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Assessing groundwater quality trends in pumping wells using spatially varying transfer functions

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Abstract When implementing remediation programs to mitigate diffuse-source contamination of aquifers, tools are required to anticipate if the measures are sufficient to meet groundwater quality objectives and, if so, in what time frame. Transfer function methods are an attractive approach, as they are easier to implement than numerical groundwater models. However, transfer function approaches as commonly applied in environmental tracer studies are limited to a homogenous input of solute across the catchment area and a unique transfer compartment. The objective of this study was to develop and test an original approach suitable for the transfer of spatially varying inputs across multiple compartments (e.g. unsaturated and saturated zone). The method makes use of a double convolution equation accounting for transfer across two compartments separately. The modified transfer function approach was applied to the Wohlenschwil aquifer (Switzerland), using a formulation of the exponential model of solute transfer for application to subareas of aquifer catchments. A minimum of information was required: (1) delimitation of the capture zone of the outlet of interest; (2) spatial distribution of historical and future pollution input within the capture zone; (3) contribution of each subarea of the recharge zone to the flow at the outlet; (4) transfer functions of the pollutant in the aquifer. A good fit to historical nitrate concentrations at the pumping well was obtained. This suggests that the modified transfer function approach is suitable to explore the effect of environmental projects on groundwater concentration trends, especially at an early screening stage.

Keywords Transfer function · Groundwater management · Convolution · Nitrate · Switzerland

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Introduction

In recent decades, changes in environmental policies were introduced by governments in order to limit the deterioration of groundwater quality observed in many parts of the world (World Water Assessment Programme 2009). Some measures of remediation to deal with agricultural contaminants have been introduced since the 1990s. In North America, for example, the concept of beneficial management practices (BMP) defines agricultural practices that are suitable for minimizing impacts on water quality (Wassenaar et al. 2006). More recently, the European Water Framework Directive (European Union 2000) has introduced guidelines for groundwater quality protection in order to reverse the deterioration of water quality in all European water bodies (including aquifers). One of the targets is to reach or maintain good water quality by 2015.

Remediation measures usually consist of limiting pollutant input in the catchment area to decrease pollutant concentration at the groundwater receptors (e.g., pumping wells, draining streams or springs). After the implementation of remediation programs, numerous studies report a delay in the groundwater quality improvement. This delay can be highly variable from one site to another, from weeks to decades (Bohlke and Denver 1995; Gutierrez and Baran 2009; McMahon et al. 2006; Meals et al. 2010; Osenbrück et al. 2006; Owens et al. 2008; Tomer and Burkart 2003; Zoellmann et al. 2001). It is crucial to know the timing required to reach water quality objectives within reasonable financial ranges. The efficiency of the methods can also be questioned when the objectives are not reached within the expected time. Therefore, it is essential to have reliable predictions to what extent the level of contaminant concentration will be reduced, as well as time frame in which the reduction will take place.

Flow and transport numerical modelling is the main approach to calculate the effect of environmental actions on the evolution of groundwater quality (Conan et al. 2003; Orban et al. 2010; Zoellmann et al. 2001). Although numerical methods can represent many physical processes such as contaminant transport, it is still challenging to use them for field studies in practical conditions, especially in terms of complexity associated with transport modelling. Uncertainties regarding the boundaries of the model domain and unknown model parameters that lead to a high predictive uncertainty as well as long computation times restrict the use of numerical methods, especially for a rapid screening of the efficiency of remediation programs.

The transfer function approach is noted as an alternative to numerical methods to model contaminant transfer in aquifers (Beltman et al. 1996; Eberts et al. 2012; Lerner and Papatolios 1993; Osenbrück et al. 2006). 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) and of solutes in the vadose zone (Jury 1982).

Transfer functions can be derived from analytical models (Jurgens et al. 2012), which can be lumped parameter models calibrated by environmental tracer (Eberts et al. 2012; Osenbrück et al. 2006) or mathematical models based on simplified aquifer geometry and flow (Beltman et al. 1996; Kazemi et al. 2006; Lerner and Papatolios 1993). Transfer functions can alternatively be derived from numerical models (Eberts et al. 2012; McMahon et al. 2008), including for instance direct age models (Cornaton and Perrochet 2006; Goode 1996; Varni and Carrera 1998). A recent review of method for modeling environmental tracers was published by Turnadge and Smerdon (2014), where the various methodologies to get the transfer functions are discussed and compared. When they are derived from analytical models, transfer function approaches generally involve simpler calculations than numerical deterministic simulations (Visser et al. 2009).

However, despite its relative ease of implementation, the transfer function approach, as usually applied up to now, is based on three restrictive conditions: (1) steady-state flow conditions; (2) homogeneous inputs of pollutant in the recharge zone; and (3) transfers of solute through the aquifer described by a single function.

Some authors have expanded the convolution-based approach to model tracer transfer by introducing time-variant forms of analytical-model transfer functions (Niemi 1977, 1990; Nir 1973; Ozyurt and Bayari 2005). Whilst such methods were developed to study transfer processes in surface flow (Nir 1973), in groundwater (Ozyurt and Bayari 2005) or in industrial processes (Niemi 1977, 1990), the required input data (variations of internal volume and/or input and output flows over the time) are difficult to obtain in groundwater domain. Their use is therefore limited for hydrogeologic applications. However, according to several authors (Badoux 2007; Baillieux 2012; Osenbrück et al. 2006; Reilly and Pollock 1996; Zuber et al. 1986, 2011), the approximation of a steady-state flow in real hydrogeological systems is valid when their mean water travel time is greater than the characteristic periods of hydrodynamic variations (Badoux 2007; Baillieux 2012; Osenbrück et al. 2006; Reilly and Pollock 1996; Zuber et al. 1986, 2011). This aspect is based on the fact that aquifers with large travel time scales have the capacity to buffer the effect of rapid variations in recharge and discharge flows. Because this situation is quite common, the steady-state flow conditions required in the transfer function approach can be relaxed in most cases.

The transfer function approach based on the convolution integral is suited for the case of a homogeneous solute flux in the input zone of the aquifer system. A homogenous input can generally be accepted for the study of environmental tracers that are associated with precipitation (Zuber 1986). However, it is rarely observed in the context of contaminant input in aquifers. For instance, in the context of a groundwater catchment covered by an agricultural area, each agricultural field may be characterized by a specific nutrient leaching history, depending on the crop management schedule, while in other zones (e.g. forests, meadows), no changes occur. Up until now, the transfer function approach was not suited for such configuration of groundwater contamination and clearly limits a widespread application.

A further limitation is that the convolution integral includes a single transfer function that describes the transfer of the solute from the input zone to the pumping well. Thus, this single transfer function has to take into account all the various flow pathways, processes of mass transport and biogeochemical interactions that occur in the aquifer system. In most cases, however, the aquifer presents at least two compartments where the transport processes are based on different physical properties: the unsaturated zone and the saturated zone. Within one aquifer, the velocities and directions of flow, as well as the transport and degradation processes, are significantly different in both unsaturated and saturated zones. Previous works have proposed analytical solutions including both the unsaturated and saturated zone in a single transfer function: exponential piston flow model (EPM; Jurgens et al. 2012) or analytical solution for coupled unsaturated–saturated transport in a homogeneous radially symmetric aquifer (Beltman et al. 1996). However, both analytical models are limited to specific cases, which are not appropriate to most aquifer and pollutant transfer configurations.

The conditions of spatially homogenous input of pollutants and single transfer compartment are therefore prohibitive for applying a transfer function approach in most groundwater quality remediation projects. That is also probably why, despite its relative ease of implementation, the transfer function approach remains largely underused.

