Validation of Travel- and Exposure-Time Based Nonlinear Reactive Transport Models

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Abstract

Groundwater resources are very important to guarantee sufficient fresh water supply worldwide. To ensure its quality, which is often endangered by natural and anthropogenic hazards, existing risks and possible protection measures need to be adequately evaluated. Mathematical models describing the transport of reactive solutes in groundwater are the key tool for this evaluation. The models help to understand the complex system of coupled physical and biogeochemical processes in the subsurface at different time and spatial scales. The parameterization and operation of such models may raise difficulties as subsurface properties are typically uncertain and computational costs for three-dimensional simulations might be immense. The travel-time based models simplify the description of reactive transport by replacing the spatial coordinates with the groundwater travel time, posing a quasi-one-dimensional (1-D) problem and potentially rendering the determination of multidimensional parameter fields unnecessary. This alternative approach is based on the assumption that the location of stationary reactive fronts i.e. concentration profiles correspond to certain groundwater isochrones which can be truth for ideal conditions that avoid solute and groundwater mixing processes: stationary flow, constant and uniform penetration of the groundwater and dissolved reactant across the entire inlet boundary, and uniform spatial distribution of the biogeochemical parameters within the domain. Travel time is defined as the time that a particle spent to achieve an observation point from the inlet boundary and it is numerically measurable through the seepage velocity field and conservative transport simulation. The stochastic behaviour of the flow field and the diffusive-dispersive transport mechanisms confer random properties to the travel time, which are expressed by local travel time probability density functions, $pdf(\tau)$, at each location. The corresponding mean travel time are commonly used as the independent variable in travel-time based models. The main hypothesis of this thesis is that the chemical-compound concentrations as function of time and travel time at each location can be a good approximation to the spatially-explicit concentrations, even when non-ideal conditions may affect the reactive behaviour. To test the validity of this hypothesis, several representative test cases are considered in this work. These test cases are inspired by real-world observations of surface water-groundwater interactions in the hyporheic zone, where dissolved organic carbon, oxygen and nitrate infiltrate into the groundwater and trigger aerobic and anaerobic degradation of organic matter by aerobic and denitrifying bacteria. In a first study, six scenarios are analysed which are differing in the variance of log-hydraulic aquifer conductivity and in the inflow boundary conditions. The results show that the conceptualization of nonlinear bioreactive transport in complex multidimensional domains by quasi 1-D travel-time models is valid for steady-state flow fields if the reactants are introduced over a wide cross-section, and dispersive mixing is adequately parameterized. Results from a second series of test cases focussing on transient time-periodic flow show that a modified version of travel-time based reactive transport models is valid if only the magnitude of the velocity fluctuates, whereas its spatial orientation remains constant. Finally, in a third study, the model is used to simulate reactive transport in geochemical and geophysical heterogeneous porous media, which request the use of the exposure time, equivalent to the time of reaction between two or more reactants, instead of travel time. The results show that the exposure-time models are able to provide good approximation of nonlinear reactive transport problems when transverse mixing is not the controlling process of the reactive system.

