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The potential for material processing in hydrological systems – a novel classification approach

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Abstract

Assessing the potential for transfer or export of biogeochemicals or pollutants from catchments is of primary importance under changing land use and climatic conditions. Over the past decade the connectivity/disconnectivity dynamic of a catchment has been related to its potential to export material, however we continue to use multiple definitions of connectivity, and most have focused strongly on physical (hydrologicaly or hydraulic) connectivity. In this paper we use a dual-lens approach, where the dynamic balance between transport and reaction is constantly in focus, and define ecohydrological connectivity as the ability of matter and organisms to transfer within and between elements of the hydrologic cycle while undergoing biogeochemical transformation. The connectivity/disconnectivity dynamic must take into account the opportunity for a given reaction to occur during transport and/or isolation. Using this definition, we define three distinct regimes: (1) one which is ecohydrologically connected and diffusion dominated; (2) one which is ecohydrologically connected and advection dominated and (3) one which is both hydrologically and ecohydrologically disconnected. Within each regime we use a new non-dimensional number, N_E, to compare exposure timescales with reactions timescales. N_E is reaction-specific and allows the estimation of relevant spatial scales over which the reactions of interest are taking place. Case studies provide examples of how N_E can be used to classify systems according to their sensitivity to shifts in hydrological regime, and gain insight into the biogeochemical processes that are signficant under the specified conditions. Finally, we explore the implications of this dual-lens framework for improved water management, for our understanding of biodiversity, resilience and biogeochemical competitiveness under specified conditions

1 Introduction

Assessing the potential for export of biogeochemicals and pollutants from catchments is of primary importance under changing land use and climatic conditions (Pringle, 2003a), yet our ability to predict that export relies on a detailed understanding of both the transport and biogeochemical processing taking place (Hornberger et al., 2001). One of the challenges for the prediction of material transfer through catchments, is the high degree of heterogeneity and its dependence on scale. Dooge (1986) suggested that scaling issues were fundamental to the development of hydrological theory, specifically the development of scaling relations across catchment scales and up-scaling from small-scale theories. Since that time there has been substantial research on small-scale process-based distributed model descriptions, however the application of these models to large catchments has at times been problematic and the preferred modes of investigation continue to vary across scales (Table 1).

In response to this, McDonnell et al. (2007) challenged hydrologists to move “beyond heterogeneity and process complexity” to better facilitate the characterization of catchments, however approaches using either an ecological or hydrological lens tend to remain embedded in discipline-specific process complexity. In a study that investigated interactions between vegetation and hydrology, Thompson et al. (2011) highlighted the co-evolution of vegetation and hydrological spatial organization, yet continued to use a hydrological lens, via a water balance approach, to characterize systems across scales. An alternative approach is to adopt a dual lens, in which the focus remains on the dynamic balance between hydrological and ecological processes. Here we focus on material fate as expressed by biogeochemical reactions.

In an attempt to identify parameters that resolved the “scale” issue, Vaché and McDonnell (2006) flagged that water residence times were integrative and meaningful across all scales, and went on to highlight the challenges in characterizing flow paths, and therefore residence times, that were of relevance to material transport; the residence time is a critical parameter within the dual lens approach. The residence time distribution (RTD), which is a function of both meteorological and hydrological forcing (Botter et al., 2011; Hrachowitz et al., 2010), has been used as a fundamental characteristic of waters aquatic systems with free surfaces (Carleton, 2002; Werner and Kadlec, 2000) and more recently of catchments (Bevan, 2001; McDonnell et al., 2010; McGuire and McDonnell, 2006). All of these authors noted the importance of the residence and transit times for the export of pollutants and biogeochemicals from catchments.

Estimates of characteristic residence times have been used in dimensionless ratios (Carleton, 2002; Hornberger et al., 2001; Ocampo et al., 2006) to improve our understanding of catchment hydro-chemical responses and chemical cycling. The dimensionless Damköhler number, Da, has been used extensively in the discipline of chemical engineering to classify a system according to the balance between transport and reaction, and is given as

$$\mathrm{Da}=\frac{\tau_\mathrm{T}}{\tau_\mathrm{R}} \tag{1}$$

where τ_T is the transport (or residence) timescale and τ_R is the reaction timescale. Thus, Da can be considered an important non-dimensional number within the dual lens approach.

Michalak (2000) used Da to characterize the appearance of chemical sorption peaks in simulation experiments. Wehrer and Totsche (2003) used Da to characterize when breakthrough of contaminants took place under non-equilibrium conditions, Ocampo et al. (2006) used Da to explore the removal of nitrate by riparian zones and demonstrated that 50 % nitrate removal occurred when $\mathrm{Da} < 1$ and increased to nearly 100 % at $\mathrm{Da} = 2$–20. Carleton (2002) used Da to explore residence time distributions in treatment wetlands and their impact on contaminant removal. Kurtz and Peiffer (2011) used a Da approach to explore turnover timescales and surface complexation reactions. Given that the Da has been successfully used to characterize the transfer of biogeochemicals under a range of transport conditions, and across a range of spatial scales from pores to wetlands and riparian zones, we suggest that Da could be used to characterize hydrological elements in a catchment. We note however that by definition the use of Da assumes connectivity i.e. that there is transport between such elements in the catchment.

The hydrological connectivity/disconnectivity dynamic is a key characteristic of many catchments (Meerkerk et al., 2009; Michaelides and Chappell, 2009; Ocampo et al., 2006; Pringle, 2003a, b) and is considered critical for ecological function, adaptation and evolution (Klein et al., 2009; Opperman et al., 2010; Pringle, 2003b). Pringle (2003b) noted the variety of definitions of connectivity, used across and within disciplines. In recent years, a commonly used definition is the ability of energy, matter and organisms to transfer within and between elements (for example sub-catchments, riparian zones, wetlands, streams) of the hydrologic cycle (Detty and McGuire, 2010; Pringle, 2003b).

Over the past decade there have been numerous attempts to characterise the connectivity/disonnectivity dynamic, most typically in terms of hydrological (surface and sub-surface pathways) or hydraulic (pathways incorporating a free surface, e.g. streams and wetlands) connectivity (Ali and Roy, 2010; Meerkerk et al., 2009; Michaelides and Chappell, 2009; Tetzlaff et al., 2007). Even where the connectivity definition of Pringle (2003b) has been used previously, conservative transfer of material is usually assumed (i.e. still using a hydrological lens). To our knowledge there have been no attempts in the hydrological literature to characterise connectivity in terms of the *effectiveness* of transferring energy, matter or organisms. Such a characteristic might be termed "ecohydrological" connectivity and must take into account both the hydrological/hydraulic transport and the biological and/or chemical fate or processing; such a definition is needed under a dual lens approach. Here we define ecohydrology as the interaction between hydrology and the biosphere, with specific regard to biogeochemical processing of material. Multiple elements of the hydrological cycle may be fully connected hydrologically, yet if organisms or material is being removed, or even settles under gravity, within a single element, the material transfer is not complete across elements, so by our definition above, the effectiveness of ecohydrological connectivity is poor. The effectiveness of ecohydrological connectivity is critical for ecological processes and outcomes.

