

The concept of the dilution index

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Abstract. In many applications, it is important to make the distinction between spreading and dilution of a plume in groundwater. Spreading is associated with the stretching and deformation of a contaminant plume, whereas dilution is associated with the increase in volume of the fluid occupied by the solute. The dilution and spreading of a Gaussian plume in a homogeneous porous medium with constant velocity are related in a simple fashion and are both characterized by the same parameters, the dispersion coefficients. However, the geological formations of interest in field applications are heterogeneous, and the plumes are irregular in shape. The dispersion coefficients that are deduced from tracer tests usually measure an overall rate at which a tracer plume spreads about its centroid and depend critically on the heterogeneity of the formation. These macroscopic dispersion coefficients are not reliable measures of the rate at which the maximum concentration is reduced because in heterogeneous formations the rates of dilution and spreading can be quite different. The main objective of this work is to introduce a new macroscopic measure of dilution, the dilution index E . Examples serve to demonstrate the usefulness of the measure. A general expression for the rate of dilution of a tracer plume is derived. The exact rate of increase of the dilution index under the idealized conditions of constant dispersion coefficients and a Gaussian plume is computed, and a lower bound is found to the same quantity for non-Gaussian plumes. For the general heterogeneous case the analysis demonstrates that the instantaneous rate of increase of $\ln E$ is proportional to the small-scale dispersion coefficients, everything else being the same. The rate of increase of $\ln E$ depends also on the degree of irregularity in the shape of the plume. Thus, in the long term, geologic heterogeneity should increase the rate of dilution because spatial variability in the flow velocity tends to deform plumes and make them less regular.

Introduction

There are many practical applications where a good grasp of dilution and mixing in groundwater is needed. For example, in a pilot study of in situ bioremediation at the Moffett site [Roberts *et al.*, 1989; Chrysikopoulos *et al.*, 1990], nonoverlapping pulses of methane and oxygen were injected into an aquifer contaminated with chlorinated solvents. Steady flow in the aquifer was induced through a production well and an injection well at a distance of a few meters with partial recirculation of the water. Oxygen was injected for a while, then methane, then oxygen, and so on. The idea was that the successive oxygen and methane pulses should not overlap near the well, to prevent excessive growth of microorganisms or “biofouling,” but should overlap at some distance from the injection point as a result of natural dilution processes; biotransformation would take place where both oxygen and methane are available to the microorganisms. Accurate evaluation of the rate at which the two pulses mix is important in timing the pulses to optimize the performance of the system.

Hydrocarbons that can serve as primary substrates to aerobic organisms usually degrade readily in the presence of dissolved oxygen. The factor limiting the transformation rate is the availability of oxygen. Thus the rate of mixing of

oxygenated with oxygen-depleted water determines the transformation rate [Borden and Bedient, 1986; MacQuarrie and Sudicky, 1990]. Sometimes, a chemical additive or substrate is injected upgradient from a pollution source; to prevent the premature utilization of the substrate, the concentration of the injected substrate is at toxic levels to the microorganisms but should decrease through dilution to levels that can sustain growth by the time the substrate reaches the pollution source. In other applications it is important to be able to evaluate whether dilution will reduce the concentration of a pollutant to safe levels at a point of regulatory compliance.

When dilution and mixing are mentioned, the word dispersion comes to mind. Dispersion in the field is measured through tracer tests involving conservative tracers injected in a well followed by the collection of concentration data and analysis of the breakthrough curve at the same or another well [Welty and Gelhar, 1989]. There are many possible tracer tests. For example, consider a two-well tracer test with partial well-to-well recirculation conducted at the Moffett site [see Chrysikopoulos *et al.*, 1990]. Bromide was mixed with the injected water continuously to form a square input pulse. The depth-averaged concentration of bromide was measured in three intermediate observation wells and the production well.

Typically, the parameters “pore water velocity” and “dispersivity” are adjusted to reproduce the observed breakthrough curve as closely as possible. The dispersivity

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that is inferred from the tracer test is influenced by the spreading of the input pulse due to variability in advective velocity among layers and the method used to interpret the results of the tracer test. Thus the bromide that is transported through a permeable sand and gravel layer breaks through considerably faster than the bromide that travels through a less permeable fine sand and silt layer. Such tests result in high values of dispersivity (of the order of 0.1–1 m) which tend to increase with the scale of the test, because the flow rates in the different layers can be considerably different.