Kurzfassung

Grundwasser ist eine bedeutende Frischwasser-Ressource weltweit. Um seine Qualität, die durch natürliche und anthropogene Gefahren vielerorts gefährdet ist, sicherzustellen, müssen die bestehenden Risiken und mögliche Schutzmaßnahmen angemessen bewertet werden. Ein wichtiges Instrument für diese Bewertung sind mathematische Modelle, mit welchen der Transport von reaktiven gelösten Stoffen im Grundwasser beschrieben werden kann. Die Modelle helfen, das komplexe System von gekoppelten physikalischen und biogeochemischen Prozessen im Untergrund in unterschiedlichen zeitlichen und räumlichen Skalen zu verstehen. Die Parametrisierung und Anwendung solcher Modelle ist mitunter schwierig, weil die Untergrundeigenschaften nicht vollständig bekannt sind und Rechenzeiten für dreidimensionale Simulationen immens sein können. Verweilzeit-basierte Modelle vereinfachen die Beschreibung des reaktiven Stofftransports, indem die Raumkoordinaten durch die Verweilzeit des Grundwassers ersetzt werden. Dadurch ergibt sich ein quasi-eindimensionales (1-D) Problem, das fallweise auch ohne die Bestimmung multidimensionaler Parameterfelder gelöst werden kann. Dieser alternative Ansatz beruht auf der Annahme, dass sich stationäre Reaktionsfronten, d.h. Konzentrationsprofile entlang bestimmter Isochronen der Grundwasserfließzeit ausbilden. Dies gilt unter idealisierten Bedingungen, d.h. wenn Mischungsprozesse des Grundwassers und darin gelöster Stoffe vernachlässigbar sind, die Grundwasserströmung stationär ist, der Stoffeintrag konstant und uniform ist, und die biogeochemischen Parameter innerhalb des Modellraums räumlich konstant sind. Die Verweilzeit ist definiert als die Zeit, die ein Wasserpartikel benötigt, um von seinem Eintragspunkt am Modellrand den jeweiligen Beobachtungspunkt im Modellraum zu erreichen. Sie kann mit Hilfe des Geschwindigkeitsfelds und einer konservativen Transportsimulation numerisch leicht bestimmt werden. Aufgrund des stochastischen Verhaltens des Strömungsfeldes und diffusiv-dispersiver Transportprozesse ist die Verweilzeit als Zufallsvariable aufzufassen, die durch lokale Wahrscheinlichkeitsdichtefunktionen der Verweilzeit, pdf(τ) beschrieben werden kann. Die aus diesen Funktionen abgeleitete mittlere Verweilzeit wird in den Verweilzeit-basierten Modellen allgemein als unabhängige Variable verwendet. Die Haupthypothese dieser Arbeit ist, dass die als Funktion von Zeit und Verweilzeit bestimmte Konzentration chemischer Verbindungen an jedem Punkt des Modellraums eine gute Näherung für die explizit räumliche Konzentration ist - auch dann, wenn nicht-ideale Bedingungen herrschen und das reaktive Verhalten der Verbindungen beeinflussen. Um die Gültigkeit dieser Hypothese zu testen, werden verschiedene repräsentative Fallbeispiele betrachtet. Diese Fallbeispiele basieren auf realen Beobachtungen von Oberflächenwasser-Grundwasser-Interaktionen in der sogenannten hyporheischen Zone, wo gelöster organischer Kohlenstoff, Sauerstoff und Nitrat in das Grundwasser infiltrieren und den aeroben und anaeroben Abbau organischer Substanzen durch aerobe und denitrifizierende Bakterien anregen. In einer ersten Studie werden in sechs Szenarien unterschiedliche Annahmen bezgl. der Varianz der hydraulischen und der Randbedingungen analysiert. Die Ergebnisse zeigen, dass die Konzeptualisierung des nichtlinearen bioreaktiven Transports in komplexen multidimensionalen Modellräumen durch quasi 1-D Verweilzeitmodelle gültig ist bei stationärer Strömung, wenn die reaktiven Verbindungen über einen breiten Querschnitt eingeführt werden, und dispersive Mischungsprozesse angemessen parametrisiert werden. Die Ergebnisse eines zweiten Fallbeispiels für periodisch wechselnde Strömungsverhältnisse zeigen, dass der reaktive Stofftransport mit einem modifizierten Verweilzeit-basierten Modell korrekt beschrieben werden kann, wenn nur die Höhe jedoch nicht die Richtung der Grundwasserströmungs

geschwindigkeit schwankt. In einer dritten Studie wurde zur Simulation des reaktiven Stofftransports in geochemisch und geophysikalisch heterogenen porösen Medien ein Expositionszeit-basiertes Modell eingesetzt. Die Expositionszeit berücksichtigt die für die Reaktion zwischen zwei oder mehreren an der Reaktion beteiligten Stoffen zur Verfügung stehende Zeit und ersetzt die Verweilzeit. Die Ergebnisse dieser dritten Studie zeigen, dass es mit Expositionszeit-basierten Modellen möglich ist, nichtlineare reaktive Transportprobleme in guter Näherung zu beschreiben, solange die transversale Mischung nicht der steuernde Prozess des reaktiven Systems ist.

