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Entropy-based critical reaction time for mixing-controlled reactive transport

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Abstract

Entropy-based metrics, such as the dilution index, have been proposed to quantify dilution and reactive mixing in solute transport problems. In this work, we derive the transient advection dispersion equation for the entropy density of a reactive plume. We restrict our analysis to the case where the concentration distribution of the transported species is Gaussian and we observe that, even in case of an instantaneous complete bimolecular reaction, dilution caused by dispersive processes dominates the entropy balance at early times and results in the net increase of the entropy density of a reactive species. Successively, the entropy of the reactant decreases until it vanishes. We show the existence of a unique critical value of dilution, which corresponds to the complete consumption of one of the reactants. This critical dilution index is independent of advective and dispersive processes, and depends only on the dimensionality of the problem, on the stoichiometry of the reaction and on the initial concentrations of the reactants. Furthermore, we provide simple analytical expressions to compute the critical reaction time, i.e., the time at which the critical dilution index is reached, for selected flow configurations. Our results show that, differently from the critical dilution index, the critical reaction time depends on solute transport processes such as advection and hydrodynamic dispersion.

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Highlights

- Derivation of the transient transport equation for the entropy of a reactive solute
- Definition of the concepts of critical reaction time and dilution index, and analytical solutions are proposed for their calculations
- The critical reaction time depends on mixing processes, whereas the critical dilution index does not

1. Introduction

The Shannon entropy has been successfully applied to describe dilution during transport of conservative tracers and it is generally expressed in terms of dilution index, which essentially quantifies the effective volume of a solute slug [Kitanidis, 1994; Cao and Kitanidis, 1998; Tartakovsky et al., 2009; Dentz et al., 2011; Rolle et al., 2013; Schneider et al., 2013; Rolle and Kitanidis, 2014; Porta et al., 2015; Ben Neriah and Paster, 2016; Boon, 2016]. A modified version of the dilution index, the flux-related dilution index, has been proposed to quantify dilution as volumetric flux carrying the solute mass flux, and has been mostly used to quantify plume dilution in the case of continuous injection [Rolle et al., 2009; Chiogna et al., 2011; Muniruzzaman et al., 2014; Cirpka et al., 2015; Ye et al., 2015a and b].

Linking the concept of dilution index with reactive mixing has been attempted by Chiogna et al., [2011 and 2012] considering steady-state flow and transport conditions; however, the entropy dynamics of conservative and reactive species has not been explored, yet, for transient transport problems. Transport and mixing exert an important control for a wide variety of subsurface reactive processes, including mineral precipitation and dissolution reactions [Molins et al. 2012; Yoon et al., 2012; Li et al., 2014], redox processes [Rolle et al., 2008, Bjerg et al., 2011] and degradation of organic contaminants at the fringe of groundwater plumes [Bauer et al., 2009; Prommer et al., 2009, Essaid et al., 2015]. For some notable cases of mixing-controlled reactions (e.g., acid-base

reactions, aerobic degradation of some organic compounds), the reactive transport problem can be solved starting from the concentration distribution of a fictitious conservative species [e.g., De Simoni et al., 2005; Luo et al., 2008; Sanchez-Villa et al., 2007; Engdahl et al., 2013]. Such species, can be defined as the mixing ratio, representing the volumetric fraction of the source water in the mixture with the ambient solution. A procedure, based on simple algebraic equations, allows computing the reactants and products concentrations based on the distribution of the conservative mixing ratio [e.g., Cirpka and Valocchi, 2007; Cirpka et al., 2012; Chiogna and Bellin, 2013; Avesani et al., 2016].

In this work, we investigate the entropy evolution during reactive transport in porous media and we derive the transient transport equation for the entropy of a reactive solute. We focus on the case of an instantaneous complete bimolecular reaction and we show that, if the mixing ratio has a Gaussian distribution, there is a unique critical value of the dilution index, quantifying a critical amount of mixing, necessary to completely consume a reactive species. This quantity, defined as the critical dilution index, is independent of mixing processes, but depends only on the stoichiometric coefficients of the reaction, on the initial concentration of the reactants and on the dimensionality of the problem. We consider cases where the solution of the advection dispersion equation for the mixing ratio leads to a Gaussian concentration distribution, since such cases have been thoroughly examined in recent literature studies focusing on mixing [Bolster et al., 2011; de Barros et al., 2012; de Barros et al., 2015], and allow quantifying the dilution index with simple analytical solutions [Kitanidis, 1994]. We analyze three cases of mixing-controlled reactive transport in: (i) uniform flow, (ii) shear flow, (iii) complex flow including shearing, vorticity and stretching, and we derive simple analytical expressions to compute the critical reaction time, i.e., the time required to reach the critical dilution index.

2. Entropy transport equation

Reactive solute transport in geophysical flows depends on the complex interplay between reaction kinetics and physical transport processes [e.g. Steefel and Lichtner, 2005; Hester et al., 2017; Li et al., 2017]. For solute transport in such systems an entropy balance equation can be derived. Here we exemplify the methodology for solute transport in saturated porous media, for which the governing advection-dispersion-reaction equation reads as [Bear, 1972]:

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (\mathbf{v}C_i) - \nabla \cdot (\mathbf{D}\nabla C_i) = r_i \quad (1)$$

where C_i [ML^{-3}] is the concentration of a reactive species i , t is time, \mathbf{v} [LT^{-1}] is the velocity vector, \mathbf{D} [L^2T^{-1}] is the dispersion tensor and r_i [$\text{ML}^{-3}\text{T}^{-1}$] is the reaction term.

In order to derive the transport equation for the entropy of a reactive solute under transient conditions we follow an approach similar to the one proposed by Chiogna et al. [2012] for steady-state transport.