The objective of this study is to make the transfer function approach more appropriate for typical configurations of environmental projects on aquifer systems. In order to extend the application of the transfer function approach, some mathematical developments are proposed. First, the convolution integral equation is modified to take multiple input zones and several transfer compartments into account. Second, the exponential model of transfer function, which is one of the most commonly used models to describe the transfer in the unsaturated zone of shallow unconfined aquifers (Zuber 1986), is derived to include partial input zones in the recharge area. Most results described in this article originate from Baillieux (2012, PhD thesis), completed by an additional review of scientific findings published since 2012. Independently of the present work and nearly at the same time of the PhD publication, the US Geological Survey published a report on analytical models, where a new formulation of the exponential model including partial input zones has been described (Jurgens et al. 2012). This model, presented as the partial exponential model (PEM), is equivalent to the derivation of the exponential model described in the present article.

The new developments of the transfer function approach are applied to predict the evolution of nitrate concentrations at the pumping well of the Wohlenschwil aquifer, a small aquifer in unconsolidated deposits located near Zurich, Switzerland. This aquifer site is well suited for testing the approach because changes in land use as a result of agriculture have been well documented since 1997; therefore, nitrate pollution from agriculture and the evolution at the pumping well are investigated. The required transfer functions to calculate nitrate values are characterized using analytical approaches. It is expected that these theoretical improvements, made to the transfer function approach and strengthened by the demonstration on a real aquifer site, will allow stakeholders to more easily quantify the response of aquifer systems to environmental measures.

New theoretical developments

The improvements brought to transfer function approach were first based on an extension of the convolution integral to cases of multiple input zones and several transfer compartments of diffuse pollutions in aquifers. Then, we reformulated the analytical models of transfer function in order to make them appropriate for such typical conditions.

Equation of convolution integral for multiple input zones and several transfer compartments

The convolution integral is the key equation of the transfer function approach. One classical formulation of the convolution integral is (Jury 1982):

The observed concentration of solute $C_{\mathrm{OUT}}(t)$ at the outlet is related to the known input function $C_{\mathrm{IN}}(t)$ of the solute on the capture zone of the outlet, through a transfer function $f(\tau)$. The transfer function $f(\tau)$ describes the travel time distribution of the solute from the input zone to the outlet, through both components, unsaturated and saturated zones. The parameter t is the observation time and τ is the travel time. In Eq. (1), $f(\tau)$ directly integrates the potential degradation of the solute during its travel in the aquifer system.

$$C_{\mathrm{OUT}}(t) = \int_0^t C_{\mathrm{IN}}(t-\tau) f(\tau)\mathrm{d}\tau \tag{1}$$

In order to extend its application to the case of distributed subareas of input solute in the input zone, the convolution integral can be modified. Considering several subareas of homogeneous solute input, the superposition principle is applied to Eq. (1). This leads to:

$$C_{\mathrm{OUT}}(t) = \frac{\sum_i Q_i \int_0^t C_{\mathrm{IN}_i}(t-\tau) f_i(\tau)\mathrm{d}\tau}{\sum_i Q_i} \tag{2}$$

where Q is the flow contribution of the input subarea and i is the index of the subarea.

For a more realistic characterization of solute transfer, the convolution integral should also separately represent the distinctive transfer characteristics of the unsaturated and saturated zones. The solute from the surface travels through the unsaturated zone according to a specific transfer function. When it reaches the water table, it is then transported in the saturated zone according to a second specific transfer function. This series of two transfer functions leads to the following double convolution (Eq. 3): 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 travel time in the saturated zone and τ is the travel time in the unsaturated zone.

$$C_{\mathrm{OUT}}(t) = \int_0^t \left[\int_0^{t-T} C_{\mathrm{IN}}(t-\tau-T) g(\tau)\mathrm{d}\tau \right] h(T)\mathrm{d}T \tag{3}$$

Finally, the partition of the transfer functions in the saturated zone and the unsaturated zone of the aquifer, as considered in Eq. (3), can be applied to various subareas of the input zone, as was done in Eq. (2). Combining Eqs. (3) and (2) leads to:

$$C_{\mathrm{OUT}}(t) = \frac{\sum_i Q_i \int_0^t \left[\int_0^{t-T} C_{\mathrm{IN}_i}(t-\tau-T) g_i(\tau)\mathrm{d}\tau \right] h_i(T)\mathrm{d}T}{\sum_i Q_i} \tag{4}$$

The equation can be quickly solved due to the simplicity of the formulation. A simple Excel spreadsheet was used in this study. This spreadsheet is available in the electronic supplementary material (ESM).

Analytical models of transfer functions

Transfer functions can be described using analytical approaches. Their applications are reported in numerous articles to estimate the evolution of groundwater quality at an aquifer outlet (Beltman et al. 1996; Eberts et al. 2012; Lerner and Papatolios 1993; Osenbrück et al. 2006; Stewart and Loague 2004).

The transfer function can be derived from the analytical equation governing the solute transport in simple configurations of aquifers, like those described by Kazemi et al. (2006). 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. Nonetheless, Luther and Haitjema (1998) suggest that the transfer function in heterogeneous unconfined shallow aquifers can be commonly described by an exponential model (Eq. 5), assuming that the main transport parameters of the aquifer (recharge rate *I*, porosity ∅ and thickness *e*) vary in such a way that the ratio $T_0 = e\varnothing / I$ is constant in the investigated domain.

$$h(t) = T_0^{-1} \exp\left(-\frac{t}{T_0}\right) \quad ; \quad T_0 = \frac{e\phi}{I} \tag{5}$$

The transfer function *g*(*t*) of solute through the unsaturated zone can be described by a dispersion model (Jury and Roth 1990). One typical formulation of the dispersion model is:

$$g(t) = \frac{1}{\sqrt{4\pi P_{\mathrm{D}} \frac{t}{T_{\mathrm{US}}}}} \frac{1}{t} \exp\left[-\frac{\left(1-\frac{t}{T_{\mathrm{US}}}\right)^2}{4P_{\mathrm{D}} \frac{t}{T_{\mathrm{US}}}}\right] \; ; P_{\mathrm{D}} = \frac{\alpha}{L} \; ; T_{\mathrm{US}} = \frac{Z \cdot \theta}{I} \tag{6}$$

The two parameters in Eq. (6) are the apparent dispersion parameter P_{D} [dimensionless] of the solute and the mean travel time T_{US} [T] through the unsaturated zone. P_{D} is defined as the ratio between the longitudinal dispersivity α [L] and the length of travel *L* [L]. Assuming a conservative and non-reactive transport, one classical way to calculate the mean travel time T_{US} of a solute in the unsaturated zone is to use the piston flow model, where *Z* [L] is the thickness of the considered layer, θ [−] is the volumetric water content of the layer [−] and *I* [L/T] is the mean annual recharge. The piston flow model (Fisher and Healy 2008; Liao et al. 2012; McMahon et al. 2006; Sousa et al. 2013; Zoellmann et al. 2001) is derived from a water balance based on the assumption of a purely vertical and advective transport of tracer.

Modification of the exponential model for a partial input zone of the recharge area

The mathematical expression of the exponential model is modified in order to better correspond to more realistic configurations of input solute, i.e. when the solute input only affects one part of the recharge area. The aquifer configuration corresponding to the exponential model was introduced to hydrogeology by Vogel (1967). The aquifer flow model is illustrated in Fig. 1. It is a horizontal aquifer, with constant thickness *e* and porosity φ, recharged by a uniform infiltration *I*. The Dupuit assumption is enforced and the solute is considered as conservative and nonreactive. Based on this configuration, the travel time is mathematically formulated as a function of the distance between the input point and the outlet, as well as a function of the dimensions of the capture zone.