Contents

1. Introduction

1.1. Motivation

Groundwater resources are increasingly intended for water uses that require excellent quality standard. Such important resource is often endangered by natural and anthropogenic hazards. In natural conditions, groundwater may present high toxicity levels due to water-rock interactions in specific geological formations, microbial activity or mixing of water from different sources. Figures 1 and 2 show the problems due to presence of arsenic (Acharyya and Shah, 2007) and fluoride in groundwater (Wang et al., 1999) at regional dimensions. Although main anthropological contaminant activities are originated in the surface (e.g. wastewater discharge into surface waters, mining or landfills), groundwater is not exempt from being affected by pollutants, which could persists given the difficulty to apply efficient treatment methods. In some cases, soil layers act as shield or buffer of pollution alleviating or suppressing negative effects on the aquifers; in other cases, pollution achieves the water table, or it is induced by poor management of wells. These circumstances justify research efforts to increase the understanding of the natural processes in the subsurface systems; however, coupled physical and biogeochemical processes at different time and spatial scales may be involved, and on occasions those are difficult to identify.

Owing to the lack of complete knowledge of the actual chemical interactions and their consequences on the natural systems, an increasing number of investigations on reactive transport processes have been conducted during the last decades. In this regards, noteworthy is the quantification of interactions between environmental compartments tackling multi-scale coupled processes to be solved numerical simulation. Fleckenstein et. al. (2010) noted about the necessity of new reactive transport methods to solve upscaling heterogeneity problems and their influence on biogeochemical processes in alluvial ecosystems. This thesis is focused on the interactions between surface water and subsurface interface.

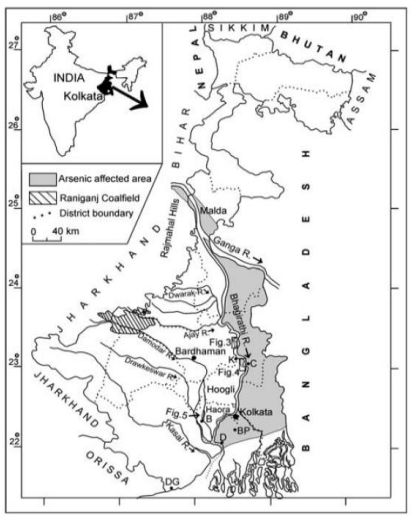

Figure 1. Map showing arsenic-affected area in West Bengal, India (Acharyya and Shah, 2007)

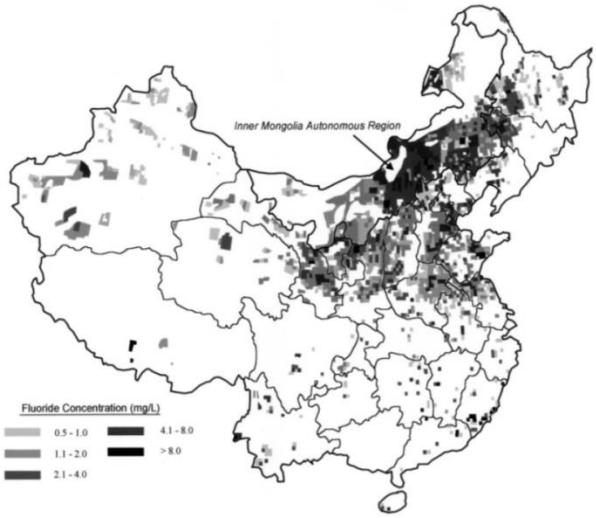

Figure 2. Distribution of fluoride concentration in the groundwater aquifers in China (Wang et al., 2002)

The reactive transport modelling is commonly based on the numerical solution of the governing flow equation and the advective-dispersive transport equation. Among the main challenges of reactive transport modelling are: to capture the scale dependence of the control processes, and the spatial variability of the key model parameters in heterogeneous media (Steefel et. al., 2005). In order to handle such limitations exist two main approaches: deterministic models, in which the reliability of the results depends on the detail of information available to represent spatial and temporal discretization of physical parameters; and stochastic models, in which the physical parameters, source/sink term, or boundary/initial conditions are defined as random variables or functions. In latter cases, the governing equations of flow and transport processes are defined as stochastic differential equations. Hence, the solution is also stochastic process expressed by probability distribution functions or statistics moments (Samper and Carrera, 1990). The stochastic modelling could be suitable in those cases where exhaustive or a priori characterization of the natural system is not possible, or when prompt evaluation of the system is requested.