We start by defining the operator \mathbf{L} as:

$$\mathbf{L} = \frac{\partial}{\partial t} + \nabla \mathbf{v} - \nabla \cdot (\mathbf{D}\nabla) \quad (2)$$

and the quantity s as:

$$\begin{aligned} s &= f(p_i(\mathbf{x}, t)) = -p_i(\mathbf{x}, t) \ln(p_i(\mathbf{x}, t)) \\ &= -\frac{C_i(\mathbf{x}, t)}{\int_V C_i(\mathbf{x}, t) dV} \ln\left(\frac{C_i(\mathbf{x}, t)}{\int_V C_i(\mathbf{x}, t) dV}\right) \end{aligned} \quad (3)$$

where $p_i(\mathbf{x}, t)$ [L^{-3}] is the concentration normalized by the total mass of the solute i , i.e., the probability distribution of the location of a tagged particle of the solute i at time t [Kitanidis, 1994].

For simplicity, and following the terminology used in other literature studies [e.g., Liu, 2007; Tehseen and Broadbridge, 2012], in this manuscript we denote s as Shannon entropy density.

Notice that for a reactive transport problem, C_i satisfies the transport equation (Equation 1), and

considering a non-zero reaction term, the integral $\int_V C_i dV$ is not constant in time. This term will decrease if C_i is the concentration of a reactant that is consumed upon reaction and will increase if C_i is the concentration of a reaction product.

Applying the operator \mathbf{L} to the function f , assuming divergence free flow, and then using the chain rule of differentiation for the different terms, we obtain:

$$\begin{aligned} \frac{\partial f(p_i(\mathbf{x}, t))}{\partial t} &= \frac{\partial f(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} \frac{\partial p_i(\mathbf{x}, t)}{\partial t} \\ \mathbf{v} \cdot \nabla f(p_i(\mathbf{x}, t)) &= \frac{\partial f(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} \mathbf{v} \cdot \nabla p_i(\mathbf{x}, t) \\ \nabla \cdot (\mathbf{D}\nabla (f(p_i(\mathbf{x}, t)))) &= \nabla \cdot \left(\mathbf{D} \frac{\partial f(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} \nabla p_i(\mathbf{x}, t) \right) = \\ &= \frac{\partial f(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} \nabla \cdot (\mathbf{D}\nabla p_i(\mathbf{x}, t)) \\ &\quad + \frac{\partial^2 f(p_i(\mathbf{x}, t))}{\partial (p_i(\mathbf{x}, t))^2} \nabla(p_i(\mathbf{x}, t))^T \mathbf{D}\nabla p_i(\mathbf{x}, t) \end{aligned} \quad (4)$$

Grouping the terms with the partial derivative of f with respect to p we obtain:

$$\mathbf{L}(f(p_i(\mathbf{x}, t))) = \frac{\partial f(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} (\mathbf{L}(p_i(\mathbf{x}, t))) - \frac{\partial^2 f(p_i(\mathbf{x}, t))}{\partial (p_i(\mathbf{x}, t))^2} \nabla(p_i(\mathbf{x}, t))^T \mathbf{D}\nabla p_i(\mathbf{x}, t) \quad (5)$$

Using the definition of $f(p_i(\mathbf{x}, t))$ given in Equation 3, then:

$$\mathbf{L}(f(p_i(\mathbf{x}, t))) = \frac{\partial f(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} (\mathbf{L}(p_i(\mathbf{x}, t))) + \frac{1}{p_i(\mathbf{x}, t)} \nabla(p_i(\mathbf{x}, t))^T \mathbf{D}\nabla p_i(\mathbf{x}, t) \quad (6)$$

in fact:

$$\frac{\partial^2 f(p_i(\mathbf{x}, t))}{\partial (p_i(\mathbf{x}, t))^2} = \frac{\partial^2 -p_i(\mathbf{x}, t) \ln(p_i(\mathbf{x}, t))}{\partial (p_i(\mathbf{x}, t))^2} = -\frac{\partial}{\partial (p_i(\mathbf{x}, t))} (\ln(p_i(\mathbf{x}, t)) + 1) = -\frac{1}{p_i(\mathbf{x}, t)} \quad (7)$$

The first term of the right hand side of the transport equation of the entropy density (Equation 5) entails the information about the reaction of C_i , namely:

$$\begin{aligned} \mathbf{L}(p_i(\mathbf{x}, t)) &= \frac{\partial p_i(\mathbf{x}, t)}{\partial C_i(\mathbf{x}, t)} \left(\mathbf{L}(C_i(\mathbf{x}, t)) \right) - \frac{\partial^2 p_i(\mathbf{x}, t)}{\partial (C_i(\mathbf{x}, t))^2} \nabla(C_i(\mathbf{x}, t))^T \mathbf{D} \nabla C_i(\mathbf{x}, t) = \\ &= \frac{\partial p_i(\mathbf{x}, t)}{\partial C_i(\mathbf{x}, t)} r_i - \frac{\partial^2 p_i(\mathbf{x}, t)}{\partial (C_i(\mathbf{x}, t))^2} \nabla(C_i(\mathbf{x}, t))^T \mathbf{D} \nabla C_i(\mathbf{x}, t) \end{aligned} \quad (8)$$

Summarizing, Equation 9 represents the transport equation for the entropy density for a reactive transport problem:

$$\begin{aligned} &\mathbf{L}(-p_i(\mathbf{x}, t) \ln(p_i(\mathbf{x}, t))) \\ &= \frac{\partial p_i(\mathbf{x}, t) \ln(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} \left(\frac{\partial p_i(\mathbf{x}, t)}{\partial C_i(\mathbf{x}, t)} r_i \right. \\ &\quad \left. - \frac{\partial^2 p_i(\mathbf{x}, t)}{\partial (C_i(\mathbf{x}, t))^2} \nabla(C_i(\mathbf{x}, t))^T \mathbf{D} \nabla C_i(\mathbf{x}, t) \right) + \frac{1}{p_i(\mathbf{x}, t)} \nabla(p_i(\mathbf{x}, t))^T \mathbf{D} \nabla p_i(\mathbf{x}, t) \end{aligned} \quad (9)$$

where we substituted Equation 8 in Equation 6, and we replaced $\mathbf{L}(C_i)$ with r_i , based on the governing reactive transport equation (Equation 1).