To illustrate our point we present two examples. Firstly, we take the example of Fe(II)-rich anoxic groundwaters being discharged into a well oxygenated stream which then flows into a lake. The groundwater, stream and lake are hydrologically and hydraulically fully connected, however Fe(II) undergoes oxidation on exposure to oxygenated waters, and likely precipitates out as Fe(III) oxide, which may affect the benthic ecology. The balance between the rate of transport, the rate of Fe(II) oxidation, the rate of precipitation and settling, and the rate of Fe(II) production from reductive dissolution, will determine the effectiveness of ecohydrological connectivity, with respect to Fe(II), of the groundwater and lake. If all Fe(II) is oxidized before reaching the lake, the system is ecohydrologically disconnected with respect to Fe(II). Secondly, we take the example of a phytoplankton-rich wetland being flushed out across a floodplain and into a lake under flooding conditions. The wetland, the floodplain and the lake are hydraulically fully connected, however in transit the phytoplankton may grow, aggregate, settle and decompose. The balance between the rate of transport, the rate of particle settling under gravity and the phytoplankton net productivity will determine the effectiveness of ecohydrological connectivity, with respect to the phytoplankton, of the wetland and the lake. If all phytoplankton settle out (or decompose) before reaching the lake, the system is ecohydrologically disconnected with respect to phytoplankton.

This paper seeks to develop a framework that could be used to conceptually classify ecohydrological systems, including systems undergoing intermittent connectivity, and thus provide insights into processes controlling the export of material from catchments. For clarity, we modify the broader connectivity definition of Pringle (2003b), to a definition of ecohydrological connectivity as *the ability of matter and biota to transfer within and between elements of the hydrologic cycle, while subject to biogeochemical or biological processing*. For simplicity, at this point we have excluded energy transfer from our definition.

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2 Conceptual framework

Our definition of ecohydrological connectivity explicitly takes into account the transfer of matter and biota across and between hydrological elements. We therefore begin the development of our framework with the scalar transport equation, or advection-diffusion-reaction (ADR) equation, that describes transport of chemical B via a homogeneous fluid (constant density and viscosity) and is given as

$$\frac{\partial[B]}{\partial t} = \underbrace{-u_i\,\frac{\partial[B]}{\partial x_i}}_{\text{I}} + \underbrace{D_{\text{eff}}\,\frac{\partial^2[B]}{\partial x_i \partial x_i}}_{\text{II}} - \underbrace{k'\,[B]}_{\text{III}} \tag{2}$$

where $[B]$ is the concentration of chemical B (mmol m^{-3}), u_i is the mean velocity in the i-direction (m s^{-1}), t is time (s), x_i is distance in the i-direction (m), D_{eff} is the *effective* diffusion/dispersion coefficient (m^2 s^{-1}) and k' is an appropriate rate constant (s^{-1}) where

$$\tau_{\text{R}} = 1/k'. \tag{3}$$

Note that outside of diffusive boundary layers, D_{eff} is likely to be significantly larger than molecular diffusivity and may describe processes such as turbulent diffusion, bioturbation or mechanical dispersion. Term I describes advective transport of chemical B, Term II describes Fickian transport of chemical B, and Term III describes the rate at which chemical B is consumed.

The non-dimensional Peclet Number, Pe, provides the balance between advection and diffusion:

$$\text{Pe}=\frac{D_{\text{eff}}}{u_i \Delta x_i} \tag{4}$$

where Δx_i is the characteristic length scale over which transport processes are operating. The Pe is used to determine which terms in Eq. (2) are retained.

The choices of appropriate control volume, and their relevant time and length scales are critical. A first assumption is that the control volume and therefore the characteristic length scale, Δx_i, are physically constrained, typically by catchment/stream/wetland geomorphology. The relevant transport timescale, τ_T, is then determined by the length scale and the transport process, whether advective or diffusive controlled (Fig. 1).

We apply Eq. (2) to an idealized one dimensional control volume or hydrological element (Fig. 2a), which has a physically constrained horizontal length scale of Δx_i, with through-flow velocity u_i and effective diffusivity D_eff. The general solution to Eq. (2) is

$$[B] = \exp(-k't)\left[\alpha_0 + \sum_{n=0}^{\infty}\left(\alpha_n \cos\left(\frac{n\pi}{\Delta x_i}(x-u_it)\right) + \beta_n \sin\left(\frac{n\pi}{\Delta x_i}(x-u_it)\right)\right)\exp\left(-\frac{n^2\pi^2 D_\mathrm{eff}}{\Delta x_i^2}t\right)\right] \quad (5)$$

where n is the summation index and α_n and β_n are Fourier cosine and sine coefficients respectively and are determined by the initial and boundary conditions that apply to the particular element being modeled.

Chemical reaction timescales

We have illustrated above the use of Pe to determine the appropriate transport or residence timescales, and we now address the estimation of appropriate chemical reaction timescales. While acknowledging that many biogeochemical processes have more complex kinetics, for simplicity we initially assume our chemical reaction of interest can be described as

$$A + B \xrightarrow{k} C + D \quad (6)$$

Equation (6) can be treated as a second order reaction where k is the second order rate constant (mmol^{-1} m^3 s^{-1}) and if we assume A to be in excess of B then Eq. (6) can then be considered "pseudo-first-order" with respect to B, $[B]$ is not limiting and

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = -k[A][B]. \tag{7}$$

The square brackets denote the chemical concentration (mmol m^{-3}) and k' is the pseudo-first-order rate constant (s^{-1}) and is used in (2).

Alternatively, if we use a Monod model (Park and Jaffe, 1995; Lendenmann and Egli, 1998; Castillo et al., 1999), the rate of consumption of chemical B can be parameterized as

$$\frac{\mathrm{d}[B]}{\mathrm{d}t} = -q[A] \tag{8}$$

where q is the specific consumption rate of the reactant B (mmol cell^{-1} day^{-1}), and the characteristic timescale of reaction, τ_R is given by Simpson and Landman (2007) as

$$\tau_\mathrm{R} = \frac{[B]_\mathrm{max}}{q_\mathrm{max}} \tag{9}$$

where $[B]_\mathrm{max}$ is the maximum expected concentration of B and $k' = 1/\ \tau_\mathrm{R}$.

Using this conceptual framework, we define three regimes, depending on the relative balances between Terms I, II and III in Eq. (2), and present a modified Eq. (5) for each regime.

2.1 Regime I: advection dominated

For systems that are hydraulically or hydrologically connected and Pe $\ll$ 1 (i.e. the system is advection dominated, Fig. 2. Term II in Eq. (2) drops out, leaving

$$\frac{\partial[B]}{\partial t} = \underbrace{-u_i\frac{\partial[B]}{\partial x_i}}_{\mathrm{I}} \underbrace{-\,k'\,[B]}_{\mathrm{III}} \tag{10}$$

The relevant (advective) transport timescale for this regime is

$$\tau_{\mathrm{T}}^{A} = \frac{\Delta x}{U_x} \tag{11}$$

where U_x is the mean velocity ($\mathrm{m\,s^{-1}}$) in the x-direction.

