, 2008; Van der Velde *et al.*, 2010; Eberts *et al.*, 2012]. The travel time distribution of particles is then calculated from the age and number of particles reaching the pumping well over time. This relatively simple method is based on a purely advective transport through the aquifer and does consequently not take into account the dispersion processes during the transport as well as the interaction of the solute with the aquifer media. It is based on a steady state flow assumption in the aquifer [McMahon *et al.*, 2008; Eberts *et al.*, 2012] or calculated for different time steps for transient state flow

[*Van der Velde et al., 2010*]. In a more complex way, *Weismann et al. [2002]* and *Frind et al. [2002]* compute travel time distribution in wells, using a backward-time particle tracking approach in a model of flow and transport simulated by a random-walk particle method, as detailed in *LaBolle et al. [1998]*. According to *Cornaton [2004]*, simple particle-tracking approach is nevertheless not a suitable method to compute travel time distribution, since groundwater volumes are not associated to the simulated ages.

According to some authors [*Jury and Roth, 1990; Zuber and Maloszewski, 2001*], the travel time pdf corresponds to the response function to an instantaneous unit mass flux impulse. As a result another numerical approach consists in a forward transport simulation of a solute impulse applied on the recharge zone [*Varni and Carrera, 1998; Zoellmann et al., 2001; Wriedt and Rode, 2006*] and the transfer function of solute from the recharge zone to the well is assimilated to the normalized mass flux breakthrough curve of solute at the pumping well. This method is very interesting because, on the contrary to the particle tracking analysis, the computed transfer function takes into account the transport parameters, particularly the dispersion, retardation and degradation parameters, included in the process. However it requires a steady state flow conditions.

The simulation of the solute breakthrough can be applied in a backward steady state flow and transport simulation. The unit injection of solute is applied in the well and the normalized breakthrough of solute, corresponding to the transfer function, is computed at any observation point of the capture zone. In this case, the calculated transfer function corresponds to the travel time distribution of a punctual solute injection at the observation point of the capture zone. In this backward configuration the probability of capture can additionally be computed by a permanent injection of a unit concentration mass of solute in the well [*Cornaton, 2004; Cornaton and Perrochet, 2006b; Lim et al., 2010*]. As a result, it is possible to calculate for each point of the capture zone first the travel time distribution and, second, the probability of capture, which statistically corresponds to the fraction of mass input that reaches the pumping well. The transfer function of the solute in the aquifer system can be calculated by combining both results. This methodology, not well described in the literature, has many advantages because the transfer function is defined at each input point of the capture zone. It is particularly suited for the study of the transfer of point source pollutions. However, the method is less suitable for the study of the transfer of pollutions from diffuse sources. Indeed, in that case, the various calculated transfer functions have to be spatially integrated over the pollution source area to obtain a transfer function representative for the input zone of diffuse pollution, which is an additional step of computation that is not easily carried out.

Another numerical approach to compute the transfer function is the reservoir theory, recently developed for three-dimensional model of flow and advective-dispersive transport in aquifers [*Etcheverry and Perrochet, 2000; Cornaton and Perrochet, 2006b*]. The reservoir

theory is based on a deterministic characterization of the internal age statistical distribution in the aquifer system, leading to the computation of the travel time pdf at each outlet boundary of the aquifer system. This method is certainly the most powerful tool for transfer functions determination, since all deterministic parameters of flow and transport in the aquifer are taken into account. Nevertheless, its application requires some specific numerical tools to resolve mathematical models, like the computational tool Groundwater [Cornaton, 2007], which are not yet widely used in hydrogeology.

From the simplest particles tracking method to the reservoir theory application, numerical tools provide a large range of approaches to compute the transfer function of an aquifer system. All these methods are based on a good characterization of the boundaries, initial conditions and parameters of the aquifer system. The calibration of the parameters of the numerical model, particularly the transport parameters, is often based on data of artificial, natural or environmental tracers. A combination of the numerical methods with tracers methods, introduced in section 2.4.4, is consequently advisable.

2.4.3. ANALYTICAL APPROACHES

Transfer functions can be defined using analytical approaches. Their applications are reported in some articles for the estimation of the evolution of groundwater quality at the outlet of aquifer systems following a transfer function approach [Lerner and Papatolios, 1993; Beltman et al., 1996; Stewart and Loague, 2004; Osenbrück et al., 2006; Eberts et al., 2012]. The expression of the transfer function can be obtained by two different means: a purely analytical model or a lumped parameter model.

The transfer function can be derived from the analytical equation governing the solute transport in aquifers in simple configurations. Some examples are described in Kazemi et al. [2006] for various conceptual 2D groundwater flow models. The formulation of an analytical equation of the transfer implies a simple geometry of the aquifer and a rather homogeneous spatial distribution of the parameters of flow and transport. Otherwise, when the spatial variation of the properties is too complex, a numerical characterization of the transfer function can be required, following the methods described in the previous section. Nonetheless, Luther and Haitjema [1998] suggests that the transfer function in heterogeneous unconfined shallow aquifers can be commonly described by an exponential model (Equation 2.7), assuming that the main transport parameters of the aquifer (recharge rate i , porosity ϕ and thickness e) vary in such way that the ratio $T = e\phi/i$ is constant in the investigated domain. When these conditions are observed, the analytical model of transfer function is interesting because the main factors controlling flows and transport in the aquifer can be quantitatively included in the calculation.

Transfer functions can also be defined using lumped parameter models (LPMs). The lumped parameters models (LPM) were introduced in hydrogeology by Maloszewski & Zuber [1982] in order to describe the transfer function of environmental tracers in aquifers and, by Jury [1982], for the characterization of transfer functions of solutes in soils. The transfer function is described by a parametric function, the LPM, with a shape related to the characteristics of the aquifer [Zuber, 1986a]. This section does not precisely analyze the criterion of choice for either of the models, nevertheless, typical examples of applications can be found in the published literature. The exponential model is rather useful for the saturated zone [Haitjema, 1995; Maloszewski and Zuber, 1996], whereas dispersion models can be used for transfers in the unsaturated zone [Jury and Roth, 1990; Beltman et al., 1996; Stewart and Loague, 2003; Mattern and Vanclooster, 2010] and in the saturated zone as well [Osenbrück et al., 2006]. More details about the aquifer configurations underlying the LPMs can be found in Zuber [1986a], Kazemi et al. [2006] and Eberts et al. [2012].

While LPMs are generally derived from the analytical equations of transport in conceptual simple models of aquifers, the parameters of the equation are however not directly linked with the intrinsic characteristics of the aquifer system. The function is generally calibrated with the known input and output data of solute or environmental tracer concentrations in the aquifer system. In published literature, this approach is mainly based on environmental tracer analyses, which find applications for groundwater ages interpretation [Maloszewski and Zuber, 1982; Zuber and Maloszewski, 2001] and for groundwater quality predictions, at pumping wells for example [Osenbrück et al., 2006; Eberts et al., 2012]. In this last case, this refers also to tracer methods, described further in Section 2.4.4.

The main LPMs of solute transfer functions are described in Maloszewski & Zuber [1982]: the piston flow model, the dispersion model, the exponential model and the combined exponential-piston flow model. The Fickian Model, reported in Jury & Roth [1990], is equivalent to the dispersion model, with the relation $P_D = \alpha_L / Z \cong D / VZ$ (neglecting the molecular diffusion, parameters defined in the caption of Table 2.2). The lognormal model [Jury and Roth, 1990] and the three-parameter gamma distribution model [Amin and Campana, 1996] can also be used as models of solute transfer subject to dispersion processes.

To date, the new formulations of LPMs, in the context of solute transfer in aquifers, has not been described since Amin & Campana [1996], with the development of the gamma distribution model in the context of various flow configurations in aquifers. These LPMs formulations are reported in Table 2.2.

Model	Lumped parameter models of transfer function	
Piston	$g(t) = \delta(t - T)$	Equation 2.6
Exponential	$g(t) = T^{-1} \exp\left(-\frac{t}{T}\right)$	Equation 2.7
Exponential-piston	$g(t) = \frac{\eta}{T} \exp\left(-\frac{\eta t}{T} + \eta - 1\right)$	$, t \geq T(1 - \eta^{-1});$ Equation 2.8
	$g(t) = 0$	$, t < T(1 - \eta^{-1})$ Equation 2.9
Dispersion	$g(t) = \frac{1}{\sqrt{4\pi P_D \frac{t}{T}}} \frac{1}{t} \exp\left[-\frac{(1 - \frac{t}{T})^2}{4P_D \frac{t}{T}}\right]$	$, P_D = \frac{\alpha_L}{Z} \cong \frac{D}{VZ}$ Equation 2.10
Fickian	$g(t) = \frac{Z}{2\sqrt{\pi D t^3}} \exp\left[-\frac{(Z - Vt)^2}{4Dt}\right]$	Equation 2.11
Log-normal	$g(t) = \frac{1}{\sqrt{2\pi\sigma t}} \exp\left[-\frac{(\ln(t) - \mu)^2}{2\sigma^2}\right]$	Equation 2.12
3-parameter gamma distribution	$g(t) = \frac{\exp\left[-\frac{(t - \gamma)}{\beta}\right]}{\beta^\alpha \Gamma(\alpha)} (t - \gamma)^{\alpha-1}; t \geq \gamma, \quad \gamma \neq 0$	Equation 2.13

Table 2.2 The lumped parameters models of transfer functions; the input parameters of the equations are: the mean travel time T [T], the ratio of the total volume of the system to the exponential flow volume η [-], the dispersion parameter P_D [-], the travel length Z [L], the dispersivity α_L [L], the effective diffusion-dispersion coefficient D [L² T⁻¹], the velocity of travel V [L T⁻¹], the mean μ [T] and the standard deviation σ [T] of the natural logarithm of the time, the scale parameter β , the location parameter γ , the shape parameter α and the gamma function $\Gamma(\alpha)$.

The lumped parameters models have originally been formulated to describe the transfer of a solute (more particularly environmental tracers) in the aquifer system, in the specific case where the solute travel times has the same characteristics as the water transit times. This means: (1) that the solute is not affected by decay and retardation processes, (2) that the input function of solute is proportional to the recharge rate of water, (3) that the input of solute affects the entire capture zone of the aquifer system.

These assumptions are very well suited for most environmental tracers because they are not affected by retardation processes, because the input functions are proportional to the recharge rate as they come into the aquifer system with precipitations, and because the solute input affects the entire aquifer recharge zone. Some tracers are affected by well known decay processes in the aquifer system (⁸⁵Kr or ³H for instance), but the decay is then directly included in the convolution integral, with an added decay term [Zuber, 1986a], as expressed in Equation 2.3.

For the use of LPMs for retarded and nonconservative transfer, Jury & Roth [1990] demonstrate that the transfer function of a solute subject to a first order decay and to a linear retardation during its transport can be deduced from the transfer function of a tracer, with the same flow conditions, that would not be subject to retardation and decay processes and to which decay and retardation factors are added following Equation 2.14:

$$g(t) = \frac{\exp(-\lambda t)}{R} g_m\left(\frac{t}{R}\right) \quad \text{Equation 2.14}$$

where $g_m(t)$ is the transfer function of a non-reactive and conservative solute, R and λ are respectively the retardation and decay factors¹.

The relation of Equation 2.14 can be applied for all the lumped models of transfer functions reported in Table 2.2. By including the retardation and decay factors R and λ , the resulting transfer functions can be applied for nonconservative solutes and reactive transport. Based on a transfer function characterized by a dispersion model (Equation 2.10), Figure 2.6 illustrates the effect of the retardation and decay factors on the characteristics of the transfer.

¹ Chemical reactions such as radioactive decay and certain forms of biogeochemical degradation can be characterized by a first-order kinetic of decay, described as an exponential decay (where C_0 is the concentration at time $t = 0$; $C(t)$ is the concentration at time t ; λ is the decay constant and $t_{1/2}$ is the half-life of the reactive mass):

$$\frac{C(t)}{C_0} = \exp(-\lambda t) \quad \text{with} \quad \lambda = \frac{\ln 2}{t_{1/2}}$$

The effect of sorption on transport can be characterized using the retardation factor, described as the ratio between the mean transit time T of transported mass affected by sorbing processes and the mean transit time T^* of the transported mass under conservative transport, assuming that the sorption is linear through the system. The retardation factor R can therefore be written as:

$$R = \frac{T}{T^*} \quad (R \geq 1)$$

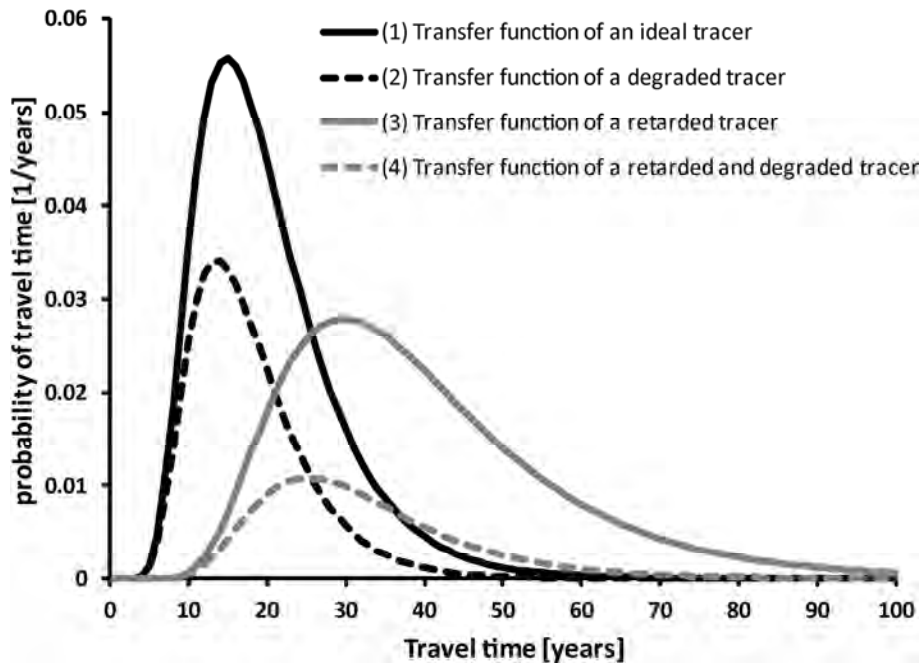


Figure 2.6 Four variants of a transfer function characterized by a dispersion model with the common parameters $T=20$ years and $P_D=0.1$. The function (1) characterizes a conservative and non reactive transport ($\lambda=0$ and $R=1$). The function (2) characterizes a non conservative and non reactive transport ($\lambda=0.035$ and $R=1$). The function (3) characterizes a conservative and reactive transport ($\lambda=0$ and $R=2$). The function (4) characterizes a nonconservative and reactive transport ($\lambda=0.035$ and $R=2$).

2.4.4. APPROACHES BY TRACERS

There is a large panel of tracers methods to characterize transfer functions or to give partial information on it. Tracers can directly give the characteristics of transfer functions only in very specific cases that are rarely encountered, as discussed in this section. Hence, they are more frequently used for the calibration of numerical and analytical methods, introduced in previous Sections 0 and 2.4.3.

The use of artificial tracing is a direct way to quantify, in the field, the transfer functions of a solute in aquifer systems, based on the assumption that the characteristics of transports are similar for the artificial tracer and the investigated solute. Theoretically, instantaneous artificial tracing gives a direct measure of the transfer function, by the breakthrough curve measured at the observation point. This technique is based on the assumption that the duration of tracer injection is considered as instantaneous, which is valid because injection time is negligible relative to the travel time in the aquifer.

Another technique consists in a constant rate injection of tracer in an aquifer point and the measure of its breakthrough curve at an outlet point, usually a pumping well, until the steady state of concentrations is reached. The transfer function between the two points corresponds to the normalized derivation of the tracer breakthrough curve. The tracing tests are usually carried using a point injection. The obtained transfer function is representative

only of the point injection and the extension of that transfer function to the entire capture zone is not obvious. Nevertheless, a transfer function representative for a diffuse input zone could be assessed by diffuse artificial tracing. Not well discussed in scientific literature, the use of artificial tracer to assess transfer functions in aquifers could theoretically be a suitable approach, particularly for point source pollutions but also for nonpoint source pollutions. However, this technique has some important limitations. First of all the applicability of artificial tracers covers a travel time range of few months, which limits investigations to small scale aquifers. The interactions of the artificial tracers with aquifer media must also be taken into account, especially degradation, adsorption and retardation processes. Finally, the injection must be carried out carefully to satisfy the assumption of an instantaneous injection.

Environmental tracers produce useful data for the determination of transfer function of an aquifer system. Traditionally, environmental tracers are used for groundwater dating and usually yield the mean age of groundwater after recharge and thus the mean transit time of water within the aquifer. A wide range of environmental tracers (such as SF₆, CFC, ³H/³He, ³⁹Ar and ¹⁴C) is well described in literature [Kazemi *et al.*, 2006; Leibundgut *et al.*, 2009; Newman *et al.*, 2010] and their applicability depends on to the travel time scale and the hydrogeological context. Traditionally, the transfer function is assimilated to a parameterized function based on a lumped parameter model [Osenbrück *et al.*, 2006; Eberts *et al.*, 2012]. Parameters of the transfer function are calibrated in an inverse problem [Zuber, 1986a; Maloszewski and Zuber, 1996]: calculated output concentrations of environmental tracer are fitted to observed values using convolution of the known function of tracer input with the parameterized transfer function (Equation 2.3).

Other environmental tracers such as temperature or electrical conductivity, generally called natural tracers because their origins are poorly related to human activities, are the object of recent researches in the domain of transfer functions assessment. This approach is particularly applied for river-aquifer interactions, where input and output time series of tracers are used to get the transfer function from the river to a well or an observation point [Cirpka *et al.*, 2007; Vogt *et al.*, 2009]. The transfer function is calculated by statistical and non-parametric deconvolution of input and output tracer functions [Skaggs *et al.*, 1998]. This mathematical approach also finds applications for the analysis of artificial tracing data [Fienen *et al.*, 2006].

Hence, the knowledge of the input and output concentration evolution of environmental tracers gives the possibility to assess the transfer function of these tracers from the input zone to the observation point. Environmental tracers can be generally considered as ideal tracers of the groundwater, because they are injected in the recharge zone proportionally to the water flow and in a spatially constant concentration and because they are generally conservative and non reactive. In the context of pollutant transfer, environmental tracers do however not necessarily represent the same input zone than pollution, when environmental

tracers are representative for the entire catchment area and when the natural tracers are only representative for a localized input zone (a river for instance).

Artificial and environmental tracers are able to provide useful information for the characterization of the transfer functions in aquifer systems. Nevertheless each of them presents advantages and limitations. If artificial tracers are able to give a direct measure of the transfer function, through tracer breakthrough curve, they can only be used for a short travel time scale, few months maximum. On the contrary environmental tracers provide information for a large range of travel time, but their use requires long time series. Natural tracers are usable only for a few hydrogeological contexts, especially for river-aquifer exchanges studies. Moreover, contrary to artificial tracers, data provided by natural and environmental tracers must be treated using mathematical inversion, such as parametric or non-parametric deconvolution.

2.4.5. TRANSFER FUNCTION THROUGH THE UNSATURATED ZONE

Travel times in the unsaturated zone of the aquifer must also be taken into account, especially for thick unsaturated zones, having a significant effect on the total travel time of the solute within the aquifer system. The scientific literature includes some well described classical methods: tracing [Tilahun *et al.*, 2004], numerical simulation of unsaturated flow and mass transport in the soil [Wang *et al.*, 2010], application of analytical transfer functions [Jury and Roth, 1990; Mattern and Vancloster, 2010], water balance [Zoellmann *et al.*, 2001; Fisher and Healy, 2008] or use of environmental tracers [Schwientek *et al.*, 2009].

2.4.6. SUMMARY AND DISCUSSION

Table 2.3 summarizes and compares the various methods that can be used to estimate the transfer functions in aquifer systems.

The numerical methods allow characterizing the transfer function of a solute from any input zone to any outlet of the aquifer system. They are usually combined with tracer data to calibrate the relevant parameters for the simulation of flow and transport in the aquifer. Hence, numerical methods and tracer methods are often combined for the characterization of the transfer functions.

The analytical methods are of a different nature. On the one hand, the analytical formulations can be based on the physical relationships governing flow and transport in the aquifer system. In this case, the characteristics of the aquifer system should be simple enough to allow simulating the transfer functions with simple analytical equations. On the other hand, in the usual case where the aquifer is more complex, such physically-based formulation of transfer functions is not possible and analytical formulations by lumped parameters models are required. The parameters of the lumped parameters models need to be calibrated using time series of environmental tracers at the inlet and the outlet of the aquifer. This calibration is also advised for physical-based analytical equations even if it is not an absolute necessity. Hence, analytical methods and tracer methods are also often combined for the

characterization of the transfer functions and, when the calibration is carried out using environmental tracers, the obtained transfer function is characteristic for a homogeneous input of tracers in the capture zone.

The tracers methods are based on three different types of tracers: environmental tracers (e.g. ^3H , ^{81}Kr), natural tracers (e.g. ^2H , ^{18}O) and artificial tracers. As previously discussed, times series of environmental tracers or artificial tracers are necessary to characterize the transfer functions using lumped parameter models or non parameterized functions. The direct characterization of the transfer function using artificial tracers is accessible in very specific cases, when tracers and solute input are comparable in terms of input configurations and transport properties. Generally artificial tracers are used to calibrate numerical models of flows and transports in the aquifer. Hence, tracers methods are more generally used for the calibration of transfer functions obtained by analytical or numerical methods than for a direct characterization of the transfer function.

Among the wide range of existing methods which one is the most suitable for assessing the transfer function in a specific aquifer?

The investigation of the distribution of travel time must be adapted to the hydrogeological characteristics of the site, which are linked to the geological nature of the aquifer, the recharge conditions, the scale of the system and the nature of the contaminant. Numerical simulations, for example, are well adapted for the investigation of aquifers for which the main parameters controlling subsurface flows and transports are well known. When the characteristics of the aquifers are more difficult to simulate, for example in the case of karst aquifers, analytical resolution of transfer functions, calibrated with field data or environmental tracers, should be more suited. When the target input zone is a river, natural tracer could give valuable data for the estimation of transfer function. Finally, for small scale aquifers, artificial tracing could also give pertinent data.

Nevertheless, data of tracers generally gives partial information about transfer functions of a specific solute coming from a specific input zone, especially because artificial and environmental tracers are not representative of the target input zone and the studied solute. On the other hand, it could be difficult to apply analytical and numerical methods, especially when the aquifer is complex or if there is a lack of field data permitting to calibrate the parameters of the transfer function.

For these last two reasons, combined approaches should be privileged by coupling the various methods. Examples of combined approaches are the calibration of a numerical simulation with environmental tracers data set [Zoellmann *et al.*, 2001] or the calibration of an analytical model of travel time distribution with tracing techniques or environmental tracers [Osenbrück *et al.*, 2006]. A combined approach could increase the reliability of the results and permit the adaptation of the investigation tools to the aquifer characteristics and the available means.

Tracers methods			Analytical methods			Numerical methods			Methods	General principles	Obtained data	Advantages	disadvantage	Conditions of application	Possible combination	References
Environmental tracer	Natural tracer	Artificial tracer	Lumped parameters model or physical-based analytical formulation	Application of the reservoir theory	Backward simulation of a pulse of solute applied at the outlet	Forward simulation of a pulse of solute applied on the catchment area										
Groundwater dating by analyzing environmental tracers (usually CFC, SF ₆ , ³ H, ³ H/ ² He)	Transfer function is calculated by statistical and non-parametric deconvolution of input and output time series of tracer data	Injection of a artificial tracer in the aquifer and measurement of the breakthrough curve in the water catchment	Transfer function is derived from an analytical equation of transport or from lumped parameters model, respectively based on the hydrogeological parameters or calibrated with environmental tracers	The reservoir theory gives the link between the distribution of water age in an aquifer and the distribution of travel times at the outlet. Based on a mathematical model of flow and transport	By Inverting of flow conditions, the breakthrough in an aquifer is simulated when an unit pulse of mass is applied at the outlet	Simulation of the breakthrough at the outlet when an unit pulse of mass is applied on the capture zone										
Mean travel time from the recharge area	Transfer function of tracer from input to output points	Travel times distribution from the injection point ; longitudinal dispersion coefficient	Travel times distribution in the water catchment	Travel times at the outlets	Travel times distribution water from one recharge point of the aquifer	Travel times distribution of water at the outlets										
Direct measurement of the mean age of water from the whole recharge area of the water catchment	No need of detailed investigations of hydrogeological characteristics, calibrations by tracer naturally present in the aquifer	Direct experimental determination of travel time and evaluation of dispersion coefficient	No need of detailed investigations of hydrogeological characteristics, calibrations by environmental tracers	Direct calculation of travel time distribution at each point of recharge or discharge	The dispersion is taking into account, the distribution of travel time can be calculated by sector of the capture zone											
Measurement of an apparent age of water, which does not consider the age distribution; Not applicable for study of sub-basin	Required particular hydrogeological context and tracer time series data set	Point investigation	Need to follow in time the environmental tracers in the water catchment	Need of a calibrated mathematical model flow and transport, specific numerical tools, steady state flow hypothesis	Need of a calibrated mathematical model flow and transport, steady state flow hypothesis											
Travel times must be in the range of environmental tracer use. Not very complex for aquifer	The fluctuations of tracer in the recharge zone must have a significant impact on the variation of the tracer at the outlet	Small scale of groundwater basin and fast travel times (few months maximum)	Require simplification on the aquifer geometry and the flow configuration or long times series of input environmental tracer concentration	Numerical methods require specific tools of calculation and the investigation of the relevant parameters for their calibration	Numerical methods require specific tools of calculation and the investigation of the relevant parameters for their calibration											
Combination with lumped parameters model approach	Combination with parameters model	Combination with numerical methods	Combination with tracers methods for the calibration of the lumped parameters	Combination with tracers methods for the calibration of transport parameters	Combination with tracers methods for the calibration of transport parameters											
[Kazemi et al., 2006; Visser et al., 2007; Leibundgut et al., 2009; Schwientek et al., 2009; Eberts et al., 2012]	[Skaggs et al., 1998; Cirpka et al., 2007; Vogt et al., 2009]	[Käss, 1998]	[Maloszewski and Zuber, 1982; Zuber, 1986a; Eberts et al., 2012]	[Cornaton and Perrochet, 2006b; a; Kazemi et al., 2006]		[Wriedt and Rode, 2006]										

Table 2.3 Main used methods for the determination of transfer function in aquifers

2.5. CONCLUSION

It is important to determine the impact of an environmental action on the evolution of groundwater quality, not only to know the groundwater quality level that can be expected after a long term but also to predict the development of groundwater quality over time. This last point brings a better understanding of the necessary time scale for environmental measures to give significant results and permits to foresee the financial repercussions.

The travel time distribution of contaminants in the aquifer is a good descriptor of hydrogeological factors controlling the delay between a contamination event on the recharge zone or the reduction of diffuse leaching of contaminant, and the observed evolution of contaminant concentration at the outlet of the aquifer, a pumping well for example. The intrinsic characteristics of the aquifer, the location of the source of contamination and the interaction of the solute with the media are the main factors controlling the distribution of travel time in the aquifer.

Two approaches are usually carried out to quantify groundwater quality evolution at the pumping well in relation to the evolution of influx contaminants in the recharge zone. The first approach is based on numerical models of flow and transport in aquifers. The advantage of the method is the possibility to take into account the spatial variability of the parameters controlling flow and transport in the aquifer. The complexity of its implementation, however, limits its use for a lot of groundwater quality remediation programs.

The second option is the transfer function approach. While its application required some assumptions, such a steady state flow and a spatially homogenous solute influx, the transfer function approach presents the significant advantages of its relative ease of implementation, once the transfer function is determined.

There is a large array of methods to evaluate the transfer function of a contaminant in the aquifer system. These methods, summarized in Table 2.3, can be classified into three types: numerical methods, analytical methods and the tracer methods.

The choice between numerical methods or analytical methods to evaluate the transfer function is mainly based on the complexity of the studied aquifer: analytical methods can be a good alternative if the system is too complex to obtain the transfer function by a numerical simulation, for technical or financial reasons. For both approaches it is possible to introduce in the mathematical resolution the retardation factor and degradation of mass during the transport. Transfer functions, determined by experimental approaches, are based on the analyses of artificial or environmental tracers, at the inlet and outlet zones. Hence, it requires less knowledge about the internal functioning of the aquifer system, which can be an advantage. However, it is associated to a specific input zone, according to the tracer used, and, if the tracer is not ideal, the obtained transfer functions are representative only for the tracer and not for the studied contaminant.

A combined approach should be favored in order to evaluate the solute transfer function with a good accuracy. Environmental tracer can for example be used to calibrate lumped parameter models of transfer functions [Osenbrück *et al.*, 2006] or to calibrate numerical simulations of transfer functions [Zoellmann *et al.*, 2001]. When the transfer functions are determined using independently numerical or analytical approaches calibrated with the same field data (such as environmental tracers), Eberts *et al.* [2012] demonstrate that both methods can give comparable results.

The necessary assumptions that are involved in the transfer function approach, limit its use for a significant part of remediation projects. The accuracy of the method can be impaired, for example when the input mass is located in a distributed manner, with a strong spatial variation, or when the flow in the aquifer is not in a steady state. Moreover the transfer function approach is based on the description of the transfer in the entire aquifer system with a unique transfer function. It could be interesting to have the possibility to consider the different transfer compartments of the aquifer (for example unsaturated and saturated zones) separately and to introduce each of them in the convolution integral equation.

A new formulation of the convolution integral is thereby required. This new formulation should permit to quantify separately the transfer function in the unsaturated and saturated zone, as it is usually the case for the most of the aquifer systems. Moreover the new formulation should permit to consider the heterogeneity of mass arrival rate in the input zone, as is generally the case in most aquifer contamination contexts. The effect of transient groundwater flow regime on the characteristics of the travel time distribution should also be studied in more details. It would allow a better understanding for which conditions the assumption of steady state flows is valid. Hence, the applicability of the transfer function approach for a larger number of remediation projects would be reinforced.

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Quantification of groundwater quality trends in pumping wells using spatially varying transfer functions

ABSTRACT

The transfer function approach is one of the methods that is used to determine the evolution of groundwater quality at the outlet of aquifers in relation to the history of pollutant inputs in the groundwater catchment. This method presents some advantages owing to its ease of implementation, which requires limited investigations of aquifer characteristics and simple computation tools. On the other hand, the application of the method is based on some conditions that limit its use for most cases of aquifer pollution: a steady-state flow conditions, a homogenous solute input on the groundwater catchment, a single solute transfer compartment in the aquifer system, a balanced flow and mass budget between the input zone and the outlet. While these conditions can be assumed in certain hydrogeological contexts, described in this study, the generalization of the approach involves new developments that are introduced.

Based on a hypothetical example, it is demonstrated that steady-state flow can be assumed when characteristic periods of the hydrodynamic fluctuations are lower than the mean travel time of solute in the system. The conditions of mass and water balance that are required to satisfy the application of a transfer function approach are described. Finally the convolution integral, a key element of the approach, is developed to include in a separate manner (1) several zones of specific solute input history and (2) several transfer compartments in the aquifer system, especially saturated and unsaturated zones of the aquifer. The solute transfer function is the central element of the convolution integral and is often described by an analytical equation. The formulation of the exponential model is enhanced to be applied for input and output zones of limited extension, notably in the context of a heterogeneous distribution of solute input in the capture zone.

3.1. INTRODUCTION

The anthropogenic pressure on the environment, mainly represented by urban, industrial and agricultural contaminant loads, is responsible for most of the groundwater pollution observed in many shallow aquifers in the world. The global increase of pollutants in groundwater observed in many parts of the world since the second half of the 20th century leads to serious problems for humans and the environment [Strebel *et al.*, 1989; *World Water Assessment Programme*, 2009; Vandenberghe, 2010].

In the last decades environmental policies were introduced in order to limit groundwater pollution, such as the European Water Framework Directive [European Union, 2000] or the Swiss Nitrate Projects [OFEV, 2002]. The decrease of pollutants level in groundwater is generally carried out primarily by limiting the source of pollution and secondly by in-situ bio- or chemical remediation, when possible. For example, groundwater pollution by nitrate, for which agriculture is the main diffuse source, is typically treated by enforcing changes of land uses: the conversion of intensive farming, which favors the leaching of nitrate in the soil, to permanent meadows or, more commonly, a decrease of nitrogen surplus in fertilizers [OFEV, 2002; Oenema *et al.*, 2005].

To better assess the financial consequences and to give more comprehensive information to land users, politicians and the public, the implementation of measures aiming to reverse the trend of increasing levels of pollutants in groundwater requires some prior knowledge of the following:

- (1) When the actions will affect the evolution of the quality of groundwater at the aquifer outlet, particularly when the improvement of quality will be significant
- (2) How the water quality will evolve in the future

As reported in many articles [Bohlke, 2002; Tomer and Burkart, 2003; Meals *et al.*, 2010; Sohler and Degre, 2010], the lag time between the remediation actions implemented on the aquifer catchment and the expected improvement of groundwater quality at the targeted aquifer outlet (which can be a pumping well, a spring or a surface stream), can be explained by the residence time of the contaminant in the aquifer, which is related to the travel time distribution of the solute between the input zones and the aquifer outlet (see Chapter 2).