The second term of the right hand side of Equation 9 depends only on the physical process of hydrodynamic dispersion and represents a source term for the entropy density. In fact, p is a probability density and therefore $p_i(\mathbf{x}, t) \geq 0$, the elements of \mathbf{D} are all positive, and hence $\nabla(p_i(\mathbf{x}, t))^T \mathbf{D} \nabla p_i(\mathbf{x}, t) \geq 0$. The first term on the right hand side of Equation 9 represents the contribution of reactive mixing and can act as the only possible sink term for the entropy. Notice

also that the asymptotic behavior for $r_i \rightarrow 0$ is consistent with the conservative case [Kitanidis, 1994]. In fact, considering the term that is multiplied by the second derivative of $p_i(\mathbf{x}, t)$ with respect to C_i , and given that the probability density p is defined as $p_i(\mathbf{x}, t) = \frac{C_i(\mathbf{x}, t)}{\int_V C_i(\mathbf{x}, t) dV}$, if $r_i \rightarrow 0$

the mass of the reactant tends to a constant (i.e., conservative tracer case) and hence its second derivative is zero. Therefore, the reactive mixing term vanishes since:

$$\begin{aligned} & \lim_{r_i \rightarrow 0} \left(-\frac{\partial p_i(\mathbf{x}, t) \ln(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} \left(\frac{\partial p_i(\mathbf{x}, t)}{\partial C_i(\mathbf{x}, t)} r_i - \frac{\partial^2 p_i(\mathbf{x}, t)}{\partial (C_i(\mathbf{x}, t))^2} \nabla(C_i(\mathbf{x}, t))^T \mathbf{D} \nabla C_i(\mathbf{x}, t) \right) \right) \\ &= \lim_{r_i \rightarrow 0} \left(-\frac{\partial p_i(\mathbf{x}, t) \ln(p_i(\mathbf{x}, t))}{\partial p_i(\mathbf{x}, t)} \left(\frac{\partial p_i(\mathbf{x}, t)}{\partial C_i(\mathbf{x}, t)} r_i \right. \right. \\ & \quad \left. \left. - \frac{\partial^2 p_i(\mathbf{x}, t)}{\partial (C_i(\mathbf{x}, t))^2} \nabla(C_i(\mathbf{x}, t))^T \mathbf{D} \nabla C_i(\mathbf{x}, t) \right) \right) = 0 \end{aligned} \quad (10)$$

and Equation 9 converges to the entropy transport equation proposed by Kitanidis [1994] for a conservative solute:

$$\mathbf{L}(-p_i(\mathbf{x}, t) \ln p_i(\mathbf{x}, t)) = \frac{1}{p_i(\mathbf{x}, t)} \nabla(p_i(\mathbf{x}, t))^T \mathbf{D} \nabla(p_i(\mathbf{x}, t)) \quad (11)$$

3. Properties of a Gaussian concentration distribution: dilution index and critical dilution index

3.1 Conservative transport

We consider now the case in which the concentration distribution of a conservative solute is Gaussian. This case represents the solution of Equation 1 for an instantaneous point injection occurring at $t=0$ and at $\mathbf{x}=0$ of a conservative quantity X , considering constant velocity and dispersion coefficients:

$$X(\mathbf{x}, t) = \frac{1}{\det(\mathbf{k})^{1/2} (2\pi)^{n/2}} \exp\left(-\frac{1}{2}(\mathbf{x} - \mathbf{vt})^T \mathbf{k}^{-1} (\mathbf{x} - \mathbf{vt})\right) \quad (12)$$

where \mathbf{k} is the covariance matrix and n is the dimension of the domain.

The peak, i.e. the maximum value, of a Gaussian concentration distribution is given by:

$$X_{peak} = \frac{1}{\det(\mathbf{k})^{1/2} (2\pi)^{n/2}} \quad (13)$$

The peak concentration therefore depends only on the covariance matrix of the concentration distribution and all Gaussian plumes with a given peak concentration have the same value of $\det(\mathbf{k})$.

The Shannon entropy S [Shannon, 1948] is the spatial integral of the entropy density s (Equation 3) and for a Gaussian distribution is [Kitanidis, 1994]:

$$S = -\ln((2\pi e)^{n/2} \det(\mathbf{k})^{1/2}) \quad (14)$$

The dilution index, defined as the exponential of Equation 14, therefore, can be expressed as a function of the peak concentration by substituting Equation 13 in Equation 14:

$$E = (2\pi e)^{n/2} \frac{1}{(2\pi)^{n/2} X_{peak}} = \frac{e^{n/2}}{X_{peak}} \quad (15)$$

The dilution index has units of $[L^n]$ where n is the spatial dimension of the problem (i.e., $n=1, 2$ or 3). Notice that the Gaussian distribution is the maxentropic distribution, i.e., it has the maximum entropy (and therefore the maximum dilution) for a given zero, first and second moment of the concentration distribution [Kitanidis, 1994].

3.2 Reactive transport

Considering a reactive transport system in which a mixing-controlled chemical reaction $aA + bB \rightarrow cC$ occurs, and assuming the same diffusive/dispersive properties of reactants and products, it is possible to compute the spatio-temporal distribution of the reacting species from the concentration of the conservative mixing ratio. For the case of an instantaneous complete bimolecular reaction

(i.e., $C_A C_B = 0$), the reactive species A injected in a domain in which only the reactant B is present, can exist as long as $X < X_{crit}$, where $X_{crit} = aB_{amb}/(aB_{amb} + bA_{in})$, a and b are the stoichiometric coefficients of A and B respectively, B_{amb} is the ambient concentration of B , and A_{in} is the inlet concentration of A [Cirpka and Valocchi, 2007]. Therefore, when the peak concentration of the mixing ratio reaches the critical value, $X_{peak} = X_{crit}$, the reactant A is completely consumed and no reaction can occur anymore.