Substituting Eqs. (11) and (3) into Eq. (4) gives the appropriate Damköhler number for Regime I as

$$\mathrm{Da}_I = \frac{k'\Delta x}{U_x}, \tag{12}$$

When Da $\gg$ 1, $\tau_{\mathrm{T}} \gg \tau_{\mathrm{R}}$ which indicates that the control volume residence time is sufficiently long for chemicals A and B to react. When Da $\ll$ 1, $\tau_{\mathrm{T}} \ll \tau_{\mathrm{R}}$ which indicates that chemicals A and B do not have sufficient time come to react before they are advected out of the control volume; in this case chemicals A and B may be treated as if they are conservative. Some examples of environments where we expect of Regime I to occur are shown in Fig. 2.

In the small Pe limit, the diffusion term can be neglected and the general solution Eq. (5) can be re-written as

$$[B] = \exp(-k't)f(x-ut) \tag{13}$$

where the function $f(x)$ represents the initial ($t = 0$) distribution of $[B]$ in the element. Physically, as time increases the initial profile of $[B]$ is advected at speed u through the element without change of form except for a reduction in magnitude due to the reaction term.

This solution and its behavior are shown in Fig. 4a and b. Figure 4a shows the case where there is no significant consumption of B (Da $\ll$ 1) before it has been advected through the element. The magnitude of the initial profile has been preserved. Figure 4b shows the case where there has been significant consumption (Da $\gg$ 1) of B as there has been a significant reduction of magnitude in the profile. Note however that B has not spread within the element since this is the advection-dominated regime (i.e. diffusion is minimal).

2.2 Regime II: diffusion dominated

For systems that are hydraulically or hydrologically connected and Pe $\gg$ 1 (i.e. system is diffusion dominated, Fig. 3, Term I in Eq. (2) drops out so we have

$$\frac{\partial[B]}{\partial t} = \underset{\text{II}}{D_{\text{eff}}\frac{\partial^2[B]}{\partial x_i \partial x)i}} - \underset{\text{III}}{k'\,[B]}, \tag{14}$$

The relevant (diffusive) transport timescale, τ_{T}^{D}, for this regime is then

$$\tau_{\text{T}}^{D} = \frac{\Delta x_i^2}{D_{\text{eff}}}. \tag{15}$$

and given Eq. (7), then

$$\text{Da}_{\text{II}} = \frac{k'\Delta x^2}{D_{\text{eff}}} \tag{16}$$

where Da_{II} is the definition of Da appropriate for this regime.

When Pe $\gg$ 1 the general solution Eq. (5) can be re-written as

$$[B] = \exp(-k't)\left[\alpha_0 + \sum_{n=0}^{\infty}\left(\alpha_n \cos\left(\frac{n\pi}{\Delta x_i}x\right)\right.\right.$$
$$\left.\left. + \beta_n \sin\left(\frac{n\pi}{\Delta x_i}x\right)\right)\exp\left(-\frac{n^2\pi^2 D_{\text{eff}}}{\Delta x_i^2}t\right)\right] \tag{17}$$

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In the absence of significant reaction of B (Da $\ll 1$), B will eventually diffuse through the entire system without significant loss of B. This is shown in Fig. 4c. Alternatively, if Da $\gg 1$ then much of B will be used up before it has a chance to diffuse through the system, which is shown in Fig. 4d.

2.3 Regime I and II boundary

We have shown how to use Pe and Da to classify eco-hydrological systems, however porous media are frequently characterized by their dispersivity,

$$\alpha_i = \frac{D_{\text{eff}}}{u_i}. \tag{18}$$

If we normalize the dispersivity by the characteristic length scale (i.e. the length of the control volume), then

$$\frac{\alpha_i}{\Delta x_i} = \frac{D_{\text{eff}}}{u_i \Delta x_i} = \text{Pe}. \tag{19}$$

Note that this relationship is dependent on scale and the empirically derived relationship

$$\alpha_i = 0.0175 \Delta x_i^{1.46} \tag{20}$$

can be applied to a flow path length less than 3500 m (Todd and Mays, 2005).

Reported horizontal field dispersivities considered of high reliability, typically range from 10^{-2} to 10^{2} m, over length scales ranging from 10^{0} to 10^{3} m (Gelhar 1992), and using Eq. (18) we get Pe numbers O(10^{-3})–O(1), indicating that both advection and diffusion are significant in the development of [B] at the upper end of the range. Under this condition, advection and diffusion act on similar time scales.

2.4 Regime III – hydrological disconnection

We have shown how to use Pe and Da to classify ecohydrological systems, however so far we have assumed hydrological/hydraulic connectivity. In temperate, semi-arid and arid environments, there may be times when elements of the hydrological cycle are hydrologically or hydraulically disconnected. During these periods, chemical and biological reactions continue within the hydrological element and biogeochemicals will accumulate or decline, creating an isolated biogeochemical reactor in the environment. Under these conditions

$$\frac{\partial[B]}{\partial t} = -k'[B] \tag{21}$$

The general solution Eq. (5) can then be re-written simply as

$$[B] = \exp(k't)f(x) \tag{22}$$

where $f(x)$ is the initial ($t = 0$) distribution of $[B]$.

Examples of aquatic systems that are hydrologically or hydraulically disconnected are shown in Fig. 5. We can assume full internal mixing of these systems due to external forcing (e.g. due to wind mixing).

If we take the reaction shown in Eq. (6) then the extent to which chemical B is removed is determined by both rate of reaction and also the timescale over which the hydrological element is physically disconnected or isolated. We will call this the *isolation* timescale, τ_I. When hydrological elements become isolated with no water fluxes in or out, the chemical reaction shown in Eq. (6) may quickly become limited by either the depletion of reactants or the build up of products. The consequences of hydrological/hydraulic isolation are no resupply of reactants and no flushing of products. Under these conditions, the change in concentration of B cannot be described by Eq. (7) and we should instead use Eq. (8), however to illustrate our conceptual framework we will assume that until chemical B is 10 % consumed, pseudo-first order kinetics can be utilized i.e. the reaction is not limited by $[B]$. In this case we revert to using Eq. (7).

We now present a new non-dimensional number to describe this Regime III as the ratio of residence or isolation timescale to reaction timescale

$$N_{\mathrm{III}} = \frac{\tau_{\mathrm{I}}}{\tau_{\mathrm{R}}} \tag{23}$$

If we take the inverse of the isolation timescale, τ_{I}, we obtain what we can term the hydrological/hydraulic *connection frequency*. Alternatively if the isolated system itself is the reference point then $1/\tau_{\mathrm{I}}$ is the disturbance frequency, k_D, a concept used extensively in terrestrial ecology (Huston, 1994).

3 Discussion

3.1 Non-dimensional numbers

The Damköhler number has been used extensively in chemical engineering and more recently in environmental and hydrological contexts and we have shown above that it provides a useful classification of eco-hydrological systems. However, the definition of Da implicitly assumes hydrological or hydraulic connectivity. Without physical connectivity, there is no transport of chemicals across hydrological elements, therefore we are unable to define τ_{T}. For example Da could not be used to describe Regime III, where we defined the system in terms of the timescale of isolation, τ_{I}. A new non-dimensional number, N_{III} was created to account for this constraint. It should be noted that N_{III} does *not* characterize material connectivity, but rather the potential for material to be disbursed once hydrological connectivity is again established. This potential for disbursal has significant implications for both small-scale and landscape-scale ecological processes, as will be discussed below.