According to Visser *et al* [2009], numerical simulations and methods based on transfer function are the two main approaches that can be used to calculate the effect of environmental actions on the evolution of groundwater quality, taking into account the travel time distribution of contaminant in the aquifer system. Numerical models of flow and transport in the aquifers is the more frequent approach: the simulation of pollutant load in the recharge and of its travel time through the aquifer is based on the aquifer characteristics and the subsurface flow and transport equations [Zoellmann *et al.*, 2001; Conan *et al.*, 2003; McMahon *et al.*, 2008; Orban *et al.*, 2010]. In spite of its high potential of accuracy, the

complexity of the simulation procedures can represent a limitation for applying this approach to most environmental projects.

The groundwater quality evolution at the outlet of an aquifer (pumping wells, springs or streams) can also be calculated by a transfer function approach [Lerner and Papatolios, 1993; Beltman *et al.*, 1996; Stewart and Loague, 2004; Osenbrück *et al.*, 2006; Eberts *et al.*, 2012]. The main advantage of such an approach resides in the fact that its application involves simpler calculations than numerical models [Osenbrück *et al.*, 2006; Visser *et al.*, 2009; Eberts *et al.*, 2012]. The transfer function approach is however based on three assumptions that limit its availability for most groundwater pollution contexts: (1) a steady state flow, (2) a homogeneous input of pollutant in the recharge zone and (3) a transfer of solute described by a single function. In real aquifer cases, these conditions are rarely met and the necessary approximations can lead to errors in the results. These limitations explain the reason that, in the published literature or in environmental applications, the transfer function approach is not often used to calculate the evolution of a pollutant at the outlet of an aquifer.

The general topic of this research is to develop a new method for the prediction of groundwater quality evolution, using an approach appropriate for most environmental projects. This chapter describes how the limitations of the transfer function approach can be partially removed and how this approach could hence represent a promising method to predict the evolution of a solute concentration at the outlets of the aquifers. In section 3.2, the transfer function approach, based on the convolution integral, is described as applied up to now, emphasizing the assumptions required for its implementation and the resulting limitations. Section 3.3 clarifies the hydrodynamical conditions where the steady state flow assumption is valid. The convolution integral is developed in section 3.4 in order to separately include in the calculation various subareas of the input zone, each of them showing a specific history of solute concentration input. The equation is also further developed in order to consider various transfer compartments in series, especially when the transfer of solute takes place across the unsaturated zone and the saturated zone of the aquifer. The transfer function is a key-element of the approach developed in this chapter and the analytical methods, introduced in Chapter 2, represent an interesting alternative for their characterization, as it is developed in Section 3.5.

3.2. ON SOME LIMITATIONS OF THE TRANSFER FUNCTION APPROACH AND NEEDS OF DEVELOPMENT

3.2.1. DESCRIPTION OF THE TRANSFER FUNCTION APPROACH

The evolution of a pollutant concentration at the outlet of an aquifer (for instance a pumping well, a spring or surface stream) can be estimated by a transfer function approach [Lerner and Papatolios, 1993; Beltman et al., 1996; Stewart and Loague, 2004; Osenbrück et al., 2006]. The key element of the transfer function approach is the convolution integral. The convolution integral (Equation 3.1) mathematically links the evolution of a contaminant concentration at the outlet of an aquifer to the history of solute input in the recharge zone and the transfer function of the solute through the aquifer system.

The formulation of the convolution integral is:

$$C_{OUT}(t) = \int_0^t C_{IN}(t - \tau)g(\tau)d\tau \quad \text{Equation 3.1}$$

$C_{OUT}(t)$ is the concentration of solute at the outlet; $C_{IN}(t - \tau)$ is the input function of solute concentration; $g(\tau)$ is the transfer function of contaminant from the input zone to the outlet; t is the observation time and τ is the travel time.

According to this approach, the evolution of the solute concentration $C_{OUT}(t)$ can be quantified from two elements:

- The history of solute concentration at the input zone of the aquifer system, represented by the function $C_{IN}(t - \tau)$. This requires defining precisely the part of the aquifer recharge zone where input flow reaches the considered outlet, in other words the capture zone of the outlet.
- The transfer function $g(\tau)$ that is defined in Chapter 2 as the probability distribution of travel times of a determinate solute, from an input zone to an outlet of an aquifer, considering the various pathways within the aquifer and the retardation and degradation processes affecting the travel duration and the loss of mass of solute into the aquifer. As reported in Chapter 2, the transfer function can be characterized by various approaches: numerical resolutions, analytical approaches and tracer methods.

For the rest of Chapter 3, the transfer function approach will be developed around the specific case of an outlet corresponding to a pumping well. Nevertheless, by analogy, it can be deduced that the results also apply to outlets of other natures, spring or river for instance.

3.2.2. LIMITATIONS OF THE TRANSFER FUNCTION APPROACH

In this section, the assumptions supporting the transfer function approach are revisited and described in more depth. The purpose is first to clarify in which conditions these assumptions can be satisfied and, second, to provide the required development to make the transfer function approach more flexible.

3.2.2.1. Steady state flow requirements

The steady state flow requirement is based on the nature of the convolution integral where the function $g(\tau)$ is time-invariant, in other words where it does not depend on the time of observation.

The temporal variations of flow velocities in the aquifer are dependent on the temporal variations of the recharge and the discharge: seasonal variations of recharge, variations of boundary conditions of head or unsteady pumping rate. Due to this transient flow, observed in most aquifers, the transfer function is actually time-variant and the first assumption of a steady state flow is violated in most cases.

Some authors proposed several techniques to estimate solute transfer and the output response of a solute concentration for non-steady state hydrological systems [Niemi, 1977; Lewis and Nir, 1978; Zuber, 1986a; Amin and Campana, 1996; Rodhe et al., 1996; Ozyurt and Bayari, 2005a; b]. For example, Zuber et al. [1986] propose a new formulation of the convolution integral, where the output solute concentration is weighted by the evolution of input flow and the total volume accessible to the solute in the system, and where the transfer function is defined according to the mean travel time of solute in the system. According to McGuire & McDonnell [2006], these techniques are not commonly used because of the complexity of their implementation.

According to several authors, the approximation of a steady-state flow in real hydrogeological systems is valid when their mean travel time of water is larger than the characteristic periods of hydrodynamic variations [Zuber et al., 1986; Osenbrück et al., 2006; Badoux, 2007; Zuber et al., 2011]. This aspect is based on the fact that aquifers with large travel time scale have the capacity to buffer the effect of fast variations of recharge and discharge flow.

3.2.2.2. Homogenous solute input flux requirements

The second assumption is generally approximated by averaging input mass flux over the entire capture zone of the well, as carried out by Osenbrück et al. [2006]. But in most real pollution contexts in groundwater catchments, spatial variations of mass input characteristics can be very large.

The example of the Sumas-Blaine aquifer is reported by Almasri and Kaluarachchi [2007], who simulate the spatial repartition of nitrate pollution in groundwater in relation to land use, dominated by various type of crops and where certain zones can also be dominated by

uncultivated land, residential communities and small industries. The soil characteristics controlling the transfer of solute are furthermore not necessarily constant in the entire domain of the capture zone, particularly if the soil characteristics vary spatially. Another example is offered by the study of Stewart and Loague [2004] for a regional-scale atrazine leaching assessment, in the San Joaquin Valley, California, where transfer functions vary spatially according to the soil texture variations and according to the spatial distribution of degradation processes over the area.

The output concentration is dependent on the input concentration and the transfer function of pollutants coming from each part of the catchment area. By averaging the input concentration and the transfer function in the entire aquifer domain, the contribution of the most remote input zones have exactly the same impact as the closest input zones, which cannot be valid for strong heterogeneous input zones.

Consequently, the transfer function approach should be applied in a spatially distributed manner in order to more adequately represent the reality of groundwater pollution contexts.

3.2.2.3. Balanced mass and flow budget requirements

The third assumption is that, in the case of a conservative solute, there is no loss or gain of mass between the input zone and the output zone, relative to the inflow and outflow rates. This leads to a balanced integral of concentration $C(t)$ over the time between the input zone and the output zone, as formulated in Equation 3.2.

$$\int_0^{\infty} Q_{IN}C_{IN}(t)dt = \int_0^{\infty} Q_{OUT}C_{OUT}(t)dt \quad \text{Equation 3.2}$$

where Q_{IN} and Q_{OUT} are respectively the inflow and outflow rates.

Three hydrogeological configurations strictly respect this condition:

- (1) **Case 1:** when the pumping well is the only one aquifer outlet, in other words when all the recharge flow and the input mass converges toward the pumping well. In that case the input zone corresponds to the recharge area of the aquifer. This case is illustrated in Figure 3.1 , Case 1.
- (2) **Case 2:** when the aquifer presents multiple outlets, the input zone considered must correspond to the capture zone of the pumping well, where all mass and flow inputs reaching the pumping well are located. The capture zone must be defined carefully in accordance with a balanced flow budget between input zone and the pumping well. This case is illustrated in Figure 3.1 , Case 2.

- (3) **Case 3:** in a multiple outlets aquifer, when the capture zone of the pumping well and the capture zone of the other outlets are not dissociable, only one part of the total input mass will be captured by the pumping well. If the assumption that the flow reaching the pumping well and the flow converging towards the other outlets have the same characteristics of travel time distribution and of recharge zone, based on the fact that the flows are mixed enough at the position of the pumping well, hence the input zone can be defined as the entire groundwater catchment of the pumping well and of the other outlets. This case is illustrated in Figure 3.1 , Case 3.

Figure 3.1 illustrates in a 2D section projection the three aquifer configuration cases, where the conditions of balanced flows and mass budget, required in a transfer function approach, are respected. This involves to delimit carefully the input zone where recharge flows are captured by the pumping well and to quantify mass influx in it.

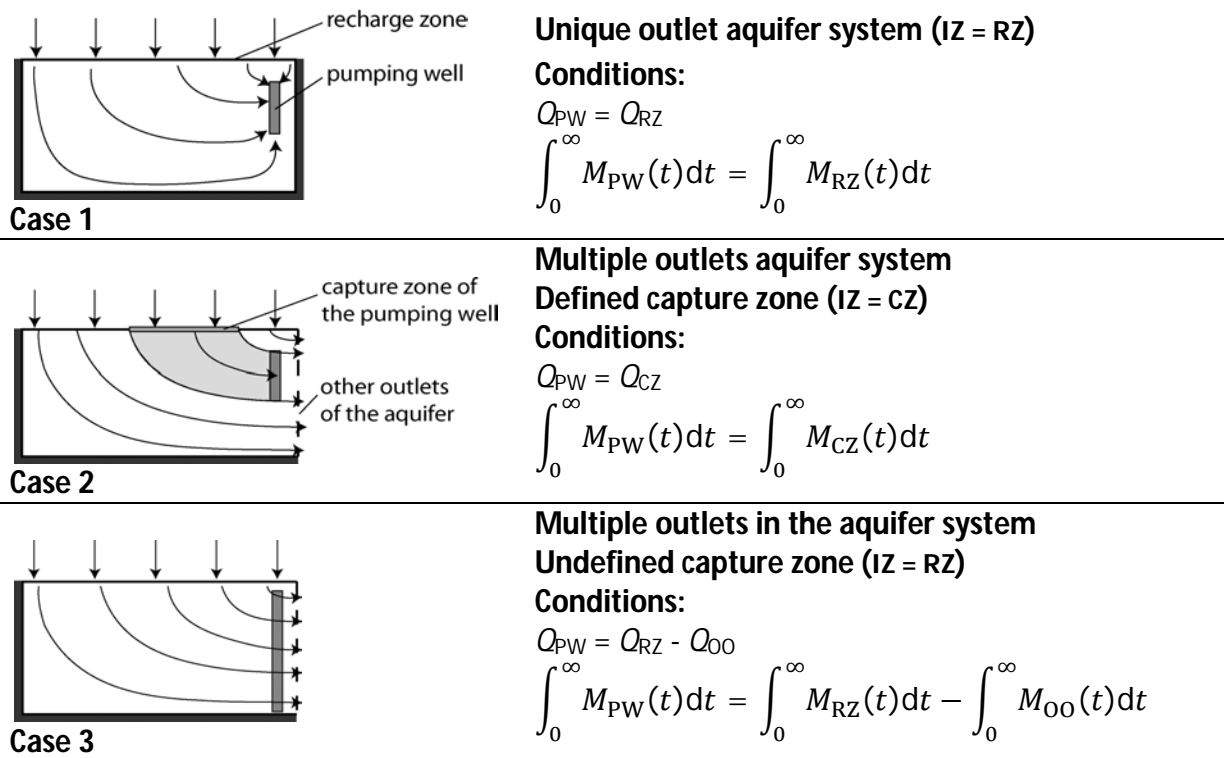


Figure 3.1 Hydrogeological characteristics and physical conditions for which the mass and the water budgets are balanced between the input zone and the pumping well; IZ: input zone where flow and mass inputs are considered to calculate $C_{IN}(t)$; PW: pumping well wherein $C_{OUT}(t)$ is resolved; CZ = capture zone of the well; RZ = recharge zone of the aquifer; OO = other outlets of the aquifer, expected the pumping well; Q : flow rate [L^3/T]; M : mass flux [M/T]

3.2.2.4. Requirement of a single transfer compartment in the aquifer

The transfer function approach is based on a single transfer function from the input zone to the pumping well. In the case of a real aquifer, travel of contaminant from the surface to the pumping well is actually carried out through different aquifer compartments and transfer of these contaminants does not have the same characteristics into the various compartments. First, these differences of transfer characteristics can be explained by the variability of flow directions, which is particularly true for the compartments represented by the unsaturated zone and the saturated zone of the aquifer: mainly vertical in the unsaturated zone, for instance, the transport is rather horizontal in the saturated zone.

In some cases, aquifer characteristics can also spatially vary and contaminants can be subject to various physical and chemical processes along their travel. Hence, the dynamic of retardation and degradation processes during the transport of contaminants are not necessarily the same in the various compartments of the aquifer. Böhlke et al. [2002], for example, describe a compartmented aquifer, where denitrification processes are observed at different locations of the aquifer: at the deepest part of the saturated zone, due to the presence of pyrite, and at the outlet of the aquifer, represented by organic-rich sediments overlying the aquifer in a river valley. On the contrary, few denitrification processes are observed in the unsaturated zone and in the shallow groundwater. Depending on the groundwater flow path, nitrate contaminant is more or less subject to denitrification. Consequently, its transfer cannot be described by a single transfer function, due to this heterogeneous behavior during the transport.

This aspect limits the characterization of the transfer of solute through the aquifer by a single transfer function. The transfer function approach should characterize the transfer through the different compartments of the aquifer in a separate manner, especially through the saturated and unsaturated zones.

3.2.3. CONCLUSION

This section lists the main limitations that can be encountered when applying the transfer function method to estimate the evolution of a solute concentration at an outlet of an aquifer system, especially at the pumping well. The first limitation is the assumption of a steady-state flow that rarely takes place in reality. Some authors assume a steady-state flow in the aquifer when the mean travel time of solute is greater than the period of hydrodynamic variations. In Section 3.3, a methodology is proposed to critically test the validity of such an approximation. The third assumption is a balanced flow and mass budget between the input zone, where flow and mass flux input determine the evolution of input solute concentration, and the outlet, where flow and mass flux output determine the evolution of output solute concentration. This requires that input zones must be defined with care. If this limitation cannot be eliminated, Figure 3.1 gives an overview of the various configurations of input and outputs zones that can be encountered and that respect the third assumption.

The second assumption of a homogeneous solute flux in the input zone of the aquifer and the fourth assumption of a single compartment of transfer through the aquifer system are susceptible to introducing strong limitations of the transfer function approach, especially for an heterogeneous distribution of solute input and when the aquifer presents various types of transfer compartments (typically the unsaturated zone and the saturated zone). A development of the convolution integral is proposed in Section 3.4, which gives the possibility to combine or separate various input zones of solute and various transfer compartments in the aquifer system, as it is observed in more realistic hydrogeological cases.

3.3. VALIDITY OF THE TRANSFER FUNCTION APPROACH FOR FLOW IN TRANSIENT STATE

3.3.1. INTRODUCTION

The travel time within the aquifer depends on temporal flow velocity variations, which is a function of the temporal recharge and discharge dynamics, observed in a transient state. For example, the travel time of contaminant is higher during a low-velocity flow period than during a high-velocity flow period. As a consequence, in transient flow conditions, the transfer function depends on the time of observation, which is in contradiction with the first assumption of the transfer function approach.

In this section, the effect of transient variations in a system with increasing travel time is tested, using a conceptual model of a simple aquifer, subject to transient conditions of recharge.

3.3.2. METHODOLOGY

The adopted methodology is to simulate the transfer function of an ideal tracer from the recharge zone to the outlet of an aquifer, subject to transient conditions of recharge flows. As reported by some authors [*Jury and Roth, 1990; Varni and Carrera, 1998; Zoellmann et al., 2001; Zuber and Maloszewski, 2001*], the transfer function is assimilated to the normalized breakthrough of the tracer at the outlet when an instantaneous tracer impulse is applied on the recharge zone. Transfer functions are simulated by applying a pulse injection at high and low recharge periods and the difference between each of these transfer functions is analyzed.

The aquifer model is 1000 m long and 3.2 m thick. The simulation is carried out in a 2D vertical projection and fully saturated media, using the numerical tools FEFLOW [*Diersch, 2009*]. The recharge zone corresponds to the surface of the aquifer. The unique outlet is represented by a boundary condition of head $H = 100$ m at the right side (1st kind/Dirichlet boundary condition). The porosity of the aquifer is homogeneous in the entire domain. The characteristics of the conceptual simulated aquifer are illustrated in Figure 3.2.

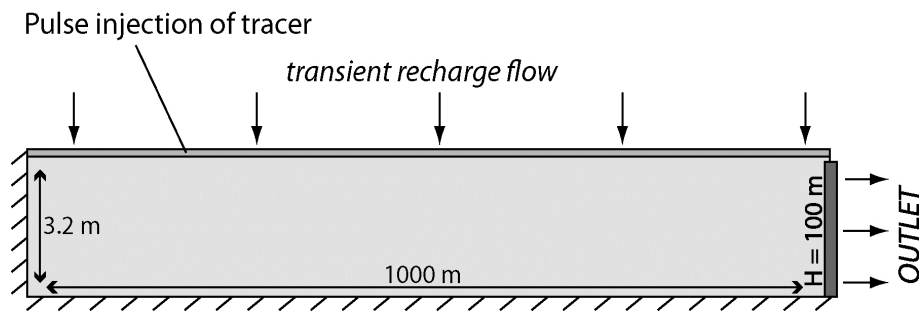


Figure 3.2 Conceptual model of the simulated aquifer and main hydrogeological characteristics

A fluctuating recharge flow is homogeneously applied at the surface of the aquifer. The characteristic period of the fluctuations is 6 months (about 180 days). Low recharge periods (January – February and July – August) correspond to a flow rate of 1 mm/day whereas high recharge periods (April – May and October – November) correspond to a flow rate of 3 mm/day. Mean annual flow rate is of 2 mm/day. Characteristics of the variations are illustrated in Figure 3.3 for a two-year period. Flow and transport are simulated during a period of 4000 days.

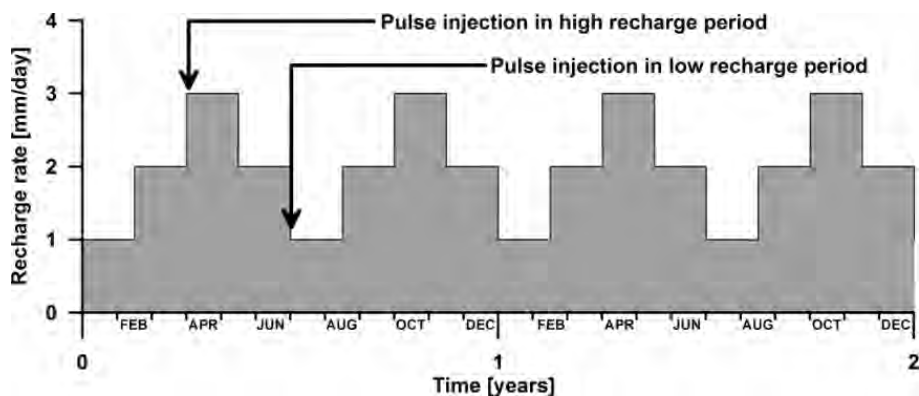


Figure 3.3 Aquifer recharge variation during two years: the recharge cycle is repeated for each period of 6 months. Low recharge periods (January – February and July – August) correspond to a flow rate of 1 mm/day whereas high recharge periods (April – May and October – November) correspond to a flow rate of 3 mm/day. Mean annual flow rate is of 2 mm/day. Arrows indicate the times of instantaneous impulse unit of tracer in a high recharge period or in a low recharge period.

Based on the previous hydrogeological characteristics, the aquifer model is simulated six times. For each of these simulations, the porosity of the aquifer is changed, according to the values of Table 3.1. The porosity varies between around 1,6% and 50%, which extreme values are not realistic but are useful for the test. The change of porosity results in varying mean travel time of flow in the aquifer, according to Equation 3.3, reported by Kazemi et al [2006] for a horizontal aquifer, with uniform thickness e and porosity ϕ and recharged by a uniform surface recharge rate i .

$$T_0 = \frac{e \cdot \phi}{i}$$

Equation 3.3

Hence, for each selected value of porosity the mean travel time in the aquifer varies (Table 3.1).

Configuration of aquifer model	1	2	3	4	5	6
ϕ : porosity [%]	1.5625%	3.125%	6.25%	12.5%	25%	50%
e : thickness [m]	3.2	3.2	3.2	3.2	3.2	3.2
i : Mean annual flow rate [m/day]	0.002	0.002	0.002	0.002	0.002	0.002
T_0 : Mean travel time [days]	25	50	100	200	400	800

Table 3.1 Parameters of the six configurations of the aquifer, leading to various mean travel time T_0

Two simulations of the transfer function are carried out for each of the six configurations of the aquifer model. One transfer function is calculated when the instantaneous unit tracer impulse is applied at the beginning of a high recharge period (the 1st of April). The other transfer function is simulated when the instantaneous unit tracer impulse is applied at the beginning of a low recharge period (the 1st of July). For each configuration of aquifer, the transfer functions are compared (Figure 3.4).

3.3.3. RESULTS

Simulated transfer functions are illustrated in Figure 3.4. Transfer functions calculated for an impulse in a low recharge period (black dashed line) are significantly different from the transfer functions in a high recharge period for aquifer models with a mean travel time scale from 25 to 100 days. Transfer functions from low recharge periods are more widely spread over time than transfer functions from high recharge periods. Consequently the transfer of a solute through the aquifer varies considerably with the input date in the aquifer.

On the contrary, the contrast between high recharge transfer functions and low recharge transfer functions is much less significant from a mean annual travel time of 200 days and the difference is nearly invisible for a mean travel time of 800 days. These results show that, once a mean annual travel time of 200 days has been reached, the transfer of a contaminant becomes nearly independent of the input time. Consequently, the difference between both transfer functions becomes negligible when the mean travel time is higher than the characteristic period of recharge variation, which is 180 days.

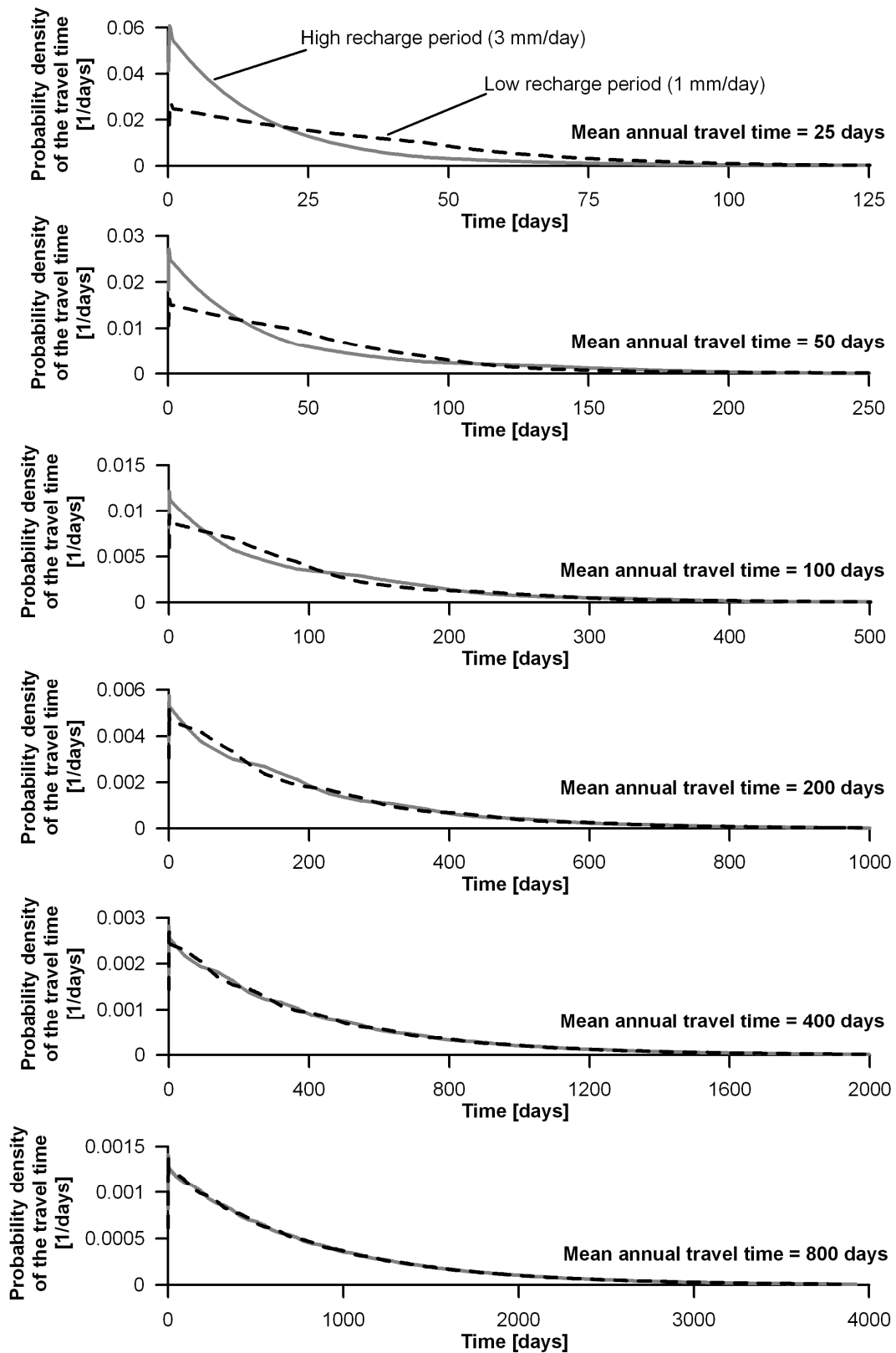


Figure 3.4 Simulated transfer functions for each configuration of aquifer (mean annual travel time of 25, 50, 100, 200, 400 and 800 days) and for a tracer impulse in high recharge flow period (grey line) and low recharge flow period (black dashed line)

3.3.4. CONCLUSION

This short study highlights the fact that the larger the travel time scale of the aquifer is, the higher the buffer effect of recharge variation on the travel time distribution of a contaminant will be. This illustrates and confirms the conclusions from previous works [Zuber *et al.*, 1986; Jury and Roth, 1990; Varni and Carrera, 1998; Zoellmann *et al.*, 2001; Zuber and Maloszewski, 2001; Badoux, 2007] : when the mean travel time in the system is larger than the characteristic periods of hydrodynamic variations, the transfer function does not vary significantly with time.

It is important to keep in mind that the previous results are only valid for the aquifer model of Figure 3.2. Nevertheless the chosen characteristics of the aquifer, a fully saturated aquifer with a unique recharge zone subject to input flow variation and a unique fully penetrated outlet, constitute a highly reactive configuration to hydrodynamic variations. Consequently aquifers with other characteristics should react less strongly than in the proposed conceptual model and the buffer effect of travel time scale in the aquifer should be higher than in the present study. In other words, the conclusions of this study, where buffer effect is minimized, should be relevant for real aquifer cases.

In conclusion, we can state that in the context of the transfer function approach to calculate the evolution of groundwater quality at pumping wells, the steady state flow condition can be assumed valid when characteristic periods of hydrodynamic variations are lower than the mean contaminant travel time in the aquifer system.

3.4. EQUATION OF CONVOLUTION INTEGRAL FOR MULTIPLE INPUT ZONES AND SEVERAL TRANSFER COMPARTMENTS

3.4.1. INTRODUCTION

The transfer function approach has the potential to be an interesting alternative to numerical simulations of flow and transport to estimate the evolution of groundwater quality at pumping wells. Nevertheless it relies on the convolution integral (Equation 3.1) that lacks flexibility compared to numerical methods for two main reasons:

- (1) the evolution of solute concentration at the pumping well is calculated based on the history of solute concentration in a single input zone
- (2) the transfer of mass from the input zone to the well is described by a single transfer function in a single transfer compartment

In this section the convolution integral is reformulated in order to remove these limitations. The aim is to make the transfer function approach more suitable to various input and transfer configurations that are encountered in aquifer systems.

3.4.2. THE CONVOLUTION INTEGRAL FOR MULTIPLE INPUT ZONES

The transfer function approach based on Equation 3.1 corresponds to the case of a homogeneous solute flux in the input zone of the aquifer system. If a homogenous input can be generally accepted for the study of environmental tracer, which are associated with precipitation [Zuber, 1986b], it is rarely observed in the context of contaminant input in aquifers. For example, in the context of groundwater catchment covered by an agricultural area, each agricultural parcel is susceptible to be characterized by a certain nutrient leaching history, depending on the crop rotation and the crops techniques employed on it (tillage for instance), as shown by Hansen & Djurhuus [1997].

Lerner and Papatolios [1993] propose a methodology to predict the evolution of nitrate concentrations at a pumping well, considering a distributed nitrate input in the capture zone of the well. The method is based on the conservation of mass and flow between the catchment area and the pumping well, where the catchment is divided into three subareas, each of them being characterized by a specific initial level of nitrate concentration in recharge. The method is partially equivalent to the transfer function approach since it integrates the distribution of travel time of nitrate from the input zones to the pumping well. However, the method gives only the evolution of the nitrate concentration $C(t)$ at the pumping well relative to an initial nitrate concentration C_0 in the aquifer system and a target nitrate concentration C continuously and constantly applied in the recharge zone from an initial moment in time. This represents a strong limitation of the method because a progressive evolution of the nitrate concentration input cannot be considered in the calculation. Moreover, the method assumes that the isochrones of travel times delimit the various input zones. This represents a second limitation: the subareas are delimited on the

basis of the spatial distribution of solute input and not on the hydrodynamic properties, which control the isochrones location.

The resolution of the transfer function approach is based on the travel time of the distribution of solute from an input zone to the well and on the evolution of input concentration of solute in the recharge zone. In order to extend its application to the case of distributed subareas of input solute in the input zone, the convolution integral (Equation 3.1) can be developed. To determine the evolution of solute concentration at the pumping well, considering several subareas of homogeneous solute input history, the superposition principle is applied on Equation 3.4. This leads to:

$$C_{OUT}(t) = \frac{\sum_i Q_i \int_0^t C_{IN_i}(t - \tau) g_i(\tau) d\tau}{\sum_i Q_i} \quad \text{Equation 3.4}$$

$C_{OUT}(t)$ is the solute concentration at the pumping well; i is the index of the subarea; $C_{IN}(t)$ is the input solute concentration; $g(\tau)$ is the transfer function of solute from the input zone to the pumping well; Q is the flow contribution of the input subarea to the pumping flow.

Figure 3.5 illustrates the various elements of Equation 3.4, for a conceptual aquifer showing five subareas of solute input. Each of the subareas is characterized by a homogeneous solute flux input history $C_{IN}(t)$. This case could be representative of an agricultural area, where each subarea could represent an agricultural parcel affected by a relatively homogeneous land use.

Equation 3.4 introduces, in the convolution integral and over time, the contribution of each subarea of the input zone to the solute concentration at the pumping well. Where some parts of the input zone present a constant solute concentration flux, these zones are considered as distinct subareas of the input zone. Equation 3.4 can be simplified as follows:

$$C_{OUT}(t) = \frac{\sum_{i \in A} Q_i \int_0^t C_{IN_i}(t - \tau) g_i(\tau) d\tau + \sum_{i \in B} Q_i C_{IN_i}}{\sum_{i \in A, B} Q_i} \quad \text{Equation 3.5}$$

Two groups of subareas have been defined in Equation 3.5: the group *A* groups together the subareas where the mass input flux is not constant in time and the group *B* groups together the subareas where the mass input flux is constant. This last equation can be very relevant when some part of the recharge zone has a constant input concentration. In this case, the characterization of the transfer function is not required for solutes coming from these parts, which simplifies the resolution of the problem.