In the category of stochastic models, several numerical approaches based on travel- and exposure-time as dependent and independent variables of the governing equations have been developed in the past decades (Dagan and Nguyen, 1989; Goode, 1996; Simmons et. al., 1982, 1995a, 1995b; Varni and Carrera, 1998; Ginn et. al., 1999, 2000, 2002; Cornaton et. al., 2006; Seeboonruang et. al., 2006). Such studies provide the basis for representing the spatial distribution of the groundwater age, and for solving conservative and reactive transport problems based on the travel or exposure time models.

1.2. Hypothesis, objectives and structure of this thesis

The fundamental hypothesis to be tested in this thesis is that, under certain conditions, the chemical-compound concentration traditionally estimated by the spatially-explicit advective-dispersive method can be approximated by concentrations expressed as function of the travel time and the simulation time. By posing a quasi 1-D problem, the computation effort and the explicitly-spatial definition of physical-biogeochemical parameters are considerable reduced. The main assumption behind this idea is that the concentration profiles of geochemical systems overlap with the groundwater isochrones, which are defined as lines of equal groundwater age mapped multi-dimensionally. It is truth when reactive systems are linear, or when nonlinear chemical reactions satisfy strictly advective transport mechanism, stationary flow systems, and spatially uniform bioreactive parameters. In contrast, when groundwater and reactive solute mixing processes controls the reactive transport mechanisms, the travel time is not able to capture the evolution of the reactive compounds, no matter those are mobile or immobile.

The current manuscript aims to address the validation of travel-time models to solve nonlinear bioreactive transport problems for those features and conditions that, albeit enhancing the groundwater and reactive solute mixing processes, do not preclude an accurate performance of the travel-time models. The thesis focuses on an aquatic ecosystem that represents surface-groundwater interaction as the hyporheic zone. There, flow and transport boundary conditions of the groundwater domain are sensitive to hydraulic and meteorological events, as well as contaminant discharge on the surface water. The bioreactive system under study represents the redox reactions that take place in a saturated sandy aquifer when dissolved organic matter (electron donor), and dissolved oxygen and nitrate (electron acceptor), are well-mixed and infiltrated from the surface water across the whole inlet boundary of the model domain triggering aerobic degradation of the organic

matter and denitrification. Both chemical reactions are catalysed by two non-competitive bacteria populations, aerobes and denitrifiers.

The following steps provide the insights into the performance of travel time models. Rather than comparing travel time simulation to a real case study or laboratory experiment, a 2-D spatially-explicit model considered as the "virtual truth" provides freedom to design the conceptual model according to the common features that enhance mixing processes into the saturated groundwater systems:

i. Map the travel time (equivalent to the mean groundwater age) in the 2-D domain.
ii. Simulate the 1-D nonlinear bioreactive transport problem.
iii. Map the 1-D concentration with respect to the mapped travel time.
iv. Simulate the 2-D spatially-explicit advective-dispersive model, as "virtual truth".
v. Estimate local residual errors at each position of the domain, along with the root mean standard errors for the whole domain.

The scope of this work covers three main drivers of mixing processes: the hydraulic heterogeneity, expressed by stochastic description of the hydraulic conductivity combined with constant and transient transport boundary conditions; transient flow systems; and coupled physical and geochemical heterogeneity. The content of this manuscript is structured in the following sections:

- Section 2 summarize and compiles the general conclusions detailed in the Appendixes and suggests the outlook of the author for further research topics that may give continuity to the travel-time based bioreactive model applications.

- Appendix A discusses the effects of physical heterogeneity coupled with transient transport boundary conditions on the travel time approach. For that purpose, a total of six case studies are defined by the combination of three degrees of physical heterogeneity, defined by the variance in the hydraulic conductivity field of value 1, 2 and 3; and the continuous and diurnal fluctuation of mobile reactants injected across the whole boundary.

- Appendix B analyses the performance of travel-time models when the flow system undergoes time-periodical fluctuations. In transient flow systems, the mixing processes may break down the application of travel time models. Here, the time-averaged mean travel time, when the inflow rate suffers diurnal and seasonal fluctuations, can be a good estimator of the transient bioreactive system. It is assumed that the flowpaths of the 2-D domain remains constant, whilst the magnitude of the mean seepage velocity fluctuates.

- In Appendix C the concept of geochemical heterogeneity coupled with physical heterogeneity is analysed. To handle the geochemical heterogeneity, travel time is substituted by exposure time, which is defined here as the time that reactive compounds are in contact and able to react. A binary physical-geochemical heterogeneous medium defines reactive lenses of low hydraulic conductivity, and non-reactive matrix of high hydraulic conductivity.