To characterise biogeochemical and material fate, under both hydrological/hydraulic connection and disconnection, we propose the use of a more general non-dimensional number

$$N_\mathrm{E} = \frac{\tau_\mathrm{E}}{\tau_\mathrm{R}} \tag{24}$$

where τ_E is an exposure timescale. This is the timescale over which the biogeochemicals or materials have the *opportunity* to be processed. This opportunity may occur during transport (when $\tau_\mathrm{E} = \tau_\mathrm{T}$ and $N_\mathrm{E} = \mathrm{Da}$ i.e. Regimes I and II depending on Pe) or during hydrological/hydraulic isolation (when $\tau_\mathrm{E} = \tau_\mathrm{I}$ and $N_\mathrm{E} = N_\mathrm{III}$ i.e. Regime III). The concept of an exposure timescale has been previously used in surface renewal theory (Dankwerts, 1951) and chemical engineering (Asarita, 1967). The proposed non-dimensional number therefore gives an indication of the extent of chemical reaction possible within the exposure timescale.

N_E can be used to determine the physical constraints on a system required to ensure, for example, that 90 % of a biogeochemical is removed. If we take the example of a pseudo-first-order reaction as shown in Eq. (6) and our definition shown in Eq. (23) then Eq. (7) can be integrated to obtain

$$\begin{aligned} [B]_* &= [B]_0 \exp(-k'\tau_\mathrm{E}) \\ &= [B]_0 \exp(-N_\mathrm{E}). \end{aligned} \tag{25}$$

When chemical B is 90 % removed,

$$\frac{[B]_*}{[B]_0} = 0.1 = \exp(-N_\mathrm{E}) \tag{26}$$

then $N_\mathrm{E} \approx 2.3$. So for a system where $N_\mathrm{E} \gg 2.3$, we expect more than 90 % removal of chemical. For a system where $N_\mathrm{E} \ll 2.3$, we expect less than 90 % removal of chemical. If we are aiming for biogeochemical removal, for example in reconstructed riparian zones, we could manipulate the physical system to ensure we have $N_\mathrm{E} \gg 2.3$, and thus achieve at least 90 % removal. We can thus use the concept of N_E to identify the required timescale, and then with knowledge of the transport mechanisms, physically size the system to ensure the opportunity timescale is appropriate. Similarly we use Eq. (24) to show that at least 10 % removal of B occurs when $N_\mathrm{E} \gg 0.1$.

3.2 Application of Pe/Da approach across scales

In the previous sections we outlined how Da and Pe can be used to classify ecohydrological systems according to the fate of chemical *B*. We will now examine this concept for several hydrological systems across different temporal and spatial scales. We will focus on the oxidation of Fe(II) which plays a prominent role in linking metabolic activities across anaerobic and aerobic components of aquatic systems (Raiswell and Canfield, 2012). Fe(II) oxidation is an ecologically significant reaction both under neutral and acidic conditions however the rate is strongly dependent on pH (Stumm and Morgan, 1996). The oxidation process typically implies precipitation of ferric oxides and through that the generation of acidity. Under well-buffered conditions, such as anaerobic ground or pore waters, the pH remains relatively constant. Under low or no-alkalinity conditions however, oxidation of Fe(II) significantly contributes to acidification of surface waters. Examples of such systems are acidic mining lakes (Peine et al., 2000) or acid sulphate soils (Burton et al., 2006) where acidity has been generated through the oxidation of pyrite, but where acidic iron cycling i.e. the combined reduction of ferric and oxidation of ferrous iron, maintains acidic conditions (Peine et al., 2000). Here we will compare three anaerobic aquatic systems containing Fe(II) and how they respond to oxygen exposure under different transport regimes. We have chosen two pH conditions: neutral (pH 7) conditions as found in many anaerobic environments, and slightly acidic (pH 4) conditions as found in many anaerobic systems receiving waters that have been exposed to pyrite oxidation (Blodau, 2006).

The oxidation of Fe(II) can be modelled using the rate law given by Stumm and Lee (1961).

$$\frac{d[\mathrm{Fe(II)}]}{dt} = -k_{\mathrm{abio}} P_{\mathrm{O_2}} [\mathrm{OH^-}]^2 [\mathrm{Fe(II)}] \tag{27}$$

where P_{O_2} is the partial pressure of oxygen (0.21 atm) and k_{abio} is the rate constant (1.5×10^{13} L^2 mol^{-2} atm^{-1} min^{-1} at 25 °C).

This rate law predicts extremely low rates under acidic conditions. Typically, Fe(II) oxidation will be accelerated by bacteria. Pesic et al. (1989) reported a decrease in microbial oxidation rate with increasing pH between pH 2.2 and pH 3. Extrapolation of their rate law (Kirby et al., 1999) demonstrates that at pH 4 the abiotic rate is still higher then the microbial rate. Hence, in our examination we will use Eq. (26) for pH 4 and pH 7.

The rate constant k in Eq. (26) can be converted into a pseudo 1st-order rate constant for ambient temperature and pressure conditions and for a pre-defined pH as

$$k' = k_{\text{abio}} P_{O_2} [OH^-]^2 \tag{28}$$

which yields the reaction times, τ_R, given in Todd and Mays (2005), that will be used for the analyses below.

3.3 Case I: porewater transport in deep lake sediments

The sediment of deep eutrophic lakes (pH neutral conditions) or mining lakes (acidic conditions) may be hydrologically connected to the surrounding groundwater but if the hydraulic conductivity of the sediment material is extremely low, groundwater inflow velocities could be $< 10^{-9}\,\text{m}\,\text{s}^{-1}$. We assume a molecular diffusion coefficient, D_{eff} of $10^{-9}\,\text{m}^2\,\text{s}^-1$.

Under this scenario, the characteristic length scale is not physically constrained. We can, however, estimate a depth at which the O_2 concentration has been decreased to a specified level. In order to fulfil the validity of pseudo-first order kinetics we assume a reduction by only 10 %, i. e. $\Delta P_{O_2} = 0.021$ atm which corresponds to $\Delta[O_2] \approx 0.03\,\text{mol}\,\text{l}^{-1}$ at ambient temperature, and stoichiometrically to an Fe(II) consumption of $\Delta[\text{FeII}] = 0.03\,\text{mol}\,\text{l}^{-1}$. Hence, the thickness of a layer will be estimated, in which the oxygen concentration does not drop below $0.27\,\text{mol}\,\text{l}^{-1}$.

Fe(II) concentrations in pH neutral lake sediments rarely exceed $0.1\,\text{mol}\,\text{l}^{-1}$ (see e.g. Baccini 1985) while in acidic environments Fe(II) concentrations of up to 10 mmol l^{-1} may be reached (Burton et al., 2006; Peine et al., 2000). Therefore, a Δ[FeII] of 0.03 mol l^{-1} is a 30 % removal at pH 7 and a 0.3 % removal at pH 4. Using Eq. (25), $N_E \approx 0.4$ and 0.003 for pH 7 and 4 respectively.

In the next step we can estimate $\Delta x_{10\,\%}$ by combining Eqs. (15) and (23) as

$$\Delta x_{10\,\%} = \sqrt{N_E \times \tau_r \times D_{\text{eff}}} \tag{29}$$

which yields 8×10^{-4} m at pH 7, and 8×10^{-2} m at pH 4. The corresponding exposure timescales, τ_E, within these contact zones are 7×10^2 s at pH 7, and 6×10^6 s at pH 4. Using these length scales, groundwater inflow velocities and molecular diffusion coefficient, Pe ranges from 1.2×10^3 at pH 7 to 1.3×10^1 at pH 4 (Table 3).