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:

$$g_{x_1x_2}(t) = \frac{L\exp\left(-\frac{t}{T_0}\right)}{T_0(x_2 - x_1)} \quad , t_2 \le t \le t_1 \tag{7}$$

$$g_{x_1x_2}(t) = 0 \tag{8}$$

; otherwise, with

$$t_1 = T_0 \ln\left(\frac{L}{x_1}\right) \tag{9}$$

$$t_2 = T_0 \ln\left(\frac{L}{x_2}\right) \tag{10}$$

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

$$\overline{t(x)}_{x_1x_2} = \frac{T_0}{x_2 - x_1}\left[x_2\left(\ln\left(\frac{L}{x_2}\right) + 1\right) - x_1\left(\ln\left(\frac{L}{x_1}\right) + 1\right)\right] \tag{11}$$

The detail of the derivation is given in the Appendix. 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*). The transfer function $g_{z_1z_2}(t)$ of a solute from the recharge zone and reaching the outlet at the interval of depth limited by z_2 and z_1 is given in the Appendix (Eq. 27).

Equation (7) was compared with the PEM described by Jurgens et al. (2012; US Geological Survey's report on lumped parameter models for environmental tracer applications, including binary mixing models leading to 25 possible models combinations). Equation (7) corresponds to the PEM and Eq. (11) also finds equivalence, which suggests the correctness of the main mathematical developments detailed in the Appendix.

Application to a case study

The Wohlenschwil aquifer was particularly well suited to test the transfer function approach because the pollution

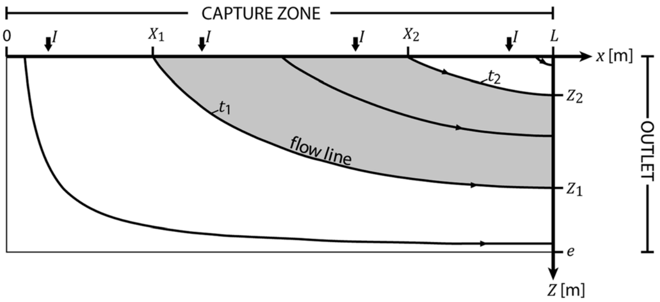

Fig. 1 Flow configuration sketch for the analytical modeling of the transfer function in 2D configuration according to an exponential model. I is the recharge rate, X_1 and X_2 are the distance of the upstream and downstream limits of the central parcel, respectively, L is the length of the capture zone, Z_1 and Z_2 are the depths of the outlet boundaries, e is the thickness of the saturated zone

history is documented in almost every agricultural parcel of the groundwater basin, and the evolution of pollution has been measured for several decades. Hence, historical observations can be compared with calculations based on the proposed method; another interest is the use of a case study to demonstrate the various investigations that can be carried out with such a transfer function approach.

Study site

The Wohlenschwil aquifer, a small-scale sand-gravel aquifer, is located in the canton of Aargau, in the central plateau of Switzerland (Fig. 2). The general characteristics of the Wohlenschwil aquifer were studied over the years 2009–2010 and have been the subject of previous studies—Geological Atlas of Switzerland 1/25,000 - Sheet 1090 Wohlen (Jäckli AG Engineering, unpublished data, 1996; "Hydrogeologische Untersuchungen zur Nitratbelastung im Groundwasser Gemeinde Wohlenschwil/AG: Resultate des Sondierkampagne" [Hydrogeological investigations on nitrate contamination in the groundwater community of Wohlenschwil/AG: results of drilling campaign]). This aquifer is located in a small valley bounded in the south and northwest by molassic hills, a typical formation of the Swiss plateau. The aquifer mainly corresponds to glaciofluvial sediments (sand and gravels) and 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 its edge. In the central part of the valley, the unconfined aquifer has a varying thickness between 10–30 m, and the water table is located at approximately 10–15 m beneath the surface. The saturated zone is generally thin (1–2 m), with a thickness reaching 15 m locally in the central part and around the pumping well. 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 approximately 10^{-2} m/s, whereas the lateral part of the aquifer, generally formed by late glacial moraine deposits, presents a lower hydraulic conductivity of 10^{-4}–10^{-5} m/s (Jäckli AG Engineering, unpublished data, 1996). Mainly direct recharge feeds the aquifer, whereas lateral inflow from surrounding slope zones plays a minor role. Tracer tests from 1993—(Jäckli AG Engineering, unpublished data, 1994; "Hydrogeologische Untersuchungen zur Nitratbelastung im Groundwasser Gemeinde Wolhenschwil/AG" [Hydrogeological investigations on nitrate contamination in the groundwater community of Wohlenschwil/AG]), including four different fluorescent tracers, were used to estimate aquifer properties (porosity, travel time and capture zone of the pumping well). The hydraulic distance between tracer input and pumping wells varied between 150 to 500 m. Hydraulic connections between several points of the hydrogeological basin and the pumping well were deduced. The average travel time of tracers in the saturated zone was in the range 40–200 days. For the interested reader, more information about the results of these tracer tests can be found in Baillieux (2012). Based on flow directions, tracers test results and drainage divide localization (Fig. 2), two outlets were identified in the aquifer. The first outlet is located in the eastern part of the aquifer, in the immediate vicinity of the pumping well, while the second outlet, located northwest of the aquifer, is most likely a loss to the lateral aquifer, which may continue until the Reuss River, located 2 km to the north. As the main interest of the authors is the evolution of the nitrate concentration at the pumping well, this study is focused on the first part of the catchment area, which approximately corresponds to the capture zone of the pumping well (Fig. 2).

The community's drinking water is obtained from a pumping well that supplies an average of 360 m^3/day of water from the Wohlenschwil aquifer. The land cover in the aquifer recharge zone is predominantly permanent meadow and intensive agriculture and, secondarily, forest and uncultivated fields (Fig. 2). A strong and continuous increase of nitrate concentrations in pumped groundwater was observed during the 1980s and 1990s with a maximum in 1996 (Fig. 3) and was attributed to intensive agriculture. Because the nitrate concentration exceeded 40 mg/L (Swiss drinking-water standard limit) in the pumping well in 1993, cantonal authorities solicited federal support in order to reduce nitrate concentration. The Nitrate Project (starting in 1997) consisted of converting agricultural parcels in the catchment area of the pumping wells from intensive agricultural practices to