When such dispersion coefficients are used in advection-dispersion-reaction equations, however, there are indications that the dilution or mixing of chemicals is overestimated. Careful analysis of the results of a bromide tracer test at the Moffett site [Roberts *et al.*, 1989] led to an estimate of longitudinal dispersivity of about 0.65 m; however, the dispersivity that had to be used in a transport and microbial kinetics model to reproduce the overlap of oxygen and methane pulses that would give the observed rate of transformation was 0.07 m, or about an order of magnitude smaller.

It is now widely understood that the dispersion coefficients that are deduced from tracer tests are macroscopic measures of the rate of spreading of the tracer. Considerable theoretical work on field-scale dispersion (or macrodispersion) has shed light on the meaning of macrodispersion and its relation to the heterogeneity of the medium [Dagan, 1982; Gelhar and Axness, 1983; Neuman *et al.*, 1987; Kitanidis, 1992]. It is questionable, however, that such macrodispersion coefficients necessarily describe rates of dilution at the scale of interest because, as we will see later, spreading and dilution are two different, although related concepts.

Intuitively, by dilution we mean the uniform dispersal of a solute in a solvent or the reduction of the maximum concentration of the chemical as it is dissolved into a larger volume of solvent. For instance, a dilution indicator is the maximum concentration value. It may be that under the idealized conditions described by the advection-dispersion equation with constant coefficients there is no real need to underline the distinction between dilution and spreading because both processes are characterized by the same dispersion coefficients. However, under more realistic conditions encountered in the field, the relation between dilution and spreading is not simple.

This work deals with the question of what is dilution and, in particular, it presents a quantitative measure of dilution that is applicable under general conditions of shape of plume or field heterogeneity. It will be demonstrated through examples that this measure agrees with our intuitive notion of what is really dilution.

In this paper, to facilitate the presentation of the key ideas, we will not concern ourselves with the mixing of two different chemicals (such as the intermingling of methane and oxygen) but, of course, dilution is relevant to mixing. Furthermore, when it comes to transport, we will focus on the case of a conservative nonreactive solute. However, the measures of degree of dilution that are presented are applicable to both reactive and nonreactive solutes.

Background: Spreading Versus Dilution

Consider a plume of an ideal tracer, i.e., a conservative nonreactive and nonsorbing solute that is too dilute to affect

the properties of the fluid. Processes of interest are advective transport, which is the movement of a chemical with some average (“grid-scale”) fluid velocity, and dispersive transport, which is scattering caused by the combined action of small-scale (“subgrid-scale”) velocity variations and molecular diffusion. Transport governed by these processes is described by the classical advection-dispersion (A-D) equation:

$$\frac{\partial c}{\partial t} + \frac{\partial(cu_i)}{\partial x_i} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial c}{\partial x_j} \right) \quad (1)$$

The concentration (mass per unit volume of solution) at location $\mathbf{x} = [x_i]$, $i = 1, \dots, n$, and time t is $c(\mathbf{x}, t)$, where \mathbf{x} is an array of the coordinates in the n -dimensional domain where solute might be found and c is the concentration of a chemical in the water in appropriate units, such as parts per million or moles per liter. Here, $\mathbf{u} = [u_i]$ is the velocity and $\mathbf{D} = [D_{ij}]$ is the local or microdispersion tensor. The velocity and the dispersion coefficients may vary in space. Einstein’s notational convention is used: Summation is implied over any index that appears exactly twice in a term.

It is important to be clear about the meaning of these quantities, particularly when discussing dilution in heterogeneous formations at the field scale. The concentration c is actually defined over an elementary finite volume and an elementary finite time period. This finite volume in our analysis could have dimensions as small as centimeters (“laboratory” or “Darcy” scale), and the finite interval could be of the order of minutes or perhaps hours. The velocity and dispersion coefficients are defined over effectively the same volume and interval. (Dispersion coefficients, in particular, could have been quite different if concentration had been defined differently.) The dispersion coefficients at this scale are typically very small. The A-D equation is an approximately valid representation if the hydraulic head ϕ and the concentration c are gradually varying functions at these elementary scales. In other words, the A-D is appropriate to try to resolve fluctuations of concentrations at scales larger than the elementary scales. The degree of approximation is better if the hydraulic parameters (especially conductivity) vary mostly at scales much smaller or much larger than the elementary scales.

It will be more convenient to work with the concentration normalized by the total mass of the solute:

$$p(\mathbf{x}, t) = \frac{c(\mathbf{x}, t)}{\int_V c(\mathbf{x}, t) dV} \quad (2)$$

where V is the total volume of the domain and $\int_V c(\mathbf{x}, t) dV$ is the total mass divided by the porosity. (In this work, the porosity will be generally assumed constant.) A useful interpretation of $p(\mathbf{x}, t)$, which has units of 1 over volume, is as the probability distribution of the location of a tagged particle of the tracer at time t .