The above calculations have two specific implications. Firstly, the thickness of the layer that remains close to O_2 saturation varies significantly between the two pH regimes. The zone of of Fe(II) production from dissimilatory iron reduction (a biogeochemical process sensitive to O_2) will be shifted to deeper sediments under acidic conditions. Secondly and more importantly, the timescales of exposure to oxygen saturation is 4 orders of magnitudes longer under acidic conditions and lasts for several weeks. Note that the calculated τ_E is an lower estimate and may be even longer at lower Fe(II) concentrations. This long time scale provides ample opportunities for interference from other biogeochemical processes that involve oxygen or consume Fe(II).

Hence, N_E can be regarded as a process-specific parameter that allows us to classify ecohydrological systems based on chemical fate. When $N_E \sim O(1)$, as was calculated under pH 7, the balance between transport and reaction is critical and the system will be sensitive to shifts in hydrological regime. When $N_E \ll O(1)$, as was calculated under pH 4, the system will not be sensitive to shifts in hydrological regime.

3.4 Case II: surface water – groundwater exchange

The advective recharge of oxygenated surface waters into Fe(II)-rich groundwater is very common in many riparian systems under so-called losing conditions. While the majority of these systems are pH neutral, wetlands affected by acid sulphate soils (Johnston et al., 2011) and mining lakes (Fleckenstein et al., 2009) may lose acidic water to groundwater.

Again under this scenario, the characteristic length scale is not physically constrained, so we can estimate the length scales over which the O_2 concentration has been decreased by 10 %. The Fe(II) boundary conditions are selected as in Case I. $\Delta x_{10\,\%}$ can be now calculated by using Eqs. (11) and (23) as

$$\Delta x_{10\,\%} = U_x \tau_\mathrm{r} N_\mathrm{E}, \tag{30}$$

Both N_E and exposure timescales, τ_E, are the same as in case I. However the distance from the riparian zone over which 10 % of O_2 is consumed differs from Case I and is 6×10^{-3} m at pH 7, and 5×10^{1} m at pH 4. In other words, after 50 m of flow across a riparian zone at pH 4 the system would still be close to oxygen saturation, allowing O_2 consuming reactions.

To calculate Pe numbers we can use Eq. (18). In porous-media flow, D_eff becomes a scale-dependent dispersion coefficient, which can be estimated from the dispersivity, α, of the aquifer into which the lake water penetrates; see Eq. (18). We get $\alpha_i = 1 \times 10^{-5}$ m and $D_\mathrm{eff} = 1 \times 10^{-1}\ \mathrm{m^2\,s^{-1}}$ for pH 7 and $\alpha_i = 6.4$ m and $D_\mathrm{eff} = 6 \times 10^{-5}\ \mathrm{m^2\,s^{-1}}$ for pH 4. Thus at pH 7, i.e. within the short distance of 6 mm, no dispersion occurs. The corresponding Pe ranges from 2×10^{-3} at pH 7 (indicating advective transport through the O_2 containing layer) to 1.1×10^{-1} at pH 4 (indicating some dispersive effects during transport).

3.5 Case III: temporarily disconnected systems

Floodplain wetlands and playas frequently become temporarily disconnected from surface and sub-surface water flow pathways. In Western Australia, groundwater-fed wetlands affected by acid sulphate soils, fill with Fe(II)-rich groundwater which is then exposed to O_2 (Nath et al., n.d.). Seasonal lowering of the groundwater table disconnects the wetlands from the source of Fe(II), and its subsequent oxidation via ongoing exposure to O_2 is controlled by the disconnection timescale, τ_D. Depending on the buffering capacity of the wetland mineralogy, both acidic and neutral conditions can be observed.

Under this scenario, the characteristic length and time scales are physically constrained. If we assume a typical $\tau_D \sim 100$ days ($\sim 10^7$ s), then using Eq. (24), we estimate the extent of Fe(II) oxidation as 100 % at pH 7 and 1 % at pH 4. The differences between Fe(II) oxidation at the different pHs can also be demonstrated by the non-dimensional number, N_E. Using (23), N_E is 5×10^3 at pH 7 (indicating the disconnection time scale provides sufficient exposure opportunity for the reaction to proceed) and 5×10^{-3} at pH 4 (indicating that the disconnection time scale does not provide enough time for the reaction to proceed).

Again, N_E can be regarded as a process-specific parameter that allows us to classify ecohydrological systems based on chemical fate. When $N_E \gg O(1)$, as was calculated under pH 7, the system will be sensitive to changes in hydrological regime; any increase in isolation timescale will cause an increase in chemical reaction. When $N_E \ll O(1)$, as was calculated under pH 4, the system will not be sensitive to shifts in hydrological regime.

4 Conclusions

4.1 Water management

We have shown that the new non-dimensional number, N_E, can be used to classify the ecohydrological systems, their potential for material transfer and their sensitivity to shifts in hydrological regimes. N_E can also be used to calculate the distance of reactive zones. Extending this idea, Eqs. (28) and (29) can be directly applied for water management purposes. For example, we propose that the width of a riparian zone in which no agricultural activity is allowed, can be calculated using the framework presented here, to ensure minimal nitrate export from groundwater to the river. The stipulated riparian width might correspond to the lengthscale, Δx, that is required to remove e.g. 90 % of the nitrate that has infiltrated to groundwater from agricultural land. To some extent the "50 day-line" typically applied to constrain drinking water zones implicitly uses this concept already.

4.2 Competiveness of reactions

We have shown that N_E numbers are reaction specific; the corresponding spatial scales are also reaction dependent and not necessarily controlled by geomorphology. In a first approach, we can therefore argue that low N_E implies ample opportunity for other reactions to proceed within a certain hydrological element. Inversely, high N_E implies predominance of the biogeochemical process of interest. N_E is thus a reaction-specific parameter that allows us to compare the effectiveness of different material processing reactions across a certain temporal (τ_E) or spatial (Δx) scale.

More generally, lower N_E implies a lower competiveness of a specific reaction. In the examples discussed above, the oxidation of Fe(II) is much more competitive at pH 7 than at pH 4. In this case competiveness is clearly controlled by the large differences in k'. However, N_E is of course also affected by the exposure timescale. We therefore propose that for a given system, N_E can be used as a general parameter to compare competiveness between different reactions of interest.

Competiveness of redox reactions is typically discussed in terms of thermodynamic arguments, for example the gain in free energy, ΔG_f, obtained from oxidation of organic matter (Huston, 1994). This concept works very well in diffusion controlled systems such as the sediment porewaters of the ocean or deep lakes. Attempts to adapt this concept to groundwater systems have been problematic. Rather, zones of intensive redox activity are observed to be spatially distributed or located at plume fringes (see e.g. Prommer et al., 2006). Considering that the rate of a reaction is proportional to ΔG_f, thermodynamics is also related to the reaction timescale. Considering further that all dissolved substances have appropriately the same diffusion coefficients and that their residence times under diffusion controlled conditions are approximately identical, then it becomes clear that ΔG_f and N_E are interrelated predictors for competiveness under diffusion-controlled (or well-mixed) conditions.