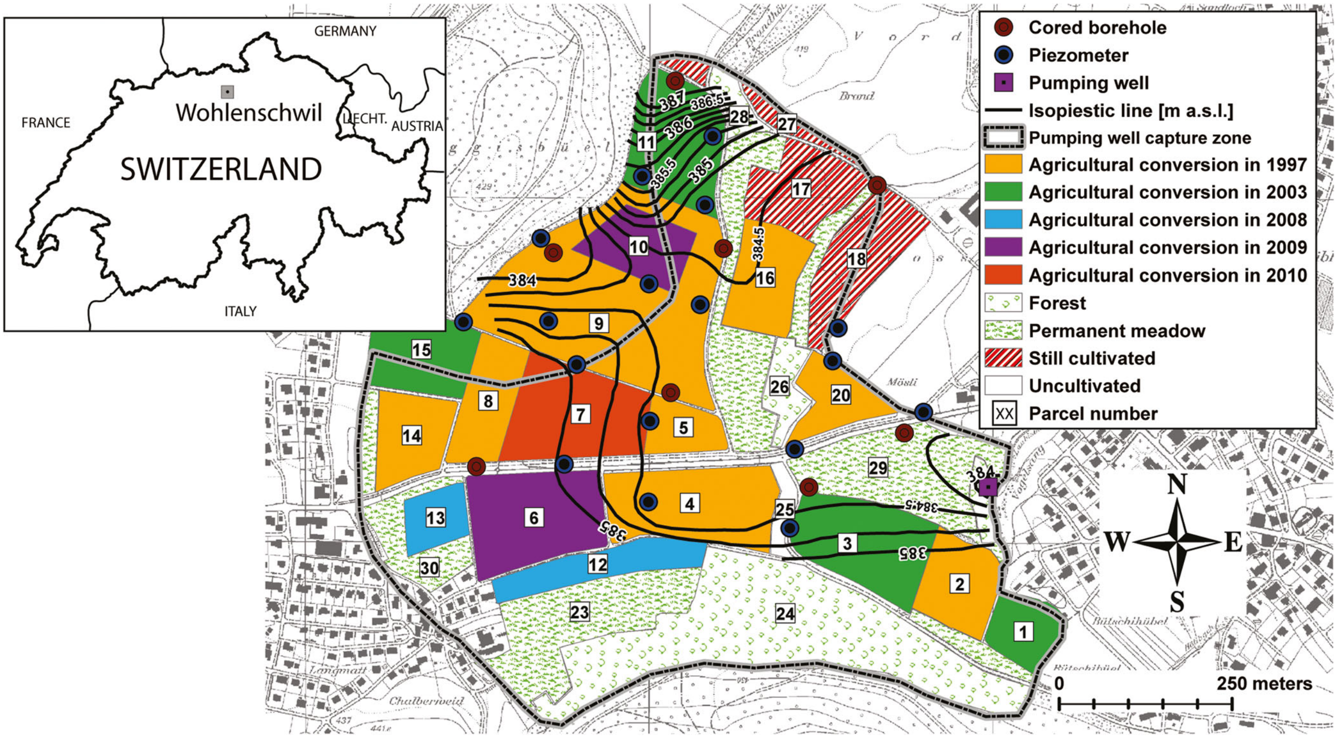

Fig. 2 Location of the Wohlenschwil aquifer in Switzerland; hydrogeological characteristics (capture zone and piezometric head [m a.s.l.] in December 2010); chronology of land-use conversions from 1997 to 2010 in *numbered parcels*

permanent meadow, leading to less fertilization and tillage within the catchment area. Conversion was carried out from 1997 to 2010 via the different steps illustrated as the solid-colored parcels in Fig. 2.

The Wohlenschwil Nitrate Project led to a rapid decrease of nitrate concentrations (Fig. 3). The initial land conversion campaign, introduced in 1997, was followed by a response spread out over a period of 6 years. However, before the observed decrease of the period 2009–2010, the second conversion campaign of 2003 was followed by an increase of nitrate concentration from 2004 to 2008, which was in contradiction with the objectives of the Nitrate Project.

Two typical questions arise in relation to the Wohlenschwil aquifer management. For a optimal management of the Nitrate Project, it is important to know to what extent the various steps of the land use change have led to the observed evolution of the nitrate concentrations, and what changes can be expected in the future, considering the planned remediation program (constant land use since 2010).

Methods

The parameters of the problem can be schematized by Fig. 4. The capture zone of the pumping well is divided

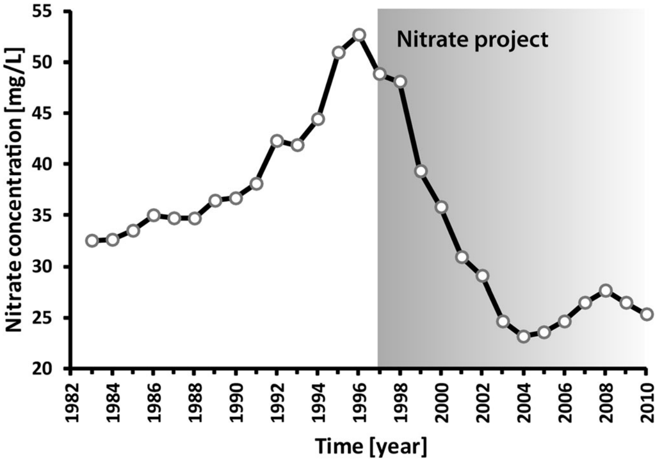

Fig. 3 Evolution of nitrate concentration (annual mean value in mg/L, 1982–2010) at the pumping well of the Wohlenschwil aquifer

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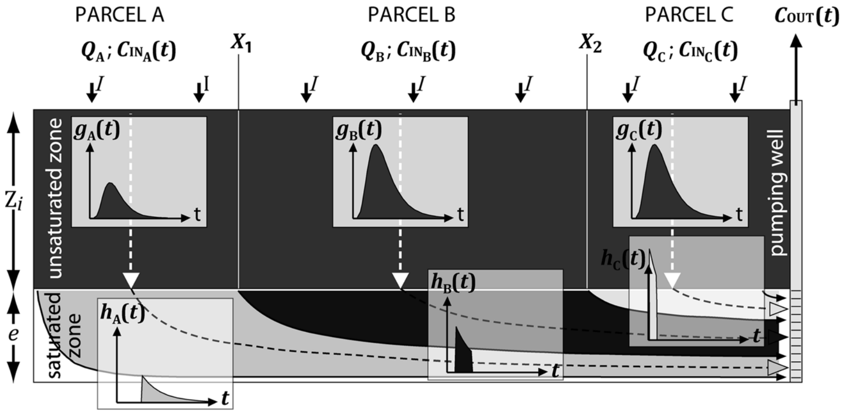

Fig. 4 Conceptual illustration of the various flow paths and of the transfer functions associated with the various transfer compartments of the aquifer system beneath the subareas *A*, *B* and *C* of the input zone

into several subareas, corresponding to the various input zones within which solute input history $C_{\mathrm{IN}}(t)$ can be considered as spatially homogeneous (parcels A, B and C). For the purpose of simplification, the general term "parcel" refers to the delimited subareas of the capture zone. Each parcel is characterized by size (i.e., the distance X_1–X_2), by a recharge rate I and by a contribution Q_i to the pumped flow. The transfer of nitrate from each parcel is described through the unsaturated zone by a transfer function $g(\tau)$ and through the saturated zone by a transfer function $h(T)$, which are dependent on the aquifer geometry (lengths Z, L, X_1, X_2 and e already described in Fig. 1), property (porosity θ) and flow conditions (recharge rate I).

The key to the resolution of the problem with a transfer function approach is based on the prior characterization of the parameters of Eq. (4) for each parcel defined within the capture zone of the pumping well. The methods used to obtain these parameters for the specific case of the Wohlenschwil aquifer are described in the following subsections.

Quantification of the input functions

For each parcel of the capture zone, the evolution of the annual average nitrate concentration $C_{\mathrm{IN_{NO_3}}}(t)$ [mg/L] in recharge water was calculated by Eq. (12):

$$C_{\mathrm{IN_{NO_3}}}(t) = \frac{M_{\mathrm{IN_{NO_3}}}(t)}{I(t)} \cdot 100 \qquad (12)$$

where $M_{\mathrm{IN_{NO_3}}}(t)$ is the annual amount of leached nitrate in [kg/ha], and $I(t)$ is the yearly groundwater recharge in [mm/year].