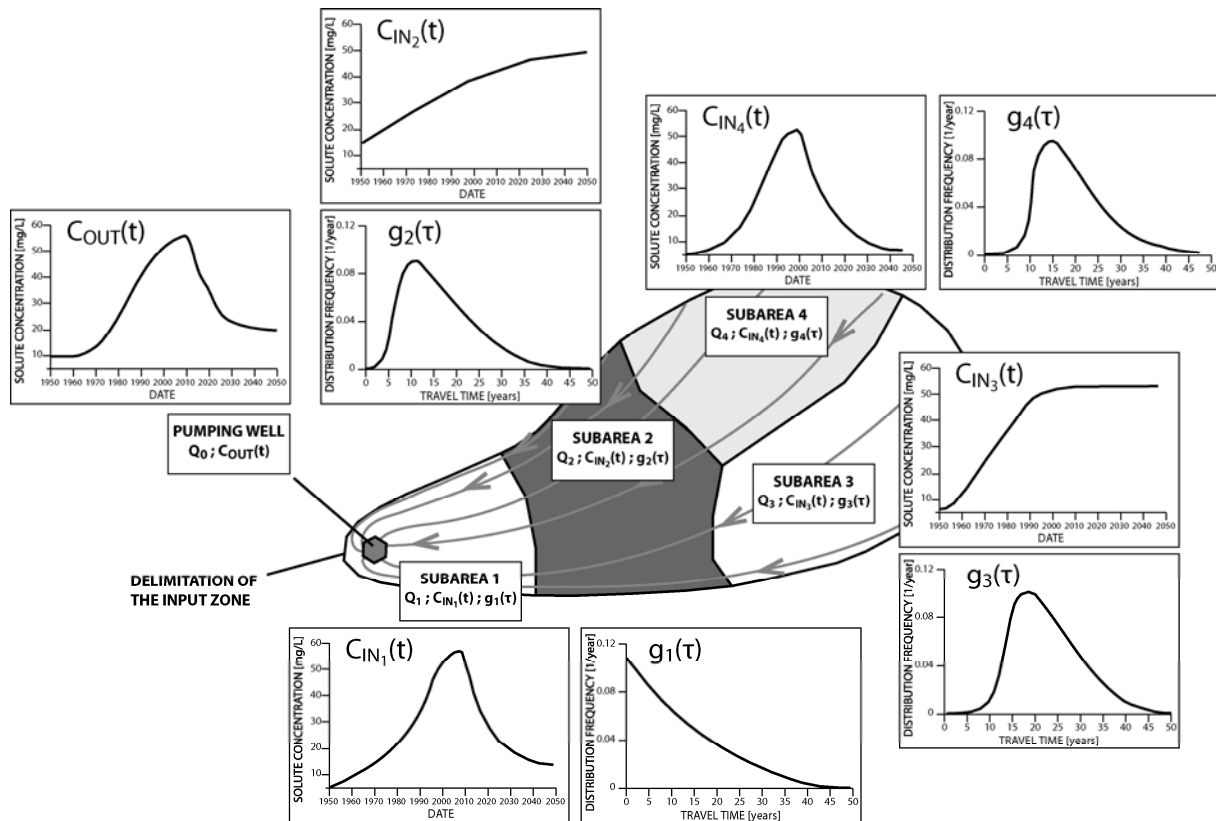


Figure 3.5 Groundwater catchment where the input zone is subdivided into four subareas of solute input; each subarea is characterized by a function of input solute concentration $C_{IN}(t)$ and by a recharge flow Q ; the solute transfer from each subarea of the input zone to the pumping well is described by a transfer function $g(\tau)$; the solute concentration evolution at the pumping well is described by the function $C_{OUT}(t)$.

3.4.3. THE CONVOLUTION INTEGRAL FOR MULTIPLE TRANSFER COMPARTMENTS

The convolution integral (Equation 3.1) is based on a single transfer function describing the transfer of the solute from the input zone to the pumping well. This implies that this single transfer function takes into account all the various flow pathways, processes of mass transport and biogeochemical interactions occurring in the aquifer system.

As these processes are not necessarily linear in the system, the characterization of the transfer function can pose a problem. In most cases, the aquifer presents two distinctive compartments where the parameters of physical laws governing transport processes are not identical: the unsaturated zone and the saturated zone. Flow and transport in the unsaturated zone are essentially vertical, whereas in the saturated zone the directions of flow have mostly a horizontal component. Hence, the velocities of flow, transport and dispersion processes are significantly different in both compartments. The biogeochemical interactions leading to retardation and degradation processes can also be significantly different in both unsaturated and saturated zones. Consequently the characteristics of the solute transfer function can significantly differ for each of these compartments.

The exponential-piston model of the transfer function has been introduced in hydrogeology in order to simulate the transfer of a solute both in the unsaturated and saturated zones of the aquifer [Etcheverry, 2001; Zuber and Maloszewski, 2001]. The transfer function in the saturated zone is simulated by an exponential model whereas the transfer function in the unsaturated zone is simulated by a piston flow model, and the total transfer function in the part of the aquifer aggregates both piston and exponential models in only one exponential-piston model. Nevertheless this exponential-piston model implies that the solute transport is only governed by advective transport in both unsaturated and saturated zones. In other words, dispersion processes are not included in the transfer model. Moreover, it is not possible to introduce separately, for each compartment, the degradation and retardation factors that could affect the transfer of solute.

For a more realistic resolution of solute transfer, in most cases, the convolution integral should separately integrate the transfer characteristics in the unsaturated and saturated zones separately. Each particle of solute reaching the groundwater table according to a transfer function in the unsaturated zone is transported in the saturated zone according to the transfer function in the saturated zone. This series of two transfer functions, illustrated in the sketch of Figure 3.6, leads to the following double convolution:

$$C_{OUT}(t) = \int_0^t \left[\int_0^{t-\tau} C_{IN}(t-\tau-T) g(\tau) d\tau \right] h(T) dT \quad \text{Equation 3.6}$$

where $g(\tau)$ is the transfer function through the unsaturated zone and $h(T)$ is the transfer function through the saturated zone; t is the observation time, T is the travel time in the saturated zone and τ is the travel time in the unsaturated zone.

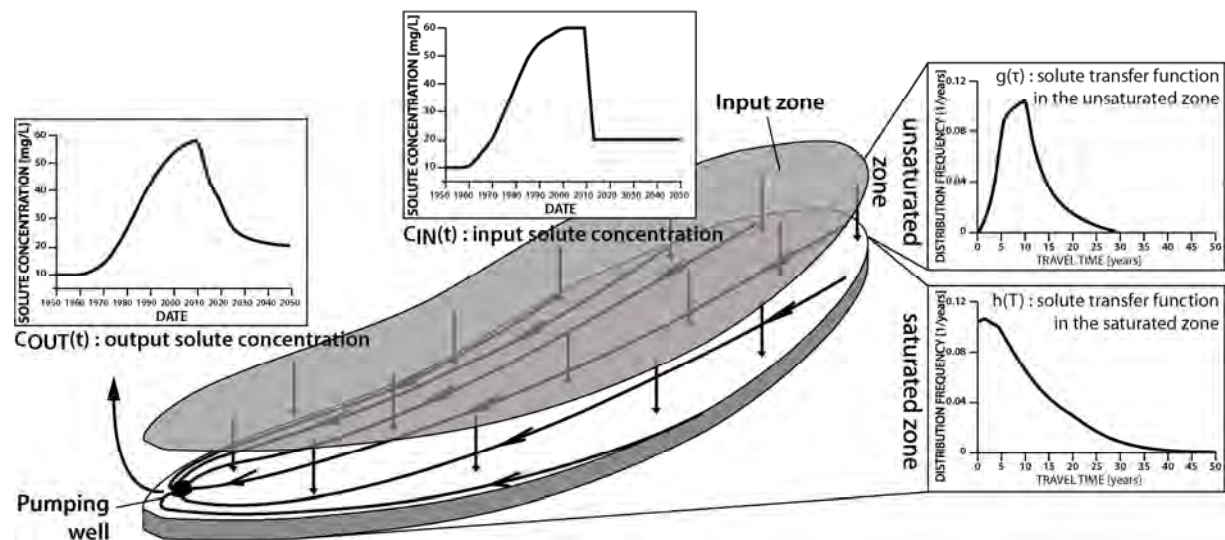


Figure 3.6 Conceptual aquifer showing an unsaturated zone and a saturated zone; the evolution of solute concentration $C_{OUT}(t)$ at the pumping well is governed by the input parameters of Equation 3.1: the evolution of solute concentration $C_{IN}(t)$ at the input zone, the solute transfer function in the unsaturated zone $g(\tau)$ and in the saturated zone $h(T)$

The advantage of the double convolution of Equation 3.6 is that the transfer functions, respectively through the unsaturated and saturated zones, can be defined in accordance with the aquifer-media and solute characteristics. Where the exponential-piston model imposes a purely advective transport, such a relationship accepts all types of transfer characteristics: exponential, piston, dispersed, simulated transfer functions, etc. (the analytical formulations of the transfer functions are developed in section 3.5).

3.4.4. INTEGRATION OF MULTIPLE INPUT ZONES AND MULTIPLE TRANSFER COMPARTMENTS IN THE TRANSFER FUNCTION APPROACH

The partition of the transfer functions in the saturated zone and the unsaturated zone of the aquifer, as considered in Equation 3.4, can be applied in the context of spatial variation of input solute concentration, at various subareas of the input zone, as considered in Equation 3.4. The combination of Equation 3.4 and Equation 3.6 leads to:

$$C_{\text{OUT}}(t) = \frac{\sum_i Q_i \int_0^t \left[\int_0^{t-T} C_{\text{IN}_i}(t - \tau - T) g_i(\tau) d\tau \right] h_i(T) dT}{\sum_i Q_i} \quad \text{Equation 3.7}$$

Solving this equation is possible with standard mathematical tools, like a spreadsheet [Olsthoorn, 2008], but the difficulty resides in determining the various parameters of the equation associated with each subarea i of the recharge zone: the input concentration functions C_{IN_i} , the contribution Q_i of each subarea to the pumping flow and finally the transfer functions h_i and g_i of solute through the saturated and unsaturated zones.

Finally it is possible to slightly reformulate the convolution integral considering both compartments of the aquifer (unsaturated zone and saturated zone) and the spatial variation of input solute concentration in the subareas of the input zone (Equation 3.7), where some parts of the subareas present a variable solute input (group A of subareas) and some parts present a constant solute input (group B of subareas as developed in Equation 3.5). This leads to:

$$C_{\text{OUT}}(t) = \frac{\sum_{i \in A} Q_i \int_0^t \left[\int_0^{t-T} C_{\text{IN}_i}(t - \tau - T) g_i(\tau) d\tau \right] h_i(T) dT + \sum_{i \in B} Q_i C_{\text{IN}_i}}{\sum_{i \in A, B} Q_i} \quad \text{Equation 3.8}$$

Equation 3.8 is the most developed formulation of the convolution integral. It allows calculating the evolution of solute concentration at a pumping well, for multiple configurations of aquifers: by considering the characteristics of the transfer in both unsaturated and saturated zones separately, by integrating the spatial distribution of solute input history on the recharge zone and by including the subareas of solute input that are constant in time.

3.5. DEVELOPMENT OF THE EXPONENTIAL MODEL OF SOLUTE TRANSFER FUNCTION IN AQUIFERS

3.5.1. INTRODUCTION

The choice of focusing the study on the transfer function approach is first governed by the relative simplicity of its implementation. The new development provided in section 3.4 removes some of their limits, by adapting it to multiple configurations of input distribution and of transfer compartments of the aquifer. The last point that has not been addressed is the characterization of the key element of the convolution integral: the transfer function of solute within the aquifer system.

In Chapter 2, analytical formulations of transfer functions in aquifers are reviewed, mainly based on the works of Maloszewski & Zuber [1982] and Jury & Roth [1990]. Including degradation and retardation parameters, these transfer functions can be used for nonconservative and reactive solute transport. Their relative ease of implementation, in spite of the required assumptions, is in line with the need to have a suitable method for most environmental projects.

The mathematical expression of one of the most frequently used analytical model, the exponential model, is developed there in order to better correspond to real configurations of input and output solute, especially when the solute input only affect one part of the recharge zone or when the transfer function must be estimated in one part of the outlet zone.

3.5.2. THE EXPONENTIAL MODEL OF TRANSFER FUNCTION

The exponential model is deduced from the simple aquifer model proposed by Vogel [1967] for the investigation of the link between the age of water and the depth of the observation point in shallow aquifers. The proposed aquifer is characterized by a uniform recharge flow I over its surface, a constant thickness e and a uniform porosity ϕ . The Dupuit assumption of a constant horizontal velocity over depth is enforced. Vogel [1967] shows that the average transit time of water through the aquifer is:

$$T_0 = \frac{e\phi}{I} \quad \text{Equation 3.9}$$

Kazemi et al. [2006] demonstrate for such an aquifer configuration that the transfer function of groundwater from the recharge area to the output section of the aquifer is:

$$g(t) = \frac{1}{T_0} \exp\left(-\frac{t}{T_0}\right) \quad \text{Equation 3.10}$$

Equation 3.10 corresponds to the exponential model of the transfer functions, reported in Table 2.2., Kazemi et al. [2006] show that this model can be applied to the fully penetrating outlet of the horizontal aquifers with a homogeneous recharge on the surface, as long as the Dupuit assumption can be respected and as long as the ratio $e\phi/I$ (Equation 3.9) is uniform throughout the entire domain. Previously, Luther & Haitjema [1998] show, in a sensibility analysis based on numerical simulations of transfer functions, that the exponential model can be a good approximation for many cases of unconfined aquifer.

Haitjema [1995] notes the possibility to use the exponential model in a transfer function approach to calculate the effect of diffuse pollutions on the groundwater quality at the outlets of aquifers. Nevertheless, when pollutants are not uniform in the recharge zone of the aquifer, the author highlights that the transfer functions should be determined on a subarea basis. The exponential model of transfer function, as formulated in Equation 3.10, is actually representative for a solute input defined in the entire recharge zone. In other words, when the input of solute only concerns one part of the recharge zone, its transfer function cannot be directly formulated by the Equation 3.10. This aspect represents a first limitation in the application of the exponential model.

Moreover the exponential model, as formulated in Equation 3.10, is representative for a fully penetrating outlet of the aquifer. Hence, when the outlet is partially represented by a pumping well in a certain depth interval of the aquifer, the exponential model is not representative of the solute transfer function for the part reaching the pumping well. This aspect represents a second limitation of the exponential model.

3.5.3. DEVELOPMENT OF THE EXPONENTIAL MODEL

In this section, the exponential model is reformulated in order to be applicable beyond these limits. For this purpose, the aquifer configuration corresponding to the exponential model is reconsidered on the basis of the works of Kazemi et al. [2006]. The aquifer flow model is illustrated in Figure 3.7: a horizontal aquifer, with constant thickness e and porosity ϕ , recharged by a uniform infiltration I . The Dupuit assumption is enforced.

Based on this configuration, the temporal relations between the recharge and discharge are mathematically formulated. It is specially defined:

- (1) the solute transfer function at the outlet, knowing the location of the solute input zone (on the conceptual example the distance interval $[x_1 ; x_2]$);
- (2) the transfer function of a solute for a certain interval of the outlet depth (in the sketch the depth interval $[z_2 ; z_1]$).

The solute is considered as conservative and nonreactive. The details of the mathematical development and the physical basis are given in Appendix A.

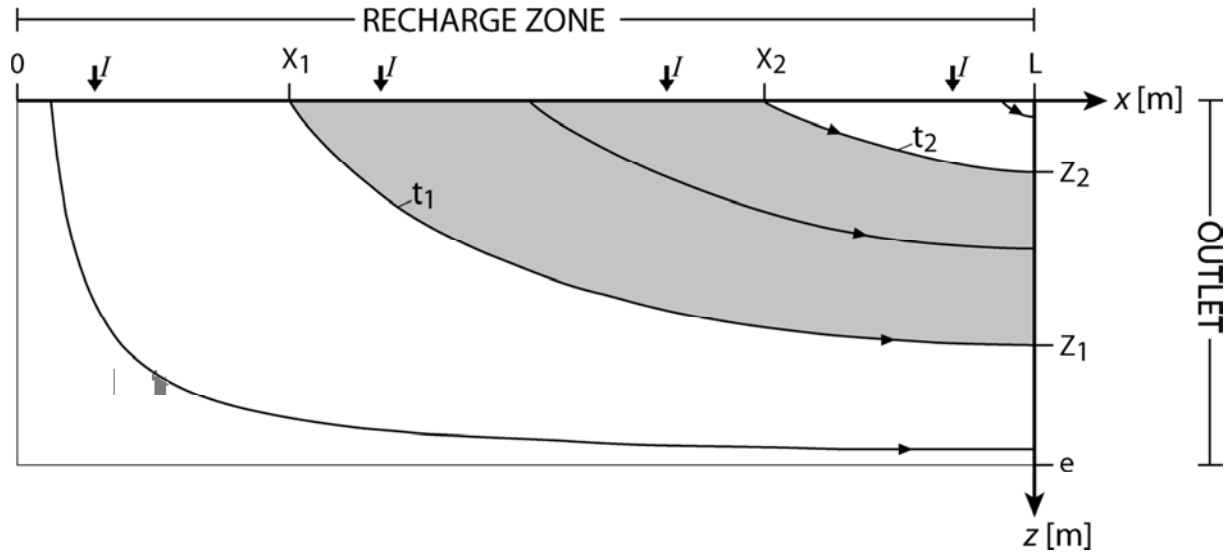


Figure 3.7 Flow configuration sketch for analytical modeling of transfer function according to an exponential model

For a solute input in a subarea of the recharge zone limited by x_1 and x_2 the solute transfer function $g_{x_1x_2}(t)$ at the outlet is:

$$g_{x_1x_2}(t) = \frac{L \exp\left(-\frac{t}{T_0}\right)}{T_0(x_2 - x_1)} \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.11}$$

$$g_{x_1x_2}(t) = 0 \quad , \text{otherwise} \quad \text{Equation 3.12}$$

$$\text{with } t_1 = T_0 \ln\left(\frac{L}{x_1}\right)$$

$$t_2 = T_0 \ln\left(\frac{L}{x_2}\right)$$

The average travel time $\overline{t(x)}_{x_1x_2}$ at the outlet for solute coming from the subarea of the recharge zone delimited is:

$$\overline{t(x)}_{x_1x_2} = \frac{T_0}{x_2 - x_1} \left[x_2 \left(\ln\left(\frac{L}{x_2}\right) + 1 \right) - x_1 \left(\ln\left(\frac{L}{x_1}\right) + 1 \right) \right] \quad \text{Equation 3.13}$$

The transfer function $g_{x_1x_2}(t)$ and the average travel time for input solute in a certain subarea (distance interval $[x_1 ; x_2]$) of the recharge zone is dependent on the size of the aquifer (parameter L).

At the interval of depth limited by z_2 and z_1 , the transfer function $g_{z_1 z_2}(t)$ of solute coming from the recharge zone is:

$$g_{z_1 z_2}(t) = \frac{\exp\left(-\frac{t}{T_0}\right)}{T_0 \left(\frac{z_1}{e} - \frac{z_2}{e}\right)} \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.14}$$

$$g_{z_1 z_2}(t) = 0 \quad , \text{otherwise} \quad \text{Equation 3.15}$$

$$\text{with } t_1 = T_0 \ln\left(\frac{1}{1 - \frac{z_1}{e}}\right)$$

$$t_2 = T_0 \ln\left(\frac{1}{1 - \frac{z_2}{e}}\right)$$

The average time of travel $\overline{t(z)}_{z_1 z_2}$ of solute at the outlet is:

$$\overline{t(z)}_{z_1 z_2} = \frac{e}{z_1 - z_2} T_0 \left[\left(1 - \frac{z_1}{e}\right) \ln\left(1 - \frac{z_1}{e}\right) - \left(1 - \frac{z_2}{e}\right) \ln\left(1 - \frac{z_2}{e}\right) + \frac{z_1 - z_2}{e} \right] \quad \text{Equation 3.16}$$

The transfer function $g_{z_1 z_2}(t)$ and the average travel time for an output solute at a certain interval of depth (depth interval $[z_2 ; z_1]$) of the outlet is independent of the size of the aquifer (parameter L). Hence $g_{z_1 z_2}(t)$ is constant over the distance x .

Equation 3.11 and Equation 3.14 can be considered separately. Equation 3.11 is formulated for the case where the input zone is defined, whereas Equation 3.14 is formulated for the case where the depth interval of the outlet is known. Equation 3.11 and Equation 3.14 are nevertheless equivalent if we consider that z_1 (or z_2) corresponds to the depth reached by a solute coming into the system at the distance x_1 (or x_2).

3.5.4. CONDITIONS OF USE OF THE EXPONENTIAL MODEL

The exponential model was introduced in Hydrogeology by Vogel [1967] in order to describe the vertical stratification of ages in an ideal unconfined aquifer, showing homogeneous properties and a constant depth (Figure 3.7). As introduced, the exponential model assumes a homogenous input in the recharge zone and a fully penetrated outlet. These requirements can be released with the new formulations introduced in this section.

The exponential model is expressed at the outlet of the aquifer for two additional cases: (1) when the input zone corresponds to a limited subarea of the aquifer recharge zone (Equation 3.11 and Equation 3.12); (2) when the transfer function is estimated for a part of

the aquifer outlet (for instance the pumping well partially penetrates the aquifer) (Equation 3.14 and Equation 3.15). Hence, the use of these new formulations of the exponential model can be very relevant when the classical formulation of the exponential model is not applicable. Nevertheless, the formulation of case (2) is based on the Dupuit assumption, that states that the velocity of groundwater flows are constant with respect to depth. Hence, this formulation is not applicable when the pumping rate significantly affects the velocities and directions of flow upstream from the well. On the contrary, when the hydraulic conductivity and the aquifer thickness are sufficiently high, the changes of flow direction and velocity due to the well are insignificant and the Dupuit assumption can be accepted.

More generally, the exponential model, from its simple formulation (Equation 3.10) to its developed formulations (Equation 3.11/Equation 3.12 and Equation 3.14/Equation 3.15), are based on a specific flow configuration, where the flows lines directions are only controlled by the recharge rate, the porosity and the dimensions of the aquifer system.

3.6. APPLICATION OF THE TRANSFER FUNCTION APPROACH FOR VARIABLY DISTRIBUTED SOLUTE INPUT AND VARIOUS TRANSFER COMPARTMENTS IN AN HYPOTHETICAL AQUIFER

Some of the new developments proposed for the transfer function approach are applied in a simple and hypothetical aquifer case, affected by changes of input rate of pollutants. The purpose of this section is to demonstrate how the transfer function approach can be used to calculate the evolution of solute concentrations at a pumping well, in accordance to the variations of solute concentrations in recharge.

3.6.1. CHARACTERISTICS OF THE AQUIFER

Figure 3.8 gives a 2D plan view of the hydrogeological context of a simple aquifer case. The groundwater catchment, where the recharge flow takes place, presents three subareas (A, B and C), each of them being affected by a specific solute input history. The distance of the subarea borders from the upper no-flow boundary and in the major direction of the flows are x_1 [m] and x_2 [m]. A pumping well is located at the distance L [m] from the upper no-flow boundary. The pumping well captures one part of the recharge and solute flux input in the catchment. As the pumping well fully penetrates the saturated zone, the capture zone of the pumping well is defined following back the flow lines until the upper no-flow boundary of the aquifer.

Figure 3.9 presents in a 3D-view the internal organization of the aquifer inside the capture zone of the well. The input surface is subdivided into three subareas (A, B and C). Each of them is characterized by a uniform recharge rate I [m/day] and a specific area S [m²].

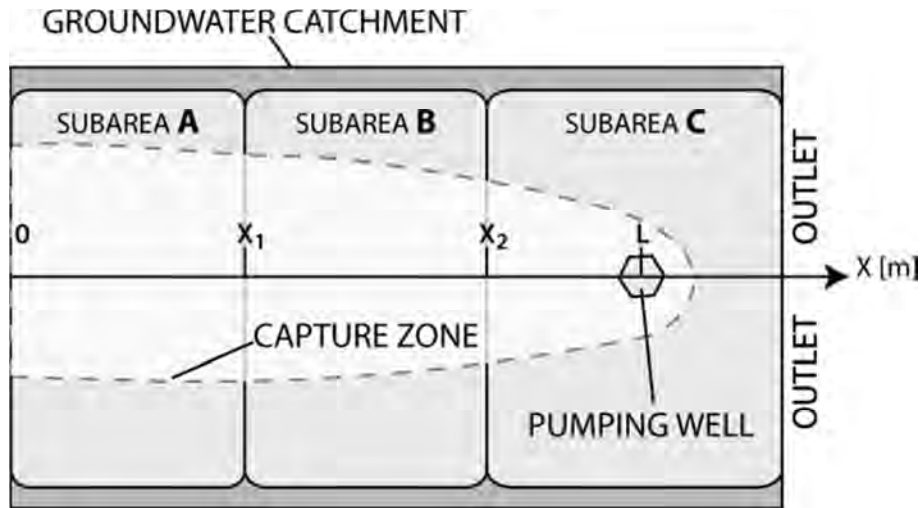


Figure 3.8 2D plan view of the hydrogeological context of the hypothetical aquifer case

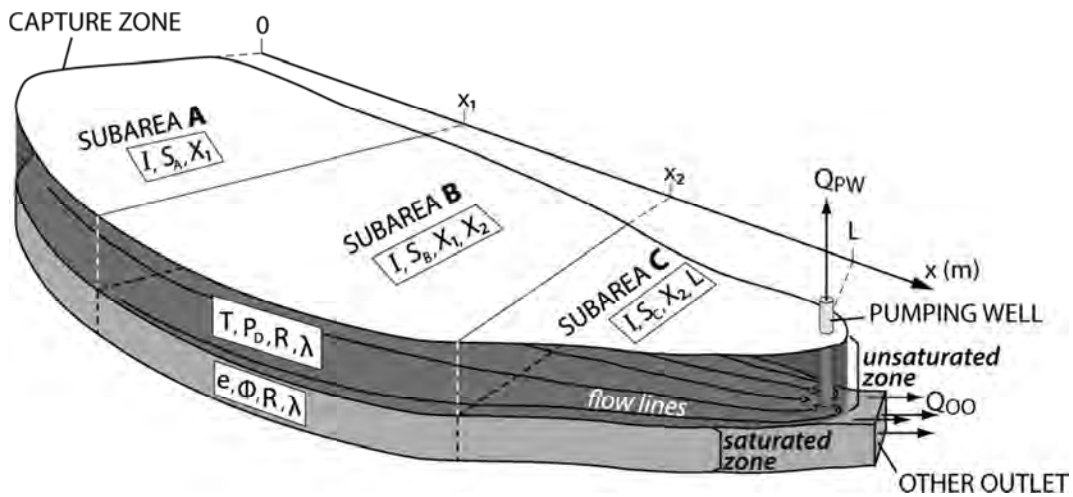


Figure 3.9 3D view of internal organization of aquifer characteristics inside the capture zone of the pumping well

The aquifer is composed by an unsaturated zone and a saturated zone. Both are characterized by homogeneous thickness and properties of the porous material. In the unsaturated zone the following parameters are known: the mean transit time of flows T [days], the dispersion parameter P_D [-], the retardation factor of the solute R [-] and the decay factor of the solute [days^{-1}]. In the saturated zone the following parameters are known: the thickness of groundwater body e [m], the effective porosity of the material ϕ [-], the retardation factor of the solute R [-] and the decay factor of the solute [days^{-1}].

Water and solute converge towards the outlet zone of the aquifer, composed by the pumping well and the other outlet. It is assumed that the pumping well has the same probability of capture as the other outlet, in other words the travel time distribution of the solute at the level of the pumping well is identical if the solute is captured by the pumping well or if it travels towards the other outlet.

3.6.2. CHARACTERISTICS OF THE SOLUTE INPUT HISTORY

Each subarea of the capture zone distinguishes itself from other by a specific function of input solute concentration over the time, which is represented in Figure 3.10.

After an initial period of invariant input of solute, where the concentrations distribution is stabilized in the aquifer system, strong changes are applied on the solute concentration of input flux at time $t = 1000$ days. In the subarea *A* the concentration of input solute varies from 20 mg/l to 40 mg/l. On the contrary, the concentration of input solute decreases from 40 mg/l to 20 mg/l for the subarea *B* and from 50 mg/l to 10 mg/l for the subarea *C*. The transition time between the two states of input solute concentration is equal to 200 days.

It is assumed that the solute is not affected by a retardation process in both unsaturated and saturated zones. In other words, the solute travel times have the same characteristics than the transit time of water. The solute is not affected by degradation process in the part of the unsaturated zone beneath subareas *A* and *B*. The solute is nevertheless subject to decay factor $\lambda = 0.0035$ in unsaturated zone beneath subarea *C*, which corresponds to a half-life $T_{1/2} = 200$ days (see footnote 1 page 27).

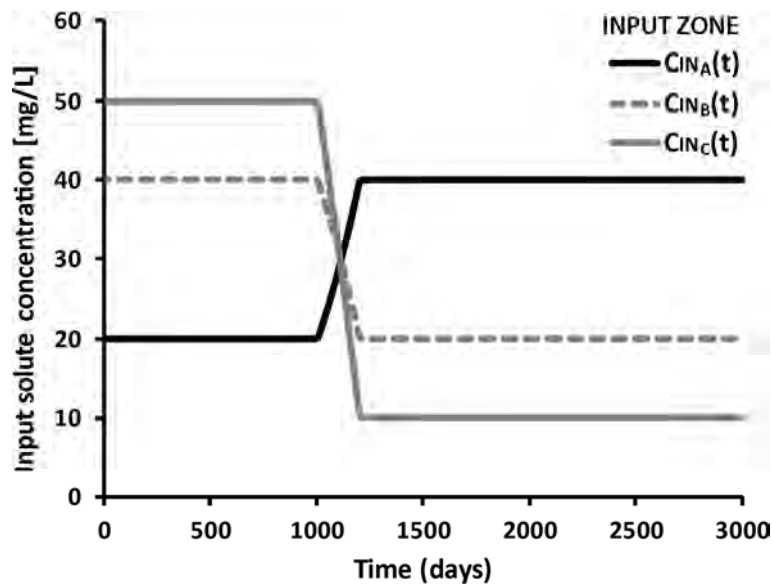


Figure 3.10 Evolution of the solute concentration $C_{IN_A}(t)$, $C_{IN_B}(t)$ and $C_{IN_C}(t)$ in recharge, in the subareas *A*, *B* and *C* respectively of the capture zone

3.6.3. PARAMETERS OF THE PROBLEM

To resolve the problem with analytical solutions a preliminary condition is to reduce the parameters of the problems in its simplest configuration. The aquifer characteristics are reduced in a 2D section projection in the longitudinal direction. This approximation tends to be valid because the flow directions are almost in the longitudinal direction and because the hydrogeological properties are laterally constant. This approximation assumes that the lateral variations of flow velocity are not significant.

Figure 3.11 illustrates the problem in a 2D vertical section. The known data of the problem are summarized in Table 3.2.

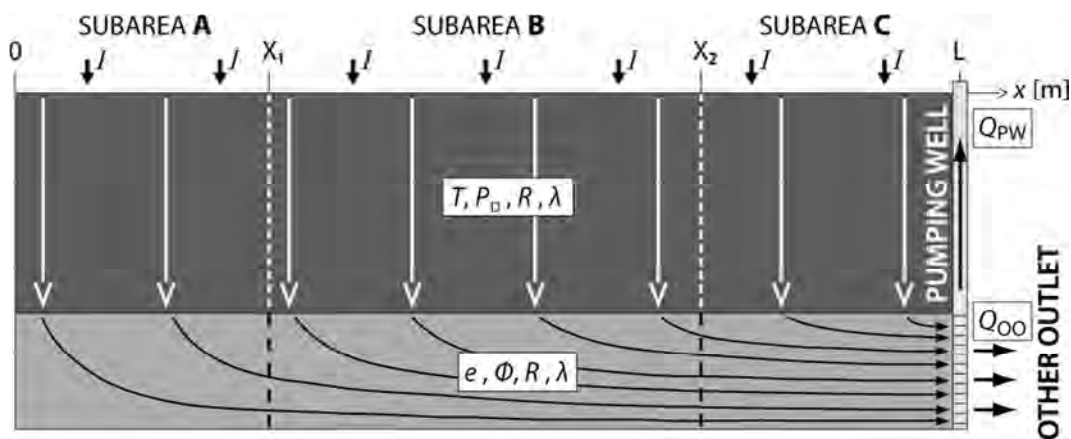


Figure 3.11 2D section projection of the aquifer

		Subarea A	Subarea B	Subarea C
Surface	Upper limit [m]	0	$X_1 = 3000$	$X_2 = 7000$
	Lower limit [m]	$X_1 = 3000$	$X_2 = 7000$	$L = 10000$
	Area [m ²]	$S_A = 3000$	$S_B = 4000$	$S_C = 3000$
	Recharge rate [m/day]	$I = 0.002$	$I = 0.002$	$I = 0.002$
Unsaturated zone	Mean transit time [day]	$T = 300$	$T = 300$	$T = 300$
	Dispersion parameter [-]	$P_D = 0.1$	$P_D = 0.1$	$P_D = 0.1$
	Decay constant [day ⁻¹]	$\lambda_A = 0$	$\lambda_B = 0$	$\lambda_C = 0.0035$
	Retardation factor [-]	$R = 1$	$R = 1$	$R = 1$
Saturated zone	Thickness [m]	$e = 2$	$e = 2$	$e = 2$
	Effective porosity [-]	$\phi_A = 0.2$	$\phi_B = 0.2$	$\phi_C = 0.2$
	Decay constant [day ⁻¹]	$\lambda_A = 0$	$\lambda_B = 0$	$\lambda_C = 0$
	Retardation factor [-]	$R = 1$	$R = 1$	$R = 1$

Table 3.2 Parameters of the problem

3.6.4. EQUATIONS GOVERNING THE RESOLUTION

The characteristics of the problem determine which of the formulation of convolution equations (among Equation 3.1, Equation 3.4, Equation 3.5, Equation 3.6, Equation 3.7 and Equation 3.8) must be considered. As the problem concerns several input zones and distinct transfer compartments within the aquifer (the unsaturated zone and the saturated zone), Equation 3.7 is appropriate.