Under advection or dispersion controlled conditions however, the timescale of exposure along a flow path, i.e. the exposure spatial scale, varies strongly depending on external forcing. Of course the flow paths and therefore exposure timescales may be distributed in space, similar to residence times, and this spatial variability will give rise to a patchwork of N_E values, paralleling the concept of "residence time distributions", with each controlled by specific biogeochemical regimes. Under these conditions, as for diffusion-controlled conditions, chemical competiveness becomes dependent on the exposure time; N_E therefore can be used as a general parameter to compare competiveness under all regimes.

4.3 Ecological consequences

Hydrological systems transition, according to external forcing, between two or three of the regimes outlined above. In particular, systems in Regime III, i.e. the disconnected state, will intermittently transition to Regime I and/or II. Estimates of N_E for Regime III systems when compared to N_E for their hydrologically connected counterparts, provide a framework for predicting the biogeochemical and ecological significance of the disconnection period (Table 4).

An example of transition between regimes is the drying and re-wetting cycles induced by oscillating groundwater tables. Typically these cycles are accompanied by transitions between anoxic and oxic conditions, and changes in biogeochemical boundaries. One consequence of such cycling would be the export of products under a high groundwater table (Regime I or II) that have accumulated under a lowering groundwater table (Regime III). We speculate that the extent to which a system is resilient to such transitions is likely controlled by the relative rates at which a microbial community can respond to environmental change or disturbance (i.e. k') and the exposure timescale of the relevant state. Hence, reactions with $N_\mathrm{E} \gg 1$ are able to process the previously accumulated reactants can be expected to be beneficial in preventing export of such products.

So far we have constrained ourselves to considering specific biogeochemical reactions occurring within and across elements of the hydrological cycle. Finally, we broaden our focus to consider landscape-scale ecological processes and their characteristic time scales. If we set the biogeochemical rate, k', to be analogous to population growth rate and the isolation timescale, τ_I, to be analogous to the reciprocal of the disturbance frequency then the two timescales in Regime III, see Eq. (22), have direct analogues to concepts in terrestrial ecology. The ratio of the population growth rate and the disturbance frequency, i.e. N_E in our framework, impacts on biodiversity and ecological resilience (Huston, 1994).

Of particular interest is the conceptual understanding that community biodiversity is maximal when there is a balance between population growth rate (or biogeochemical reaction rate) and disturbance frequency, i.e. when $N_\mathrm{E} \sim \mathrm{O}(1)$ (Fig. 6). The biodiversity in turn affects ecosystem resilience (Gunderson, 2000; Scheffer and Carpenter, 2003) however the stability space within which ecosystem resilience operates is determined by external factors, and has been related to characteristic spatial or temporal scales of external forcing (Scheffer and Carpenter, 2003). We have shown above that N_E are process specific so the question arises whether we can describe the resilience of a system in terms of its N_E distribution. We speculate that highest resilience may be expected under conditions where all processes operate at comparable N_E values, i.e. mean value of $N_{\mathrm{E},i} \sim \mathrm{O}(1)$.

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Table 1. Different preferred modes of investigation used for different scales of elements in hydrological systems.

	Soil pore scale	Superficial aquifer scale	Vegetation scale	Riparian scale	Catchment scale
Vertical length scale	O(mm-cm)	O(m-10m)	O(10 cm–1 m)	O(10 cm–1 m)	O(1–10 m)
Horizontal length scale	O(mm-cm)	O(10 m–100 km)	O(10 cm–1 m)	O(10–100 m)	O(10–1000 km)
Timescale	O(minutes)	O(days-decades)	O(mins-seasons)	O(hrs-years)	O(days-decades)
Typical modes of investigation	Laboratory Numerical	Numerical Field	Laboratory Field	Field Fumerical	Numerical Field

Table 2. Pseudo-first order rate constants, k', and reaction timescales, τ_R, for the oxidation of iron(II) under different pH conditions.

pH	(min^{-1})	(s)
7	3×10^{-2}	2×10^{3}
4	3×10^{-8}	2×10^{9}

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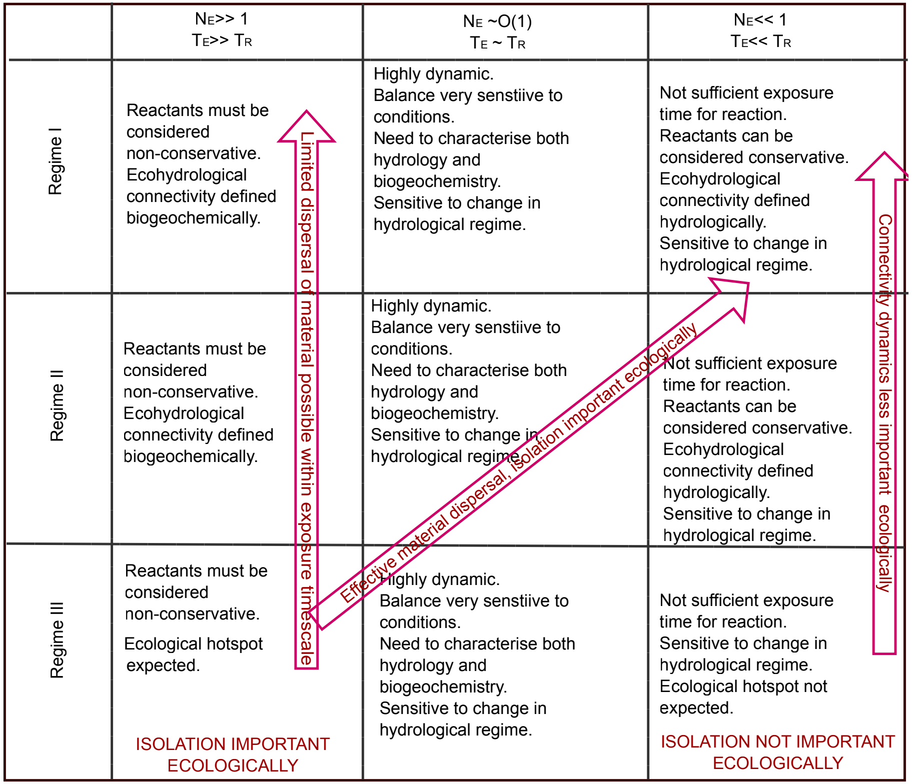
Table 3. Estimates of relevant parameters and non-dimensional numbers at pH 4 and 7.

pH	Fe(II) in porewater (mmol l^{-1})	N_E	$\Delta x_{10\,\%}$ (m)	(s)	Pe
7	0.1	0.4	8×10^{-4}	7×10^{2}	1.2×10^{3}
4	10	0.003	8×10^{-2}	6×10^{6}	1.3×10^{1}

Table 4. A summary of system characteristics under the different regimes and as a function of N_E. Note that once elements become connected after a period of disconnection, it is possible for them to rapidly move across regimes. The balance between disconnection timescales, reaction timescales and connected transport timescales determines the ecological signficance of the disconnection/isolation period.