Considering the entropy for this reactive transport problem, we can interpret Equation 15 as the amount of dilution required to completely consume reactant A , i.e. what we define as the critical dilution index E_{crit} . This quantity only depends on the dimensionality of the system, on the stoichiometry of the reaction and on the initial concentrations of the reactants A and B . In fact, substituting the definition of the critical mixing ratio X_{crit} in Equation 15 we obtain:

$$E_{crit} = \frac{e^{n/2}}{X_{crit}} = e^{n/2} \frac{bA_{in} + aB_{amb}}{aB_{amb}} \quad (16)$$

We can now define a new important quantity, the critical reaction time t_{crit} , which is the time at which the entropy reaches the value of the critical dilution index, $E(t_{crit}) = E_{crit}$, and the reactant A is completely consumed. As will be shown in the following examples, the critical reaction time is influenced by the complexity of the flow field and by the matrix variance describing the mixing processes.

Notice that the critical dilution index is computed based on the maxentropic Gaussian distribution. Therefore, the critical reaction time t_{crit} is the time required to reach a given peak concentration for an optimally mixed system.

4. Illustrative examples for the critical dilution index and the critical reaction time

In this section we consider three illustrative examples of mixing-controlled reactive transport in two dimensional flow fields with increasing complexity, for which we analyze the entropy evolution and we derive analytical expressions to compute the critical dilution index and the critical reaction time.

We consider a uniform flow field, a shear flow field and a complex flow field. The latter two cases have been described by Bolster et al. [2011] and de Barros et al. [2012] and the reader is redirected to those work for more details. Focusing on the entropy analysis for conservative and mixing-controlled reactive transport we have computed the concentration distribution of a conservative tracer introduced instantaneously (Dirac pulse) in two-dimensional unbounded domains. The concentration distribution of the reactive species is computed following the mixing ratio approach of Cirpka and Valocchi [2007]. The analytical solutions for the concentration distributions in the uniform, shear flow and complex topology cases are provided in the studies of Kitanidis [1994], Bolster et al., [2011] and de Barros et al., [2012], respectively.

4.1 Uniform flow

As a first case, we consider uniform flow in an infinite homogeneous porous medium. Under these conditions, the peak concentration of a Dirac pulse for a conservative tracer decreases with time since $\mathbf{k} = 2\mathbf{D}t$ [Kitanidis, 1994]:

$$X_{peak} = (2\pi t)^{-n/2} \det(2\mathbf{D})^{-1/2} \quad (17)$$

Therefore, considering $X_{peak}=X_{crit}$, we can define this critical reaction time as:

$$t_{crit} = \left((2\pi)^{n/2} X_{crit} \det(2\mathbf{D})^{1/2} \right)^{-2/n} \quad (18)$$

The dilution index is a correct measure of plume dilution, which “scales as the peak concentration” [Kitanidis, 1994]. In the case of a Dirac pulse injection in a uniform flow field, the dilution index can be computed as:

$$E(t) = (2\pi et)^{n/2} \det(2\mathbf{D})^{1/2} \quad (19)$$

Substituting now the critical reaction time as defined in Equation (18) into Equation (19), we can show that the value of the dilution index at $t=t_{crit}$ is independent from transport parameters such as the flow velocity and the dispersion coefficient, but depends only on the stoichiometry of the reaction and on the dimensionality of the problem:

$$E(t_{crit}) = ((2\pi)^{n/2} \exp(n/2) \det(2\mathbf{D})^{1/2}) ((2\pi)^{n/2} X_{crit} \det(2\mathbf{D})^{1/2})^{-1} = \frac{\exp(n/2)}{X_{crit}} \quad (20)$$

This is consistent with the general result shown in the previous section (Equation 16).

Always considering the case of the instantaneous release of a solute in an infinite homogeneous domain, we now analyze the time evolution of the dilution index for both a conservative and a reactive species. Figure 1 illustrates the temporal dynamics of the entropy density for a reactive solute (Equation 9) and shows the comparison between the dilution index for conservative (black lines) and reactive (blue lines) species, considering different values for X_{crit} and D (for the sake of simplicity the tensor \mathbf{D} is considered isotropic). Independently of the values of X_{crit} and D used in the four examples shown, we can observe that the shapes of the curves describing the time evolution of the entropy of the conservative and reactive solutes are the same. The entropy of the reactive solute is always framed between the entropy of the conservative species and the line $t=t_{crit}$. Whereas the entropy of a conservative solute increases linearly with time, the entropy of a reactive species shows a non-monotonic temporal behavior, as expected considering the right hand side terms in Equation 9. This is due to the opposite contribution of the mixing and reactive terms in the entropy balance of a reactant (Equation 9). At early times, the entropy of the reactant increases following the trend of the conservative case. This result, obtained for the case of uniform flow, is notable since it shows that at such early times, even in the case of instantaneous reaction kinetics, physical mixing processes clearly dominate the entropy balance. The dilution index trend for a reactant reaches a maximum and then starts decreasing when the reactive processes become

effective enough to reduce the entropy of the reactive solute until $t=t_{crit}$. At that time the reactant is completely consumed, its concentration becomes 0 everywhere in the domain, and its dilution index becomes unity. Increasing values of D translates the frame parallel to the time axis to the left. This means that for the same value of E_{crit} , we obtain smaller critical reaction times as D increases. An increase in X_{crit} translates the frame along the line of the entropy for a conservative solute towards lower values of dilution.