In Equation 3.7, the term $C_{IN_i}(t)$ is known for each subarea (Figure 3.10), i being the index of the subarea (A , B or C). The unknown terms are: the recharge flow Q_i of each subarea of the input zone and the transfer functions through the unsaturated zone $g_i(\tau)$ and through the saturated zone $h_i(T)$ for solute coming from each subarea of the input zone.

The recharge flow can be defined as:

$$Q_i = S_i \cdot I \quad \text{Equation 3.17}$$

The solute transfer function in the unsaturated zone can be represented by a dispersion model [Jury and Roth, 1990], reported in Table 2.2, assuming a vertical 1D flow configuration. As the solute is subject to decay, the dispersion model can be formulated to include the decay factor, following Equation 2.14. For solute coming from each subarea of the capture zone, the solute transfer function in the unsaturated zone is:

$$g_i(t) = \frac{1}{\sqrt{4\pi P_D \frac{t}{TR}}} \frac{1}{t} \exp \left[-\frac{(1 - \frac{t}{TR})^2}{4P_D \frac{t}{TR}} \right] \exp(-\lambda_i t) \quad , P_D = \frac{\alpha}{e} \quad \text{Equation 3.18}$$

where i is the index of the subarea (A , B or C), the dispersion parameter P_D is a ratio between the dispersivity α and the thickness of the unsaturated zone e .

Resolving Equation 3.18 with the data of Table 3.2, the solute transfer functions in the unsaturated zone are determined beneath each subarea of the catchment (Figure 3.12).

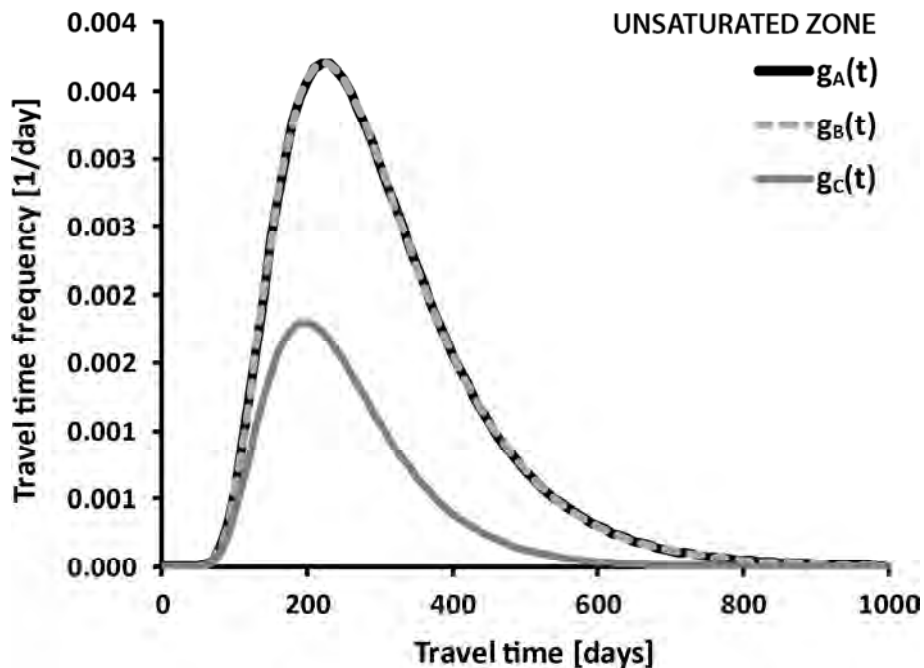


Figure 3.12 Transfer functions $g_A(t)$, $g_B(t)$ and $g_C(t)$ in the unsaturated zone for solute coming respectively from the subareas A, B and C of the capture zone. The characteristics of the transfer functions are based on a dispersion model.

In the saturated zone the aquifer configuration, characterized by a uniform recharge rate in the water table, a constant thickness of the groundwater body, a homogeneous porosity and a fully penetrating pumping well, is favorable to an exponential model of solute transfer function. As the distribution of solute input is not homogeneous in the recharge zone, the transfer function of solute must be specific to each subarea of solute input. Following the exponential model for distributed solute inputs (Equation 3.11 and Equation 3.12), and using the parameters of Table C5, the solute transfer functions in the saturated zone are determined for solute coming from each subarea of the input zone (Figure 3.13).

Summarizing the previous results, the Figure 3.14 conceptually shows the transfer functions that are characterized in the various compartment of the aquifer system.

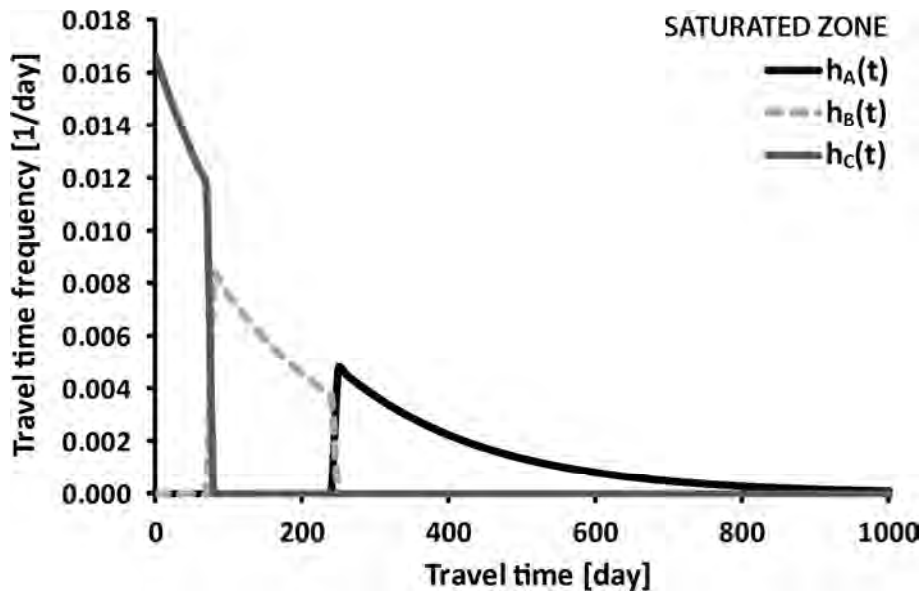


Figure 3.13 Transfer functions $h_A(t)$, $h_B(t)$ and $h_C(t)$ in the saturated zone for solute coming respectively from the subareas A, B and C of the capture zone. The characteristics of the transfer functions are based on an exponential model.

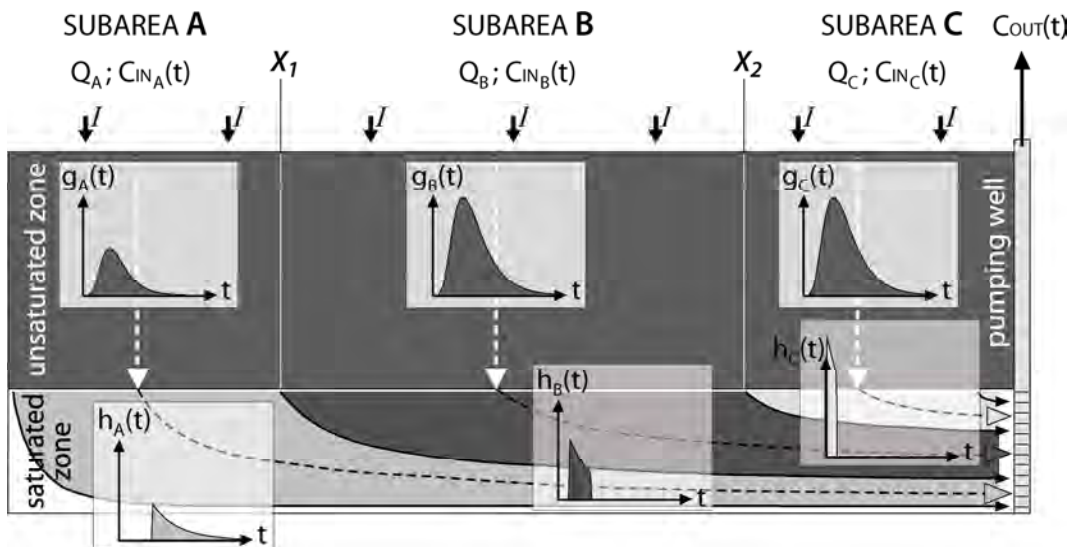


Figure 3.14 Conceptual illustration of the various flow paths and of the transfer functions associated to the various transfer compartments of the aquifer system, beneath the subareas A, B and C of the input zone.

3.6.5. RESULT

As the parameters of Equation 3.7 have been defined and quantified, the evolution of solute concentration at the pumping well can be calculated. The results are illustrated in Figure 3.15. Several aspects can be pointed out.

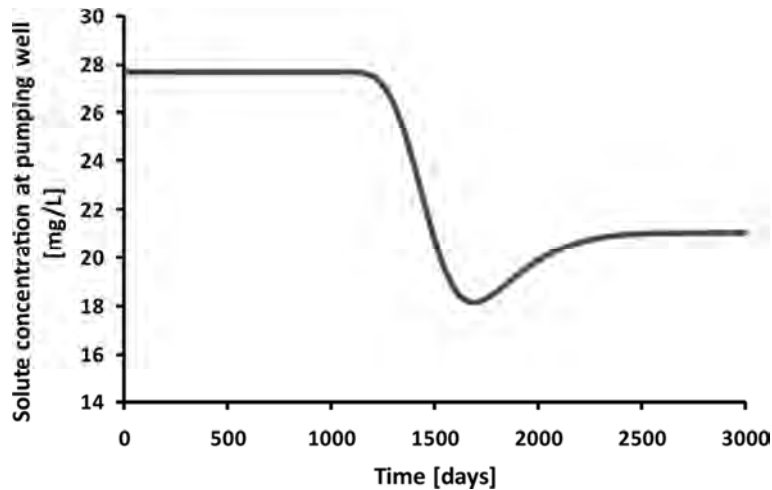


Figure 3.15 Calculated evolution of solute concentration at the pumping well [mg/l]

First, the change of mass input in the recharge zone, occurred at time 1000 days (Figure 3.10), has a significant impact on the concentration of solute at the pumping well: after an initial level of around 28 mg/L, the concentration tends to decrease from the time 1200 days, which involves a lag time of about 200 days between changes of mass flow rate in the input zone and the reaction at the pumping well. Hence, 200 days is the safe period of the aquifer to pollution events at the surface.

Second, the changes on input concentrations occur over a period of 200 days, whereas, after an initial constant level, the changes of concentration at the pumping well are observed over a period of around 1200 days. Hence, the transfer function approach effectively simulates the spreading over of the arrival time of the solute at the pumping well, which is attributed to the travel time distribution of solute through the aquifer, characterized by the transfer functions illustrated in Figure 3.12 and Figure 3.13.

Third, the trend of the concentration evolution is not univocal. The decrease of concentration reaches about 10 mg/L at the time 1700 days, with a concentration of 18 mg/L. After the time 1700 days, a reversal trend occurs, with a 3 mg/L increase over a period of around 700 days. From the time 2500 days, the concentration tends to be stabilized at the level 20 mg/L. These fluctuations can be explained by the spatial distribution of solute input history. The decrease of solute input concentration at the subarea B and C, the closest subarea in terms of distance and travel time, firstly leads to a decrease of solute concentration at the pumping well. The subarea A, which is the furthest subarea (in distance and travel time terms) and which is characterized by an increasing solute concentration of the recharge, subsequently have a delayed impact on the evolution of solute concentration at the pumping, which is visible by the increase observed from the time 1700 days.

3.7. CONCLUSION

This chapter explores the various aspects of the transfer function approach for estimating the evolution of groundwater quality at pumping wells or, more generally, at the outlets of the aquifers. It proposes new developments to make the approach suited to the largest number of remediation projects.

The new formulation of the convolution integral (Equation 3.8) strongly reduces the drawbacks of the transfer function approach, as applied up to now: multiple input zones with specific history are considered in a separate manner and the specificity of solute transfer at the various compartments of the aquifer system (in particular the unsaturated zone and the saturated zone) can be also separately included in the resolution of the equation. In this direction, several developments of the exponential model of transfer function are therefore proposed (Equation 3.11/Equation 3.12 and Equation 3.14/Equation 3.15) considering partial input zones and partial outlets.

Hence, it is easily possible to directly consider the transfer of solute both in the saturated and unsaturated zones at multiple parts of the aquifer catchment, in a single computation. This last aspect is not obvious for numerical models: the numerical simulation of flow and transport in both unsaturated and saturated zones requires solving partial differential equations that are highly non-linear, which may cause non-convergence problems.

The main limits of the transfer function approach can be found in the context of the variations of flow conditions of low frequency or flow conditions that are not constant over time (for instance a trend due to climate changes). In this case, the assumption of steady state cannot be made because the transfer functions are dependent on the time of observation. In this specific case, the simulation by a numerical procedure remains certainly the most appropriate approach to predict the evolution of a solute at the outlet of an aquifer. In every instance, as well as in the numerical simulations, a calibration procedure by observation data is strongly recommended to carry out such a transfer function approach.

To summarize, by including the theoretical developments proposed in this chapter, the transfer function approach is a promising method for the calculation of the evolution of groundwater quality at the outlets of the aquifers, when steady-state flow can be assumed. In Section 3.6, some of the new developments are applied on a conceptual aquifer system, where solute inputs are partially captured by a pumping well. In spite of this conceptual example, the application of the transfer function approach on a real case study is required to complete the demonstration of its reliability and its accuracy. The aquifer of Wohlenschwil, presented in Chapter 4, provides this opportunity.

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APPENDIX 3.A

DEVELOPMENT OF THE EXPONENTIAL MODEL OF TRANSFER FUNCTION FOR A LOCALIZED INPUT ZONE AND A LOCALIZED OUTLET

A saturated aquifer system of length L is assumed with a uniform thickness e , a uniform porosity ϕ and an uniform surface infiltration rate I (illustration in Figure 3.7). This conceptual case is already introduced by Kazemi et al. [2006] and one part of the mathematical development comes from this reference (Equation 3.A.1, Equation 3.A.2, Equation 3.A.4, Equation 3.A.5 and Equation 3.A.8). According to the hypothesis of Dupuit, horizontal velocity constant over depth, the Darcy flux along the distance corresponds to $q(x) = Ix/e$ and the real velocity along the distance x is $v(x) = Ix/e\phi$. The travel time $t(x)$ required for a solute coming from a point x to reach the outlet at the distance L is:

$$t(x) = \int_x^L \frac{dx}{v(x)} = \frac{e\phi}{I} \int_x^L \frac{dx}{x} = \frac{e\phi}{I} \ln\left(\frac{L}{x}\right) = T_0 \ln\left(\frac{L}{x}\right) \quad \text{Equation 3.A.1}$$

with

$$T_0 = \frac{e\phi}{I} \quad \text{Equation 3.A.2}$$

The cumulated flow Q_{oz} at the outlet (located at the distance L) from the surface ($z = 0$) to a certain depth z is equal to $Q_{oz} = zIL/e$. The cumulated recharge Q_{xL} at the surface from an input point x to the outlet ($x = L$) is $Q_{xL} = I(L - x)$. If $z(x)$ is the depth reached by flows coming from an input point located at the distance x , Q_{oz} and Q_{xL} are equal and the following relation can be written: $z(x)IL/e = I(L - x)$. Equation 3.A.3 can be deduced by isolating $z(x)$ from the last relation:

$$z(x) = e \left(1 - \frac{x}{L}\right) \quad \text{Equation 3.A.3}$$

Equation 3.A.1 gives the mathematical relation between the travel time t and the distance x of the input point, whereas Equation 3.A.3 gives the mathematical relation between the depth at the outlet reached by solute coming from input point at distance x .

By putting together Equation 3.A.1 and Equation 3.A.3, it follows that:

$$t(z) = T_0 \ln \left(\frac{1}{1 - \frac{z}{e}} \right) \quad \text{Equation 3.A.4}$$

$$x(z) = \left(1 - \frac{z}{e} \right) L \quad \text{Equation 3.A.5}$$

$$x(t) = L \exp \left(-\frac{t}{T_0} \right) \quad \text{Equation 3.A.6}$$

$$z(t) = e \left[1 - \exp \left(-\frac{t}{T_0} \right) \right] \quad \text{Equation 3.A.7}$$

As reported by Kazemi et al. [2006], the transit time probability density function is defined as:

$$\varphi(t) = \frac{1}{Q_0} \frac{dQ(t)}{dt} \quad \text{Equation 3.A.8}$$

Q_0 is the total discharge flow; $Q(t)$ is the portion of discharge flow which has a residence time in the system less than or equal to t . If solute enters in the same conditions than flow, and if the solute travel has the same characteristics than flow transit, the transit time probability density function $\varphi(t)$ is the transfer function $g(t)$ of solute in the aquifer.

The transfer function of solute reaching the outlet and coming from the area bounded by the distances $x = x_1$ and $x = x_2$, can be defined as:

$$g(t) = \frac{1}{Q_{0x_1x_2}} \cdot \frac{dQ_{x_1x_2}(t)}{dt} \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.A.9}$$

$$g(t) = 0 \quad , \text{otherwise} \quad \text{Equation 3.A.10}$$

$$\text{with } t_1 = T_0 \ln \left(\frac{L}{x_1} \right)$$

$$t_2 = T_0 \ln \left(\frac{L}{x_2} \right)$$

where $Q_{0x_1x_2}$ is the total discharge flow at the outlet for water coming from the subarea of the recharge zone delimited by x_1 and x_2 ; $Q_{x_1x_2}(t)$ is the part of the discharge flow that has a residence time in the system in the interval $[t_2; t]$.

Based on Equation 3.A.6, $Q_{0x_1x_2}$ and $Q_{x_1x_2}(t)$ are:

$$Q_{0x_1x_2} = I(x_2 - x_1) = IL \left[\exp\left(-\frac{t_2}{T_0}\right) - \exp\left(-\frac{t_1}{T_0}\right) \right] \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.A.11}$$

$$Q_{x_1x_2}(t) = I(x_2 - x(t)) = IL \left[\exp\left(-\frac{t_2}{T_0}\right) - \exp\left(-\frac{t}{T_0}\right) \right] \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.A.12}$$

The transfer function $g_{t_1t_2}(t)$ of solute reaching the outlet in the travel time interval $[t_2 ; t_1]$ can be derived from the discretisation of Equation 3.A.9, inserting Equation 3.A.11 and Equation 3.A.12:

$$g_{t_1t_2}(t) = \frac{\exp\left(-\frac{t}{T_0}\right)}{T_0 \left[\exp\left(-\frac{t_2}{T_0}\right) - \exp\left(-\frac{t_1}{T_0}\right) \right]} \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.A.13}$$

$$g_{t_1t_2}(t) = 0 \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.A.14}$$

Inserting Equation 3.A.4 in Equation 3.A.13, the transfer function $g_{z_1z_2}(t)$ of solute reaching the outlet at the depth interval $[z_2 ; z_1]$ is:

$$g_{z_1z_2}(t) = \frac{\exp\left(-\frac{t}{T_0}\right)}{T_0 \left(\frac{z_1}{e} - \frac{z_2}{e} \right)} \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.A.15}$$

$$g_{z_1z_2}(t) = 0 \quad , \text{otherwise} \quad \text{Equation 3.A.16}$$

$$\text{with } t_1 = T_0 \ln \left(\frac{1}{1 - \frac{z_1}{e}} \right)$$

$$t_2 = T_0 \ln \left(\frac{1}{1 - \frac{z_2}{e}} \right)$$

Inserting Equation 3.A.1 in Equation 3.A.13, the transfer function $g_{x_1x_2}(t)$ of solute coming from the subarea of the recharge zone delimited by the distance interval $[x_2; x_1]$ is:

$$g_{x_1x_2}(t) = \frac{L \exp\left(-\frac{t}{T_0}\right)}{T_0(x_2 - x_1)} \quad , t_2 \leq t \leq t_1 \quad \text{Equation 3.A.17}$$

$$g_{x_1x_2}(t) = 0 \quad , \text{ otherwise} \quad \text{Equation 3.A.18}$$

$$\text{with } t_1 = T_0 \ln\left(\frac{L}{x_1}\right)$$

$$t_2 = T_0 \ln\left(\frac{L}{x_2}\right)$$

The average time of travel $\overline{t(z)}_{z_1z_2}$ over the depth interval $[z_1; z_2]$ is the mean value of the function $t(z)$ (Equation B4) in the interval $[z_1; z_2]$, which, applying the mean value theorem, corresponds to:

$$\overline{t(z)}_{z_1z_2} = \frac{1}{z_1 - z_2} \int_{z_2}^{z_1} t(z) dz = \frac{1}{z_1 - z_2} \int_{z_2}^{z_1} T_0 \ln\left(\frac{1}{1 - \frac{z}{e}}\right) dz \quad \text{Equation 3.A.19}$$

$$\overline{t(z)}_{z_1z_2} = \frac{e}{z_1 - z_2} T_0 \left[\left(1 - \frac{z_1}{e}\right) \ln\left(1 - \frac{z_1}{e}\right) - \left(1 - \frac{z_2}{e}\right) \ln\left(1 - \frac{z_2}{e}\right) + \frac{z_1 - z_2}{e} \right] \quad \text{Equation 3.A.20}$$

Similarly, the average time of travel $\overline{t(x)}_{x_1x_2}$ for solute coming from an input zone defined in the interval $[x_1; x_2]$ is:

$$\overline{t(x)}_{x_1x_2} = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} t(x) dx = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} T_0 \ln\left(\frac{L}{x}\right) dx \quad \text{Equation 3.A.21}$$

$$\overline{t(x)}_{x_1x_2} = \frac{T_0}{x_2 - x_1} \left[x_2 \left(\ln\left(\frac{L}{x_2}\right) + 1 \right) - x_1 \left(\ln\left(\frac{L}{x_1}\right) + 1 \right) \right] \quad \text{Equation 3.A.22}$$

$$\overline{t(x)}_{x_1x_2} = T_0 \left[1 + \ln(L) + \frac{x_1 \ln(x_1) - x_2 \ln(x_2)}{x_2 - x_1} \right] \quad \text{Equation 3.A.23}$$

From a practical point of view, Equation 3.A.23 is relevant to calculate the mean travel time of solute pumped at a pumping well, where the screen section of the well corresponds to a certain depth interval of the aquifer. As it was discussed in Chapter 2, the mean travel time gives a first approximation of the order of magnitude of reaction time of the aquifer system.

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Chapter 4

Predicting the evolution of nitrate concentration at the pumping well of the Wohlenschwil aquifer

ABSTRACT

Among the various methods to predict the evolution of groundwater, Chapter 3 describes a new development in the transfer function approach. The aim of this chapter is to illustrate this approach on the case study of the Wohlenschwil aquifer, which is the subject of a "Nitrate Project" since 1997. In particular, this chapter describes and compares the analytical and numerical methods that can be used to characterize the transfer functions in the aquifer system.

The study area, located near Zurich, Switzerland, consists of an unconfined Quaternary sand and gravel aquifer with a recharge area of around 1km². In the central part of the aquifer, the water table is located around 12 m below the surface. The conversion to extensive agriculture has led to a rapid decrease of the nitrate concentration in the pumping well from about 50 mg/l in 1997 to around 25 mg/l from 2003 to 2010.

In order to assess the relevant parameters and functions required in the transfer function approach, a number of different methods were used. The seasonal variability of groundwater recharge was quantified using a soil water balance model based on measured meteorological and water content data. The transfer function of nitrate through the unsaturated zone is first analytically characterized by a dispersion model, where the transit time parameter is estimated by a piston flow model, depending on the distribution of soil moisture content. In parallel, the transfer functions through the unsaturated zone are also simulated by the numerical model HYDRUS-1D. In the saturated zone, the transfer functions are analytically characterized using graphical methods based on tracing tests and, in parallel, are numerically simulated using the FEFLOW tool. As the periods of fluctuations of the hydrodynamics conditions are lower than the calculated range of travel time, permanent conditions of flows can be assumed and a transfer function approach is applicable.

Based on the obtained transfer functions and the history of land use which is well known, the response of the system to land use changes was reconstructed and the key factors that controlled the dynamics of the response was identified. Thus, the evolution of nitrate concentration can be estimated in the future as well as the impact of recharge variations and the effect of the various steps of agricultural conversions. Analytical and numerical methods can be used to characterize transfer functions through the aquifers; the choice of one or the other mainly depends on the availability of reliable and relevant data for their implementation.

4.1. INTRODUCTION

4.1.1. PROBLEMATIC OF AGRICULTURAL POLLUTION OF GROUNDWATER

Since the second half of the twentieth century, shallow aquifers, which are one of the most important groundwater resources, are threatened by anthropogenic pressures not only on groundwater quantity but also on groundwater quality. One of the most common pollutants is nitrate, whose concentration tends to increase in many shallow aquifers [Strebel *et al.*, 1989]. Elevated nitrate concentrations usually originate from intensive agriculture that promotes the use of fertilizers and pesticides. When added above the assimilation capacity of soil and plants, fertilizers and pesticides tend to be leached through soil toward the water table. The National Observatory of Groundwater in Switzerland, representing 500 monitoring sites, estimated that, in 2005, 19% of the NAQUA monitoring sites exceeded the standards of the Water Protection Ordinance (GSchV) of 25 mg/l of nitrate and 60% of the sampling sites located in areas dominantly used for arable farming exceeded this level [OFEV, 2009]. In the same year, 4% exceeded the tolerance value of the Ordinance on Foreign Substances and Constituents in Food (FIV) of 40 mg/l and this value is exceeded in 13% of the sites located in agricultural zones [OFEV, 2009]. According to the last communication of the Swiss Federal Office for the Environment (FOEN), about the same level of pollution is observed in 2010¹.

In the specific case of diffuse contamination by agricultural land uses, remediation programs were introduced following agronomical considerations: limitation of fertilizers, land use changes or crops rotation [Cuttle and Scholefield, 1995; Wendland *et al.*, 1998; Spalding *et al.*, 2001; Owens and Bonta, 2004; Kyllmar *et al.*, 2005]. By limiting the source of pollution at the surface, these measures aim for an improvement of groundwater quality, simply due to the renewal of water in the aquifer system. During the 1990's and 2000's such environmental actions have produced significant changes on trends of groundwater quality evolution. While nitrate concentrations tended to increase between the 60's to the 80's in Europe [Strebel *et al.*, 1989], a stabilization seemed to occur during the 90's, according to the data base of the European Environment Agency [Lindinger and Scheidleder, 2004].

These inversions of tendency are observed at large scale. Nevertheless at the local scale, environmental actions produced variable results. In some cases, significant improvement of groundwater quality occurred [Wendland *et al.*, 1998; Owens and Bonta, 2004; Owens *et al.*, 2008]. In other cases, after a certain observation time, environmental actions did not show a significant effect [Meals *et al.*, 2010].

¹ See <http://www.bafu.admin.ch/grundwasser/07500/07563/07577/index.html?lang=en>

The effect of environmental measures can be observed when excess pollutants begin to be removed from the aquifer system. After implementation of environmental measures, an effect of groundwater quality usually only occurs after a lag time corresponding to the time required for pollutants to travel through the aquifer system, as developed in chapter 2. This lag time can lead to an inaccurate interpretation of the efficiency of the project. When low or no improvement of groundwater quality is observed a certain time after the introduction of remediation measures, it does not necessarily mean that the project has failed, but rather that pollutants are still present in the aquifer and that more time is required to reach the expected objectives. This situation was observed in many studies [Bohlke, 2002; Tomer and Burkart, 2003; Osenbrück et al., 2006; Hund-Goschel et al., 2007; McMahan et al., 2008; Visser et al., 2009a; Meals et al., 2010].

The knowledge of the lag time of the environmental measures is of crucial importance for the management of the project for several reasons: (1) to predict the time required to reach the expected target of the measures; (2) to determine at any time whether previous measures are effective and environmental goals will be reached. The most direct way to characterize the lag time of remediation measures is to simulate the evolution of groundwater quality in relation with evolution of pollutant inputs.

According to Visser et al. [2009b] transfer functions and numerical models remain the most valuable methods to estimate future groundwater quality trends. Most environmental projects are nonetheless not accompanied with such studies. This can be mainly explained by the fact that numerical simulations of flow and transport are often considered too costly and time-consuming for environmental projects, requiring specific tools and field investigations. The transfer function methods are also rarely applied for several reasons: by lack of specific field data, when the required conditions of the approach are not fulfilled, or simply because of unawareness of the existence of the method. Hence, there is a lack of an appropriate approach, both sufficiently simple and accurate to be applicable for most groundwater quality remediation projects.

4.1.2. PREDICTION OF GROUNDWATER EVOLUTION BY A TRANSFER FUNCTION APPROACH

In chapter 3, a new method based on transfer functions is described with the aim of predicting the evolution of groundwater quality at a pumping well (or more generally at an outlet) of an aquifer. The method is based on an extension of the classical convolution integral, which was introduced in hydrogeology for the study of the transfer of environmental tracers in aquifers [Jury, 1982; Maloszewski and Zuber, 1982]. The main condition of use of this method is that the flow of the aquifer system is in a steady state. In the new proposed formulation, transfer functions in the unsaturated and saturated zones are introduced in a separate manner and for each subarea of the input zone. The main approaches to determine the relevant transfer functions are summarized in chapter 2.

The formulation of such a convolution integral is (Equation 4.1):

$$C_{\text{OUT}}(t) = \frac{\sum_i Q_i \int_0^t \left[\int_0^{t-T} C_{\text{IN}_i}(t - \tau - T) g_i(\tau) d\tau \right] h_i(T) dT}{\sum_i Q_i} \quad \text{Equation 4.1}$$

where $g(\tau)$ is the transfer function across the unsaturated zone; $h(T)$ is the transfer function across the saturated zone; t is the observation time, T is the travel time in the saturated zone and τ is the travel time in the unsaturated zone, i is the index of the sub-area.

Equation 4.1 allows for the prediction of how groundwater quality will evolve at an outlet of an aquifer. The theory of this approach is described in detail in Chapter 3, and the methods to determine the required transfer function are detailed in Chapter 2. Then, it should be confronted by a practical application.

4.1.3. OBJECTIVES OF THE STUDY

The objective of this chapter is to test the applicability of the transfer function method, developed in chapter 3, for a real field site with a known history of land use.

The transfer function method developed in chapter 3 is applied for the prediction of the evolution of nitrate concentration at the pumping well of the Wohlenschwil aquifer, located in the canton of Aargau, in Switzerland. This case study is well suited because the change on land use by agriculture, which is the main source of nitrate pollution, as well as the evolution of nitrate at the pumping well, are well known since 1997.

The field data investigated in the Wohlenschwil site allows the characterization of the required transfer functions by two different approaches: by numerical methods and by analytical methods. The different approaches are tested and compared.

4.2. STUDY SITE

4.2.1. CONTAMINATION PROBLEMATIC OF THE WOHLenschWIL Aquifer

Wohlenschwil is a relatively small town of around 1400 inhabitants (local statistics, 2010) located in the canton of Aargau, in the central plateau of Switzerland. Drinking water of the community is obtained from a pumping well, supplying an average of 360 m³/day of water from the Wohlenschwil aquifer. The land cover in the aquifer recharge zone is mainly forest, permanent meadow and intensive agriculture (Figure 4.1). A strong and continuous increase of nitrate concentrations in pumped groundwater has been observed during the 1980's and 1990's (Figure 4.2). The increase of nitrate concentrations in groundwater has been attributed to intensive agriculture. Because the nitrate concentration has exceeded 40 mg/l (drinking standard limit in Switzerland) in the pumping well in 1993, cantonal authorities solicited federal support in order to introduce the Nitrate Project in 1997. The Nitrate Project consisted of converting agricultural parcels in the catchment area of the pumping wells from intensive agricultural practices to permanent meadow, which lead to less fertilization and tillage within the catchment area. Conversion has been carried out from 1997 to 2010 at different steps illustrated in Figure 4.1.

The Nitrate Project of Wohlenschwil led to a rapid decrease of nitrate concentrations since 1997 (Figure 4.2). Nevertheless, several observations can be made in the evolution of nitrate concentration. First, the initial land conversion campaign, introduced in 1997, is followed by a reaction spread out over a period of 6 years. Second, before the observed decrease of the period 2009 – 2010, the second conversion campaign of 2003 is followed by an increase of nitrate concentration from 2004 to 2008, which is in contradiction with the expected results.

