



Exposure times rather than residence times control redox transformation efficiencies in riparian wetlands



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SUMMARY

The concept of Damköhler numbers have been extensively used in the discipline of chemical engineering and lately increasingly found its application into environmental science in order to describe the integrated behavior of hydrological systems with respect to their physical transport and biogeochemical transformation capabilities. Defining characteristic time scales of transport and reaction, as part of the Damköhler concept, however is not trivial especially for non-well mixed systems like catchments where physically controlled transport and biogeochemical moderated reactions can be highly variable among individual flow paths. Often, system specific residence times alone are not useful to describe the time-scales of transport in the Damköhler concept, because it neglects that degradation of redox-sensitive compounds depend on dynamically changing and non-uniformly distributed hydro-biogeochemical boundary conditions that either facilitate or suppress biogeochemical reactions. In this study an approach is presented that highlights the importance to specifically distinguish between residence and exposure times if system specific transformation efficiencies are evaluated. We investigate the inter-relationship between residence and exposure time distributions for different biogeochemical processes in a virtual wetland environment that is exposed to different hydrological conditions. The relationship between exposure and residence times is mathematically described by a composition matrix that linearly relates the two identities to each other. Composition matrices for different hydrological conditions are analyzed by using the singular value decomposition technique. Results show that especially the type of couplings between the surface and subsurface flow domain control how exposure and residence times are related to each other in the wetland system and that timescales of residence and exposure typically differ by orders of magnitude. Finally, results also indicate that the assessment of system specific transformation efficiencies can be very error-prone if residence instead of exposure times are being used to derive system specific Damköhler numbers.

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1. Introduction

Understanding the fundamental couplings between physical controlled transport and biogeochemical moderated reactions of solutes, nutrients and contaminants in terrestrial ecosystems is a very challenging topic in environmental research. Profound process knowledge about how compounds or solutes are being transported and processed in natural systems like catchments, is especially essential in the context of climate change with its potential to fundamentally affect local to regional hydrologic cycles, biogeochemical cycles as well as the interactions and feedbacks among them (Lohse et al., 2009). In recent years, many interdisciplinary research efforts started to investigate how physical transport and biogeochemical reaction of solutes are related at the

various spatial and temporal scales and how interactions between hydrology and biogeochemistry affect nutrient cycling and solute mobilization within terrestrial ecosystems (reviews are given in Reich et al. (2006) and Lohse et al. (2009)). Despite the increased interest, a lot of knowledge gaps still exist, and especially the relevance of couplings between hydrology and biogeochemistry, on scales that are important to ecosystem functions and human interactions, remains an open field of research (Hyvönen et al., 2007).

The fate and behavior of redox-sensitive solutes in hydrological systems, such as nitrate or sulfate, either originating from anthropogenic or natural sources, depends on (1) their in-situ reactivity including the dependency on (bio)-geochemical and hydrological boundary conditions that either favor or suppress biogeochemical transformation processes and (2) how and on which timescales these solutes are being transported within the system. One possibility to express this inter-dependency between timescales of

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physically controlled transport and biogeochemical moderated reaction is the dimensionless Damköhler number (in the latter referred to as Da) (Eq. (1)). The Da number, by definition, relates the timescales of transport τ_T [T] to a process specific, characteristic reaction time τ_R [T]. It can be used to characterize engineered or natural systems according to their transformation- or removal efficiencies with respect to a specific solute or compound. The situation where $Da \gg 1$ represents a system where timescales of transport are much higher compared to the timescales of reaction. In such a case, removal efficiencies of a system are very high and the system acts as an effective sink for that specific solute. The opposite case ($Da \ll 1$) represents low removal efficiencies. Here, physical transport occurs on much faster timescales compared to (bio)-geochemical reaction. In modeling, systems can be effectively simplified by knowing their typical Da numbers. Systems that are characterized by very low Da numbers ($Da \ll 1$) can be treated as conservative systems, neglecting biogeochemical degradation and transformation entirely. On the other hand, for systems where $Da \gg 1$ the proceeding reactions can be simplified to equilibrium reactions rather than kinetically controlled reactions that are often non-linear and difficult to solve numerically.

$$Da = \frac{\tau_T}{\tau_R} \quad (1)$$

The concept of Da numbers has been extensively used in the discipline of chemical engineering and lately increasingly found its application in environmental science, where it improved our general understanding of catchment hydro-chemical responses (Oldham et al., 2013). Ocampo et al. (2006) used the Da concept to understand nitrate removal efficiencies of riparian areas and Kim et al. (2003) investigated the effects of dissolved organic matter and bacteria availability on contaminant transport in riverbank infiltration. Flewelling et al. (2012) characterized nitrate removal capacities of the hyporheic zone and streambed sediments by relating timescales of reaction and transport as part of a Da framework. Maher and Chamberlain (2014) presented a conceptual model for solute production in catchments, that linked the hydrologic regulation of chemical weathering to climate regulations and tectonic forcing, by calculating solute concentrations as a function of Da numbers. Briggs et al. (2014) investigated the sink and source functions of the hyporheic zone for dissolved nitrogen, where they concluded that nitrate hot moment dynamics can be explained by dynamical changes in physical hydrology and associated residence times that lead to shifted Da numbers during these events.