2. Summary and outlook

2.1. Summary and general conclusions

The aim of this thesis is to improve the understanding of the conditions under which travel- and exposure-time bioreactive transport models could be considered as a good approximation to the traditional numerical methods based on spatially-explicit description of the physical-biogeochemical parameters and the resulting dependent variables. Hence, the chemical-compound concentrations commonly expressed as function of time and space in multi-dimensional domains could be simplified as function of time and travel time (exposure time), posing a quasi-one-dimensional simulation in stationary systems. Furthermore, the substantial save in computation resources enables stochastic analysis to assess effective values of key model parameters (e.g. by Monte Carlo simulations), which may manage the uncertainty in their spatial description. The travel-time approach could be exact when strictly advective transport is considered in steady-state flow and reactive properties are uniform in the porous media. Nonetheless, the effects of transverse mixing processes may compromise the application of the travel time models in nonlinear reactive systems. In this work the system of biochemical degradation reactions typically occurring in groundwater is nonlinear and controlled by Monod kinetic parameters. For this reactive system, the role of mixing effects, the error that might be introduced through travel-time based models, and options to account for these mixing effects are quantified and analysed. This is done for different model setting with respect to principal features and boundary conditions of groundwater flow and transport and solute and groundwater mixing processes: spatial variability of physical and geochemical parameters, key variables of the model, as well as transient boundary conditions in flow and transport processes.

The conceptual model of the test case characterizes usual interactions between the well-mixed subsurface water masses, containing dissolved organic carbon (DOC, as electron donor), dissolved oxygen and nitrate (DO, NO_3^-, as electron acceptors) in saturated sandy aquifers. Here, a two-dimensional domain represents the first five meters from the inlet boundary where river water infiltrates, as being prone to great biochemical activity. The (nonlinear) kinetically-controlled reactive system is commonly found beneath the riverbed when it is well connected with a shallow aquifer. Thus, the redox degradation of organic matter by aerobic and anaerobic non-competitive bacteria populations triggers microbial metabolism and redox zonation in the so-called hyporheic zone.

Hereafter, it is presented a brief summary of the work done and the most relevant findings exposed in detail in the corresponding research papers.

The first study (Appendix A) analyses in total six scenarios of the aforementioned test case: the variance of log-hydraulic conductivity defines three two-dimensional stochastic fields from mild to middle physical heterogeneity; for which continuous injection and diurnal fluctuations of the dissolved oxygen inflow concentration are considered. Each scenario is simulated by the following mathematical frameworks:

- Travel time accounting for strictly advective transport mechanism, in which the independent variable is named kinematic age, or advective arrival time and represent a unique value at each location (1-D model).
- Travel time accounting for advective-dispersive transport mechanisms, in which the independent variable is named travel time, or mean groundwater age, and represent the mean value of an inverse Gaussian distribution at each location. Two alternative definitions of dispersion coefficient are evaluated: (i) a constant value for each location; and (ii) an effective coefficient product of the parameterization of mixing processes based on a positive linear correlation with the travel time (2x 1-D model).
- A conservative spatially-explicit transport model provides the necessary information to produce the 2-D mapping of the travel time, later used for the 2-D mapping of the 1-D concentrations with respect to travel time (2-D model).
- An additional simulation of the traditional spatially-explicit reactive advective-dispersive equation is considered throughout this work as the virtual reference or “virtual truth”, which is compared with the approximated estimations of the travel-time models (2-D model).

In all the domains the mean travel time, hereinafter named travel time or mean groundwater age, is successfully estimated by the two first temporal moments derived from the local breakthrough curves generated in the conservative transport simulation (Harvey and Gorelick, 1995). The spatial distribution of the mean travel time ratifies its strong dependency with the flow field, by getting older in slow flowpaths and within low hydraulic conductivity lenses. While the injected water penetrates into the domain, the age difference between longitudinal neighbouring streamtubes becomes more evident. The location of the highest values of the variance of travel time observed in the model domain, estimated by the third-order temporal moment of the travel time local breakthrough curves, corresponds with physical features and hot spots where two water parcels with considerable different age signature mix. These transitory zones involve inaccuracies in the estimation of the groundwater age, and consequently denote possible errors in the concentrations of chemicals subjected to nonlinear reactions. Nevertheless, the small variability observed in the 2-D spatially-explicit concentrations expressed as function of travel time suggests an accurate estimation of the independent variable concerning to the test case. Regarding the 2-D mapping of the 1-D concentrations expressed as function of travel time, the mild heterogeneous medium shows excellent fitting between the travel-time concentrations and the “virtual truth”, whilst the scenarios with stronger heterogeneity provide moderate deviations between the simplified approach and the results obtained in the spatially-explicit model. Such deviations are more perceptible in the earlier transient periods of the simulation, rather than in the achievement of stationary state.