The standard rate of nitrate leaching for each crop type (Table 1) was already reported in an unpublished work of the Wohlenschwil Nitrate Project (Ziltener C, unpublished report, 2008; "Verlängerung des Nitratprojekts Wohlenschwil: Planung und Antrag für die zweite Projektphase 2009–2014 zur Verminderung des Nitratbelastung des Grundwasservorkommens im Gebiet "Münzel" und der Grundwasserfassung "Frohberg" aus der landwirtschaftlichen Bewirtschaftung" [Extension of the Wohlenschwil Nitrate Project: planning and proposal for the second step 2009–2014 to reduce the nitrate contamination of groundwater in the "Münzel" area and "Frohberg" pumping well]) where the calculation was performed using the regional scale nutrient-flow simulation model MODIFFUS (MOdel for the estimation of DIFFUSe nutrient losses; Prasuhn and Sieber 2005). Historical land use and crop rotation, in particular, had been documented for most of the parcels since 1997 (Table S1 of the ESM). For the period before 1997, it was assumed that most of the agricultural parcels were used for intensive agriculture. Based on these data, the annual amount of leached nitrate $M_{\mathrm{IN_{NO_3}}}(t)$ [kg/ha] was quantified for each parcel of the aquifer catchment and for each year since 1990 (Table S2 of the ESM).

The yearly groundwater recharge $I(t)$ [mm/year] was calculated from 1990 to 2010 taking the following into account: (1) the climatic data of the Buchs weather station, located 12 km from the aquifer; (2) evapotranspiration estimated by the Penman-Monteith equation (Allen et al. 1998); and (3) the 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). Results of groundwater recharge are given in Table S3 of the ESM).

According to Eq. (12), the input concentrations $C_{\mathrm{IN_{NO_3}}}(t)$ are only related to the variations of recharge rate $I(t)$, simply by a dilution effect. Changes in nitrate loss for a given crop due to varying climate conditions are not considered, assuming that these variations are considered small compared to those brought about by land-use changes.

Characterizations of the nitrate transfer functions by analytical models

To solve Eq. (4), it is necessary to determine the transfer functions of the nitrate 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, as

Table 1 Nitrogen leaching rate estimated by the MODIFFUS model for the various types of crops cultivated in the recharge zone of the Wohlenschwil aquifer

Type of culture	Initials	Nitrogen leaching rate [kg N/ha/year]
Potatoes	P	150
Winter barley	WB	90
Cereals	C	90
Maize	M	60
Sunflower	SF	60
Winter wheat with intermediate crop	WW	60
Grain maize	GM	50
Sugar beet	SB	40
Artificial meadow	AM	35
Winter rapeseed oil	WR	20
Permanent meadow	PM	10
Forest	F	10
Unknown cultivation	UC	69[a]

[a] When the type of culture was unknown, the leaching average in known cultivated areas was applied

schematized in Fig. 4. Analytical methods are used to characterize these functions.

The transfer functions $g(\tau)$ of solute through the unsaturated zone were described by the dispersion model of Eq. (6). It is assumed that the solute transport is conservative, which is the case for nitrate under the non-denitrifying conditions of the Wohlenschwil aquifer. Without any data to estimate the spatial distribution of the dispersivity, a constant ratio of P_D is assumed to be a reasonable approximation to describe the dispersion of the solute in the unsaturated zone. Based on a synthesis of tracer studies provided by Gelhar et al. (1992), a value of $P_D = 0.1$ was assumed for the entire unsaturated domain.

For each of the types of soils identified by core drilling campaigns and coring augers (layers 1, 2 and 3), mean values of volumetric water content were determined using the dry gravity method, combined with bulk-density estimations. The layered structure of the subsurface and the isohypse map of the bedrock were interpreted using electrical tomographies combined with lithological observations. Data about the structure and volumetric water contents of the soil are provided in Table S4 of the ESM). For each parcel, the total travel time T_{US} [T] of Eq. (6) is the sum of the transit times of water through the identified subsurface layers.

The transfer functions $h(T)$ of solute through the saturated zone were described by the exponential model (Eq. (7)). Data necessary to resolve Eq. (7) are reported in Table S4 of the ESM and were calculated as follows. For each parcel of the capture zone, the flow line passing through its centroid was identified using the piezometric map (Fig. 2); in this flow line, the distance of the upper x_1 and lower x_2 boundaries of each parcel was quantified, as well as the length L of the flow line from the upstream no-flow boundary of the aquifer to the pumping well (see illustration, Fig. 4). The average thickness e of the aquifer was calculated by comparing the piezometric contour map with the isohypse map of the bedrock. The value of the effective porosity φ has been evaluated using the following method: at each of the four injection points of the fluorescent tracers, the difference between the calculated travel time using Eq. (11) and the observed average travel time of tracing tests is minimized, by adjusting ϕ.

Contribution of each parcel to the pumped flow

The recharge flow rate $I(t)$ [mm/year] was assumed homogeneous on the surface. The contribution of each parcel to the pumped flow Q_i [m^3/year] is simply weighted by the area A_i [m^2] of each parcel. Using this approach, the probability that water reaches the pumping well is independent of the location of the recharge within the capture zone. It is also assumed that Q_i does not vary over time.

By solving Eq. (4), the evolution of nitrate at the pumping well was calculated for the period 1997–2020 and compared to the observed values for the period 1997–2010 (Fig. 5). For the calculation after 2010, constant land use in the future and a constant annual recharge of 510.3 mm/year, corresponding to the average value of the recharges calculated from years 1990 to 2010, were assumed. The calculation was performed with an Excel spreadsheet, according to a methodology analogous to the one described by Olsthoorn (2008).

Evolution of nitrate concentrations

In Fig. 5, the trends and levels of the calculated nitrate concentrations relatively well match the observed concentrations from 1997–2010. However, there are some discrepancies, especially where the calculation significantly underestimates the observed nitrate concentrations from 1998 to 2001. The maximum difference reaches 4.34 mg/L in 1998. The average absolute error is 2.23 mg/L, which represents 7.2 % of the average observed nitrate concentrations. Since the observed fluctuations of the nitrate concentrations are relatively large compared to the differences between calculations and observations and because the general levels of nitrate fit globally well, the errors are considered acceptable.

Finally, based on the scenario that the land use of 2010 does not change in the future (which is realistic because the nitrate project is maintained for several years after 2010), the nitrate concentration should decrease continuously by 2020, with a mean decrease of 1.1 mg/L/year as of 2010. Nitrate concentrations could reach a value of 13.7 mg/L in 2020.

In order to give a more robust validation the reader is referred to additional investigations that can be found in the PhD thesis of Baillieux (2012), from which most results described in this article are originated. This study compared the calculated nitrate concentrations at the pumping well using both analytical-model-and numerical-model transfer functions. The results were quite similar. Observed small differences were explained by the spatial distribution of capture probability, which is spatially variable in the numerical method but spatially homogeneous in the analytical method. This comparison

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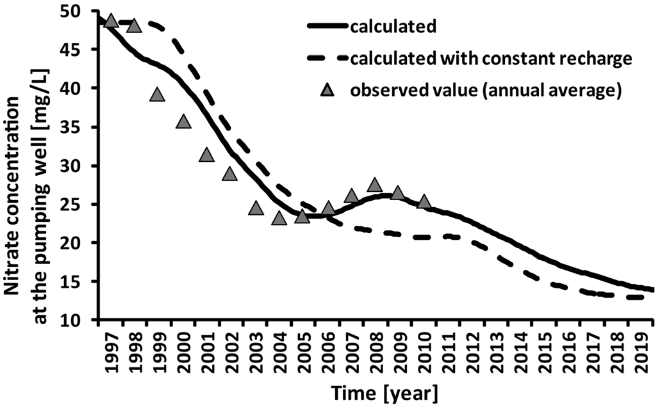

Fig. 5 Observed evolution of nitrate concentration (*triangles*) at the pumping well from 1997 to 2010, and calculated values (*lines*) from 1997 to 2020. The *dashed line* represents the results when the variations in recharge are neglected

confirms the reliability of transfer function approach when analytical-model transfer functions are used.