In the groundwater literature the same term “dispersion” is used to describe the spreading and the dilution of a plume. Let us start by quantifying spreading through the lower spatial moments. The location of the centroid of the plume in direction i is the first spatial moment:

$$\alpha_i(t) = \int_V p(\mathbf{x}, t) x_i dV \quad (3)$$

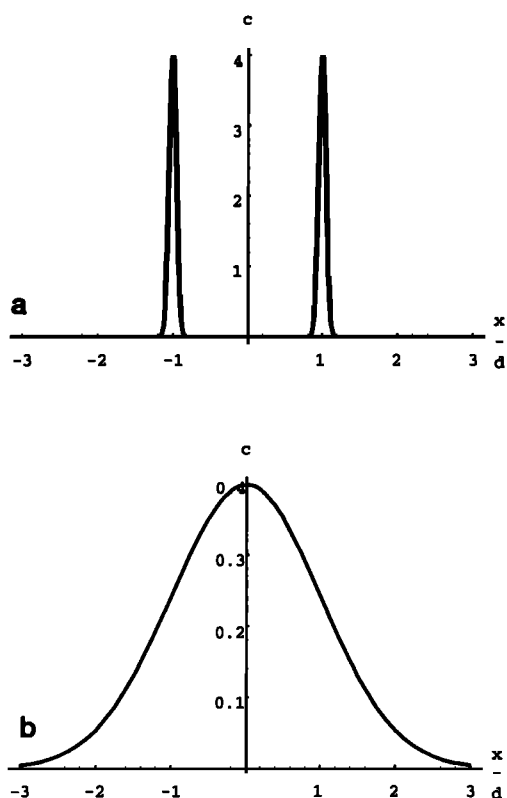


Figure 1. (a) Mass in two small plugs versus (b) mass distributed normally.

and the mean square distance or dispersion (not to be confused with dispersion coefficients) from the centroid in directions i and j is the second spatial moment:

$$\Delta_{ij}(t) = \int_V p(\mathbf{x}, t)(x_i - \alpha_i)(x_j - \alpha_j) dV \quad (4)$$

Note that $\alpha = [\alpha_i]$ is a vector with dimensions $[L]$ and $\Delta = [\Delta_{ij}]$ is a second-order tensor or dyadic with dimensions $[L^2]$.

The second moment is commonly used to describe the extent of a plume. The higher the value of Δ_{ii} , the larger the spread in direction i . Furthermore, half the time rate of change of dispersion may be used to define the effective dispersion coefficients (or macrodispersion coefficients):

$$D_{ij}^{ef} = \frac{1}{2} \frac{d\Delta_{ij}}{dt} \quad (5)$$

The macrodispersion coefficients are macroscopic measures of the rate of spreading of a plume. In many cases, macrodispersion is taken as evidence or even direct measure of dilution of the solute. However, it is not difficult to demonstrate that spreading does not necessarily mean dilution. For example, if a plume consists of two small plugs of equal mass at distance $2d$ from each other (Figure 1a), the dispersion is d^2 . This plume is certainly spread out. However, the chemical is not well dissolved because good dilution implies that the mass is distributed over a large volume of water. Compare with the case where the distribu-

tion of the mass is bell shaped (Figure 1b). These two cases are characterized by the identical mass, centroid location, and dispersion, but the degree of dilution is certainly higher in Figure 1b.

This simple example illustrates clearly the difference between spreading and dilution. Thus it is not appropriate to quantify dilution only through dispersion. In the same vein, it is not appropriate to quantify the rate of dilution increase solely through macroscopic dispersion coefficients.

An important question is, How can we quantify the degree of diluteness and the rate of change of dilution? In the general fluid mechanics literature [Hill, 1976; Ottino, 1989, 1990], this subject is studied under "mixing" which is typically the study of kinematics of flow and the associated stretching and deformation of material surfaces. These processes affect the rate of dilution or mixing by increasing the interface between the plume and the surrounding "clean" water. One of the primary reasons the study of mixing has stopped short of addressing the whole problem is that the literature does not provide a satisfactory way to quantify diluteness. The main contribution of this work is to propose and study such a measure.