The Wohlenschwil case study raises the two typical questions in relation with the introduction of a groundwater quality remediation program by the limiting of agricultural pollution sources: (1) how the present and past evolution of nitrate concentration can be explain by the remediation measures already introduced? (2) what is the evolution that can be expected in the future, considering the planned remediation program?

The transfer function approach applied to this site will focus on the period from 1997 to 2010, during which land use and nitrate concentration evolution are well known. The observed evolution of nitrate will be compared to the calculated values. Then, the method will be applied to predict nitrate evolution after 2010, based on a hypothesis of a constant land use since 2010.

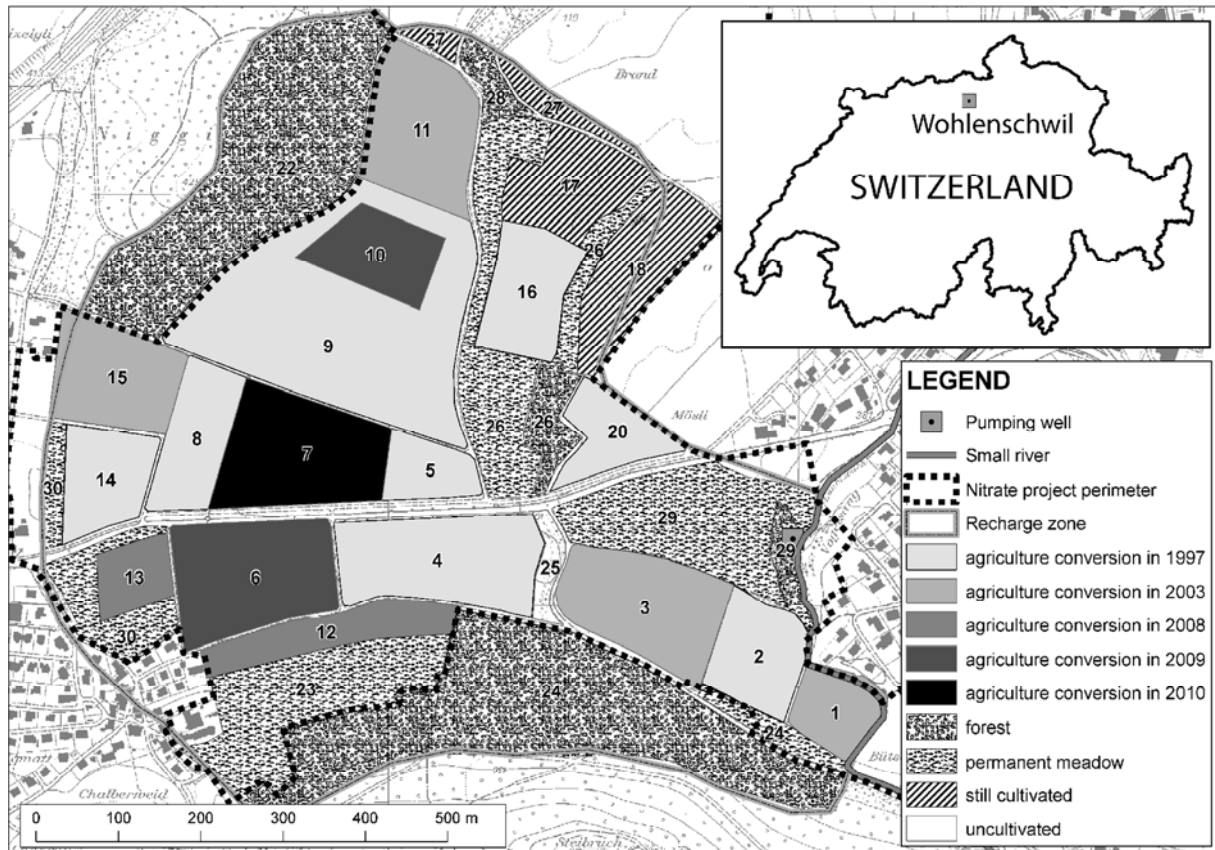


Figure 4.1 Location of the Wohlenschwil aquifer; delimitation of the recharge zone of the aquifer; Perimeter of the “Nitrate project” where environmental measures are introduced; delimitation and numbering of parcels; Chronology of land use conversion of agricultural parcels from 1997 to 2010.

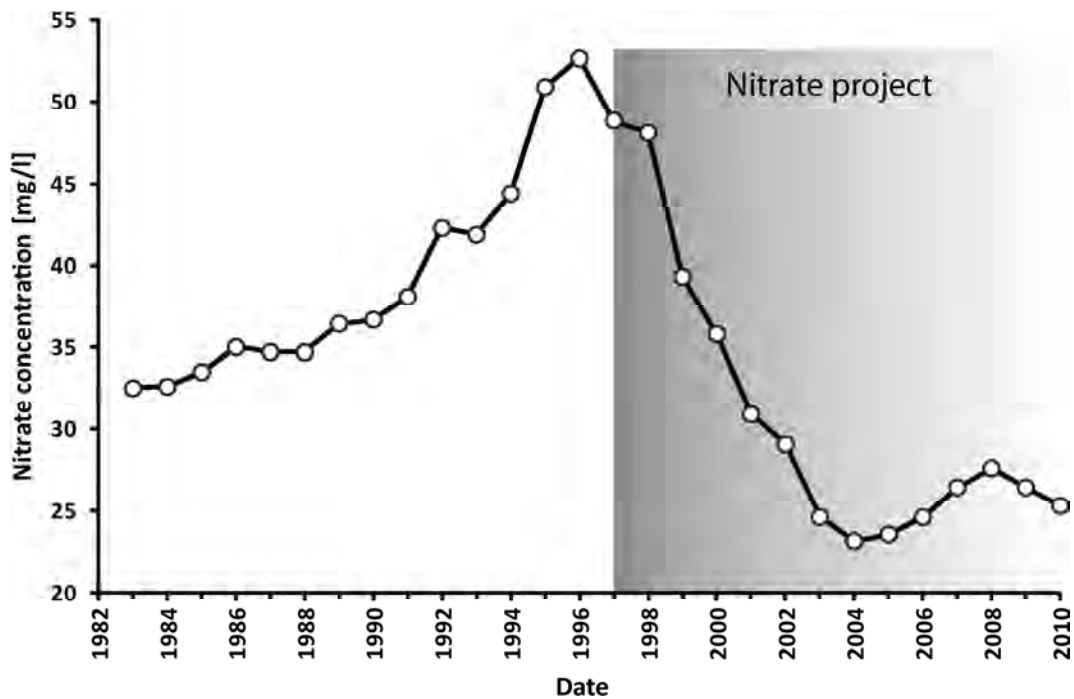


Figure 4.2 1982 – 2010 evolution of nitrate concentration (annual mean value in mg/l) at pumping well of the Wohlenschwil aquifer

4.2.2. HYDROGEOLOGICAL CONTEXT OF THE WOHLenschWIL SITE

It can be globally acknowledged that a good description of the hydrogeological characteristics of an aquifer site is a prerequisite for any project assessing groundwater quality. Specific field investigations are required depending on the study's objectives and proposed analytical methods.

The general characteristics of the Wohlenschwil aquifer have been investigated during the years 2009 – 2010 and have been addressed by previous studies [Jäckli, 1966; 1996]. This section gives the main geological and hydrogeological interpretations for the Wohlenschwil aquifer.

4.2.2.1. Geological context

The geology of the Swiss Plateau is mainly comprised of Molasse deposits dating from the Oligocene (lower fresh Molasse or USM) or Miocene (Upper marine Molasse or MMO), with thicknesses reaching up to several hundred meters in the central parts of the plateau. The Molasse is composed of sandstones, argillites and marls with alternating freshwater limestone. The topographic relief of the Plateau has been formed mainly by erosive processes during various glacial and inter-glacial periods. These valleys have been partially filled with quaternary glaciofluvial sediments and ground-moraine since the last glacial-period (Würm). The Wohlenschwil aquifer is located in a small valley bounded in the south by MMO molassic hill and in the northwest by molassic USM hills as illustrated in Figure 4.3 [Jäckli, 1966].

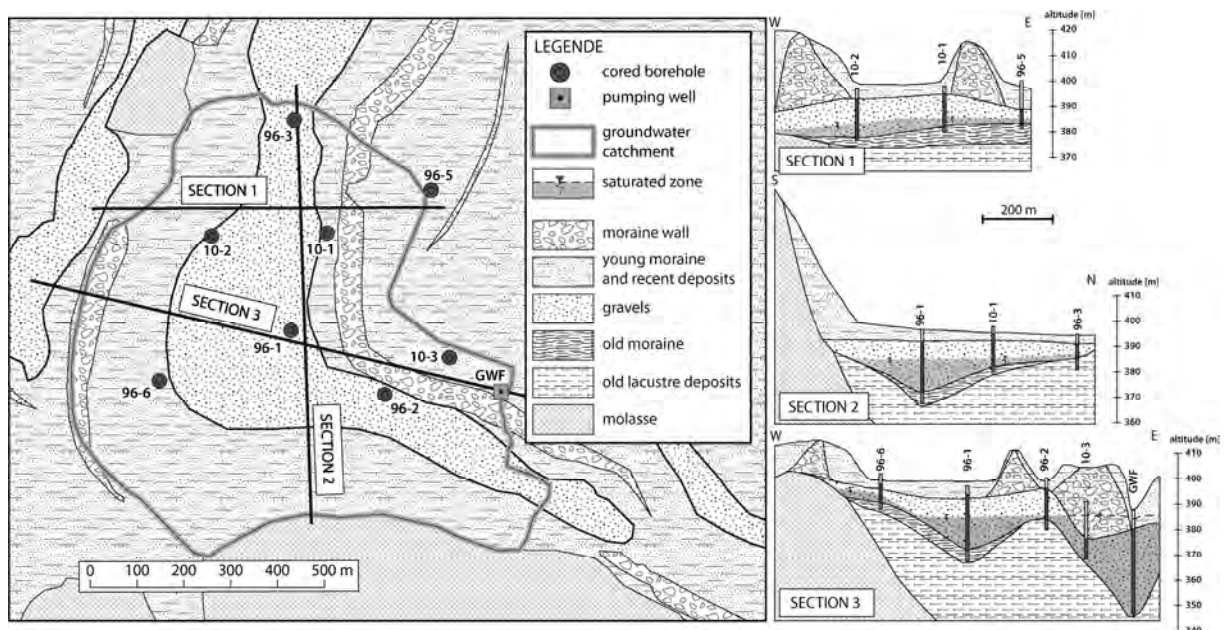


Figure 4.3 Simplified geologic map, modified from [Jäckli, 1966], and cross-sections of the Wohlenschwil aquifer, modified from [Jäckli, 1996]

According to Jäckli [1966], the deepest deposits mainly consist of low permeability ground moraine (old moraine) and lacustrine clays (old lacustrine deposits) and can be considered as aquitard. These deposits eroded during the Würm glacial-period, forming alluvial channels that reached several tens of meters in depth. These channels were filled by glaciofluvial sediments. These deposits are heterogeneous but in general, are represented by permeable sediments, like unconsolidated gravels and sands and by silty lenses with limited horizontal extent. The shallowest layers consists of the last moraine deposits of the Würm glacial-period, represented by hills of moraine walls, limiting the West and East of the valley, and by heterogeneous frontal moraines, semi-permeable, and recent deposits covering gravely sediments of the valley.

4.2.2.2. The Wohlenschwil aquifer

Observations from 8 boreholes logs and 17 piezometers (Figure 4.4), associated with results of tracing tests, pumping tests and electrical tomography studies, provided the basis for the characterization of the structure and hydrogeological properties of the aquifer.

The aquifer mainly corresponds to the glaciofluvial sediments (sand and gravels) and to a less extent to superficial deposits of moraine. The lower confining bed is formed by old clayey moraine and lacustrine deposits in the central part of the aquifer and molasse sandstone at the border (Figure 4.3). In the central part of the valley, the unconfined aquifer has a thickness of around 10 – 30 m, the water table is located around 10 – 15 m beneath the surface. The saturated zone is generally thin (1 – 3 m), with a maximum thickness reaching 15 m locally in the central part (Figure 4.3). The thickness of the aquifer tends to increase with a channel developed from the central part to the eastern part of the aquifer domain and the depth of the bottom of the aquifer reaches several tens of meters around the pumping well. The central channelized part of the aquifer has a high hydraulic conductivity of around 10-2 m/s, whereas the lateral part of the aquifer, generally formed by last glacial moraine deposits, presents a relatively low hydraulic conductivity of 10⁻⁴ – 10⁻⁵ m/s [Jäckli, 1996]. The main recharge sources are direct infiltration of rainfall in the valley and lateral inflow from surrounding slope zones (south and west by molasse and moraine hills and north and east by moraines). According to the geological map, the molasse outcrop in the upper part of the southern (southern part of Figure 4.3) hills generally dips to the south [Jäckli, 1966], which leads us to assume that this part is not contributing to the aquifer recharge. The influence of the creek flowing in the south-east near the pumping well is considered as insignificant for the groundwater quality, based on two observations: (1) the strong seasonal variations of water quality of the creek do not affect the evolution of groundwater quality at the pumping well; (2) the aquifer surrounding the pumping well is locally confined, preventing direct vertical recharge.

Based on flow directions and the determination of a drainage divide, two outlets of the Wohlenschwil aquifer are identified (Figure 4.4). The first outlet, located north-west of the

aquifer, is due to probable connections between the Wohlenschwil valley and a lateral valley that is filled with sandy sediments and that extends until the Reuss River 1800 m to the north. The creation of this connection could be explained by a former glacier mouth in this location, but this assumption has not been studied in more detail. The second outlet is located in the eastern part of the aquifer, mainly due to the effect of the pumping well. A third suspected outlet zone could exist in the same part as indicated by the existence of a former spring, which vanished when the pumping well was implemented. The water balance in the aquifer catchment shows that the annual volume of inflow in the recharge zone converging toward the pumping well is bigger than the annual pumped volume. This reinforces the assumption of a third outlet located around the pumping well, but its location has not been clearly identified due to lack of piezometric data. Based on the piezometric data and the hypothesis on outlets, the catchment area can be divided into two parts (Figure 4.4): (1) the first part is located in the west of the drainage divide, where groundwater flows converge toward the north-west outlet; (2) the second part is located in the east of the drainage divide, where the flows converge toward the pumping well and the third eastern outlet. This study will be focused on the second part, which corresponds to the capture zone of the well.

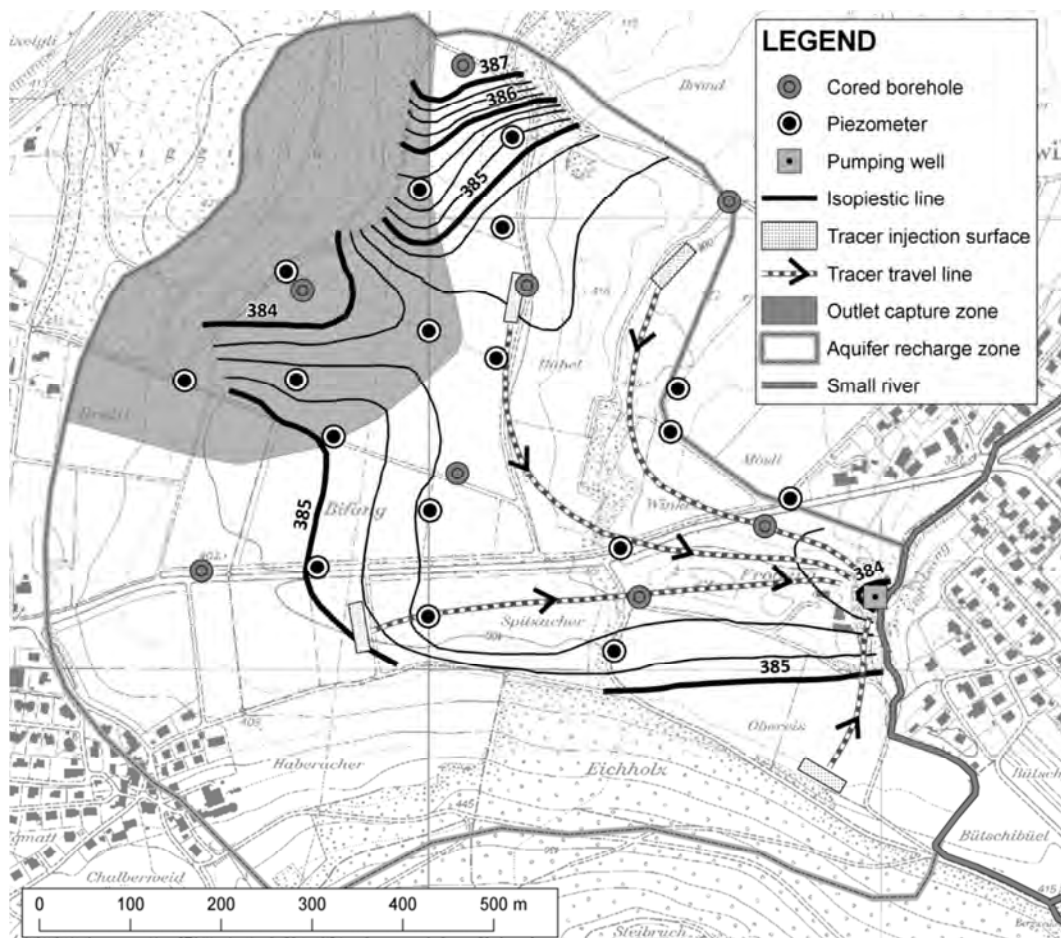


Figure 4.4 Delimitation of the Wohlenschwil aquifer recharge zone, isopiestic surface (state in December 2010), observation points, estimated tracer pathways and location of the North-West outlet capture zone

4.3. METHODOLOGY

4.3.1. INTRODUCTION

This study illustrates the transfer function approach developed in Chapter 3, focusing on the evolution of the nitrate concentration at the pumping well of the Wohlenschwil aquifer. It especially outlines the methods to derive and parameterize the relevant functions that are required.

Only the methods that are particularly well suited for the Wohlenschwil case study (small aquifer) are applied. At other sites, the application of the transfer function approach could be carried out using other methods, depending on the characteristics of the aquifer and on the available data.

Figure 4.1 shows that land use varies in the capture zone of the pumping well: first spatially, by the nature of land use (forest, agricultural parcel, urban area, waste land); secondly in the time, by differentiated crops rotation and different date of agricultural conversions. These aspects lead to a heterogeneous distribution of nitrate input history in the capture zone of the pumping well. The input zone can be then divided in several subareas, corresponding to the various agricultural parcels illustrated in Figure 4.1, and within which nitrate input history can be considered as homogeneous. Subsequently, the general term “parcel” will be used to define the delimited subareas of the capture zone of the pumping well.

As the aquifer of Wohlenschwil is characterized by a relatively thick unsaturated zone (Figure 4.3), the nitrate transfer must be considered both for saturated and unsaturated zones.

The concentration $C_{OUT}(t)$ of nitrate at the pumping well SWG of Wohlenschwil is calculated at various observation times t , based on the different elements of the Equation 4.1 that are:

- $C_{IN_i}(t)$: the input function of nitrate concentration for each parcel
- Q_i : the contribution of each parcel to the pumping rate
- $g_i(\tau)$: the transfer function of nitrate through the unsaturated zone
- $h_i(T)$: the transfer function of nitrate through the saturated zone

The key to the resolution of the problem is based on the prior characterization of these elements for each parcel defined within the capture zone of the pumping well, illustrated in Figure 4.1. In the following subsections, the methods to get these elements are introduced.

Two methods reported in chapter 2 are used to characterize the transfer functions through the saturated and unsaturated zones: on the one hand using an analytical approach and on the other hand using numerical tools. The accuracy of the transfer function approach is analyzed by comparison with the nitrate concentration observed from 1997 to 2010 (Figure 4.2). The results obtained by the analytical approach are compared to results from the numerical approach. The validated method is then applied to estimate the evolution of nitrate concentration in the future based on the scenario of a constant land use after 2010 (considering the last agricultural conversion of the “nitrate project”).

4.3.2. QUANTIFICATION OF THE INPUT FUNCTIONS

For the Wohlenschwil site, historical land use and particularly crop rotation, is known for most of the parcels since 1997. For the period before 1997, it is assumed that most of the parcels were used for intensive agriculture. This knowledge about the land use history is a key to determine nitrate concentration input function $C_{IN_i}(t)$ for each parcel of the recharge zone, as a required parameter for the calculation of Equation 4.1.

The nitrate inputs at each parcel correspond to nitrate leaching, which is dependent on land use and particularly on crop type. The standard rate of nitrate leaching (kg/ha/years of nitrogen) for each crop type are provided by an internal and non-published document of the Nitrate Project [Ziltener, 2008] and reported in Table 4.1. The methods to estimate nitrogen leaching is based on the mathematical tool MODIFFUS (MODEL for the estimation of DIFFUSE nutrient losses) [Prasuhn and Sieber, 2005]. These values have been calculated for land uses, characteristics of the soil and climate representative for the area. There is a significant uncertainty in the data provided by MODIFFUS, because these values are considered as constant in time and independent of meteorological conditions, which is not strictly true. The nitrogen cycle processes are strongly influenced by meteorological conditions, which can significantly vary from one year to the next, and have a strong effect on the nitrate leaching rate under the root zone [Stuart et al., 2011]. Despite these aspects, the data provided in Table 4.1, based on typical properties of the agricultural soil of the region and on regional characteristics of the climate, are supposed sufficiently reliable to be used.

Type of culture	Nitrogen leaching rate	
	[kg N/ha/year]	[kg NO ₃ /ha/year]
Potatoes	150	664
Flowers	130	576
Winter barley	90	399
Cereals	90	399
Maize	60	266
Sunflower	60	266
Winter wheat with intermediate crop	60	266
Winter barley with intermediate crop	60	266
Grain maize	50	221
Sugar beet	40	177
Artificial meadow	35	155
Winter rapeseed oil food	20	89
Permanent meadow	10	44
Forest	10	44

Table 4.1 Nitrogen and nitrate leaching rate estimated by the MODIFFUS tools for the various types of crops cultivated in the recharge zone of the Wohlenschwil aquifer

Based on Table 4.1 and the known annual crops rotations, the annual amount of leached nitrate $M_{\text{INNO}_3}(t)$ [kg/ha] can be quantified for each parcel of the aquifer catchment and for each year since 1997.

Using the Penman-Monteith equation [Allen *et al.*, 1998], the standard evapotranspiration in the recharge zone is calculated from 1990 to 2010, for a daily time step. The Penman-Monteith equation parameters are provided by the weather station of Buchs, located 12 km around Wohlenschwil at the same altitude. The yearly groundwater recharge $R(t)$ [mm/year] is calculated from 1990 to 2010 taking into account (1) measured rain in weather station; (2) evapotranspiration estimated by the Penman-Monteith equation; (3) estimated field capacity of the soil (with a soil water holding capacity of 100 mm), following a modified Thornthwaite-Mather monthly water balance method [Richter and Lillich, 1975].

Finally for each parcel the evolution of the annual average nitrate concentration $C_{\text{INNO}_3}(t)$ [mg/L] in recharge water is calculated by Equation 4.2:

$$C_{\text{INNO}_3}(t) = \frac{M_{\text{INNO}_3}(t)}{R(t)} \cdot 100 \quad \text{Equation 4.2}$$

According to Equation 4.2, the variations of recharge rate $R(t)$ have a strong effect on the input concentration $C_{\text{INNO}_3}(t)$, simply by a dilution effect. Nevertheless changes in nitrate loss for given crop due to varying climate conditions are not considered, assuming that these variations are considered small compared to changes brought about by land use changes.

It must be noticed here that the variations of recharge rate have a significant effect on the solute concentration in recharge, which is taken into account in this section. However it is assumed that these annual recharge rate variations have not influence on the other functions and parameters used in the transfer function approach, which requires steady state conditions of flows. Hence, it is assumed that the different elements of the Equation 4.1, which are the transfer functions $g_i(\tau)$ and $h_i(T)$ and the contribution of each parcels to the pumping rate Q_i , are independent on the observation time and are calculated using a mean recharge rate R . Moreover it is assumed that the capture zone extension is not influenced by the annual variations of the recharge rate. Based on the results of Chapter 3, these assumptions can be valid because the range of travel times of solute within the aquifer are larger than characteristic period of fluctuations, which is of 1 year, as it will be reported later.

4.3.3. CHARACTERIZATION OF THE NITRATE TRANSFER FUNCTIONS

The resolution of Equation 4.1 requires determining the transfer functions of the nitrate coming from each parcel of the capture zone of the well, $g(\tau)$ and $h(T)$, respectively through the unsaturated and the saturated zones of the aquifer. Analytical methods or numerical methods can be used to characterize these functions. The resolution by each type of method is developed and compared.

4.3.3.1. Analytical models of the nitrate transfer functions

- *Analytical transfer function through the unsaturated zone*

According to [Jury and Roth, 1990] the transfer function $g(\tau)$ of solute through the unsaturated zone can be described by a dispersion model, which is characterized by Equation 4.3:

$$g_i(t) = \frac{1}{\sqrt{4\pi P_D \frac{t}{T_{USi}}}} \frac{1}{t} \exp \left[-\frac{(1 - \frac{t}{T_{USi}})^2}{4P_D \frac{t}{T_{USi}}} \right], P_D = \frac{\alpha}{L} \quad \text{Equation 4.3}$$

Equation 4.3 has two parameters: the apparent dispersion parameter P_D [dimensionless] of the solute and the mean travel time T_{USi} [year] through the unsaturated zone of the aquifer. P_D is defined as the ration between the longitudinal dispersivity α and the length of travel L ; i is the index of the parcel.

It is assumed that the solute is conservative and the transport is not reactive, which is the case for nitrate under the non-denitrifying conditions of the Wohlschwil aquifer. Collected field data are not sufficient to provide information about the dispersivity in the unsaturated and saturated zones aquifer system. Based on results from numerous tracer studies [Gelhar *et al.*, 1992], a value $P_D = 0,1$ is assumed for the entire unsaturated domain. This assumes that the dispersivity of the solute is linearly proportional to the distance of travel. If the dispersivity is often considered as dependent on the length scale of the travel, several studies shows that the ratio between length and dispersivity is actually not constant in most cases: the longitudinal dispersivity initially increases linearly with travel distance and gradually approaches a constant asymptotic value [Pickens and Grisak, 1981; Dagan, 1984; Gelhar *et al.*, 1992]. Nevertheless, without any data to estimate the spatial distribution of the dispersivity, the constant ratio of P_D is supposed to be a reasonable approximation to describe the dispersion of the solute in the unsaturated zone.

The mean transit time of water through a layer of the unsaturated zone is calculated by Equation 4.4, where Z is thickness of the considered layer, θ is the volumetric water content of the layer [dimensionless] and R [m/year] is the mean annual recharge. Equation 4.4,

already reported in literature [Zoellmann *et al.*, 2001; McMahon *et al.*, 2006; Fisher and Healy, 2008; Liao *et al.*, 2012], is derived from a water balance on the assumption of a purely vertical and advective transport of tracer.

$$T_{layer} = \frac{Z \cdot \theta}{R} \quad \text{Equation 4.4}$$

For each parcel, the total transit time in the unsaturated zone is the sum of the travel times through subsurface layers. As the transport of nitrate is assumed not reactive, it can be considered that the transit time of water is equal to the travel time of nitrate.

The following procedure is used to calculate the parameter T_{US} of Equation 4.3:

- (1) The difference between topographic altitude and water table altitude gives the total thickness of the unsaturated zone.
- (2) For each of the types of soils identified by campaigns of core drilling and coring augers (layers 1, 2 and 3), mean value of volumetric water content is determined using drying-gravity method, combined with bulk-density. The layered structure of the subsurface is interpreted using electrical tomographies combined with lithological observations.
- (3) For each parcel, transit time of water in a layer is calculated with Equation 4.4.
- (4) For each parcel, the total travel time T_{US} of Equation 4.3 is the sum of the transit times of water through the identified subsurface layers.

- *Analytical transfer function through the saturated zone*

Equation 3.11, introduced in chapter 3, is a new formulation of the exponential model of the transfer function, for limited input zones of diffuse pollution. This model appears suited for the Wohlenschwil case study, because each parcel of limited size is characterized by a specific history of pollution. However, two aspects limit its use in the case of the Wohlenschwil aquifer. First, the use of the exponential model is based on the hypothesis of homogeneous properties of the aquifer, which is not observed at the Wohlenschwil site where the aquifer thickness spatially varies significantly (Appendix 4.A.4). Second, the use of Equation 3.11 requires quantifying the distances of the upper and lower boundaries of each of the 28 parcels of the capture zone, which can be time-consuming. Consequently, the transfer functions through the saturated zone were not characterized by an exponential model.

According to Zuber [1986] the transfer function of solute $h_i(T)$ through the saturated zone can also be described by a dispersion model, which has the same general formulation than Equation 4.3 and which corresponds to:

$$h_i(t) = \frac{1}{\sqrt{4\pi P_D \frac{t}{T_{S_i}}}} \frac{1}{t} \exp \left[-\frac{(1 - \frac{t}{T_{S_i}})^2}{4P_D \frac{t}{T_{S_i}}} \right] \quad \text{Equation 4.5}$$

where T_S [year] corresponds to the mean travel time of the studied solute (nitrate) in the saturated zone, from the parcel to the pumping well, P_D is the dispersion parameter in the saturated zone and i is the index of the parcel.

In the saturated zone, the dispersion model is applied between the centre of a parcel and the pumping well, i.e. variations in travel time between different parts of the parcel are not taken into account. Despite this fact, the dispersion model is well suited for the case of the Wohlenschwil aquifer because the length of the parcel is small compared to the distance of travel through the saturated zone. Hence, it is considered that all the mass coming from the entire surface area of each parcel can be reduced to one input point at the water table, corresponding to the average travel time of the solute in the saturated zone. Then, the solute is transferred from the water table toward the pumping well, according to a 1D horizontal transfer model. This model of transfer in 1D configuration is illustrated in Figure 4.5, for both unsaturated and saturated zones.

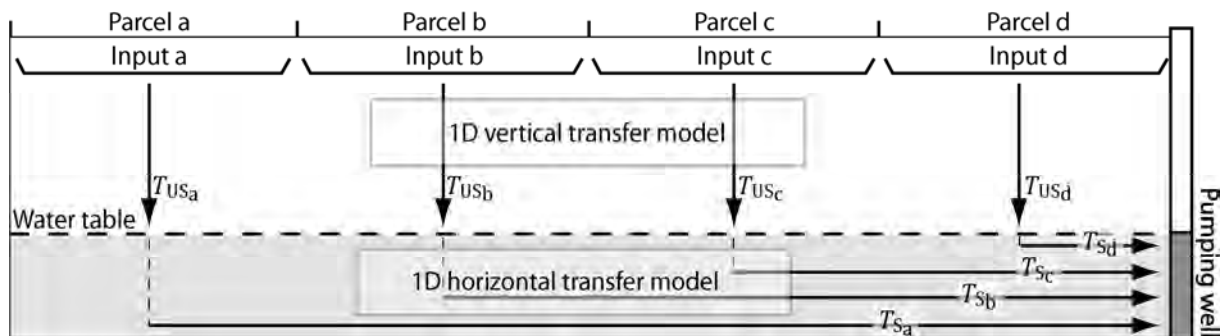


Figure 4.5 Schematic illustration of the transfer of solute from the surface of each parcel (parcels a to d) to the pumping well successively through the unsaturated zone and through the saturated zone following a 1D transfer model

In 1993, a multi tracing test has been carried out at the Wohlenschwil aquifer in order to characterize flow directions in the aquifer, capture zone and protection zones of the pumping well [Jäckli AG, 1994]. Four tracers (*Fluorescein*, *Pyranin*, *Amidoflavin* and *Duasyne*) were injected on the surface and flushed through the soil with a large amount of water. The results of the tracing test are reported in Appendix 4.B.1. This injection procedure does not

permit to characterize the recovery rate and the dispersion processes in the saturated zone because a large amount of tracer may be retained in the unsaturated zone and because dispersion can be affected by the conditions of flushing. Nevertheless it permits conducting a tracing test without boreholes. Furthermore, because a large amount of water is used, transit time of tracer through the unsaturated zone can be considered as insignificant compare to transit time in saturated zone.

The concentration measured at the pumping well was less than 0.1 ppb. This small concentration can be explained by three hypotheses: (1) a large fraction of the tracer is retained in the unsaturated zone due to the chosen injection procedure, (2) the dilution of tracer in the aquifer is high and (3) a part of the injected mass reaches another outlet, probably located in the vicinity of the pumping well, as reported in Section 4.2.2.2.

While it is not possible to use the data on tracer recovery under these conditions, it is still possible to estimate the travel time distribution in the aquifer and it is reasonable to assume that the tracer data mainly reflect the travel time in the saturated zone.

Based on mean transit time of tracers in saturated zone to the pumping well and the distance of transport along flow-lines, mathematical distance-time relations are determined in various directions of flows using quadratic regression equations, with the condition $d(t = 0) = 0$ (where d is the distance from the well and t the travel time of tracer).