Effect of temporal recharge variations

Figure 5 shows a comparison of the calculated nitrate concentrations using, on the one hand, a variable recharge rate over the years (variable recharge resolution: black lines) and, on the other hand, a constant recharge rate over the years (constant recharge resolution: gray line). In the latter case, the history of nitrate concentration input is calculated with a constant recharge rate of $I = 510.3$ mm/year, corresponding to the average recharge rate of the last 21 years (1990–2010). The calculated nitrate concentrations better match the observed values when the calculation takes a temporally variable recharge into account. This observation highlights the importance of taking the annual fluctuations of recharge rate into account to correctly estimate the history of input concentrations in the recharge area.

During the period from 2006 to 2009, the variation of the recharge rate led to a significant increase of the nitrate concentrations at the pumping well. The difference between both results reached 5 mg/L in 2008. The low recharge period from 2003 to 2005, associated with the dry years observed in Switzerland, could explain this increase in nitrate concentration. More generally, it is suggested that the dry period from 2003 to 2005 could explain the general tendency of the increase of nitrate concentrations observed during the middle of the last decade in the majority of aquifers in Switzerland, which has already been the subject of discussion by the Swiss Federal Office for the Environment (OFEV 2009).

Sensitivity analyses

A sensitivity analysis was carried out to evaluate in which frame the uncertainty on the value of the input parameters can explain the difference between observations and calculations, as observed in Fig. 5. The impact of the

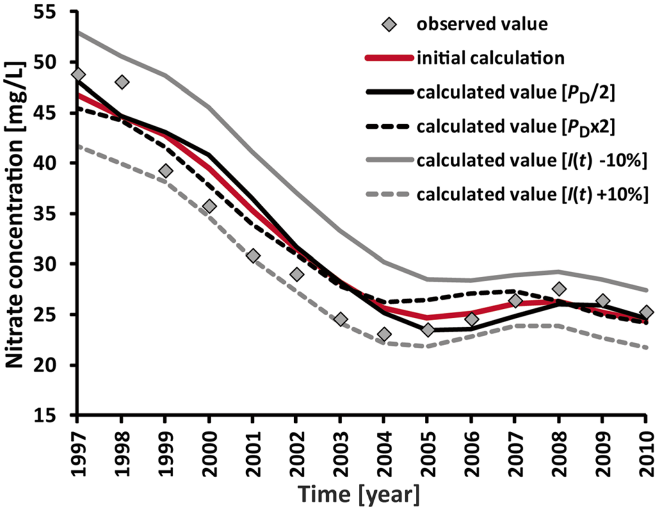

Fig. 6 Results of a sensitivity analysis of the parameter recharge rate $I(t)$ and dispersion parameter P_D on the calculated nitrate concentrations from 1997 to 2010. The *red line* shows the initial calculation with initial values of P_D and $I(t)$. *Continuous* and *dashed black lines* represent results with P_D divided and multiplied by 2, respectively. *Continuous* and *dashed gray lines* represent results with $I(t)$ reduced and increased by 10 %, respectively

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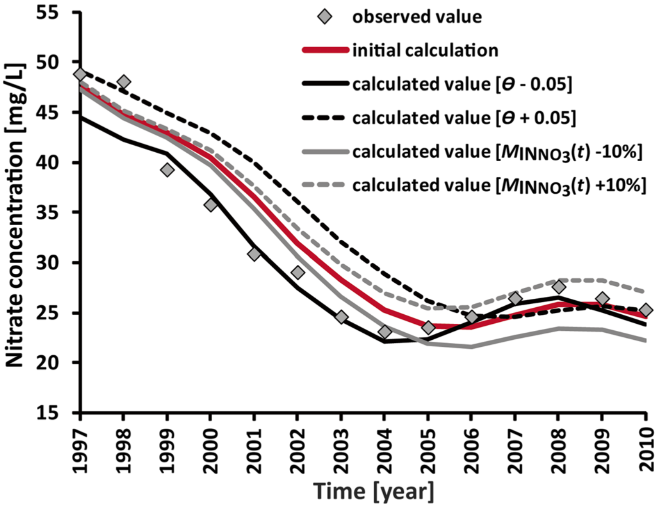

Fig. 7 Results of a sensitivity analysis of the parameters, volumetric water content θ and nitrate leaching rate $M_{\mathrm{IN_{NO_3}}}(t)$, on the calculated nitrate concentrations from 1997 to 2010. The *red line* represents the initial calculation. The *continuous* and *dashed black lines* represent results with a volumetric water content θ reduced and increased by 0.05, respectively. *Continuous* and *dashed gray lines* represent results with a nitrate leaching rate $M_{\mathrm{IN_{NO_3}}}(t)$ reduced and increased by 10 %, respectively

variations of the input parameters of Eq. (6), (12), (4) and (7) are tested and include: the recharge rate $I(t)$, the nitrate leaching rate $M_{\mathrm{IN_{NO_3}}}(t)$, the volumetric water content θ in the unsaturated zone, the dispersion parameter P_D and the effective porosity φ in the saturated zone. Figures 6 and 7 show the calculated nitrate concentrations from 1997 to 2010, when these parameters vary within the range of their realistic values, which are reported in Table 2. Results about the sensitivity of the effective porosity were not reported in the figures because changes were not visually significant.

Figure 6 shows that variations in the recharge rate $I(t)$ can strongly influence the concentrations calculated. The difference with the initial calculation reached 6.2 mg/L in 1997 when the recharge rate was 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 was multiplied by 2. Figure 7 shows that a variation of ±10 % of the nitrate leaching rate led to a variation of ±10 % on the output nitrate concentrations, which is explained by the direct mathematical link between output and input concentrations of Eq. (4) (linear relationship). The variation of the volumetric water content in the unsaturated zone has two consequences on the output nitrate concentration. First, the evolution of the 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 maximum difference with the initial calculation was 5.2 mg/L in 2001 when the volumetric water content was reduced by 0.05.

Table 2 provided the average deviation in terms of nitrate concentrations when the values of the input parameters vary within the range of their uncertainties. An average deviation of 12 % 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 4 % for the dispersion parameter. The recharge rate is the most sensitive parameter, influencing nitrate concentrations in the recharge as well as travel times in the unsaturated and saturated zones. The nitrate leaching rate and the volumetric water content in the unsaturated zone also have a considerable influence. The uncertainty associated with the dispersion parameter seems to have less influence on the accuracy of the calculated concentration. Finally the less sensitive parameter is the effective porosity within the saturated zone. The variation of the effective porosity

Table 2 Range of uncertainty of each parameter of the transfer function approach and mean relative difference of nitrate concentrations in comparison with the initial calculation of nitrate concentrations

Parameter	Range of uncertainty	Average relative difference compared to the initial calculated values of nitrate concentrations from 1997 to 2010
Recharge rate $I(t)$	±10 %	12 %
Nitrate leaching rate $\boldsymbol{M_{\mathrm{IN_{NO_3}}}(t)}$	±10 %	10 %
Volumetric water content θ	+/−0.05	8 %
Dispersion parameter P_D	Between 0.05 and 0.2	4 %
Effective porosity φ	Between 0.1 and 0.2	1 %