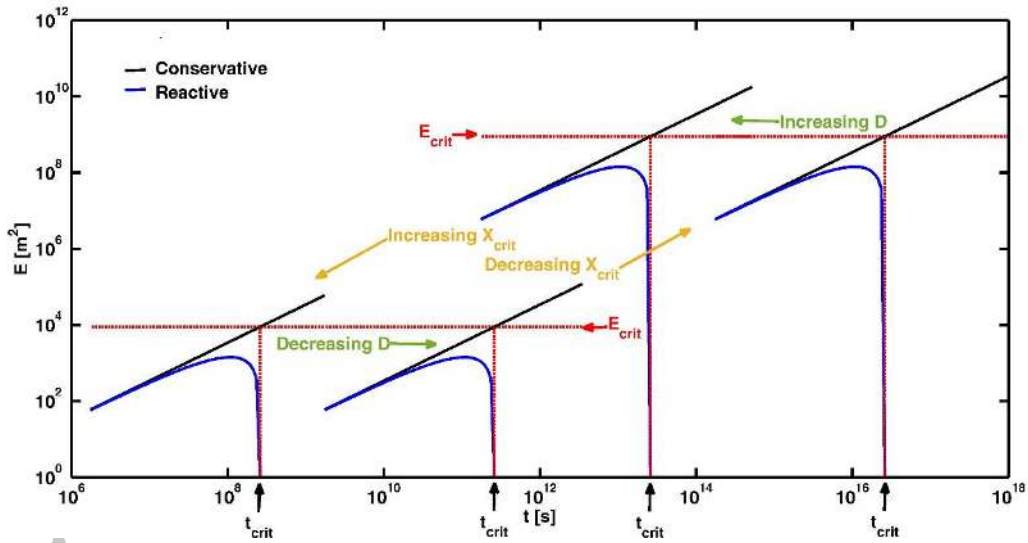


Figure 1. Relation between critical reaction time and critical dilution index in the uniform flow case for different X_{crit} and D values. The applied values of X_{crit} are 1×10^{-9} and 1×10^{-4} (top and bottom curves, respectively) and of D are $1 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ and $1 \times 10^{-6} \text{m}^2 \text{s}^{-1}$ (right and left curves, respectively).

4.2 Shear flow

The effects of shear flow on plume deformation, conservative and mixing-controlled reactive transport have been investigated in a number of recent contributions [e.g., Bolster et al., 2011; Paster et al., 2015, Bandopadhyay et al., 2017]. The work of Bolster et al. [2011] has shown that the concentration profile in a two-dimensional (i.e., in this case $n=2$) shear flow computed in a Lagrangian framework is also Gaussian. In this case, however, the variance of the Gaussian

distribution does not depend only on the local dispersion properties as in the uniform flow case, but also on the shear rate α [T^{-1}]:

$$\det(\boldsymbol{\kappa}(t)) = \left(2D_1t + \frac{2}{3}D_2\alpha^2t^3\right)(2D_2t) - (\alpha D_2t^2)^2 = 4D_1D_2t^2 + \frac{1}{3}D_2^2\alpha^2t^4 \quad (21)$$

where D_1 [L^2T^{-1}] is the dispersion coefficient in the main flow direction and D_2 [L^2T^{-1}] is the dispersion coefficient in the transverse direction. Considering that the critical dilution index is constant and independent of the mixing mechanisms, the critical reaction time can be computed as follows:

$$E(t_{crit}) = \frac{e}{X_{crit}} = 2\pi e \sqrt{4D_1D_2t_{crit}^2 + \frac{1}{3}D_2^2\alpha^2t_{crit}^4} \rightarrow t_{crit} = \sqrt{\frac{-b + \sqrt{b^2 - 4ac}}{2a}} \quad (22)$$

where $a=1$, $b=12D_1/(D_2\alpha^2)$ and $c=3/(2\pi X_{peak}D_2\alpha)^2$.

4.3 Complex flow topology

The impact of flow topology on plume stretching, folding and mixing has been studied at different scales in both 2-D and 3-D domains [e.g., Weeks and Sposito, 1998; Sposito, 2001; De Dreuzy et al., 2012; Piscopo et al., 2013; Chiogna et al., 2015; Crevacore et al. 2016; Lester et al., 2016]. Here we consider the work of de Barros et al., [2012], who investigated the dependence of the dilution index on the topology of the flow field in a Lagrangian framework. Despite the complexity of the considered two-dimensional flow field, also in that case it is possible to represent the concentration as a Gaussian distribution. Notice that, as discussed in de Barros et al. [2012], the validity of their solution for the concentration in a moving coordinate system is obtained assuming times smaller than the diffusion time scale, while the results for the covariance matrix $\boldsymbol{\kappa}$ are valid for times smaller than the advection time scale. The covariance of the Gaussian plume is given by:

$$\begin{aligned}
\det(\boldsymbol{\kappa}(t)) = \frac{4D^2}{\theta^6} \{ & [(\gamma^2 + \xi^2 - \xi\omega)\sinh(\theta t) + \theta\gamma\cosh(\theta t) \\
& - \theta(\gamma - (\xi - \omega)\omega t)][(\gamma^2 + \xi^2 + \xi\omega)\sinh(\theta t) - \theta\gamma\cosh(\theta t) \\
& + \theta(\gamma - (\xi + \omega)\omega t)] - [\gamma\omega\sinh(\theta t) + \theta\xi\cosh(\theta t) - \theta(\xi + \gamma\omega t)]^2 \}
\end{aligned} \tag{23}$$

where γ is the stretching deformation, ξ is shear deformation, ω is the vorticity and θ is the square root of the Okubo-Weiss parameter [Okubo, 1970; Weiss, 1991].

Again, the critical dilution index is constant and independent of the mixing properties of the system, and reads as:

$$E(t_{crit}) = \frac{e}{X_{crit}} = (2\pi e)\det(\boldsymbol{\kappa}(t_{crit}))^{1/2} \tag{24}$$

In this case, it is not possible to provide an explicit solution for t_{crit} , but Equation 23 can substituted into Equation 24, which can be solved iteratively for the critical reaction time.

5. Results and discussion

Figure 2 shows the concentration distribution and plume dilution for the cases of solute transport in uniform flow, shear flow and complex flow topology fields. All cases refer to infinite two-dimensional domains and the results are visualized for a $35 \text{ m} \times 6 \text{ m}$ setup (Figure 2). For the cases of shear flow (Figure 2C and 2D) and of flow with complex topology (Figure 2E and 2F), we also show the results which would be obtained in the limiting case of uniform flow; this allow appreciating the effect of mixing enhancement driven by the advective flow field. Table 1 summarizes the parameters used for the different examples shown in Figure 2.

Table 1. Values of the parameters used for the simulations shown in Figure 2.