	$N_E \gg 1$ $T_E \gg T_R$	$N_E \sim O(1)$ $T_E \sim T_R$	$N_E \ll 1$ $T_E \ll T_R$
Regime I	Reactants must be considered non-conservative. Ecohydrological connectivity defined biogeochemically.	Highly dynamic. Balance very senstiive to conditions. Need to characterise both hydrology and biogeochemistry. Sensitive to change in hydrological regime.	Not sufficient exposure time for reaction. Reactants can be considered conservative. Ecohydrological connectivity defined hydrologically. Sensitive to change in hydrological regime.
Regime II	Reactants must be considered non-conservative. Ecohydrological connectivity defined biogeochemically.	Highly dynamic. Balance very senstiive to conditions. Need to characterise both hydrology and biogeochemistry. Sensitive to change in hydrological regime.	Not sufficient exposure time for reaction. Reactants can be considered conservative. Ecohydrological connectivity defined hydrologically. Sensitive to change in hydrological regime.
Regime III	Reactants must be considered non-conservative. Ecological hotspot expected. ISOLATION IMPORTANT ECOLOGICALLY	Highly dynamic. Balance very senstiive to conditions. Need to characterise both hydrology and biogeochemistry. Sensitive to change in hydrological regime.	Not sufficient exposure time for reaction. Sensitive to change in hydrological regime. Ecological hotspot not expected. ISOLATION NOT IMPORTANT ECOLOGICALLY

Limited dispersal of material possible within exposure timescale

Effective material dispersal, isolation important ecologically

Connectivity dynamics less important ecologically

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Table A1. Notation

α_i	Dispersivity (m)
α_n	Fourier cosine coefficients
β_n	Fourier sine coefficients
$[B]$	Concentration of chemical B (mmol m^{-3})
$[B]_{\mathrm{max}}$	Maximum expected concentration of B (mmol m^{-3})
$[B]_*$	Final concentration of B (mmol m^{-3})
$[B]_0$	Initial concentration of B (mmol m^{-3})
D_{eff}	Effective diffusion/dispersion coefficient ($\mathrm{m}^2\,\mathrm{s}^{-1}$)
Da	Damköhler number
k	Second order rate constant ($\mathrm{mmol}^{-1}\,\mathrm{m}^3\,\mathrm{s}^{-1}$)
k'	Pseudo-first-order rate constant (s^{-1})
k_{abio}	rate constant for the oxidation of Fe(II) (s^{-1})
k_{D}	Disturbance frequency (s^{-1})
K_{S}	Substrate saturation constant (mmol m^{-3})
J	Fickian flux (mmol $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$)
n	Summation index
N_{E}	Exposure non-dimensional number
Pe	Peclet number
P_{O_2}	Partial pressure of oxygen (atm)
q	Specific consumption rate of the reactant B (mmol $\mathrm{cell}^{-1}\,\mathrm{day}^{-1}$)
q_{max}	Maximum specific substrate consumption rate (mmol $\mathrm{cell}^{-1}\,\mathrm{day}^{-1}$)
t	Time (s)
τ_{D}	Disconnection or isolation timescale (s)
τ_{T}	Transport timescale (s)
τ_{R}	Reaction timescale (s)
τ_{E}	Exposure timescale (s)
μ_i	Mean velocity in the i-direction ($\mathrm{m\,s}^{-1}$)
U_x	Mean velocity in the x-direction ($\mathrm{m\,s}^{-1}$)
x_i	Distance in the i-direction (m)
Δx_i	Characteristic length scale over which transport processes are operating (m)
$\Delta x_{10\,\%}$	Distance required for a 10 % change in concentration of B (m)

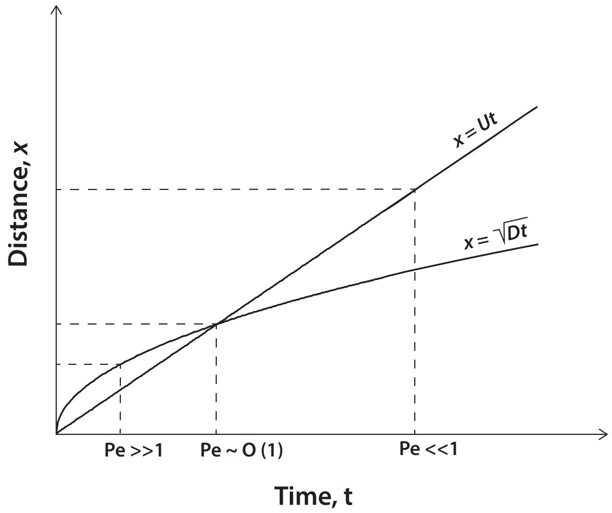


Fig. 1. The relationship between characteristic length, Δx, and time, t, scales under varying Peclet number conditions. Under Pe $\ll$ 1, advective processes dominate (Regime I); under Pe $\gg$ 1 diffusive processes dominate (Regime II); when Pe $\sim$ O(1), the characteristic length and time scales are set where the advection and diffusive lines intersect.

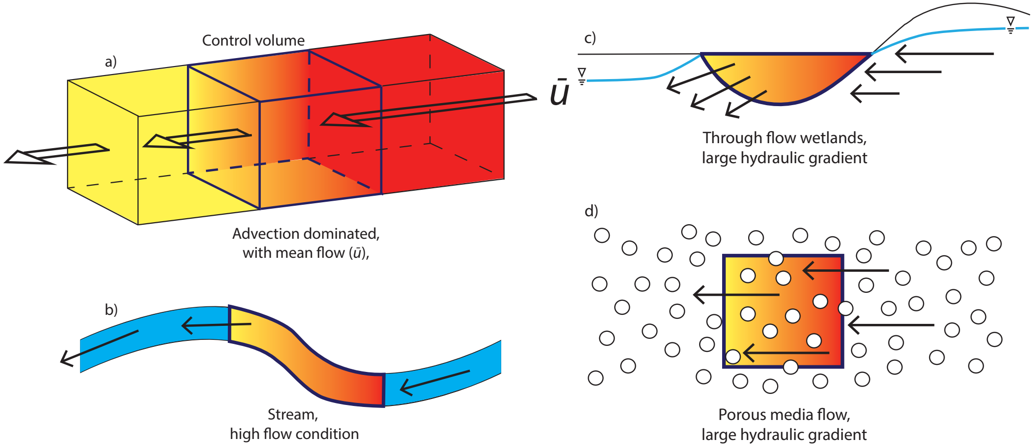
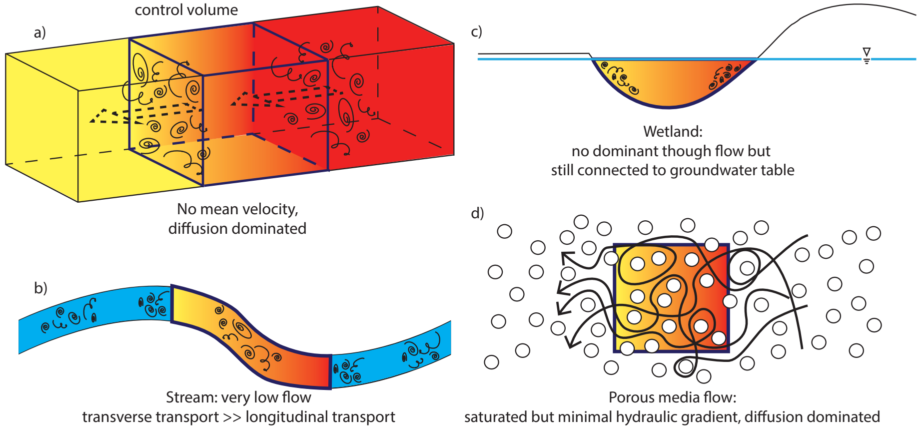


Fig. 2. Regime I. **(a)** Transport and fluxes of chemical *B* across hydrologically or hydraulically connected elements are dominated by advection. Examples of this regime are a river under high flow conditions **(b)**, a wetland with groundwater throughflow under a large hydraulic gradient **(c)** and porous media flow under a large hydraulic gradient **(d)**.