Such relations are graphically extrapolated until the limits of the recharge zone, following flow lines, and the results are plotted in a map (Appendix 4.B.2). Based on this map, the isochrone located in the center of each parcel is considered as representative for the considered parcel. Hence, the mean travel time of tracer in the saturated zone T_S [year] is estimated for each parcel of the aquifer catchment.

In the absence of field data allowing the estimation of the dispersion of solutes in the saturated zone of the aquifer, the dispersion parameter P_D is estimated with typical values of the scientific literature for porous media. Based on the article of Gelhar et al. [1992], a value $P_D = 0.1$ is assumed in the saturated domain. As previously discussed, a constant ratio between length of travel and dispersivity is enforced in the entire saturated domain, while the ratio is actually not constant in most cases [Pickens and Grisak, 1981; Dagan, 1984; Gelhar et al., 1992]. Lacking any indication on the dispersivity in the aquifer, this assumption is supposed to be a good approximation of the reality.

4.3.3.2. Numerical models of the nitrate transfer functions

In the case study of Wohlenschwil, the transfer function of nitrate through the aquifer is numerically simulated for each parcel of the recharge zone. Transfer function are independently calculated (1) in the unsaturated zone using the HYDRUS-1D flow and transport model and (2) in the saturated zone using the FEFLOW flow and transport model [Diersch, 2009]. For each simulation the procedure consists in simulating the applications of an initial unit mass of tracer in the recharge zone, with a zero background concentration, and the transfer function corresponds to the simulated breakthrough of mass tracer at the outlet [Zoellmann *et al.*, 2001]. Recharge zone and outlet are the land surface and the water table, respectively for the unsaturated zone, and the water table and the pumping well, respectively for the saturated zone. Nitrate is assumed in this study-case as conservative and non-reactive solute, consequently simulations are carried out with no degradation and retardation parameters.

- *Transfer through the unsaturated zone using 1D-HYDRUS*

HYDRUS-1D model is a numerical tool to simulate water and solute movement in a variably saturated media. Water flow is computed using the Richard's equations in a homogeneous soil. The soil hydraulic properties are calculated with the equation of van Genuchten–Mualem. HYDRUS-1D includes the semi-empirical pedotransfer functions model ROSETTA, which allows estimating soil hydraulic parameters from soil texture and related data. Parameters required for ROSETTA computation are bulk density [g/cm^3] and grain size distribution (ratio of sand, silt and clay).

Bulk-density and grain size distribution were measured in 55 samples from 3 bore cores (respectively until the depth of 5.3 m, 6.4 m and 19.4 m). These analyses, accompanied with comparison of lithologic description, lead to distinguish three different types of horizons in the unsaturated zone of the Wohlenschwil aquifer: superficial deposits (loam), young moraines (sandy loam) and gravel deposits (sand).

The properties of soil profiles are implemented in HYDRUS-1D for each parcel. Steady state flow and transient transport of nitrate is simulated through each soil profile with two boundaries conditions: (1) constant recharge rate in the upper boundary, 510.3 mm/year corresponding to the mean recharge of the last 20 years; (2) average groundwater table depth as lower boundary condition. Transfer functions $g_i(\tau)$ of nitrate through soil profiles of each agricultural parcel are calculated by simulating recovery curves of a tracer pulse injection. The tracer is assumed representative for nitrate.

- *Transfer through the saturated zone using FEFLOW*

FEFLOW model is a numerical tool to simulate groundwater flow and subsurface transport, especially in saturated zone of porous aquifers, resolving groundwater flow and transport equations (Darcy's law, equation of continuity and advective-dispersion equation). Nitrate transport in the Wohlenschwil aquifer is modeled using the FEFLOW 5.3 version. The model configuration is a 2D confined aquifer, steady state flow and transient transport. The capture zone of the pumping well, the second part of the aquifer recharge zone delineated in Figure 4.4, is simulated assuming a diffuse recharge on the surface and two boundary conditions are fixed: a flow boundary condition of $360 \text{ m}^3/\text{day}$ to the well, which is the mean value of the last 5 years, and a constant head boundary condition in the eastern limit of 383.8 m, which corresponds to the hypothesis of an outlet at this part of the aquifer, probably emerging in the bed of the small river (Figure 4.4 and Appendix 4.A.2). Diffuse recharge of the aquifer is fixed to 1 mm/day in the major part of the recharge zone, 0.5 mm/day under forest and 0 mm/day in the confined part of the aquifer (spatial distribution is given in Appendix 4.A.2). Small input of the small river is simulated by a recharge zone of 35 mm/day in the river bed. 17 observation points of groundwater table altitude (measured in December 2010, Appendix 4.A.1) are used to calibrate distribution of hydraulic conductivity, using the PEST tool, a module of automated calibration implemented in the FEFLOW software. The simulated travel time in the aquifer is fitted to the observed mean travel time during the tracing test of 1993, using porosity and dispersivity as calibration parameters (fixed porosity $\phi = 0.14$, longitudinal dispersivity $\alpha_L = 3 \text{ m}$ and transverse dispersivity $\alpha_T = \alpha_L/10 = 0.3 \text{ m}$). Results of the fitting procedure are given in Appendix 4.C. The distributions of the main parameters of the numerical model are reported in Appendix 4.A.

A pulse injection of tracer in the recharge is simulated on the area of each parcel. Simulated recovery curves at the pumping well correspond to the transfer function of nitrate in the saturated zone from each parcel to the pumping flow. Resulting transfer functions are normalized in order to have an integral equal to 1 corresponding to conservative transport between the input and the output (see section 2.3.2). The simulated tracer is assumed representative for nitrate.

4.3.4. CONTRIBUTION OF EACH PARCEL TO THE PUMPING RATE

The contribution Q_i [m^3/year] of each agricultural parcel to the pumping flow is needed for the resolution of Equation 4.1. Both analytical methods and numerical methods can be used to evaluate this parameter.

4.3.4.1. Analytical approach

Assuming a homogeneous recharge flow rate R [mm/year] on the surface, the contribution of each parcel to the pumping flow Q_i [m^3/year] is simply weighted by the area A_i [m^2] of each parcel, leading to Equation 4.6. Using this approach, the probability that water reaches the pumping well is independent of the location of the recharge within the capture zone. The second assumption is that the contribution Q does not vary with the time.

$$Q_i = R \cdot A_i / 1000$$

Equation 4.6

4.3.4.2. Numerical approach

In the conceptual model of the Wohlenschwil aquifer, two outlets are assumed for flows converging towards the pumping well: the pumping well and an eastern outlet not clearly located. Analytically it is not possible to distinguish which parts of the flow is captured by the pumping well and which parts of the flow converge toward the eastern outlet. In contrast, numerical methods, which take into account the various hydrogeological properties of the aquifer, give the possibility to calculate the contribution of each parcel to the pumping based on the simulation of the capture probability. Of course the numerical results are dependent on the assumption done on the location of the eastern outlet.

The probability field of capture by the pumping well can be simulated by the FEFLOW model using a steady state inverse flow mode. An injection of a permanent unit concentration in the pumping well is simulated and the result provides the spatial distribution of concentration, which corresponds to the probability field of capture by the pumping well. By integrating this probability field of capture in the whole area of each parcel, the contribution of each parcel to the pumping flow can be calculated.

Another way, which is more precise but requires more computation time, consists of simulating a transport of mass from each parcel to the pumping well, followed by comparing the effective mass captured by the pumping well to the injected mass.

For each parcel, the recovery rate P of the injected mass is obtained. Hence the contribution Q_i [m^3/year] of each parcel to the pumping flow can be estimated using Equation 4.7, which weights the rate of recharge with the probability of capture.

$$Q_i = R \cdot A_i \cdot P / 1000 \quad \text{Equation 4.7}$$

where R [mm] is the mean annual rate of recharge (510.3 mm/year for the period 1990 – 2010), A_i [m^2] is the area of the parcels and i is the index of the parcel.

4.4. RESULTS

4.4.1. QUANTIFICATION OF THE INPUT FUNCTION

The three graphs of Figure 4.6 illustrate: (1) the annual recharge rate of groundwater during the period 1996 – 2010 (in mm/year), with a calculated mean recharge rate of 510.3 mm/year for the period 1990 – 2010; (2) the average rate of nitrogen mass input in the capture zone of the pumping well (in kg $\text{NO}_3/\text{ha}/\text{year}$), according to the leaching values of Table 1 estimated by the MODIFFUS tool; (3) the annual evolution of nitrate concentration in the recharge water (in mg/L) averaged in the capture zone of the pumping well, using Equation 4.2. Figure 4.6 illustrates the fact that dry years, for instance in the period from 2003 to 2005, are associated with higher nitrate concentrations in the recharge water by concentrating the mass input. On the contrary, wet years, for instance in the period from 1999 to 2001, favor the dilution of nitrate in recharge water. The input function of nitrate concentration for each parcel $C_{\text{IN}_i}(t)$ is calculated in the same way, but in a distributed manner within the capture zone.

For years prior to 1997, the lack of data about land use leads to having to estimate an average mass input value of nitrate for the agricultural parcels of the capture zone. The estimation was carried out by a fitting procedure between the values of nitrate concentration observed at the pumping well and the calculated values prior to 1997. The result gives an estimation of nitrate mass input of 400 Kg/ha/year in agricultural parcels prior to 1997, which is in the range of the values of Table 4.1.

Using Equation 4.2, the nitrate concentration input evolution for each parcel $C_{\text{IN}_i}(t)$ is then calculated from 1980 to 2020, using the annual recharge rate calculated from 1990 to 2010, based on weather station data, and the mean annual recharge rate of 510.3 mm/year for years after 2010. Figure 4.7 illustrates the results for the parcel 7 of the capture zone as an example (Figure 4.1).

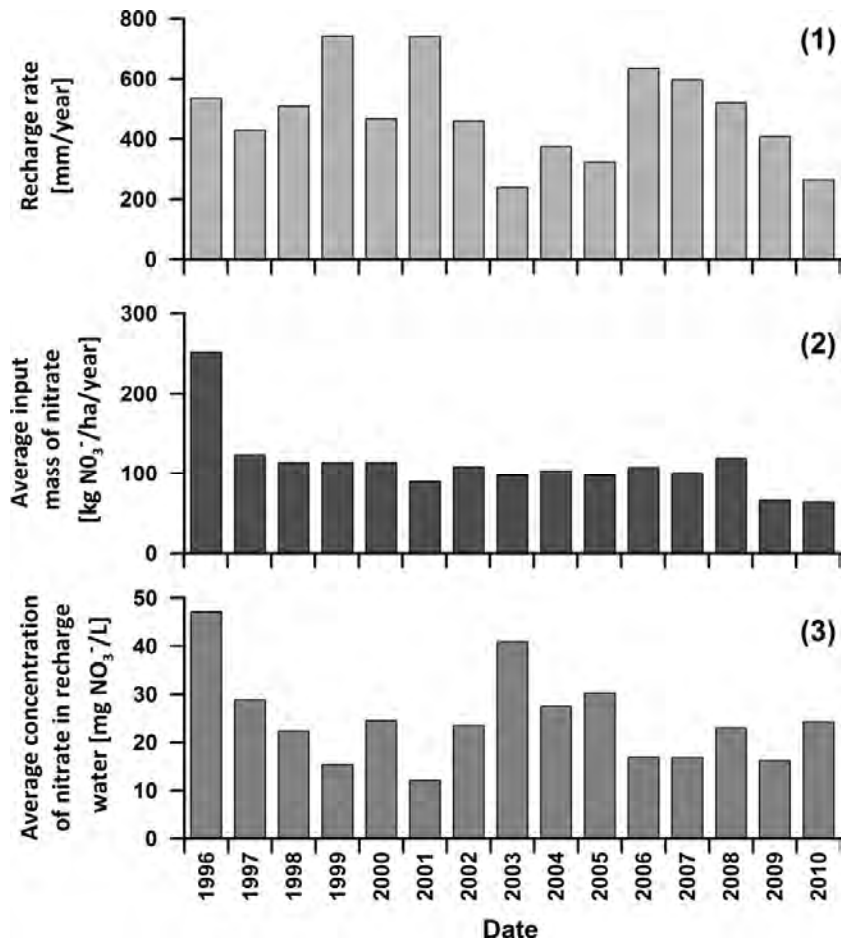


Figure 4.6 Average of nitrate concentration in recharge in the capture zone of the pumping well from 1996 to 2010 (3), based on (1) the annual recharge rate and (2) the input rate of nitrate mass.

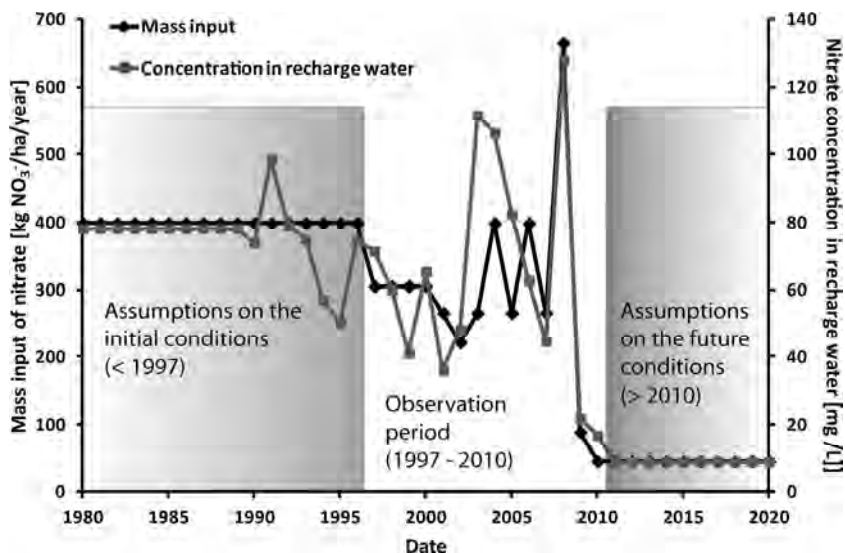


Figure 4.7 Values of nitrate concentration in recharge water [mg/L] (gray line) and mass input rate of nitrate [Kg NO₃⁻/ha/year] (black line) for the period 1980 – 2020 in the parcel 7 (Figure 4.1). The values prior to 1997 are estimated by a fitting procedure and the assumptions on the values after 2010 are based on a constant leaching mass rate from 2010 and a constant recharge, corresponding to the average of the period 1990 – 2010.

4.4.2. CHARACTERIZATION OF THE NITRATE TRANSFER FUNCTIONS

4.4.2.1. Analytical models of the nitrate transfer functions

- Analytical transfer function through the unsaturated zone

Table 4.2 gives the values of measured volumetric water content θ [%] and of the estimated thickness Z [m] for each soil layer under each parcel of the capture zone. Using Equation 4.4 the mean travel time of nitrate through each layer is then calculated. For each parcel, the total transit time T_{US} in the unsaturated zone (Table 4.2), is the sum of the travel times through the subsurface layers.

Parcels <i>i</i>	Area A_i [m ²]	Contribution to pumping flow Q_i [m ³ /year]	Thickness Z [m]			Volumetric water content θ [%]			Transit time T [years]	
			Layer 1	Layer 2	Layer 3	Layer 1	Layer 2	Layer 3	Unsaturated zone T_{US}	Saturated zone T_S
1	9210	4641	2,0	2,0	14,0	29%	26%	10%	5,0	0,08
2	13440	6768	2,0	2,0	12,0	29%	26%	10%	4,6	0,04
3	22980	11576	1,7	2,3	12,0	29%	26%	10%	4,5	0,08
4	25320	12757	2,2	1,8	11,0	29%	26%	10%	4,4	0,22
5	7610	3832	2,6	1,8	8,6	29%	26%	10%	4,1	0,22
6	25170	12680	0,0	10,0	0,0	29%	26%	10%	5,2	0,55
7	22680	11428	2,5	2,5	7,0	29%	26%	10%	4,1	0,41
8	9010	4537	4,1	1,1	1,8	29%	26%	10%	3,3	0,71
9	24300	12243	2,6	1,8	8,6	29%	26%	10%	4,1	0,49
10	2650	1337	0,3	1,7	10,0	29%	26%	10%	3,0	0,55
11	18830	9486	0,2	3,3	5,5	29%	26%	10%	2,9	1,10
12	12800	6450	0,0	16,0	0,0	29%	26%	10%	8,3	0,55
13	7260	3659	0,0	12,0	0,0	29%	26%	10%	6,2	1,10
14	12500	6298	0,0	8,0	0,0	29%	26%	10%	4,1	1,10
15	5900	2971	0,0	13,0	0,0	29%	26%	10%	6,7	1,04
16	14910	7510	0,0	21,6	4,4	29%	26%	10%	12,0	0,27
17	15550	7831	0,0	19,6	0,0	29%	26%	10%	10,1	0,33
18	9800	4937	0,7	10,7	4,6	29%	26%	10%	6,8	0,16
20	10020	5046	0,0	12,0	2,0	29%	26%	10%	6,6	0,14
23	28920	14567	0,0	28,0	0,0	29%	26%	10%	14,5	0,60
24	75920	38248	0,0	30,0	0,0	29%	26%	10%	15,5	0,27
25	3270	1645	1,7	2,3	11,0	29%	26%	10%	4,3	0,11
26	35640	17954	0,0	19,6	2,4	29%	26%	10%	10,6	0,27
27	5790	2915	0,0	10,0	5,0	29%	26%	10%	6,2	1,10
28	3950	1990	0,0	10,0	5,0	29%	26%	10%	6,2	1,10
29	33470	16863	0,0	20,0	0,0	29%	26%	10%	10,3	0,05
30	14390	7249	0,0	16,0	0,0	29%	26%	10%	8,3	1,23

Table 4.2 Parameters for the analytical characterization of nitrate transfer functions through the Wohlenschwil aquifer

The transfer function of nitrate $g_i(\tau)$ through the unsaturated is calculated for each parcel, using the dispersion model formulated in Equation 4.3, with the values of mean transit time T_{US_i} [year] reported in Table 4.2 and a dispersion parameter $P_D = 0,1$ as previously discussed.

- *Analytical transfer function through the saturated zone*

The graphic approach provided the map of isochrones of travel times, presented in Appendix 4.B. Based on this map, the mean travel time of nitrate in the saturated zone T_S [year] is visually estimated for each parcel of the aquifer catchment. Results are reported in Table 4.2. The transfer function of nitrate $h_i(T)$ through the saturated is characterized for each parcel with the Equation 8, using the values of mean transit time T_{S_i} [year] reported in Table 4.2 and a dispersion parameter $P_D = 0,1$ as previously discussed.

4.4.2.2. Numerical models of the nitrate transfer functions

- *Transfer through the unsaturated zone using HYDRUS-1D*

Based on the measured bulk-density and grain size distribution each sample is associated to one of the three main types of soils observed in the aquifer: superficial deposits (layer 1), young moraines (layer 2) and gravels deposits (layer 3). The mean value and standard deviation of the bulk density data and of the grain size distribution data are reported in Table 4.3 for each of these three types of soils.

	% > 50 μm (sand)		2 μm < % < 50 μm (silt)		% < 2 μm (clay)		Bulk density [-]	
	Mean value	Standard deviation	Mean value	Standard deviation	Mean value	Standard deviation	Mean value	Standard deviation
Layer 1	0,33	0,06	0,50	0,03	0,17	0,03	1,35	0,16
Layer 2	0,69	0,05	0,18	0,06	0,13	0,06	1,42	0,08
Layer 3	0,92	0,05	0,05	0,03	0,03	0,02	1,94	0,18

Table 4.3 Bulk density [dimensionless] and proportion of clay, silt and sand [%] of each of the three main soil horizons of the unsaturated zone of the Wohlenschwil aquifer

For the simulations, the thickness and spatial distribution of different layers reported in Table 4.2 are used. Soils hydraulics parameters of each soil type are estimated with the ROSETTA model, using input parameters of Table 4.3. Using these parameters and the mean annual recharge from 1990 to 2010, the transfer functions of nitrate through the unsaturated zone $g_i(\tau)$ are simulated with HYDRUS-1D under each parcel of the capture zone.

- *Transfer through the saturated zone using FEFLOW*

The transfer functions of nitrate through the saturated zone $h_i(T)$ are simulated by the numerical model computed with FEFLOW. Because the transport of nitrate is assumed to be conservative, resulting transfer functions are normalized in order to have an integral equal to 1.

Moreover, the isochrones of advective transit times of groundwater reaching the pumping are calculated using a particle tracking method. This gives a good spatial visualization of the mean travel times in the studied saturated zone. The results are illustrated in Figure 4.8.

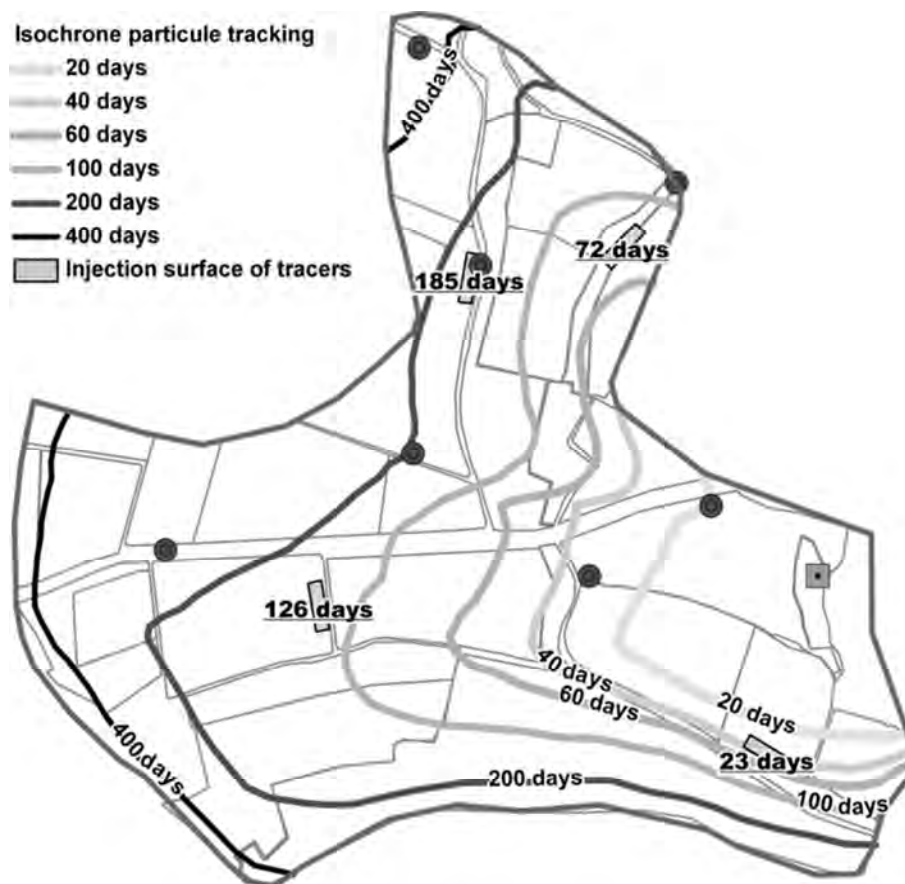


Figure 4.8 Isochrones of travel time in the saturated zone of the aquifer simulated by particles tracking

4.4.2.3. Comparison of the analytical and numerical results

Figure 4.9 and Figure 4.10 show the results of transfer functions that were calculated with numerical and analytical methods for nitrate coming from the parcels 3 and 11. The calculated transfer functions are compared for the unsaturated zone in Figure 4.9 and for the saturated zone in Figure 4.10. The parcel 3 is located close to the pumping well, whereas parcel 11 is located close the northern boundary of the aquifer. The thickness and structure of the unsaturated zone are significantly different for both parcels, as reported in Table 4.2. Hence, parcels 3 and 11 are considered as representative of the diversity of configurations that can be encountered in the Wohlschwil case study, that is why they were chosen for a comparison of the transfer functions characterized, on the one side, by an analytical method and, on the other side, by a numerical method.

Two main observations can be outlined. First, the range of travel time is of about 0 to 800 days in the saturated zone versus 1 to 5000 days in the unsaturated zone. Hence, the travel time is higher in the unsaturated zone than in the saturated zone. Second, a significant difference can be observed between the analytical and the numerical approach. For the unsaturated zone of parcel 3, the travel times computed by the numerical approach are higher than travel times computed by an analytical approach, while the contrary is observed for parcel 11 (Figure 4.9). Despite these differences, the general range of travel times is similar between the numerical and analytical methods. Also, the distribution of the travel times is very similar and the time lag is about 300 days, which is relatively small compared to the mean travel times (20 to 30% of the mean values).

In the saturated zone the shape of the transfer functions calculated by the analytical and numerical methods are very close for the parcel 3. In the parcel 11, the analytical method provides a transfer function in the saturated zone that is more dispersed than the transfer function calculated by the numerical method.

One explanation of these significant differences is that the parameterizations of the equations governing the analytical and numerical approaches do not rely on the same field data. The numerical approach used in the saturated zone takes into account the observed hydraulic head as calibration parameter while the isochrones of travel times estimated in the analytical approach are mainly based on the results of tracers. Similarly, the numerical approach used in the unsaturated zone takes into account bulk density and grain size distribution, implemented in the ROSETTA model, while the analytical approach, simply based on the volumetric water content, does not. The numerical methods tend to be more precise because more factors are taken into account. However, the results given by the analytical methods seem satisfying considering the simplicity of the approach.

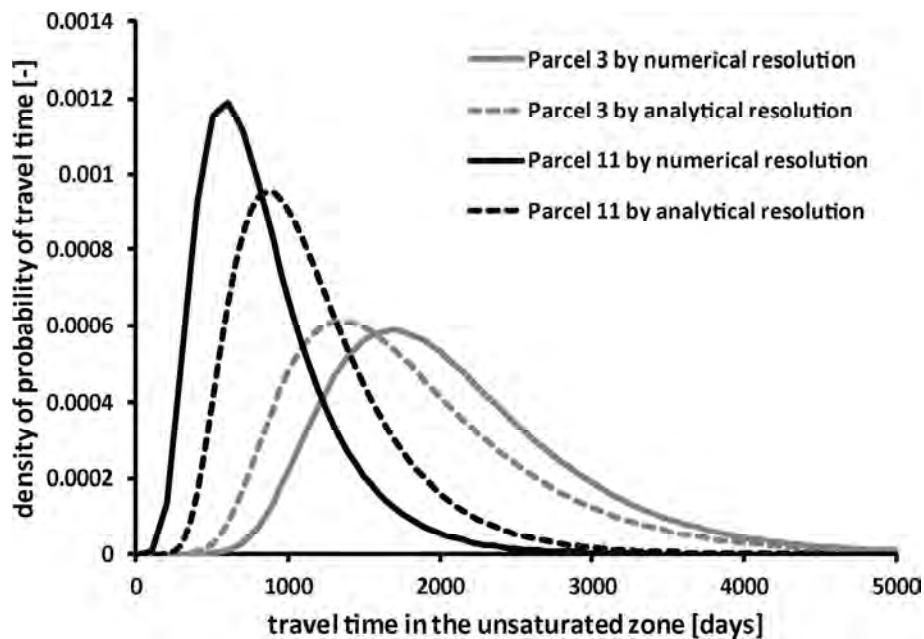


Figure 4.9 Transfer functions through the unsaturated zones for nitrate coming from parcel 3 (gray lines) and from parcel 11 (black lines), calculated with a numerical method (continuous lines) and an analytical method (dashed-lines)

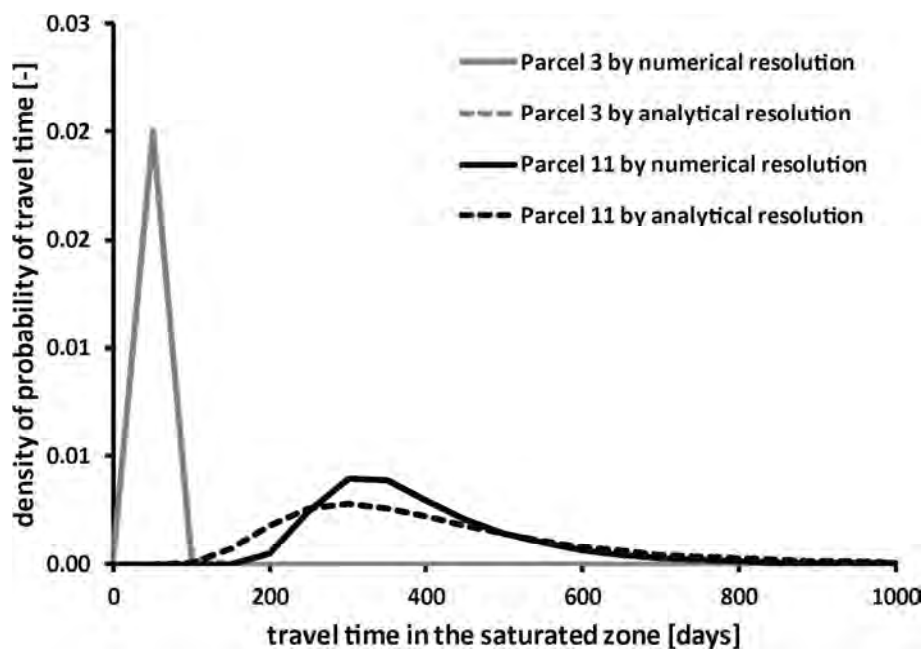


Figure 4.10 Transfer functions through the saturated zones for nitrate coming from parcel 3 (gray lines) and from parcel 11 (black lines), calculated with a numerical method (continuous lines) and an analytical method (dashed-lines)

4.4.3. CONTRIBUTION OF EACH PARCEL TO THE PUMPING RATE

The resolution of Equation 4.1 requires an estimation of the contribution Q_i [m^3/year] of each parcel of the capture zone to the pumping flow. Both analytical methods and numerical methods can be used to evaluate this parameter.

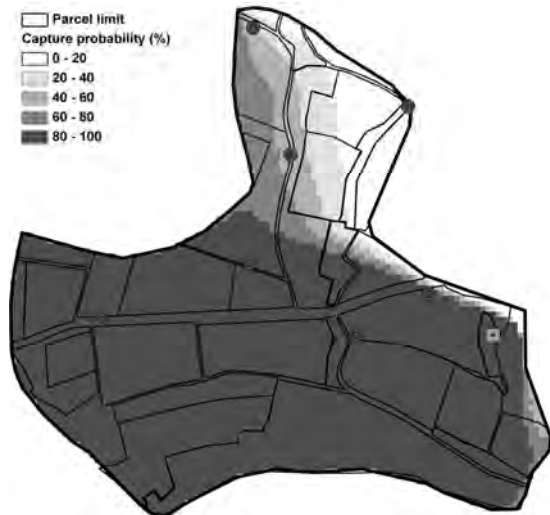
4.4.3.1. Analytical approach

In the analytical approach the contribution Q_i of each parcel is evaluated using Equation 4.6. The average annual groundwater recharge R for the last 20 years is 510.3mm/year. Areas A_i of the parcels and the resulting Q_i are reported in Table 4.2.

4.4.3.2. Numerical approach

The probability field of capture by the pumping well is calculated in a steady state inverse flow mode and illustrated in Figure 4.11. This map shows that the southern median part of the catchment area is the most contributing zone to the pumping well, while the probability of capture in the northern part is lower.

The forward mode is performed to calculate the recovery rate at the pumping well of a mass injected at each parcel of the capture zone. This leads to the recovery rate P and the contribution Q_i resulting from Equation 4.7 and reported in Table 4.4.



Parcel i	Recovery rate P	Contribution to pumping flow Q_i [m^3/year]	Parcel i	Recovery rate P	Contribution to pumping flow Q_i [m^3/year]
1	77%	3575	14	87%	5462
2	100%	6768	15	50%	1495
3	100%	11576	16	29%	2158
4	100%	12757	17	14%	1121
5	95%	3646	18	6%	302
6	100%	12680	20	54%	2714
7	84%	9609	23	100%	14567
8	78%	3551	24	100%	38248
9	71%	8707	25	100%	1645
10	46%	619	26	23%	4215
11	41%	3936	27	10%	301
12	100%	7365	28	17%	336
13	100%	6421	29	75%	12580
			30	96%	13494

Figure 4.11 Probability field of capture by the pumping well

Table 4.4 Values of mass recovery rate and the contribution Q_i of each parcel to the pumping flow calculated by numerical method

4.4.4. CALCULATION OF THE NITRATE CONCENTRATION EVOLUTION

Using the relevant parameters and functions of the Equation 4.1 ($C_{\text{INNO}_3}(t)$, $g_i(\tau)$, $h_i(T)$ and Q_i), estimated by analytical and numerical methods, the evolution of nitrate at the pumping well is calculated for the period 1997 – 2020 and compared to the observed values for the period 1997 – 2010 (Figure 4.12). The calculation is performed with an Excel spreadsheet, as described by Olsthoorn [2008]. An example of such a spreadsheet is described in Appendix 5.A.