Parameter	Symbol	Value
Isotropic dispersion coefficient [m^2/s]	D	1.0×10^{-9}
Velocity [m/s]	v	1.2×10^{-7}
Shear rate [$1/\text{s}$]	α	5.5×10^{-8}
Stretching deformation [$1/\text{s}$]	γ	5.5×10^{-8}
Shear deformation [$1/\text{s}$]	ξ	5.5×10^{-8}
Vorticity [$1/\text{s}$]	ω	8.0×10^{-8}

Figure 2A shows the concentration distribution for a conservative solute transported in a uniform flow field for $t=t_{crit}$. We set $X_{crit}=0.5$ and we plot, in Figure 2B, the temporal increase of the plume dilution. In particular, we observe that at time $t=t_{crit}$ (vertical black dashed line) the value of the dilution index is equal to the value of the critical dilution index (horizontal red dashed line). This means that a reactive plume would be completely consumed after a time equal to t_{crit} (1.6×10^8 s).

We consider now two limiting cases [Bolster et al., 2011] for the shear flow example. The concentration distribution is shown in Figure 2C for the base case (i.e., rotated ellipsoid obtained with $\alpha=5.5 \times 10^{-8}$ 1/s), as well as for a second case, in which the shear rate is set to a very small value (i.e., $\alpha=1 \times 10^{-11}$ 1/s), resulting in the same concentration distribution as in the uniform flow field. Figure 2D illustrates the temporal evolution of dilution and shows that, in presence of significant shearing ($\alpha=5.5 \times 10^{-8}$ 1/s), plume dilution increases faster than in the uniform case. We can also observe how the rotation of the plume leads to a significant reduction of the critical reaction time ($t_{crit}=9.4 \times 10^7$ s, blue dotted line) in comparison to the uniform flow field case. In fact, if α is very small (i.e., $\alpha=1 \times 10^{-11}$ 1/s), the plume vanishes at the same time as in the uniform flow field case (vertical black dashed line in Figure 2D). However, both plumes have the same critical dilution index, E_{crit} (horizontal red dashed line).

Similar findings were obtained in the example with complex flow topology. The tilted and elongated ellipsoid in Figure 2E corresponds to the plume undergoing stretching, vorticity and shear deformation with the parameters listed in Table 1, whereas the second plume was obtained with larger values of vorticity (i.e., $\omega=5\times 10^{-4}$ 1/s), while keeping the same stretching and shear deformation and approaches the concentration distribution in the uniform flow field. This is due to the fact that rapid rotation of the plume indeed prevents its persistent deformation in a preferential direction. We can observe that with the chosen set of parameters the conservative tracer reaches a peak concentration equal to X_{crit} and the dilution reaches its critical value at an earlier critical reaction time ($t_{crit}=8\times 10^7$ s, magenta dashed line in Figure 2F), which is approximately half the value for the uniform flow case. In the case of large vorticity in comparison to shear deformation and stretching, the critical reaction time approaches the value of the uniform field (black dashed line in Figure 2F).

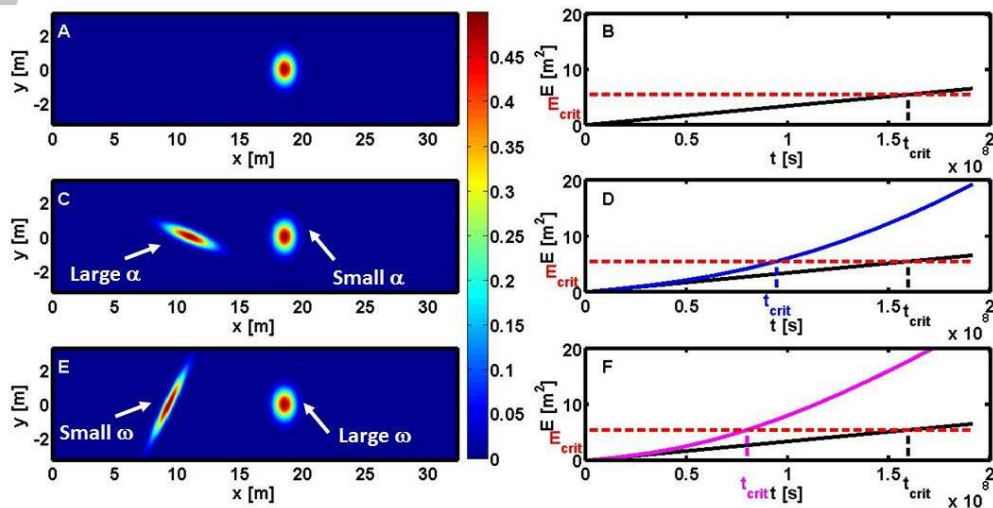


Figure 2. Concentration distribution of a conservative tracer injected in a uniform flow (A), shear flow (C) and complex flow topology (E) fields. All plumes are represented at $t=t_{crit}$. Panels B, D and F show the dilution index and the value of the critical dilution index (horizontal red dashed line) reached at different critical reaction times (vertical dashed lines).

It is also interesting to examine the dependence of the critical reaction time on the critical mixing ratio and, thus, on the stoichiometry and initial concentration of the reactants. Decreasing trends of

t_{crit} with increasing X_{crit} have been found for all three illustrative examples as shown in Figure 3A and 3C.

To better appreciate the effect of the advective flow field on mixing enhancement, we compute the ratio between the critical reaction time for the shear flow and the complex flow topology, respectively, and the critical reaction time for the uniform flow field case. We can observe (Figure 3B and 3D) that the larger the value of X_{crit} , the less effective is mixing enhancement driven by the advective properties of the flow field (i.e., the ratio between the critical reaction times approaches 1). This means that the larger the initial concentration of the injected compound A is (with respect to the ambient concentration of B), the more effective is mixing enhancement driven by advection. Moreover, the ratio between the critical reaction times depends on the parameters of the flow fields: it increases with decreasing shear rate in case of shear flow, while it increases with increasing vorticity in case of the complex flow field. In fact, the shear flow converges to a uniform flow by reducing the shear rate, while the complex flow field converges to the uniform flow field by increasing vorticity.