The consequence of neglecting dispersive coefficients in strictly advective travel time models is the increase of inaccuracies until the reactive system achieves the steady state; such that in long-term stable ecosystems, the kinematic age could capture nonlinearity trends of the reactive components. The results slightly improve when the 1-D model accounts for simple values of local and constant longitudinal dispersivity in the governing equation. An optimized version of the travel-time model considers the parameterization of the dispersive coefficient in the two-dimensional domain described by a linear relationship, such that the mixing coefficient increases with the mean groundwater age. The travel-time based predictions in terms of the magnitude and the patterns of the reactive compound concentrations are excellent, even before steady conditions are achieved. Nonetheless, the finding of the

effective dispersive coefficients is subject to perform feasible conservative tracer tests in real sites, or the setup conservative transport model able to handle with the adequate level of hydraulic parameter´s uncertainty.

The diurnal fluctuation of dissolved oxygen concentration in the inflow is designed as a sinusoidal curve reproducing similar dynamics in the net balance between photosynthesis and respiration processes observed in the surface water (the peak of DO concentration at midday, the valley at midnight, and the wavelength approximately third parts of the inflow concentration in the continuous injection scenario (Diem et. al., 2013). As expected, the diurnal perturbation is almost unnoticed by the microbial population with slow response capacity, due to their small effective growth and decay rates selected in the present test case. Nonetheless, there is an interest to test the potential errors on the estimated mobile reactant concentrations (DO). In comparison with the continuous injected scenario, temporal dynamics in inflow concentration resulted in slightly higher errors maintained over time.

Take away message: travel-time models can provide extremely good agreement with the "virtual truth" for an adequately parameterized dispersive coefficient when mobile reactants are introduced over a wide cross-section, flow is at quasi steady state, and uniform reactive properties; it is expected a good tendency when simple conceptualization of dispersive coefficient are considered (Sanz-Prat et. al, 2015).

The second study (Appendix B) addresses the dynamic hydrological conditions that commonly affect shallow aquifers well-connected with riverbeds. The natural fluctuations of the seepage velocity induce temporal alterations in the local values of the mean groundwater age, therefore also alters the corresponding estimated chemical concentrations. To assess such effects in the travel time model, the study addresses the definition and evaluation of a time-independent characteristic travel time as proxy of bioreactive transport in transient flow systems; in particular when the hydraulic field is affected by time-periodic fluctuations of the inflow boundary conditions and the following assumptions are met: (i) the groundwater storage is neglected in order to keep the magnitude of the seepage velocity uniquely affected by hydraulic dynamics along the inlet boundary; (ii) the spatial orientation of the groundwater flowpath are constant, whereas only the magnitude of the seepage velocity is adjusted by the inflow rate at the boundary; otherwise, intervals of convergence-divergence among flowpaths may cause meaningless counter-clockwise during the groundwater age tracking; (iii) the value of the bioreactive parameters are uniform in the whole domain. Here, the test case is analysed in the following mathematical frameworks of bioreactive transport:

- Conservative transport simulations accounting for (a) strictly advective and (b) advective-dispersive transport mechanisms in: (i) steady flow, and (ii) time-periodic flow conditions. Then, the kinematic age, and the local mean travel time at steady state can be estimated and simultaneously compared with their corresponding mean (or time-averaged) value in transient flow conditions (4x 1-D model; 4x 2-D model).
- Reactive transport travel time simulation accounting for advective and local longitudinal dispersive coefficient in steady flow, for diurnal and seasonal fluctuations (b-i, 2x quasi 1-D model).
- Spatially-explicit reactive advective dispersive simulation, considered the "virtual truth" of the test case reproducing time-periodic flow conditions, for diurnal and seasonal fluctuations (b-ii, 2x 2-D model).