No mean velocity,
diffusion dominated

Stream: very low flow
transverse transport >> longitudinal transport

Wetland:
no dominant though flow but
still connected to groundwater table

Porous media flow:
saturated but minimal hydraulic gradient, diffusion dominated

Fig. 3. Regime II. **(a)** Transport and fluxes of chemical *B* across hydrologically or hydraulically connected elements are dominated by diffusion. Examples of this regime are a river under very low flow conditions, where for example transverse transport exceeds longitudinal transport **(b)**, a wetland at equilibrium with the local groundwater **(c)** and porous media flow under minimal hydraulic gradient **(d)**.

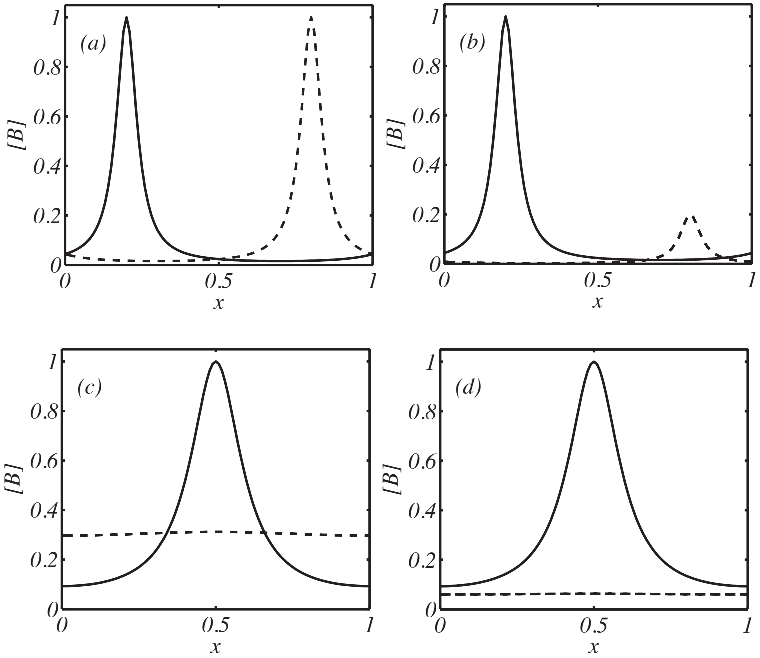


Fig. 4. Example profiles of $[B]$ from the model problem for small (solid line) and large (dashed line) times illustrating the evolution of $[B]$ under different conditions: **(a)** $\mathrm{Pe} \ll 1$ and $\mathrm{Da} \ll 1$, **(b)** $\mathrm{Pe} \ll 1$ and $\mathrm{Da} \gg 1$, **(c)** $\mathrm{Pe} \cong 1$ and $\mathrm{Da} \ll 1$, **(d)** $\mathrm{Pe} \cong 1$ and $\mathrm{Da} \gg 1$. Note that in this figure, B and x have been normalized for illustrative purposes.

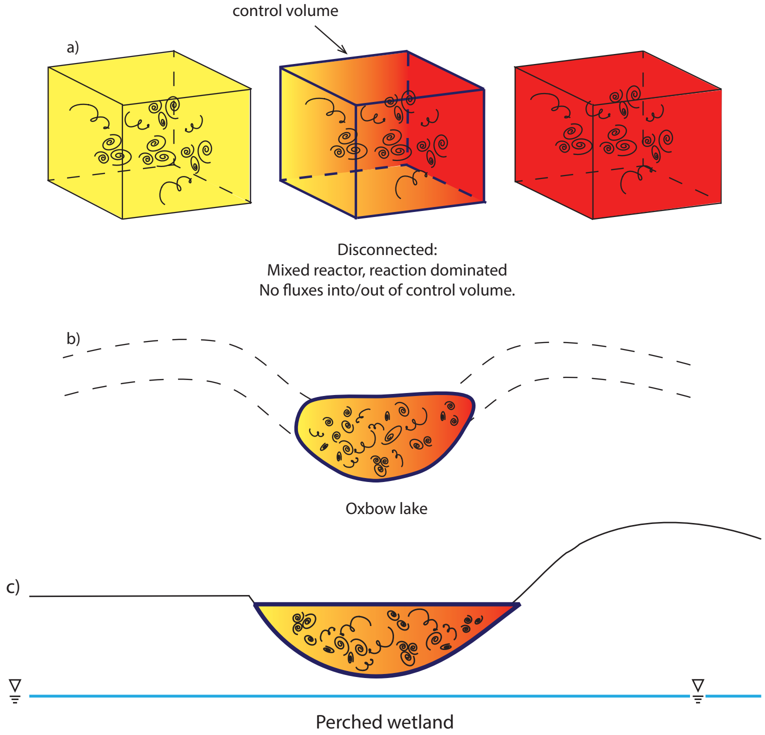


Fig. 5. Regime III. **(a)** The elements of interest are hydrologically and hydraulically disconnected. Examples of this regime are an oxbow lake which has disconnected from its river **(b)**, and a wetland perched above the groundwater table **(c)**.

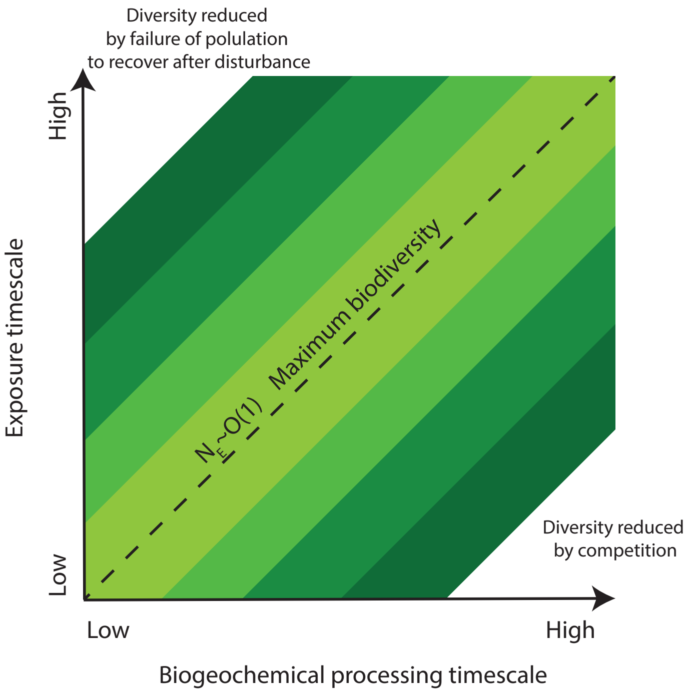


Fig. 6. The relationship between N_E and biodiversity. This is likely to hold true for microbial diversity as well as landscape-scale biodiversity. Modified from (Huston, 1994).