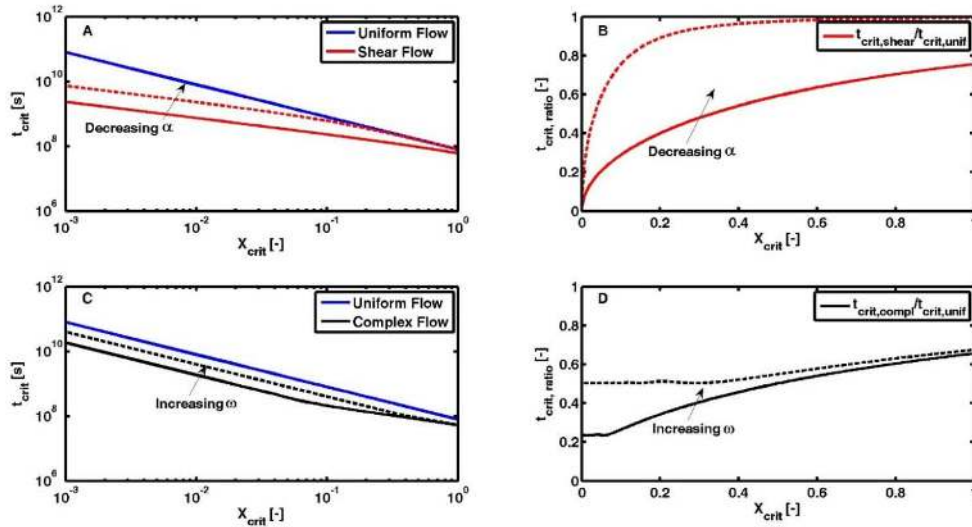


Figure 3. Relation between the critical reaction time and the critical mixing ratio for uniform flow (blue line), shear flow (red line, Panel A) and complex flow topology (black line, Panel C). Ratio between the critical reaction time in the shear flow field and in the uniform flow field (Panel B), and between the critical reaction time in the complex flow field and in the uniform flow field (Panel C), as a function of the critical mixing ratio.

6. Concluding remarks

This work has investigated the entropy evolution for mixing-controlled reactive transport. The transient entropy density transport equation derived for a reactive species allowed identifying dilution terms that provide a positive contribution and act as entropy sources, as well as reactive mixing terms that act as sinks in the entropy balance. Despite this work only considered Gaussian plumes and instantaneous complete bimolecular reactions, the proposed approach and the transient entropy density transport equation can be used to investigate the temporal evolution of the dilution for reactive species in different flow fields and in case of more complex reactions (e.g., biologically mediated, reversible bimolecular equilibrium reactions etc.). Moreover, quantities like the critical dilution index and the critical reaction time have been computed for maxentropic plumes and idealized reaction kinetics. We argue, therefore, that they could both represent lower limits for more complex situations (i.e., incomplete mixing and incomplete or slow reactions).

An interesting outcome of the analysis was that, even in the case of instantaneous complete bimolecular reaction, dilution processes dominate over reaction at early time. We focused on cases in which the solute concentration is Gaussian. Under these conditions, we have shown that it is possible to find simple analytical solutions that relate the entropy of conservative and reactive plumes with the peak concentrations. Three examples have been selected to illustrate the concepts of critical dilution index and critical reaction time. The critical dilution index quantifies the value of conservative dilution at which a transient reactant plume is completely consumed. It does not depend on mixing processes but only on the dimensionality of the problem and on the stoichiometry and initial concentration of the reactants. The newly introduced concept of the entropy-based critical reaction time, represents the time at which the critical value of dilution is reached and the reactant plume vanishes. Both the critical reaction time and the critical dilution index have been computed analytically only for Gaussian plumes. The applicability of these concepts to non-Gaussian plumes has still to be tested. Moreover, the effects of incomplete mixing and spatial

fluctuations in concentration fields on reactive solute transport [e.g., Tartakovsky et al., 2012; Chiogna and Bellin 2013] have not been explicitly considered in this work, but deserve future investigation.

The analysis provided in this study offers interesting insights for the characterization of dilution and its interaction with reactive processes in different geophysical flows. Besides the simple analytical cases illustrated in this study, the analysis of the critical dilution index and the critical reaction time can be applied for mixing-controlled reactive transport in numerical simulation in complex two-dimensional and three-dimensional flow fields. Interesting outcomes, shading light on the interplay between mixing and reactions, are envisioned for mixing-controlled reactive transport in different heterogeneous and anisotropic media, for Fickian and anomalous transport.