The time-periodic feature of the transient flow one-dimensional and two-dimensional systems clearly induces null variability of the mean travel time value, and the mean kinematic age, in locations which values are integer of periodic fluctuations. Meanwhile, the in-between areas exhibit maximal but acceptable variability values. In spite of differences and uncertainties in the estimation of the independent variable, the four approaches provide similar results of the time-invariant characteristic travel time.

The comparison between the simplified one-dimensional reactive transport model and the two-dimensional "virtual truth" is excellent for mobile compounds. Regarding nonlinearities in the immobile biomass components, small deviations are observed due to the slow response of microbes to diurnal alterations. The resulting aerobic zonation increases or decrease at the same time than seepage velocity, which causes a transition zone with presence of both bacteria populations. However, the seasonality of flow rates provides a better spatial differentiation between the two degradation pathways (location of aerobic and denitrifying bacteria).

Assuming available transient flow information in real sites, by physically-sampled data or statistically approximated, the time-averaged mean seepage velocity still could be estimated and used in a stationary flow simulation expecting similar results to the traditional transient flow simulation. Nonetheless, an important limitation of the proposed simplified model in real applications is to obtain accurate representativeness of non-periodical hydraulic events that define the transient flow system.

Take away message: the one-dimensional steady state simulation of the time-averaged travel-time based model is able to effectively reproduce a multi-dimensional time-periodic simulation of bioreactive transport problem when flow direction does not change (Sanz-Prat et. al, 2016).

The third study (Appendix C) considers the coupled effect of physical and geochemical heterogeneity of the porous medium. Both are defined in the presented work as binary spatial property; such that highly heterogeneous reactive lenses, acting as quasi-infinite sources of dissolved organic matter, which are embedded in an inert matrix with one order of magnitude higher hydraulic conductivity. The principal novelty of this work with respect to the previous ones is that the reactive properties are only spatially uniform in the reactive zones. This assumption implies the use of the exposure time, defined here as the time that an idealized water parcel is exposed to two or more reactive materials, as substitute for the travel time. As expected, the difference between travel time and exposure time is more evident the further it gets form the inlet of the domain. The modified test case is simulated for the following mathematical frameworks:

- Exposure time based reactive transport simulation, for homogeneous and heterogeneous domain (2x 1-D model).
- Conservative advective-dispersive transport simulation, to estimate travel time, mean exposure time (hereinafter exposure time), and time difference at each location (2-D model).
- Reactive transport spatially-explicit based advective-dispersive simulation, as the reference case or virtual truth (2-D model).

Notice that the simplified approach is not able to reproduce concentrations corresponding to non-reactive areas, which may cause overestimation of the chemical-compound

concentrations. Although the uncertainty is significantly higher than in the first and second studies, the exposure-time based model captures the same tendency and magnitude than the “virtual truth” concentrations inside the reactive lenses. With the purpose to simulate more realistic conditions, the test case is designed such that the reactions could take place downstream the reactive lenses due to the excess release of dissolved organic matter not consumed within the reactive lenses.

Take away message: the compound concentrations in the reactive zones estimated by the multi-dimensional and highly heterogeneous spatially-explicit reactive transport model can be successfully replaced by the one-dimensional homogeneous exposure time model, when quasi-steady state is achieved and reactive activity is clearly restricted to certain locations (Sanz-Prat et. al, 2016 submitted).

In general, the travel- and exposure-time bioreactive transport models are good approximations to the traditional numerical methods. The chemical-compound concentrations in 2-D domains simplified as function of time and travel time by posing a quasi 1-D simulation in stationary systems reduces significantly the computation effort a lot. The reduction of computation effort offers an alternative, from small to large scale, to perform numerical models as: uncertainty analysis in multi-dimensional stochastic flow and transport models; calibration or sensitivity analysis of physical and biogeochemical parameters; or the application for inverse models.