From a practical standpoint it would also be convenient to have a representative number that expresses how close is a plume to complete dilution. However, the concept of complete dilution should be qualified on the setup and conditions of the transport process. In the case of a confined batch reactor, for example, complete dilution means that the concentration is uniform. But if the contents of a well-mixed reactor are emptied without intermingling into a larger reactor, the new mixture may not be homogeneous anymore and the system may not be well mixed. Similarly, when a well-mixed tracer is injected into a small well located in a relatively large aquifer, we cannot think of completeness of mixing as uniformity in concentration over the whole aquifer; instead, the degree of mixing should depend on the size and spreading of the plume. We will see, however, that all different cases can be treated in a conceptually unified framework.

Dilution Index and Reactor Ratio

An index will be defined here that quantifies the degree of dilution of a tracer in a system. In particular, this index should satisfy the following criteria:

1. It should correspond to our intuitive notions of what is degree of dilution. For example, if we have two cases of clearly unequal degree of dilution, the index should reflect the difference.
2. The index should be proportional to the volume of fluid occupied by the solute. The index should be inversely proportional to an average normalized concentration.
3. The maximum degree of dilution for a certain setup should correspond to the concentration that formally maximizes the value of the index.

Consider first the discrete case. Assume that the domain or container where the transport is taking place is subdivided into n discrete bins or elementary volumes of volume ΔV ; see Figure 2. Let P_k be the ratio of mass in bin i divided by the total mass; P_k may be interpreted as the probability that a tagged particle is found in bin k . The degree of dilution is measured through the number

1	2	3	4
			n

Figure 2. Subdivision of reactor into n bins.

$$E = \Delta V \exp \left(- \sum_{k=1}^n P_k \ln (P_k) \right) \quad (6)$$

which is defined as the dilution index. Note that the dilution index has dimensions of volume.

It will later be demonstrated through examples and derivations that this number is representative of the degree of uniformity of the mass distribution among the n possible bins. For now, consider that all the mass is distributed uniformly in m bins ($m < n$), while $n - m$ bins in the reactor contain no solute mass; the value of E of (6) then is $m\Delta V$. The larger the number m , the better the mixing. In this example we can interpret E as the volume of the bins where a tagged solute particle can be found with equal chance. Also, the concentration in the bins that contain chemical is inversely proportional to the dilution index, because the concentration is inversely proportional to the volume over which the chemical is distributed. Here, neglecting variability in porosity, we will use as ΔV the total volume of the bin (solids and pores). Thus E expresses the volume of the porous medium that is occupied by the solute.

Consider now the mass distribution that would result in the theoretically maximum value of E . Of course, it makes sense to consider only distributions that would be consistent with the given experimental or field setup and the other physical parameters of the problem. For this reason the maximum value will vary from case to case, as will be seen later. We will call this maximum value E_{\max} . In the previous example, $E_{\max} = n\Delta V = V$, the volume of the container.

The reactor ratio is defined as the ratio of the actual dilution index to the maximum dilution index that is theoretically possible consistent with other limitations:

$$M = E/E_{\max} \quad (7)$$

This is a dimensionless number between 0 and 1 that describes how complete is the actual dilution compared to the theoretically maximum dilution that is possible given the setup (or available information). A value near 0 indicates incomplete dilution, and a value near 1 indicates a high degree of dilution under the specified conditions. The larger the value of M , the closer is the system to a state of "equilibrium." The reason it is called reactor ratio will become obvious later when it will be shown that in some

simple cases, it is the ratio of the reactor volume that is occupied by the solute. For example, $M = 0.50$ means that the solute is distributed over 50% of the reactor. The reactor ratio can also be interpreted as a shape factor of the plume.

In some applications it is more convenient or appropriate to consider that the mass is distributed in a continuous fashion. That is, instead of specifying the distribution of mass among n bins, we specify the distribution of mass continuously within a reactor through $p(\mathbf{x}, t)$, the distribution function of the mass. In this case it turns out that by considering the continuous case as the limit of the discrete case as the number of bins increases we obtain from (6) the expression

$$E(t) = \exp \left[- \int_V p(\mathbf{x}, t) \ln (p(\mathbf{x}, t)) dV \right] \quad (8)$$

where $p(\mathbf{x}, t)$ is the distribution function of the mass. See Appendix A for details on how one can advance from the discrete case to the continuous one in a consistent way. Notice that E has the units of volume for three-dimensional domains (or area or length, for the two- and one-dimensional cases, respectively). The reactor ratio is defined in the same way (equation (7)) as for the discrete case.