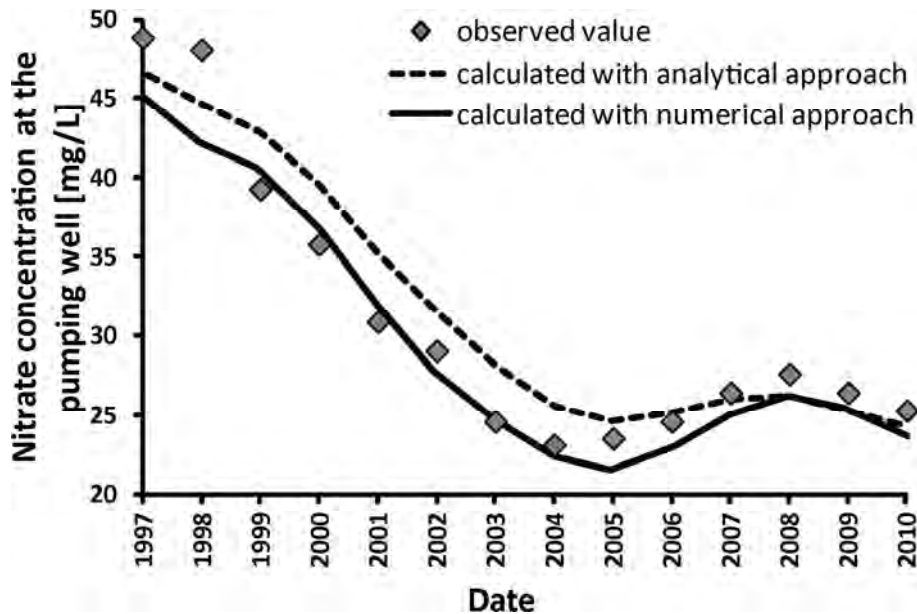


Figure 4.12 Annual calculated (black lines) and observed (grey rhombus) evolution of nitrate concentration in Wohlschwil aquifer from 1997 to 2010

The calculated concentrations generally agree well with observed values for both numerical and analytical methods: trends and levels of observed nitrate concentrations are relatively well reproduced. Nevertheless, Figure 4.13 shows some discrepancies between observed and calculated values, especially for the highest concentration observed in 1997 and 1998, where the calculation underestimates the nitrate concentration for both numerical and analytical methods. Table 4.5 provides the main information about the differences between observed and calculated values. The mean absolute error is 1.72 mg/L for the numerical resolution and 2.23 mg/L for an analytical resolution. The maximum difference reaches 5.94 mg/l in 1998 for the numerical approach and 4.34 mg/L for the analytical approach. The average differences between the observed values and the calculated values are 7.2% for the analytical method and 5.6% for the numerical method.

A general interpretation is that the differences between the observed and calculated values can be attributed to the uncertainties on the aquifer characteristics (geometry, flow lines, hydraulic parameters, lithological structures), on the input characteristics (recharge, mass

leaching rate, capture zone) and on the internal parameters controlling the transport (porosity and mean travel times in the saturated zone, volumetric water content, bulk density and grain size distribution in the unsaturated zone), as well as the assumptions required for the analytical and numerical approaches (particularly the hypothesis of a steady state flow condition).

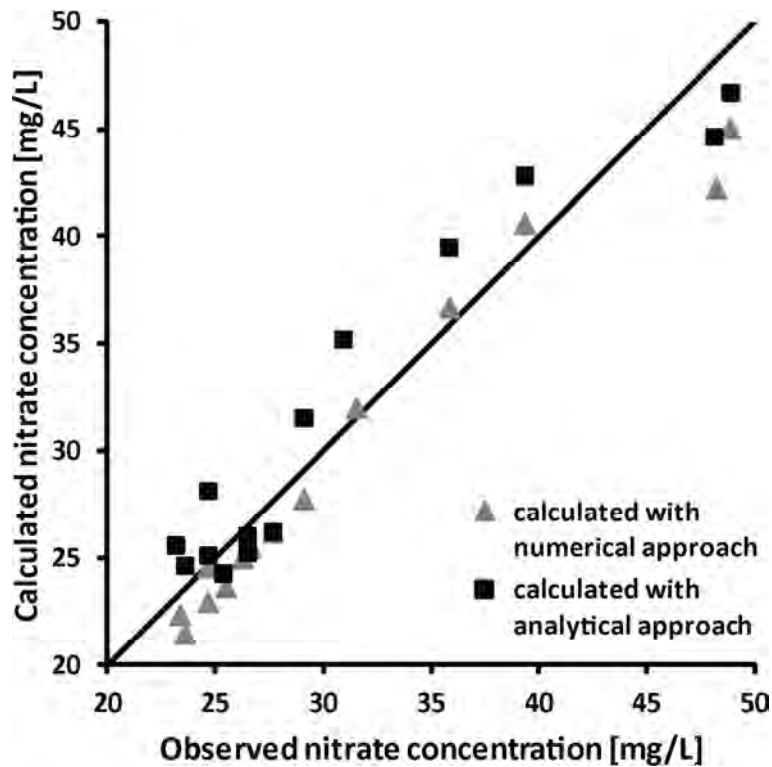


Figure 4.13 Calculated values of nitrate concentration for the period 1997 – 2010 as a function of observed values

	Numerical method	Analytical method
Mean absolute difference [mg/L]	1.72 mg/L	2.23 mg/L
Maximum difference	5.94 mg/L (in 1998)	4.34 mg/L (in 2001)
Mean relative difference (compared to the average of nitrate concentrations observed from 1997 to 2010)	5.6%	7.2%

Table 4.5 Statistical values of the difference between observed and calculated values of nitrate

More precisely, a sensitivity analysis of the parameters used in the analytical method was carried out, the objective being to know if the uncertainty of the value of these parameters can explain the difference between observations and calculations.

Without considering geological factors and the delimitation of the capture zone, the results provided by the analytical approach are mainly dependent on four factors: the nitrate leaching rate, the volumetric water content in the unsaturated zone, the recharge rate and the dispersion parameter P_D .

According to Equation 4.2 and Equation 4.4, the recharge rate $R(t)$ has an influence on the concentration of nitrate in the recharge and on the mean travel time through the unsaturated zone. The uncertainty of its value was estimated as +/- 10%. The dispersion parameter P_D has an influence on the travel time distribution of nitrate in the unsaturated and saturated zone. According to Gelhar et al. [1992], its value is very variable and can fluctuate between half and double of the typical value 0.1 used in this study. The rate of nitrate leaching $M_{\text{INNO}_3}(t)$ has a direct influence on input nitrate concentration, according to Equation 4.2, and thus, on the output nitrate concentration, following Equation 4.1. It is assumed that the uncertainty of its value is about +/- 10%. Finally, according to Equation 4.4, the volumetric water content θ has an influence on the mean travel time of nitrate through the unsaturated zone. The uncertainty on the value of the water content is assumed to be about +/- 0.05 according to the variability of the water content analyzed in each soil layer. Figure 4.14 and Figure 4.15 show the calculated concentration in nitrate concentrations from 1997 to 2010, when such parameters vary within the range of their uncertainties.

Figure 4.14 shows that the recharge rate $R(t)$ strongly influences the calculated concentrations, the difference with initial calculation reaching 6.2 mg/L in 1997 when the recharge rate is reduced by 10%. The results seem to be less sensitive to the dispersion parameter, but the deviation remains significant with a calculated difference reaching 1.9 mg/L in 2006 when the dispersion parameter is multiplied by 2. Figure 4.15 shows that a variation of +/- 10% on the nitrate leaching rate leads to a variation of +/- 10 % on the output nitrate concentrations, which is explained by the direct mathematical link between output and input concentrations of Equation 4.1. The variation of the volumetric water content in the unsaturated zone has two consequences on the output nitrate concentration. First, the evolution of nitrate concentration is smoother when the volumetric water content increases. Second, the variation of volumetric water content leads to a lag of the arrival time of the pollutant: the trough and the peak of the curve are delayed or brought forward. The maximum difference with the initial calculation of nitrate concentrations is of 5.2 mg/L, in 2001, when the volumetric water content is reduced of 0.05.

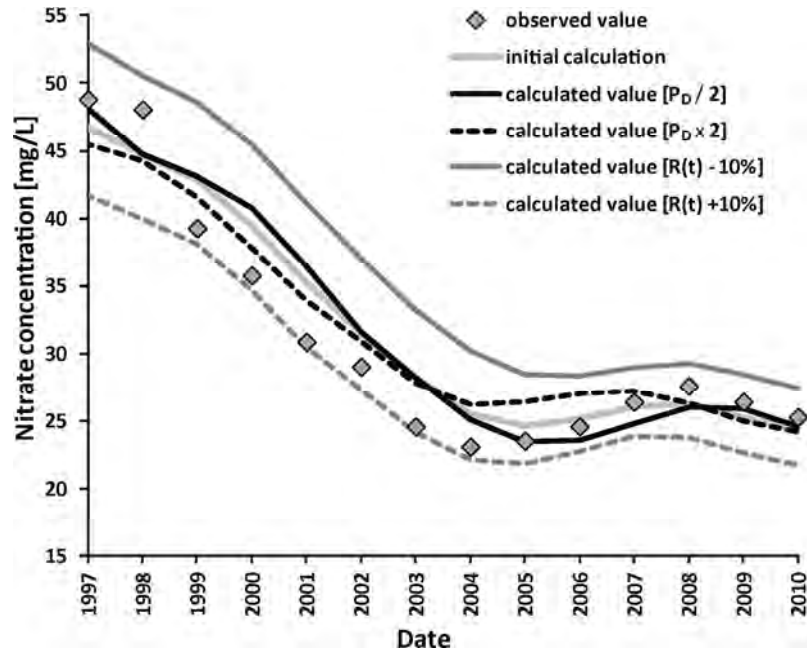


Figure 4.14 Results of a sensibility analysis of the parameters recharge rate $R(t)$ and dispersion parameter P_D , on the calculated nitrate concentrations from 1997 to 2010. Initial calculation with $P_D = 0,1$ and $R(t)$ (calculated in section 0) are shown in light grey line. Continuous and dashed black lines represent results with a P_D respectively divided and multiplied by 2. Continuous and dashed grey lines represent results with a $R(t)$ respectively reduced and increased by 10%.

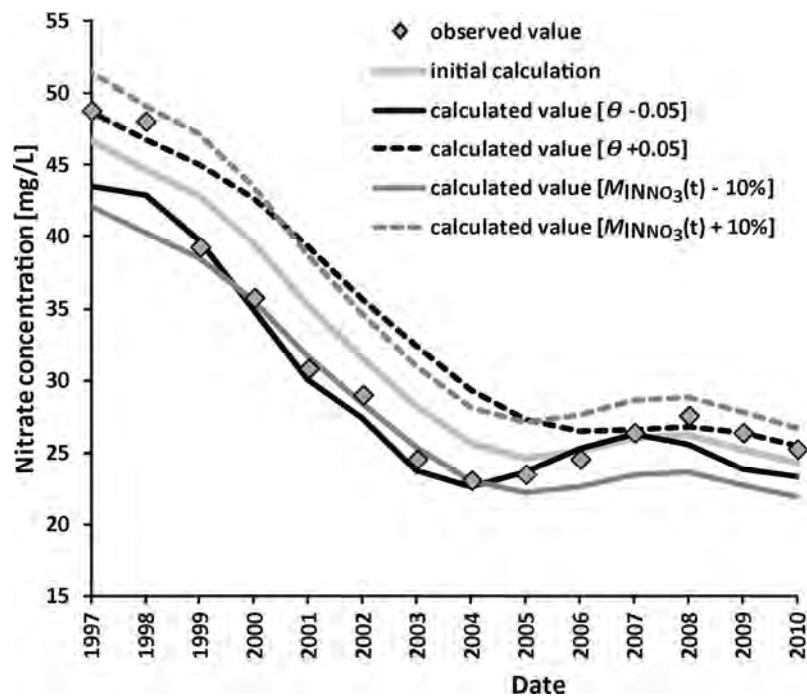


Figure 4.15 Results of a sensibility analysis of the parameters volumetric water content θ and nitrate leaching rate $M_{INNO_3}(t)$ on the calculated nitrate concentrations from 1997 to 2010. Initial calculation is illustrated in light grey line. Continuous and dashed black lines represent results with a volumetric water content θ respectively reduced and increased of 0.05. Continuous and dashed grey lines represent results with a nitrate leaching rate $M_{INNO_3}(t)$ respectively reduced and increased by 10%

Parameter	Range of uncertainty	Mean relative difference (compared to the average of nitrate concentrations observed from 1997 to 2010)
recharge rate $R(t)$	+/- 10%	15%
nitrate leaching rate $M_{\text{INNO}_3}(t)$	+/- 10%	10%
volumetric water content θ	+/- 0,05	8%
dispersion parameter P_D	between 0,05 and 0,2	3%

Table 4.6 Results of a sensibility analysis of the parameters recharge rate, nitrate leaching rate, volumetric water content and dispersion parameter, on the value of nitrate concentration calculated by analytical method when the parameters vary in the range of their uncertainty. Table shows the range of uncertainty of each parameter and the mean relative difference in comparison with initial calculation of nitrate concentrations.

In Table 4.6 the average deviation in term of nitrate concentrations are calculated when the values of the input parameters vary within the range of their uncertainties. An average deviation of 15% of the calculated nitrate concentration can be attributed to the variation of the recharge rate of 10%. The variation of the other parameters within the range of their uncertainty leads to the following deviations in comparison with the initial calculations: 10% for the nitrate leaching rate, 8 % for the volumetric water content and 3 % for the dispersion parameter. The recharge rate is the most sensitive parameter, influencing at the same time nitrate concentration in recharge and travel times in the unsaturated zone. Nitrate reaching rate and volumetric water content in the unsaturated zone have also a considerable influence, with a mean variation of around 10%. The uncertainty associated to the dispersion parameter seems to have less influence on the accuracy of the calculated concentration.

To summarize, the values of the nitrate concentration at the pumping well calculated with the analytical or numerical methods fit relatively well the observed concentration, in terms of evolution and absolute values. The error is below 8% for both methods, which is relatively small and acceptable for an environmental project. The uncertainty associated with the value of the parameters used in the analytical method can have an influence on the accuracy of the calculated values and could explain in part the difference between observed and calculated concentrations. An effort should be made to reduce these uncertainties, particularly concerning the estimation of the recharge rate, of the nitrate leaching rate and of the volumetric water content in the unsaturated zone.

4.4.5. PREDICTION OF NITRATE EVOLUTION TRENDS AT THE PUMPING WELL

In the Nitrate Project of Wohlenschwil, most of the parcels used for intensive agriculture were converted to permanent meadows step by step until the year 2010 (Figure 4.1), which constitutes the final stage of the project with the conversion of parcel 7. After 2010, only two parcels in the capture zone of the pumping well are still used for intensive agriculture.

The transfer function approach allows determining how the implemented measures will influence the future evolution of nitrate concentration at the pumping well. Equation 4.1 is solved to evaluate the evolution of nitrate concentration from 2011 to 2020, assuming a constant land use in the future and a mean recharge of 510.3 mm/years (average of annual recharge in the period 1990 – 2010). The results are illustrated in Figure 4.16, using the analytical and numerical approaches.

This projection does not take into account additional pollution occurring in the future or the effect of climatic variations (recharge variations have an effect on the input concentration according to Equation 4.2). Based on the hypotheses of constant recharge rate and mass input, nitrate concentration should decrease continuously by 2020, with a mean decrease of 1.3 mg/L/year (numerical approach) or 1.1 mg/L/year (analytical approach) since 2010. In 2020, nitrate concentration could reach a value of 11.1 mg/L or 13.7 mg/L, respectively calculated by a numerical approach or an analytical approach. The difference between the latter results is mainly explained by the contribution of the parcels to the pumping rate (see section 0), which are different depending on the used approach.

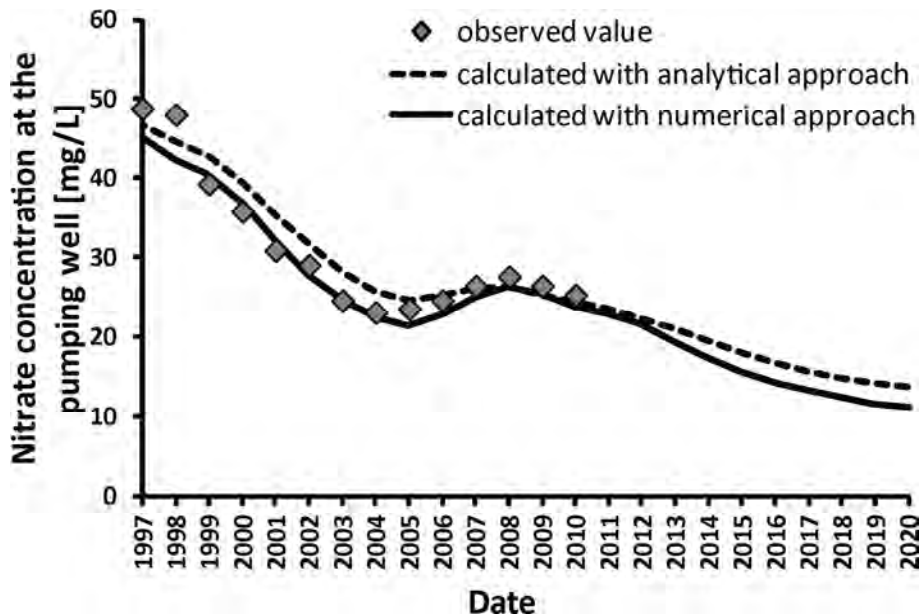


Figure 4.16 Observed evolution of nitrate concentration (black rhombus) at the pumping well from 1997 to 2010 and calculated values (lines) from 1997 to 2020. Transfer functions are calculated by numerical approach (continuous-line) and by analytical approach (dashed-line).

4.4.6. CONTRIBUTION OF EACH PARCEL TO THE NITRATE CONCENTRATION AT THE PUMPING WELL

The Nitrate Project was carried out in different steps from 1997. Among the 18 parcels used for intensive agriculture at least until 1996 and located in the capture zone of the pumping well, 9 parcels were converted to permanent meadow in 1997, 4 parcels in 2003, 5 during the period 2008 – 2010 (Figure 4.1).

The effect of these different conversion steps on the nitrate concentration at the pumping well is determined. It particularly permits quantifying how the last environmental measures (conversion of 2008-2010) will impact the future nitrate concentration.

The contribution of each parcel to the nitrate concentration in pumping well is calculated using Equation 4.1, parameterized by numerical approach. The parcels concerned by the same conversion step are grouped together (conversions of 1997, of 2003 and of 2008 – 2010) and for each group $C_{OUT_i}(t)$ are summed in order to quantify the effect of each conversion group on the nitrate concentration at pumping well.

Figure 4.17 illustrates the results, in a cumulative diagram. This graph shows the impact of the Nitrate Project on the water quality. Each conversion step results in a decrease of the nitrate contribution at the pumping well for the concerned conversion group. For example, the conversion in 1997 leads to a strong decrease in the nitrate contribution of this group starting in 1999. The graph highlights the fact that the expected improvement is delayed in time. For example, the last conversions of the period 2008-2010 should have a visible and significant effect after 2011, where the contribution of these parcels to the nitrate concentration decreases significantly.

Based on these results it is possible to quantify, in a differentiated way and for each of the parcels group, the impact of the conversions to nitrate concentration at the pumping well. Figure 4.18 shows the relative contribution of each parcels group, in comparison with the contributions levels in the year 1997. This analysis quantifies the effectiveness of the Nitrate Project in the past and the future.

For example 12 mg/L are gained in 6 years with the conversions introduced in 1997 and this gain reaches 14.3 mg/L after 20 years of conversion (in 2017). Conversion introduced in 2003 lead to a decrease of 7.2 mg/l of nitrate concentration since 2015. The last conversions of the period 2008-2010 would permit gaining 11.3 mg/l for the next 10 years (period 2011 – 2020), compared to 1997.

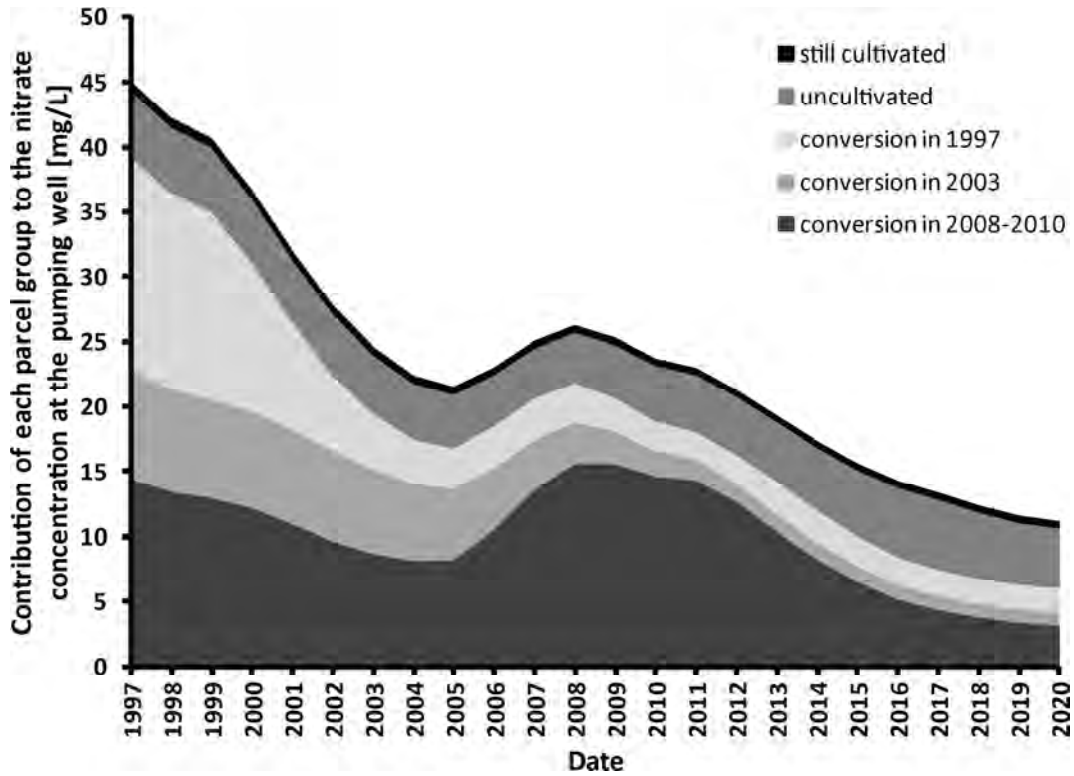


Figure 4.17 Contribution of each parcel to the evolution of nitrate concentration from 1997 to 2020; Results are presented for groups of parcels respectively converted to permanent meadow in 1997, 2003 and 2008 – 2010. Transfer functions are calculated by numerical approach.

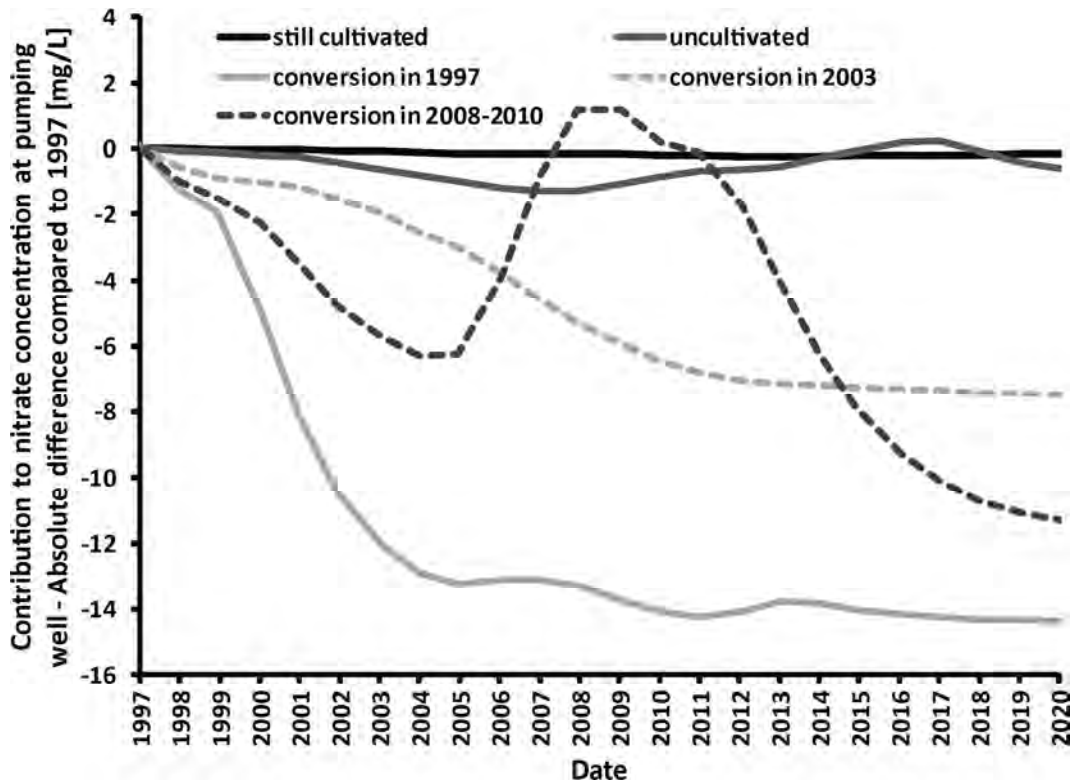


Figure 4.18 Difference between the contribution of each group of parcels to the nitrate concentration at the pumping well and the contribution in the reference year 1997. Transfer functions are calculated by numerical approach.

4.4.7. EFFECT OF CLIMATIC FORCING ON NITRATE CONCENTRATION BASED ON CHANGING RECHARGE RATES

Contrary to what could be expected, the Nitrate Project introduced since 1997, does not result in a continuous decrease of the nitrate concentration at the pumping well. In Figure 4.17, both calculated and observed evolution of nitrate concentration show an increase during the period 2005 – 2008. In the same way, Figure 4.18 shows a strong increase of nitrate contribution during the period 2005 – 2008 for the parcels group of the 2008 – 2010 conversions.

This evolution should be explained by an increase of nitrate concentration input in the recharge zone. According to Equation 4.2, the nitrate concentration C_{INNO_3} [mg/L] in recharge water can be influenced by two factors:

- (1) the mass of nitrate that is leached through soils M_{INNO_3} [Kg/ha/year];
- (2) the recharge rate R [mm/year]

The graphic (2) of Figure 4.6 shows that the average nitrate leaching rates under the agricultural parcels does not significantly increase during the period preceding the year 2005 (based on only one culture specific nitrate leaching rate, with the assumption that variations in leaching rates due to climate factors are insignificant). Hence, the increase of nitrate concentration observed at the pumping well in 2005 – 2008 could not be explained by an increase of nitrate mass input during previous years.

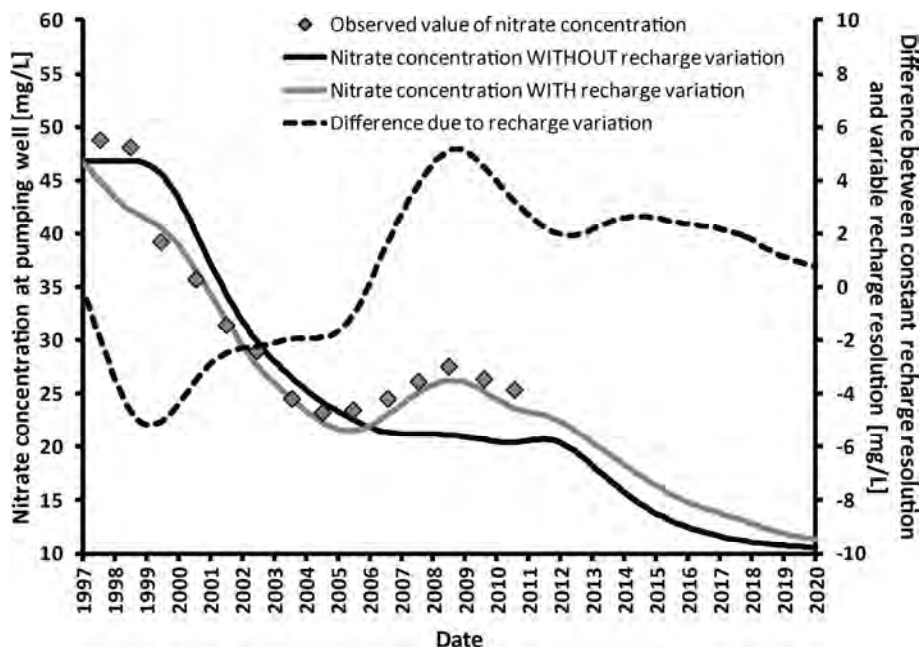


Figure 4.19 Evaluation of the evolution of the nitrate concentration taking into account the variation of recharge (black line) and considering constant recharge (grey line). Observed value of nitrate concentration (grey rhombus); absolute difference between constant recharge resolution and variable recharge resolution (dashed line)

Figure 4.19 shows a comparison of nitrate concentration (evaluated by resolution of Equation 4.1) taking into account on the one hand a variable recharge rate over the years (variable recharge resolution – black line) and on the other hand a constant recharge rate over the years (constant recharge resolution – grey line). In the latter case, the history of nitrate concentration input is calculated using Equation 4.2, with a constant recharge rate $R = 510.3$ mm/year, corresponding to the average recharge rate of the last 21 years (period 1990 – 2010).

The first observation is that the calculated nitrate concentrations agree better with the observed values when the calculation takes into account a variable recharge. For example, the observed increase of the nitrate concentrations during the period from 2005 to 2008 is well simulated for variable recharge and poorly simulated for constant recharge.

The second observation is the difference between the nitrate concentrations that are calculated for constant recharge and a variable recharge (right ordinate – dashed black line). It allows quantifying the impact of recharge variations on the nitrate concentration at the pumping well. Two main observations can be made:

- (1) The high recharge period between 1993 and 1995 (average recharge rate of 670 mm/year) is certainly responsible for a high dilution of the nitrate mass input, which is reflected in the evolution of the concentration since 1996. The increased recharge leads to a decrease in the nitrate concentration in 1999 of nearly 5 mg/L
- (2) The impact of the dry period 2003 – 2005, accompanied with a low recharge rate, has an important repercussion on nitrate concentration in the period 2007 – 2010, when the nitrate concentration increases as much as 5 mg/L.

These results highlight the necessity of considering the annual fluctuations of recharge rate to estimate the input concentrations. This can be very important for the accuracy of the transfer function method developed in this chapter. These results also suggest that recharge volume could play a key role rather than changes in leaching rates to explain the increase in nitrate concentrations in the period 2005 – 2008. More generally, this result demonstrates on a study case that the dry period 2003 – 2005 could explain the general tendency of the increase of nitrate concentration observed during the middle of the last decade in the majority of aquifers of Switzerland [OFEV, 2009].

Nevertheless, if the transfer function approach seems to reproduce the effect of climatic variations on the nitrate concentration at the pumping well, the physical and biochemical processes leading to this increasing tendency of nitrate concentration are not entirely simulated by such an approach. Indeed, the approach calculates an increasing concentration of nitrate in recharge due to the decreasing recharge rate. The concentrated pool of nitrate is then transported to the pumping well according to the transfer functions that are

independent on the recharge variations. In reality the pool of nitrate is more probably stored in the soil during the dry years from 2003 to 2005 and flushed by the high recharge of the years 2006 and 2007. This last mechanism, which could be reproduced by numerical simulations of flow and transport, is conceptually different from what is simulated by the transfer function approach. Moreover, as explained in Section 0, the methodology applied in this case study does not take into account the effect of climatic variations on the nitrogen cycle and consequently on the leaching rate of nitrate.

To conclude, the transfer function approach is able to reproduce increases or reductions of solute concentration in recharge, due to variations of climatic conditions, but the link between climatic variations and input-output nitrate concentrations is incomplete: the internal processes of transport and transformations of the solute in the aquifer, also due to climatic variations, are not fully taken into account.

4.5. DISCUSSION AND PERSPECTIVES

The transfer function approach developed in chapter 3 enables (1) to highlight the predominant role of the unsaturated zone in the transfer of nitrate in the Wohlschwil aquifer; (2) to simulate the past and present evolution of nitrate concentration at the pumping well; (3) to predict the evolution of nitrate concentration; (4) to distinguish the climatic effect from the effect of land use changes on the nitrate evolution; (5) to quantify the impact of each of the agricultural conversions on the nitrate evolution.

Based on these results, the efficiency of the agricultural conversion can be evaluated in time and a prediction on the future nitrate concentration evolution can be carried out. The management of the Nitrate project gains in precision.

This study compares the results of a transfer function approach for two cases: (1) when transfer functions are entirely characterized by analytical methods; (2) when transfer functions are entirely characterized by numerical methods. Based on the results of this case study, it is not possible to recommend one or the other approach. This aspect is in line with the results of the study introduced by Eberts et al. [2012]: the choice of using one or the other depends on the availability of the required parameters for their implementation and on the uncertainty in estimating the value of these parameters.

There is some contradiction in using numerical methods in a transfer function approach. The transfer function approach should stay simple and flexible to present a real advantage in comparison with numerical methods. Nevertheless the computation of transfer functions by numerical methods can constitute a real advantage because it permits to separately characterize the transfer process in different compartments of the aquifer. The numerical computation of flow and transport in the entire aquifer domain, in particular in both

unsaturated and saturated zones and at different parts of the aquifer catchment, can on the contrary be difficult to carry out. Indeed this problem is highly non-linear and hence the model might not converge. Moreover simulations methods integrating both unsaturated and saturated zones require specialized numerical tools, specific field data and involve time of calibration and calculation. A numerical characterization of the transfer functions, in a separated manner for each compartment of the aquifer (unsaturated and saturated zone, various input zone of the aquifer catchment), simplifies the computation.