2.2 Outlook

The findings presented above prove that the performance of travel- and exposure-time based reactive transport models in non-ideal circumstances deserves more thorough attention. As the presented work was pretty much focused on one specific test case (the redox reactions in the hyporheic zone), more diversified sets of real problems should be considered in future, for instance, different sorts of coupled physical and biogeochemical heterogeneities, e.g. as anisotropic hydraulic fields, different compositions of geochemical facies, and stratigraphic profiles. Besides, the evaluation can be extended to nonlinear chemical reactions, which is not controlled by transverse (and vertical) mixing processes, such as: rock-water interactions; reversible chemical reactions as precipitation/dissolution; to account for retardation factor in attachment/detachment processes (e.g. in active mineral bounds). An interesting research field that increases complexity of exposure time approach is the inclusion of microbial transport processes. The application in the unsaturated zone implies novel findings in the required assumptions to deal with the effects of diffusive processes and multi-phase transport of certain chemical compounds.

The advantage of the comparing idealized travel time models and the spatially-explicit model (“virtual truth”) is to avoid disruptions from non-controlled factors that typically appear in real site applications. Nonetheless, testing travel-time models’ estimates against observed data in laboratory and field experiments may better proof whether travel time models could infer reactive transport behaviour in real systems.

In three-dimensional domains the effect of vertical and transverse mixing processes get more relevance and may compromise the accuracy of the mean groundwater age value, and its capture of nonlinear behaviour of reactive components, but simultaneously the computational

reduction is more profitable than that in the two-dimensional domains (sixfold faster than in the presented test case). The stochastic groundwater field improves the description of effective flow and transport parameters (Dentz et. al., 2000, 2004, Cirpka, 2002, among others). In this sense, research efforts on the development of parameterization methods according to the effective dispersive coefficients represent a successful strategy to improve the performance of simply one-dimensional advective-dispersive travel-time models.

Another frequent limitation factor is the estimation of travel time in transient flow systems. Here, the proposed case study implies conditions mainly found in confined aquifer where the groundwater storage coefficient could be neglected, and well-connected to recharge areas with the same pattern of inflow rate. However, in the unconfined aquifers with significant specific yield value, or groundwater subsurface undergoing critical changes in flowpath direction are outside the scope of this work. For the author´s knowledge, relevant advances in analytical and numerical solutions have been proposed for other sort transient flow systems by Cornaton (2012) and Soltani et. al. (2013).

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Appendix A: First publication

Title

On the validity of travel-time based nonlinear bioreactive transport models in steady-state flow

Authors

Alicia Sanz-Prat, Chuanhe Lu, Michael Finkel, Olaf A. Cirpka

Journal

Journal of Contaminant Hydrology (Volume 175-176, pages 26-43)

Year

2015

Highlights

- We test whether travel time is a good proxy for reactive-species concentrations.
- The agreement is very good for moderate heterogeneity and steady-state flow.
- Effective longitudinal mixing must adequately be addressed.
- Travel-time based simulations thus simplify nonlinear reactive transport.
- The approach is invalid when macroscopically transverse mixing is relevant.

Appendix B: Second publication

Title

Using travel times to simulate multi-dimensional bioreactive transport in time-periodic flows

Authors

Alicia Sanz-Prat, Chuanhe Lu, Michael Finkel, Olaf A. Cirpka

Journal

Journal of Contaminant Hydrology (Volume 187, pages 1-17)

Year

2016

Highlights

- Velocity fields with periodically fluctuating magnitude and constant direction.
- Perform nonlinear bioreactive transport in 1-D domain.
- Transfer 1-D results to 2-D domains by mean groundwater age at steady state.
- Application to oxygen-inhibited denitrification.
- Excellent agreement between mapped and spatially explicit results.

Appendix C: Third publication

Title

Effects of nonlinear reactive-transport processes in physical-geochemical heterogeneous media on the exposure time approach

Authors

Alicia Sanz-Prat, Chuanhe Lu, Richard Amos, Michael Finkel, David Blowes, Olaf A. Cirpka

Journal

Manuscript submitted to the Journal of Contaminant Hydrology

Year

2016

Highlights

- Exposure time as a good proxy of geochemical heterogeneity in nonlinear bioreactive transport in 1-D domain.
- Coupled physical-geochemical heterogeneity is defined as binary properties in a 2-D domain.
- Perform nonlinear bioreactive transport in the 2-D domain and in a homogeneous 1-D domain.
- Map 2-D exposure time by using travel time exclusively activated in reactive zones.
- Good agreement of trends and magnitudes of chemical-concentrations as function of exposure time between the 2-D and 1-D model.
- Significant reduction of computation effort with the exposure time approach when transverse mixing does not control the reactive system and reactions are strictly located.