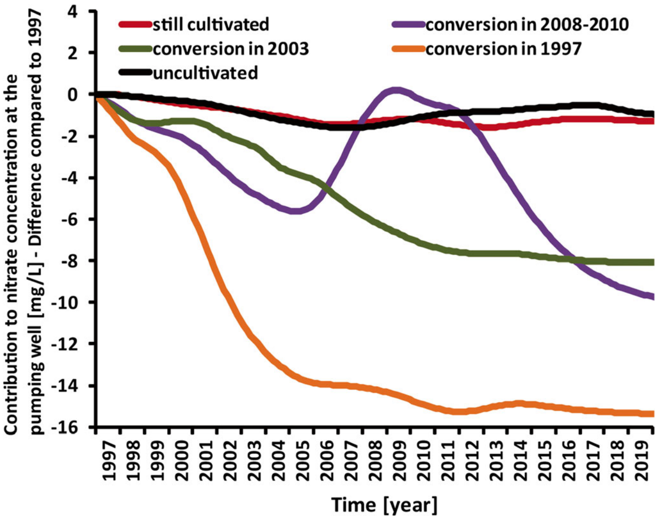

Fig. 8 Difference between the contribution of each group of parcels to the nitrate concentration at the pumping well and their contribution in the reference year 1997

in the saturated zone between 0.1 and 0.2 leads to a variation of 1 % of the calculated nitrate values. This result must be strongly mitigated because, in the case study, the average travel time in the saturated zone (0.6 years) represents only 8 % of the average total travel time in the aquifer (7.3 years; see Table S4 of the ESM). Thus, the sensitivity of calculated concentrations to a parameter affecting only the travel time within the saturated zone is relatively low in comparison with other parameters.

Contribution of each conversion step to the nitrate concentration

The contribution of each parcel to the nitrate concentration in the pumping well was calculated using the following steps: the parcels consistent with the same conversion step are grouped together, which corresponds to the agricultural conversions of 1997, of 2003 and of 2008–2010 (Fig. 2); inside each group, Eq. (4) is resolved for each parcel (considering a time variable recharge), and the outputs $C_{\mathrm{OUT}i}(t)$ are summed in order to quantify the effect of the targeted conversion group on the nitrate.

Figure 8 shows how each conversion group influences changes in the nitrate concentration at the pumping well during the development of the Nitrate Project, taking 1997 as the reference year. 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 leads to a decrease of 7.2 mg/L of nitrate concentration as of 2015. The last conversions of the period 2008–2010 would make it possible to gain 11.3 mg/L for the next decade (period 2011–2020), compared to 1997.

Conclusion

This article introduces new developments for the application of a transfer function approach to the study of the evolution of groundwater quality at aquifer outlets, taking land-use history in the capture zone into consideration. The approach was successfully tested in the case study of the Wohlenschwil aquifer.

The extension of the convolution integral, to multiple input zones with specific land-use history and multiple transfer compartments (e.g. unsaturated and saturated zone), increases the applicability domain of the transfer function approach. Transfer functions can be derived from analytical equations or numerical models. However, in order to make the approach achievable for most practitioners and remediation programs in a relatively easy and cost-effective way, several developments of the exponential model of the transfer function are proposed in this article (Eqs. 7 and 25 of the Appendix), for the purpose of considering partial input zones or partial outlet configurations. Equations (7) and (11) have already been described in the literature as the partial exponential model (PEM; Jurgens et al. 2012), which supports the results presented here.

The results obtained in the Wohlenschwil aquifer are encouraging and lend credibility to transfer function approaches for quantifying the evolution of groundwater quality in pumping wells. The application to other sites, to types of outlets other than a pumping well and to contaminants other than nitrate is conceivable. A minimum of information 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 subarea of the recharge zone to the flow at the outlet; and (4) the transfer functions of the considered pollutant in the distinct transfer compartments of the aquifer, whose required detailed characterization depends on the methodology used (analytical or numerical procedures). In the Wohlenschwil aquifer, the analytical-based transfer functions were characterized without strong investigations, mainly using the quite basic hydrogeological settings. While the approach allowed us to quantify the evolution of nitrate contents at the pumping well, this was also a useful tool to identify the driving parameters of the nitrate transfer in the studied aquifer, which are the recharge rate and volumetric water content in the unsaturated zone. For other study sites, other parameters might be increasingly important such as the effective porosity of the saturated zone in more saturated aquifer.

The main limit of the approach is that it relies on the strong assumption of steady-state flow conditions. It is assumed that the different elements of Eq. (4) (except the input concentration functions) are independent of the observation time and are calculated using a mean recharge rate *I*. Moreover, it is assumed that the capture zone extension is not influenced by the annual variations of the recharge rate. According to previous studies (Badoux 2007; Osenbrück et al. 2006; Reilly and Pollock 1996; Zuber et al. 1986, 2011), these assumptions can be valid when the range of travel times of solute within the aquifer is greater than the characteristic fluctuation period. Thus, in the context of the variations of flow conditions of low frequency or flow conditions that are not constant over time (for example, a trend due to climate changes), simulations in transient mode using numerical models are certainly more appropriate approaches to predict the evolution of a solute at an aquifer outlet than the transfer function approach. Thus, one improvement that should be addressed is the adaptation of the approach to highly hydrodynamic environments, notably to karstic systems. This requires the use of time-varying transfer functions, which have been introduced in previous studies (Niemi 1977, 1990; Nir 1973; Ozyurt and Bayari 2005) but show restricted conditions for application in aquifers.

The new developments for the application of transfer function approaches are demonstrated here with a specific chemical compound, nitrate, whose transport can be assumed to be nonreactive and conservative under certain conditions. The applicability of the method to substances that are subject to degradation and absorption in aquifers should be analyzed in another case study. Furthermore, to determine the saturated zone parameters using artificial tracer tests is fairly specific to the site. Most of the time there are no tracer tests across the capture zone available or achievable. When no artificial tracer data are available, one approach is to use groundwater dating to calibrate the transfer functions in the saturated zone, using ^{3}H/^{3}He dating method for instance, which only reflects the travel time in the saturated zone, and to ensure that all the transfer functions together reproduce the measured data. An alternative approach is to use a numerical groundwater model for the saturated zone only. This way, it is possible to extract ages directly from flow models, which is much simpler than setting up a full flow-transport model for the vadose and saturated zone. Coupling the transfer function approach to simulate the transfers in the unsaturated zone with numerical simulations and/or environmental tracers in the saturated zone should be tested for more complex or larger-scale aquifer cases.

Before even considering these further developments, the transfer function approach is a relevant method that can now be put into practice to resolve groundwater pollution problems. Due to its relative ease of implementation and its capacity to be adapted to various aquifer environments, it could be more frequently associated with environmental projects focused on nitrate contamination, particularly when the level of strategic importance does not require or allow the use of more sophisticated numerical simulations of solute transport in the aquifer. The approach could be particularly useful in local studies to meet the objectives of good qualitative status of groundwater bodies as set out in the European Water Framework Directive.