One approach that is not described in this study is to combine the numerical and analytical methods: one for the characterization of the transfer functions through the unsaturated zone and the other for the saturated zone. The combination of the numerical and analytical methods could be relevant in several scenarios: (1) when the availability of the data does not enable using one or the other method in one part of the aquifer; (2) when the numerical method is particularly more appropriate than the analytical method, which could be especially the case in the saturated zone (the dispersion model of the analytical approach (Equation 4.5) is defined for a 1D domain, whereas the transport takes place in a 2-dimensional or even 3-dimensional domain, which can be taken into account by a numerical model); (3) when the complexity of the aquifer prevents the use of numerical methods; (4) when the specific tools for numerical modeling are not available.

In first view, a logical combination would be to use an analytical method to characterize the transfer functions through the unsaturated zone and a numerical method to characterize the transfer functions through the saturated zone. For the unsaturated zone, the analytical method, described in this chapter, is based on the combination of a piston flow model (Equation 4.4) and a dispersion model (Equation 4.3) that are straightforward to implement and whose results can be correct if the required parameters are well characterized.

To summarize, the combination of analytical methods and numerical methods could represent a real gain for the transfer function approach because accuracy and simplicity of implementation of each of the methods are optimized in the characterization of the transfer in each compartment of the aquifer system.

The advantages of the transfer function approach reside in its simplicity and its flexibility. The comparison of observed and calculated value of nitrate concentration at the pumping of the Wohlenschwil aquifer shows that the approach can be accurate, at least if relevant functions and parameters of Equation 4.1 are correctly characterized. By analogy, this approach can be applied for other pollutants than nitrate, integrating the reactivity of the transport and the degradation of the pollutant during its travel through the aquifer system. These aspects are discussed in chapter 3.

A second advantage that could be highlighted is that, once the transfer functions are defined, a large range of scenarios can be calculate very rapidly (e.g. different land use patterns) or the calculation can very easily be updated when additional measures are taken. Hence, the effect of the different measures becomes immediately apparent, the various

scenarios can be compared and the management of the environmental project gains in precision.

Finally, the choice of using a transfer function approach could be also relevant when the effect of land use changes on a smaller subsection of an aquifer (a single parcel for instance) is to be evaluated (leading to results presented in Figure 4.18). A numerical simulation of the reaction at the pumping well would require characterizing flow and transport parameters in the entire aquifer domain, which would involve doing strong investment for field investigations and computations. By a transfer function approach, the transfer function of only this subsection needs to be evaluated (by resolution of Equation 3.5 or Equation 3.8) and not of the entire aquifer, which strongly simplifies the procedure of calculation and allows concentrating the investigations on the subsection concerned.

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APPENDIX 4.A



Figure 4.A.1 Observation points of groundwater table (measured in December 2010) in the Wohlenschwil aquifer

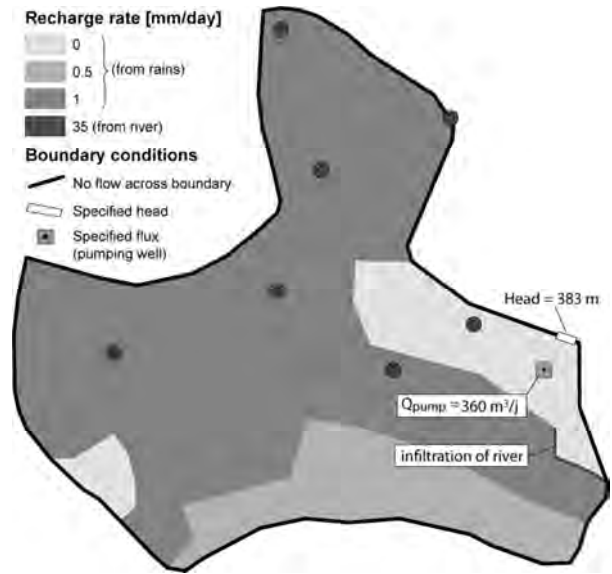


Figure 4.A.2 Distribution of diffuse recharge rate and boundary conditions (well abstraction, constant head and no flow boundaries) of the numerical model

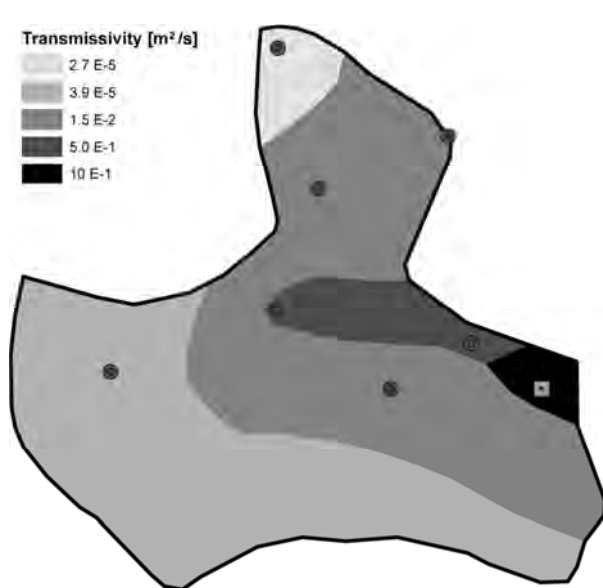


Figure 4.A.3 Distribution of transmissivity in the numerical model of the Wohlenschwil aquifer

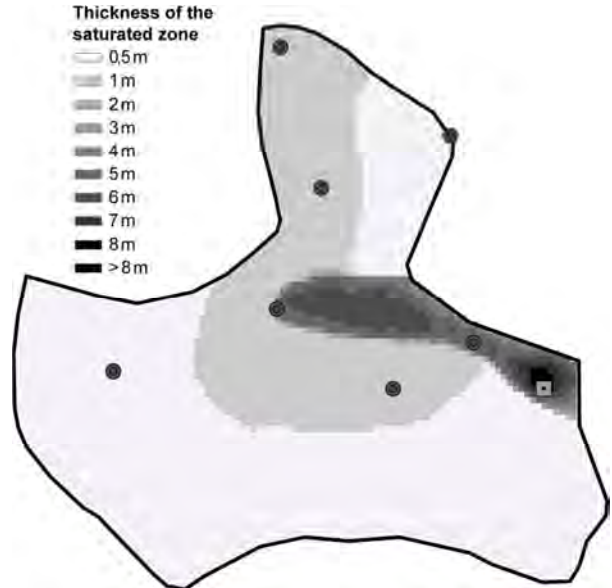


Figure 4.A.4 Distribution of thickness of the saturated zone in the numerical model of the Wohlenschwil aquifer

APPENDIX 4.B

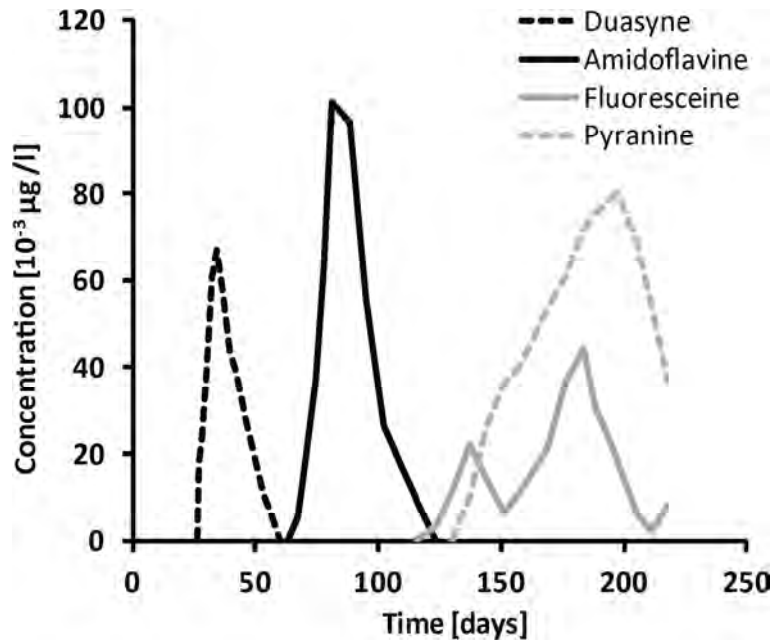


Figure 4.B.1 Breakthrough curves of the tracing test carried out in 1993

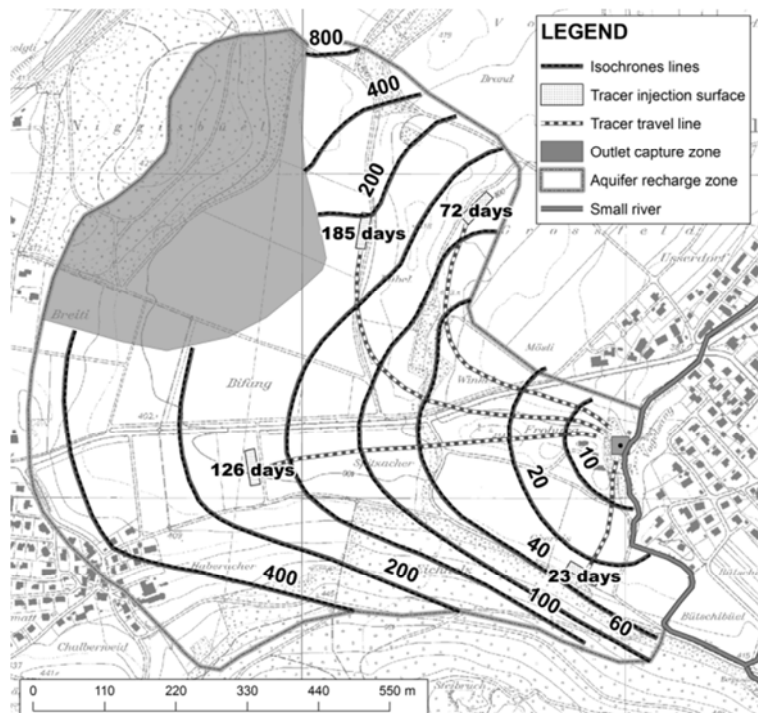


Figure 4.B.2 Isochrones of travel time in the saturated zone of the aquifer determined by a graphical approach

APPENDIX 4.C

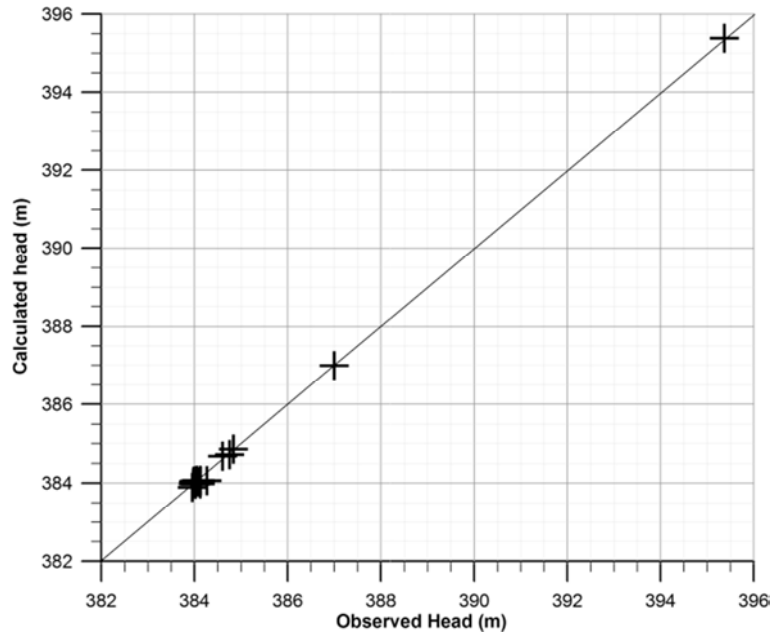


Figure 4.C.1 Calculated heads of groundwater as function of observed heads after calibration procedure of flow parameters of the numerical model of Wohlenschwil aquifer

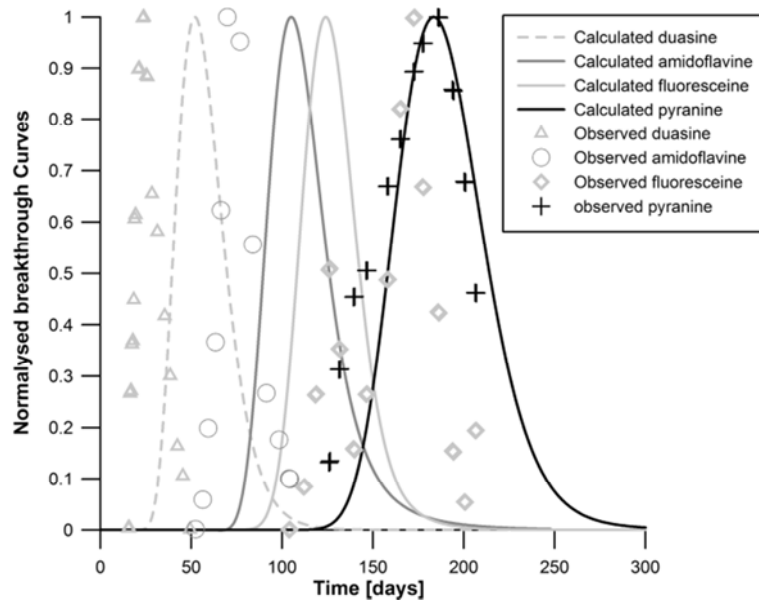


Figure 4.C.2 Comparison between calculated and observed recovery curves of tracers (normalized values) after calibration procedure of transport parameters of the numerical model of the Wohlenschwil aquifer

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Chapter 5

Conclusions and outlook

The introduction of targeted environmental measures for the improvement of groundwater quality requires prior knowledge of their effectiveness. This thesis introduces and develops the transfer function approach, which has been described infrequently in the scientific literature, for establishing predictions on the evolution of groundwater quality at the outlets of aquifers.

Chapter 2 emphasizes that the distribution of travel time plays an important role in explaining the observed lag time between the introduction of environmental measures and the effective improvement of groundwater quality at the aquifer outlet. This distribution of travel time can be addressed by employing a transfer function approach. The initial limitations of this approach are, particularly, (1) the homogeneous distribution of the input history on the catchment area, (2) a description of their transfer through the aquifer system through a single function, (3) the difficulty of characterizing the transfer function and (4) the need to assume steady-state hydrodynamic conditions. These could explain the relatively low popularity of this approach to date for studies aiming to predict the evolution of groundwater quality at the outlet of an aquifer.

Nevertheless once the transfer function is determined, which can be carried out by numerous methods summarized in Table 2.3, the transfer function approach can be implemented with a relative ease. This justifies further consideration and development concerning the conditions of its implementation.

Chapter 3 provides a better framework and extends the range of applicability of the approach. The conditions for which the hydrodynamic characteristics of the aquifer system can be considered in steady-state are analyzed. In transient state, the temporal variations of the recharge rate influence the distribution of travel time of the solute, which becomes dependent on when the solute enters the system. However, when the average travel time increases, the effect of changes in recharge tends to be increasingly buffered by the aquifer system. It is confirmed that the distribution of travel time at the outlet tends to be independent of the observation time when the mean travel time is greater than the characteristic period of hydrodynamic variations. Hence, this condition may justify the application of the transfer function approach to systems with a transient character.

By adjusting the formula for the convolution integral, which is the mathematical relationship at the center of the transfer function approach, this study attempts to redefine its domain of applicability. When the spatial distribution of pollution inputs on the capture zone cannot be considered homogeneous over its entire area, its redistribution into subareas is necessary. In

this context, the convolution integral is redefined to independently take into account the different subareas of the input zone. Similarly, the convolution integral incorporates the possibility to independently characterize the different compartments of transfer that are crossed by the solute during its travel toward the outlet. This aspect corresponds to the typical case of a transfer from the surface towards the outlet, through the unsaturated and saturated zones of the aquifer. These developments represent a significant improvement for the application of the method in most common cases of unconfined aquifers affected by diffuse pollution, non-uniformly distributed over the recharge area.

The evaluation of the impact of a "nitrate project" on the water quality of the Wohlenschwil aquifer pumping well is presented as a case study in Chapter 4. The global efficiency of the project can be evaluated in terms of the reduction of the nitrate levels over time. The assessment can also be made at the scale of the parcels or following the date of the agricultural conversions involved (1997, 2001, 2003 and 2008–2010). The calculation is performed using a basic spreadsheet, such as Excel (Appendix 5.A), with which the problem can be solved very quickly, once the various parameters of the convolution integral are established. The Wohlenschwil site allows for the importance of the travel time of pollutants due to their passage through the unsaturated zone to be emphasized. The unsaturated zone is sometimes underestimated by hydrogeological studies that are often more focused on the saturated zone, however, both zones should be evaluated with the same consideration.

Another interesting aspect that is highlighted in the case study is the quantification of the impact of changes in recharge rates on the nitrate concentrations that are observed at the pumping well. Thus, the increase in nitrate due to the dry years from 2003 to 2005 caused a natural rise in the levels of nitrate at the pumping well up to 5 mg/L in 2008. This local result could be used to explain the origin of the higher levels of nitrate observed in Switzerland during the same period over most groundwater monitoring stations [OFEV, 2009].

The results of the Wohlenschwil case study are encouraging and lend credibility to the transfer function approach for quantifying the evolution of groundwater quality in the context of environmental projects. The application of the approach to other sites is possible whenever the required parameters of the convolution integral can be determined. Application to other outlets than a pumping well and to other contaminants than nitrate is conceivable. A minimum of information needed is required: (1) the delimitation of the capture zone of the outlet of interest, (2) the spatial distribution of historical and future pollution input within the capture zone, (3) the contribution of each sub-area of the recharge zone to the flow at the outlet and (4) the transfer functions of the considered pollutant in the aquifer, using one or a combination of the methods introduced in Chapters 2 and 3 and taking into account the possible factors of degradation and retardation of the substance within the aquifer.

Depending on the characteristics of the site, this information is more or less easily obtainable.

- (1) The delimitation of the capture zone can be generally estimated in shallow aquifers with relatively well known methods, reported for example in Bussard et al. [2004], mainly based on the water balance and flow lines. However, when the aquifer is affected by several outlets, when the recharge has various origins or when the subsurface flow system is complex, this evaluation can be less obvious and requires more detailed hydrogeological investigations, such as tracing tests, drilling and piezometric monitoring.
- (2) Pollutant inputs in the capture zone depend on the nature of the pollutant, its solubility and reactivity, on the climate, on the land use and on the soil properties. Hydrogeologists could take advantage of agronomic studies or tools for the evaluation of agricultural pollutants inputs.
- (3) The contribution of flow from each sub-area of the capture zone to the pumping well can be assumed proportional to the surface of the sub-area, with a probability of capture of 100%, as carried out for the Wohlenschwil case study. For a more detailed estimation, numerical methods are quasi indispensable.
- (4) The characterization of the transfer functions is the key element of the transfer function approach. Whereas transfer functions can be calculated by numerical methods or analytical methods, both methods should be validated or calibrated by tracer data. In the saturated zone, the use of an exponential model of transfer can be considered. The required parameters, the recharge rate, the porosity and the aquifer thickness, are generally available in basic hydrogeological studies or straightforward to obtain. However, the application of an exponential model of transfer is limited by the requirement of homogeneous properties of the aquifer. The dispersion model is well adapted to simulate the transfer of solute through the unsaturated zone. However, its use requires an estimation of the mean travel time. This knowledge is not usually available in most hydrogeological reports and additional investigations of the soil can be necessary, as carried out in the Wohlenschwil case study (where the recharge rate and the distribution of residual water content were investigated).

The question remains as to the most suitable method between an approach using transfer functions and a direct numerical simulation of subsurface flow and transport. When correctly constructed and calibrated, the numerical simulation can take into account all the aspects of the problem, whether it be in regards to the geological, hydrogeological, pedological and agronomical parameters, which control the pollutant input, the travel dynamics and the hydrodynamic conditions, within the aquifer and at the outlet. When these factors are correctly incorporated, a numerical simulation, whether deterministic or stochastic, is without question more accurate than the transfer function approach. Moreover, the solution to the problem by numerical simulation can be carried out in a transient state, while the transfer function approach assumes a steady state of the

hydrodynamic conditions. However, the transfer function approach may be appropriate in many specific but common situations. For example, a project often requires a prediction of the evolution of groundwater quality considering the planned environmental actions and the fact that the financial, technical or temporal means of the project will not allow for the implementation of a numerical model of subsurface flow and transport. The transfer function approach, in this case, could provide an alternative method since, once the transfer functions are established, the calculation requires only simple spreadsheets (Appendix 5.A) and is almost instantaneous. This allows for the quick study of the different scenarios of actions in the environmental project. Similarly, when additional environmental measures are taken, as the project is progressing, the data calculation can be easily updated.

A second case, where the transfer function approach could be relevant, is when the project concerns a small part of the capture zone. In this case, it is sufficient to know the transfer function describing the transfer of solute from this area, for example through an artificial tracing experiment, in order to directly calculate the effect of land use changes on the quality of water at the outlet. In this case, the lateral contribution of solute can be considered constant. Hence, it is not necessary to define the hydrogeology of the entire capture zone: rather investigations can be focused just on the area where the environmental actions are planned. If the transfer function can be accurately established for solutes coming from this zone, the approach can provide results with relatively low uncertainty.

In a few words, the choice between the transfer function approach and a classical numerical simulation of solute transport, to resolve the link between pollutant input and pollutant concentration at the outlet, depends on (1) the characteristics of the aquifer, particularly its level of complexity and the transient character of the hydrodynamic conditions, (2) the available or obtainable data and (3) the level of accuracy that must be reached, with regard to the importance of the environmental project and the time available for the study. The numerical simulation of transport is more sophisticated but is applicable whatever the complexity of the system, as long as the characteristics of the aquifer system are well known. When the properties of the aquifer are highly variable and when the system is subject to high hydrodynamic fluctuations for instance, numerical simulations of transport should be applied. But for systems of simple hydrogeological configuration, a common situation for shallow aquifers, numerical simulation and transfer function approach could be equivalent in terms of accuracy, while the transfer function approach is certainly more easily and quickly implemented.

It should be noted that a transfer function approach and a classical numerical simulation of water flow and solute transport could be used in a combined manner for solving groundwater quality problems. For example, it would be interesting to use the transfer function approach in the unsaturated zone in order to generate the input concentration time series for the numerical groundwater flow and transport model in the saturated zone.

The characterization of the transfer functions in the various compartments and for the different sub-areas of the capture area is an essential step of the approach. This step can be carried out by numerous methods, summarized in Chapter 2, developed in Chapter 3 and partially applied in Chapter 4, depending on which data are available and on the hydrogeological characteristics of the site. The choice of the method is, for example, directly linked to the size of the studied aquifer: artificial tracers are for example suited to investigate the transfer functions for a range of travel times of few month maximum, as it is the case in the Wohlenschwil aquifer, while environmental tracers are reasonably more suited for aquifers of larger size characterized by travel time range of several years. However, analytical methods and numerical methods are suitable in both cases.

If each of the numerical, analytical or tracers methods can lead to an independent characterization of the transfer functions, a combination of methods is also possible. For example an artificial tracer test could be carried out to calibrate analytical models, as it is carried out at the Wohlenschwil aquifer. For aquifers of larger size than the Wohlenschwil case, the analytical or numerical model used to characterize the transfer function could be calibrated by groundwater age data. To summarize, a coupled approach should increase the reliability of the results and should generally be favored.

With the new developments presented in this study, the transfer function approach turns out to be a promising method. Nevertheless, it should be tested in more detail to be more largely disseminated in environmental projects. Its development potential is still important, which deserves further research. First, a direct comparison of the transfer function approach with a classical numerical simulation of solute transport, carried out independently in the same case study, is missing in this thesis and should be tested. Second, the improvements for the transfer function approach are demonstrated with a specific chemical compound, nitrate, whose transport can be assumed nonreactive and conservative under certain conditions. Some theoretical elements were introduced in Chapter 3 to adapt the method to substances subject to degradation and absorption in aquifers, as is the case of pesticides for instance. The applicability of the method to such substances should be studied and demonstrated in a case study. The combination of an agronomical tool, to simulate the leaching of agricultural pollutants below the root zone, such as MODIFFUS [Prasuhn and Sieber, 2005] or AGRIFLUX [Banton and Larocque, 1997], with the transfer function approach should be tested in other agricultural sites. Similarly, the possibility of coupling the transfer function approach, to simulate the transfer of the pollutant in the unsaturated zone, with a direct simulation of flow and transport in the saturated zone should also tested for more complex aquifer cases. The transfer function approach should also be tested for aquifers of larger dimension than the Wohlenschwil aquifer, using in these cases, time series of environmental tracer data to calibrate the transfer functions. Finally, the approach should be adapted to more dynamic hydrogeological environments (in hydrodynamic terms) than porous aquifers, notably in karstic systems. This requires, however, studying the problem

related to the transient state of the hydrodynamic conditions, which currently remains unresolved.

Finally, the recent decision of the European Commission to refer France to the EU Court of Justice for “failing to take measures to guarantee that water pollution by nitrates is addressed effectively” [*European Commission - Press Release, 2012*] emphasizes the urgency of implementing relevant actions of groundwater quality remediation. To gain in efficiency such remediation programs require optimizing the relevant actions to reach a good quality status of groundwater within a given time. By its relative ease of implementation and its capacity to be adapted to various aquifer environments, the transfer function approach appears to be a relevant method that could be more frequently associated with environmental projects, where the level of strategic importance does not require the use of more sophisticated simulations of flow and solute transport in the aquifer.

APPENDIX 5.A

Once the input functions of concentration are characterized for each subarea of capture zone and once the transfer functions are characterized, using for example one of the methods introduced in Chapter 2, the evolution of a solute concentration at the outlet can be calculated by a transfer function approach, using the convolution integral or its derivatives, introduced in Chapter 3 of this thesis. Intuitively, the convolution could have to be performed by specific mathematical tools, such as MATLAB or MAPLE. However, Olsthoorn [2008] shows that the discretization of the equation of convolution allows processing the resolution by a simple EXCEL spreadsheet.

The numerical version of this thesis comes with an EXCEL file, called *convolution calculator.xls*, which allow solving the convolution integral or its derivatives. This tool can be used in a transfer function approach for the prediction of the evolution of solute concentration at the outlet of an aquifer, a typical need of the projects of groundwater quality remediation in aquifers affected by diffuse pollution.

The file is divided into 5 spreadsheets:

- *CONFIGURATION*: the sheet of input parameters
- *RESULTS*: the sheet showing the results of the convolution
- *CALCULATION UNSZ*: the sheet of the resolution of the convolution into the unsaturated zone
- *CALCULATION SZ*: the sheet of the resolution of the convolution into the saturated zone
- *CALCULATION OUTPUT*: the sheets that aggregates the various sub-results for the resolution at the considered outlet of the aquifer system

To summarize, the user has to enter the input parameters in the spreadsheet *CONFIGURATION* and the results of calculation are given in the spreadsheet *RESULT*. The other spreadsheets are only used for the internal calculations of the tool *convolution calculator.xls*. Note that the concentration and time data and the data have not specified units.

The input parameters have to be entered in the yellow cells of the spreadsheet *CONFIGURATION*, in the given order from (1) to (18). In order to avoid any hazard of introducing an error in the calculations, the writing in the spreadsheets is only allowed in the cells reserved for input parameters. Off course this limitation can be removed using the password "convolution" (in Excel version 2007-2010 go in the Review tab and click Unprotect Sheet).

The input parameters are summarized and described in Table 5.A.1.

Parameter	Value to be enter	Description of the parameter
(1) Number of parcels	Entire value between 1 and 30	This parameter specifies the number of subareas in the capture zone, called in the context of agricultural area as " <i>parcel</i> ". It is assumed that the input function is spatially homogeneous within each parcel. The program does not permit more than 30 parcels.
(2) Do you separately take into account the unsaturated zone?	Enter the response yes or no	This parameter specifies if the transfer functions within the unsaturated and saturated zones are separate or not. If no, the transfer functions will describe the transfer from the surface of each parcel to the outlet. If yes, the transfer functions are described in a separate manner in the unsaturated and saturated zones.
(3) Time step	Enter a positive value	This parameter specifies the time step of the calculation, which is the same for each time series: the transfer functions, the input functions, the results
(4) Beginning of calculation	Number	This parameter specifies the date of the first value of concentration in recharge. This date should be chosen in accordance with the period of interest for the results. Indeed, as explained by Olsthoorn [2008], there is a need of initializing the calculation by an average value of input concentrations during a time that should be at least equal to the maximum time of transfer. As the transfer functions are 100 time step long, the beginning of calculation should be at least 100 or 200 time steps before the period of interest, depending if the transfer function in the unsaturated zone is taken into account or not (value reported in the cells C37-38. Clearly if the period of interest begins in the year 2000 and that the time step is 0.5 years, the beginning of calculation should be maximum 1950 if the unsaturated zone is not separately taken into account in the transfer functions or 1900 otherwise. The first time of the available results are reported in the cells C39-C40.
(5) End of calculation	Number	This parameter specifies the date of the end of calculation, in other words the maximum time of the results. The spreadsheet is limited to 2000 data of calculation. Hence, the range between the beginning of calculation, step (4) and the end of calculation cannot be higher than 2000 times the time step defined in point (3).
(6) Would you like to normalize the transfer function in the unsaturated zone?	Enter the response yes or no	This parameter specifies if the calculation tool has to normalize the transfer functions of the unsaturated zone. If the solute is not affected by degradation processes during its travel within the unsaturated zone, the transport is conservative and the integral of the

		transfer function should be equal to 1: the transfer function has to be normalized. If the transport is not conservative and if the entered transfer functions already take into account the degradation factor, thus they should not be normalized.
(7) Would you like to normalize the transfer function in the unsaturated zone?	Enter the response yes or no	Idem than above for the transfer function in the saturated zone.
(8) Would you like mixing your concentration by an additional input of constant concentration?	Enter the response yes or no	This parameter specifies if there is an additional input of constant solute concentration that is mixed to the solute at the outlet, for instance due to surface stream infiltrations. If yes the user has to specify points (9) and (10).
(9) Rate of additional input at the outlet	Enter a value between 0 and 1	This parameter specifies the rate of water coming from the additional input. For example, a value of 0.2 means that 20% of water at the outlet comes from the additional input.
(10) Constant concentration of additional input	Enter a positive value	This parameter specifies the concentration of solute in the additional input.
(11) Have you got observed data?	Enter the response yes or no	This parameter specifies if there is observed data, for a comparison with calculated value. This observed data are plotted in the graphics of calculated values. If yes the user have to specify points (12) and (13)
(12) Beginning of observed data	Number	This parameter specifies the first date of observed data. This date has to be in the time of interest, in other words it has to be at least equal to the first time of the available results (cells C39-C40).
(13) End of observed data	Number	This parameter specifies the last date of observed data. This date have to be in the time of interest, in other words it has to be lower or equal than the end of calculation, point (5).
(14) Area / rate reaching the outlet	Number / value between 0 and 1 , for each parcel	This parameter specifies the area of each parcel and the rate of mass that effectively reach the considered outlet. The impact of the history of solute concentration in recharge is proportional to the size of the parcel and to the rate of mass reaching the outlet. For instance, a value of 0.2 means that 20% of mass dissolved in the recharge water reaches the outlet.
(15) Observed values	Number for each date of observation	This parameter specifies the observed data in the range of times defined at points (12) and (13). These values have typically the dimension of a concentration [M ³ /L]. Empty cells are allowed.

(16) Concentration in recharge	Number for each time step	This parameter specifies the history of solute concentration in recharge for each parcel. The values are specified for each time step of calculation between the beginning and final time of calculation, points (4) and (5). A maximum of 2000 data is allowed for each parcel. Empty cells are not allowed.
(17) Transfer functions in the unsaturated zone	Enter a number for each time step	This parameter specifies the value of the transfer functions for each time step of the travel time, defined between 0 and 100 time steps, within the unsaturated zone subjacent to each parcel. A maximum of 100 data is allowed for each parcel. Hence, the maximum travel time is 100 time steps long. Empty cells are not allowed.
(18) Transfer functions in the saturated zone	Enter a number for each time step	This parameter specifies the value of the transfer functions for each time step of the travel time, defined between 0 and 100 time steps, within the saturated zone and for solute coming from each parcel. A maximum of 100 data is allowed for each parcel. Hence, the maximum travel time is 100 time steps long. Empty cells are not allowed.

Table 5.A.1 Description of input parameters of the Excel spreadsheet convolution calculator.xls

The resolution of the evolution of nitrate concentration at the pumping well of the Wohlenschwil aquifer, introduced in Chapter 4, is given in the following Excel spreadsheets, attached with the numerical version of this thesis:

- *convolution_calculator_analytical_TF.xls* : the transfer functions are characterized by analytical models.
- *convolution_calculator_numerical_TF.xls* : the transfer functions are characterized by numerical simulations.

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Je me sens déjà
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Capitaine Haddock**