Defining the characteristic time scales for transport τ_T , as part of the Da concept, however is not trivial, especially for non-well mixed and transient systems like catchments, where timescales of transport can be highly variable between individual flow paths (Oldham et al., 2013). In many studies that use the Da framework, it is frequently assumed that system specific residence times (RT) can be used as a proxy to define the characteristic timescales of transport τ_T . Basu et al. (2011) e.g. used a relationship between RT distributions and processing timescales to explain nutrient exports from catchments. Botter et al. (2010) calculated Da numbers based on RT distributions to explain the chemical composition of stream flows and Literathy and Laszlo (1996) mentioned that quality of bank filtered water is affected by the RT in the aquifer. Migration of nitrate in catchments is a very special case. Here it is often argued that subsurface transport processes are so slow (very long RT) compared to the timescales of biogeochemical transformation, so that removal efficiencies must be very high ($Da \gg 1$). However, observations like e.g. high concentrations of dissolved oxygen or nitrate in deep and very old groundwater (e.g. Strohmeier et al., 2013 or Bartsch et al., 2014) clearly proof, that transformation efficiencies for nitrate can't be very high.

Findings like these proof that catchment specific RT alone might not be appropriate to be used in the Da framework in order to define the characteristic timescales of transport. By using mean RT or RT-distributions, as a proxy for τ_T , one assumes that conditions that favor biogeochemical reactions are uniformly present along subsurface transport pathways. However, for non-well mixed systems like catchments, this is almost never the case where biogeochemical reactions, that occur along different subsurface flow path lines, depend on dynamically changing and non-uniformly distributed hydro-biogeochemical boundary conditions (Frei et al., 2012), that either facilitate or suppress biogeochemical reactions.

To account for these heterogeneous conditions in space and time in non-well mixed systems, a modified version of the Da concept was proposed that uses exposure times (ET) rather than RT to define τ_T (Ginn, 1999; Seeboonruang and Ginn, 2006; Oldham et al., 2013). By definition, ET represent the timescales along individual flow paths over which material has the opportunity to be processed (Oldham et al., 2013). Denitrification along subsurface transport path ways e.g. can only occur under anaerobic conditions where oxygen concentrations are low and where organic carbon is available. The specific period of time where the subsurface water is flowing through this area, where oxygen is absent and organic material is available, defines the ET for denitrification. The idea of using ET rather than RT to describe the "effective" timescales of physical transport in the Da concept was postulated by Ginn (1999) and later by Oldham et al. (2013). However, estimation of ET for natural systems is extremely difficult or sometimes even impossible, especially for non-well mixed systems like catchments, because it requires a combined and integrated perspective on how and under what specific circumstances physical controlled transport and (bio)-geochemical reaction occurs in hydrological systems. Modern tracer techniques, such as "smart tracers" (Haggerty et al., 2008; Liao et al., 2013), that are potentially able to track changes in redox conditions, look promising and may offer a possibility to estimate ET for hydrologic systems in the future.

Although very difficult to estimate for real systems, both RT and ET represent important system characteristics, providing us with key information about the nature of physically controlled transport and (bio)-geochemical moderated reactions. Understanding how ET and RT are related to each other under different hydrological conditions can help us to improve our knowledge about how hydrological systems are functioning. But how can we investigate and describe such a relationship between ET and RT for non-well mixed and in-homogenous hydrological systems where different landscape elements such as riparian areas, wetlands or upslope areas contribute differently to the transformation and mobilization of a solute? And how is this relationship between RT and ET affected by different hydrological conditions and (bio)-geochemical processes?

In this study an approach is presented where we mathematically evaluate the relationship between RT- and ET-distributions. The framework is applied to a virtual model environment, exposed to non-uniform hydrological conditions, for which typical biogeochemical processes (aerobic respiration, denitrification, iron(III)- and sulfate reduction) are being simulated. The framework uses particle tracking methods to specifically distinguish between RT and ET, similar to the concept which was described in Seeboonruang and Ginn (2006). Different model realizations are being used, in order to investigate how the relationship between ET- and RT-distributions depends on different transport and reaction specific parameters and to identify first order controls that affect the relationship between RT and ET. A central aspect of the study is to highlight the importance to specifically distinguish between ET and RT when it comes to an evaluation of transformation efficiencies for natural systems by applying the Da concept.

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