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Appendix: Mathematical development of the exponential model for the transfer function at localized input zone and outlet

A saturated aquifer system of length *L* is assumed with a uniform thickness *e*, a uniform porosity θ and a uniform surface infiltration rate *I* (illustration in Fig. 1). This conceptual case has already been introduced by Kazemi et al. (2006), and one part of the mathematical development is taken from this reference—Eqs. (13), (14), (16), (17) and (20). According to the hypothesis of Dupuit, assuming horizontal velocity constant over depth, the Darcy flux over the distance corresponds to $q(x)=Ix/e$, and the real velocity over the distance x is $v(x)=Ix/e\varphi$. The travel time $t(x)$ required for a solute from a point x to reach the outlet at distance L is:

$$t(x) = \int_x^L \frac{\mathrm{d}x}{v(x)} = \frac{e\phi}{I}\int_x^L \frac{\mathrm{d}x}{x} = \frac{e\phi}{I}\ln\left(\frac{L}{x}\right) = T_0\ln\left(\frac{L}{x}\right) \quad (13)$$

with

$$T_0 = \frac{e\phi}{I} \quad (14)$$

The cumulated flow Q_{0z} at the outlet (located at distance *L*) from the surface ($z = 0$) to a certain depth z is equal to $Q_{0z}=zIL/e$. 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 from an input point located at distance x, Q_{0z} and Q_{xL} are equal and the following relationship can be written as: $z(x)IL/e=I(L-x)$. Equation (15) can be deduced by isolating $z(x)$ from the last relationship:

$$z(x) = e\left(1-\frac{x}{L}\right) \tag{15}$$

By combining Eqs. (13) and (15), it follows that:

$$t(z) = T_0 \ln\left(\frac{1}{1-\frac{z}{e}}\right) \tag{16}$$

$$x(z) = \left(1-\frac{z}{e}\right)L \tag{17}$$

$$x(t) = L\exp\left(-\frac{t}{T_0}\right) \tag{18}$$

$$z(t) = e\left[1-\exp\left(-\frac{t}{T_0}\right)\right] \tag{19}$$

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

$$\varphi(t) = \frac{1}{Q_0}\frac{\mathrm{d}Q(t)}{\mathrm{d}t} \tag{20}$$

where Q_0 is the total discharge flow and $Q(t)$ is the portion of discharge flow that has a residence time in the system of less than or equal to t. If solute enters in the same conditions as flow, and if the solute travel has the same characteristics as flow transit, the transit time probability density function $\rho(t)$ 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:

$$g(t) = \frac{1}{Q_{0_{\mathrm{x_1x_2}}}} \cdot \frac{\mathrm{d}Q_{\mathrm{X_1X_2}}(t)}{\mathrm{d}t} \quad , t_2 \le t \le t_1 \tag{21}$$

$$g(t) = 0 \tag{22}$$

; otherwise, with

$$t_1 = T_0 \ln\left(\frac{L}{x_1}\right) \tag{23}$$

$$t_2 = T_0 \ln\left(\frac{L}{x_2}\right) \tag{24}$$

where $Q_{0_{\mathrm{x_1x_2}}}$ is the total discharge flow at the outlet for water from the subarea of the recharge zone delimited by x_1 and x_2, and $Q_{\mathrm{X_1X_2}}(t)$ is the part of the discharge flow that has a residence time in the system in the interval $[t_2; t]$.

Based on Eq. (18), $Q_{0_{\mathrm{x_1x_2}}}$ and $Q_{\mathrm{X_1X_2}}(t)$ are:

$$Q_{0_{\mathrm{x_1x_2}}} = I(x_2-x_1) = IL\left[\exp\left(-\frac{t_2}{T_0}\right)-\exp\left(-\frac{t_1}{T_0}\right)\right] \quad , t_2 \le t \le t_1 \tag{25}$$

$$Q_{\mathrm{X_1X_2}}(t) = I(x_2-x(t)) = IL\left[\exp\left(-\frac{t_2}{T_0}\right)-\exp\left(-\frac{t}{T_0}\right)\right] \quad , t_2 \le t \le t_1 \tag{26}$$

The transfer function $g_{\mathrm{t_1t_2}}(t)$ of solute reaching the outlet in the travel time interval $[t_2; t_1]$ can be derived from the discretization of Eq. (21), inserting Eqs. (25) and (26):

$$g_{\mathrm{t_1t_2}}(t) = \frac{\exp\left(-\frac{t}{T_0}\right)}{T_0\left[\exp\left(-\frac{t_2}{T_0}\right)-\exp\left(-\frac{t_1}{T_0}\right)\right]} \quad , t_2 \le t \le t_1 \tag{27}$$

$$g_{\mathrm{t_1t_2}}(t) = 0 \quad \text{, otherwise} \tag{28}$$

Inserting Eq. (16) in Eq. (27), the transfer function $g_{\mathrm{z_1z_2}}(t)$ of solute reaching the outlet at the depth interval $[z_2; z_1]$ is:

$$g_{\mathrm{z_1z_2}}(t) = \frac{\exp\left(-\frac{t}{T_0}\right)}{T_0\left(\frac{z_1}{e}-\frac{z_2}{e}\right)} \quad , \mathrm{t_2 \le t \le t_1} \tag{29}$$

$$g_{\mathrm{z_1z_2}}(t) = 0 \tag{30}$$

; otherwise, 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 Eq. (13) in Eq. (27), the transfer function $g_{\mathrm{x}_1\mathrm{x}_2}(t)$ of solute from the subarea of the recharge zone delimited by the distance interval [x_2; x_1] is:

$$g_{\mathrm{x}_1\mathrm{x}_2}(t) = \frac{L\exp\left(-\frac{t}{T_0}\right)}{T_0(x_2-x_1)} \quad , t_2 \leq t \leq t_1 \tag{31}$$

$$g_{\mathrm{x}_1\mathrm{x}_2}(t) = 0 \tag{32}$$

; otherwise, with

$$t_1 = T_0\ln\left(\frac{L}{x_1}\right) \tag{33}$$

$$t_2 = T_0\ln\left(\frac{L}{x_2}\right) \tag{34}$$

Applying the mean value theorem, the average time of travel $\overline{t(z)}_{\mathrm{z}_1\mathrm{z}_2}$ over the depth interval [z_1;z_2] is the mean value of the function $t(z)$ (Eq. 16) in the interval [z_1;z_2], which corresponds to:

$$\overline{t(z)}_{\mathrm{z}_1\mathrm{z}_2} = \frac{1}{z_1-z_2}\int_{z_2}^{z_1} t(z)\mathrm{d}z = \frac{1}{z_1-z_2}\int_{z_2}^{z_1} T_0\ln\left(\frac{1}{1-\frac{z}{e}}\right)\mathrm{d}z \tag{35}$$

$$\overline{t(z)}_{\mathrm{z}_1\mathrm{z}_2} = \frac{e}{z_1-z_2}T_0\left[\left(1-\frac{z_1}{e}\right)\ln\left(1-\frac{z_1}{e}\right)-\left(1-\frac{z_2}{e}\right)\ln\left(1-\frac{z_2}{e}\right)+\frac{z_1-z_2}{e}\right] \tag{36}$$

Similarly, the average travel time $\overline{t(x)}_{\mathrm{x}_1\mathrm{x}_2}$ for solute from an input zone defined in the interval [x_1;x_2] is:

$$\overline{t(x)}_{\mathrm{x}_1\mathrm{x}_2} = \frac{1}{x_2-x_1}\int_{x_1}^{x_2} t(x)\mathrm{d}x = \frac{1}{x_2-x_1}\int_{x_1}^{x_2} T_0\ln\left(\frac{L}{x}\right)\mathrm{d}x \tag{37}$$

$$\overline{t(x)}_{\mathrm{x}_1\mathrm{x}_2} = \frac{T_0}{x_2-x_1}\left[x_2\left(\ln\left(\frac{L}{x_2}\right)+1\right)-x_1\left(\ln\left(\frac{L}{x_1}\right)+1\right)\right] \tag{38}$$

$$\overline{t(x)}_{\mathrm{x}_1\mathrm{x}_2} = T_0\left[1+\ln(L)+\frac{x_1\ln(x_1)-x_2\ln(x_2)}{x_2-x_1}\right] \tag{39}$$

From a practical point of view, Eq. (39) 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. The mean travel time provides a first approximation of the order of magnitude of reaction time of the aquifer system (Fenton et al. 2011; Sousa et al. 2013).

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