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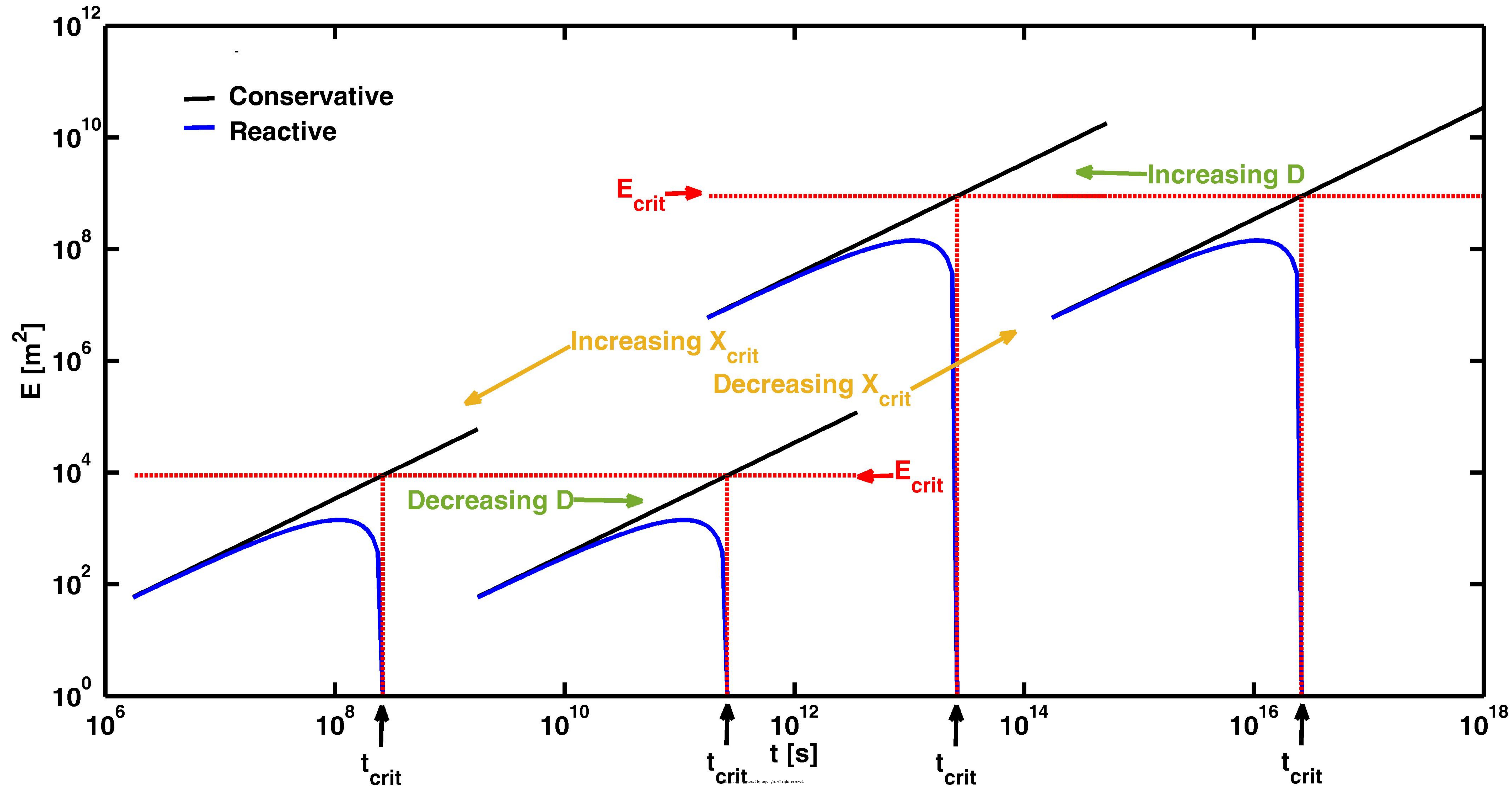
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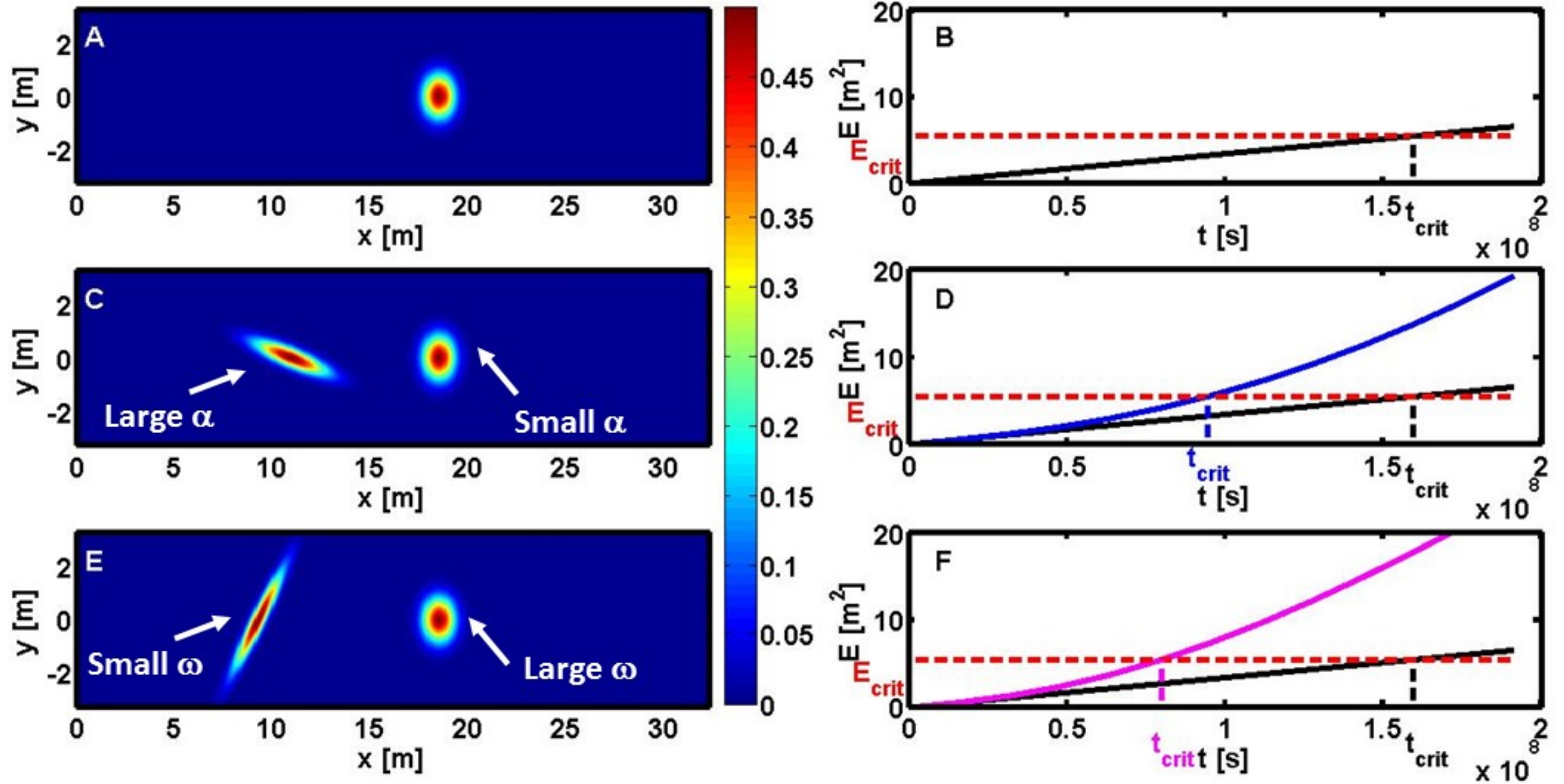
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Figure 1.



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Figure 2.



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Figure 3.