Relation to Entropy and Interpretation

Entropy

The logarithm of the dilution index is a familiar expression that is known as "entropy" or "information." Mathematically, entropy is a functional of a probability function that has been used in different fields to quantify degree of disorder, information in a source, average uncertainty, ambiguity, multiplicity, etc.

The term entropy was coined by Clausius but it was Boltzmann, in 1871, who first developed a far-reaching statistical interpretation of the concept, according to *Jaynes* [1984a], who traced the development of the second law of thermodynamics. Entropy figures prominently in chemical thermodynamics, which studies the energy changes that accompany chemical reactions. A central notion of thermodynamics is that a physical system will "spontaneously" approach a stable condition, known as equilibrium. At equilibrium, the entropy, which is a measure of the disorder of a system, is the maximum possible. Entropy is a key concept in thermal and quantum physics where it is defined generally as the multiplicity of quantum states [*Jaynes*, 1957; *Kittel and Kroemer*, 1980]. In information theory, pioneered by *Shannon* [1948], entropy is the amount of information in a source. The entropy of any source is the fewest number of bits able to represent the source in a message. For example, a source that transmits a "yes" or "no" message has an entropy or information of 1 bit. Entropy is also a fundamental concept in problems of inference, especially within the context of the so-called Bayesian statistics, as discussed by *Jaynes* [1983, 1984b] and *Woodbury and Ulrych* [1993].

It is remarkable that the same expression can describe so many seemingly different concepts. However, in all of its uses entropy measures "number of possibilities." Its bearing on dilution is that the entropy of the probability of location of a tagged particle measures, in a sense, the number of locations where this particle can be found and

hence can be used (as will be discussed in this work) to find the size of the volume occupied by the solute plume.

However, the concept of entropy does not seem to have been associated with the concept of dilution in a formal way. In solute transport in groundwater the author is familiar with only one work where entropy has been mentioned. However, in that work [Smith and Schwartz, 1981], entropy was used as a measure of uncertainty in solute transport prediction [Smith and Schwartz, 1981, p. 353] due to insufficient information about the hydraulic conductivity. The dilution index that has been proposed herein is not an average over the ensemble of realizations of conductivity but a volume-averaged measure of the degree of dilution in a "single realization." Smith and Schwartz presented results for zero local dispersion coefficients (p. 352) for which the entropy showed a pronounced increase over time (p. 360), whereas, as will be shown in equation (18), the dilution should in this case remain constant. This demonstrates that the entropy used in the Smith and Schwartz paper is not a measure of dilution but a measure of ensemble uncertainty.

There are important practical difficulties in trying to use an entropy measure to describe dilution, which may explain why the approach has not been used in the past. The conventional expression for entropy is

$$H_d = - \sum_{k=1}^n P_k \log(P_k) \quad (9)$$

for the discrete case, where the mass is distributed in n bins and P_i represents the ratio of mass in bin i . In information theory and quantum mechanics the logarithm is to base 2 and the entropy is measured in bits. Not only is it awkward to measure dilution in bits, but a more substantial problem is that the numerical value of the entropy depends strongly on the domain discretization. The finer the discretization grid, the more the bins and the higher the entropy. The entropy expression never converges (i.e., it never becomes independent of the grid) no matter how smooth the distribution. Thus the conventional expression for the entropy is not directly usable to measure plume dilution in a spatial domain where there is no inherent discretization.

Furthermore, for the continuous case, the entropy that is used is

$$H_c = - \int_V p(\mathbf{x}) \ln(p(\mathbf{x})) dV \quad (10)$$

where $p(\mathbf{x})$ is the distribution function of the mass. (Incidentally, this expression appears to be less favored in the literature on entropy than (9).) Notice that H_c has unwieldy units, and this expression cannot be obtained from the discrete case as a limit when the grid step diminishes to zero.

These concerns may be less important in other applications of entropy where the objective is to determine the distribution that maximizes the entropy ("equilibrium"). It is emphasized that entropy maximization is not among the main objectives of this work. Instead, the motivation for this work is to establish a measure of dilution so that it may subsequently be used to study kinetics, i.e., the rate of change of dilution.

The dilution index that has been proposed in this work is an adaptation of the entropy expression that was made to

avoid the above mentioned difficulties. The dilution index depends only weakly on the discretization grid; i.e., for smooth distribution functions the index for the discrete case converges to the index for the continuous case as the grid becomes finer. The dilution index for either case has the dimensions of the space occupied by the solute. Such units are appropriate since the standard definition of dilution is "the act of distributing solute mass over a larger volume".

Interpretation

A key assertion in this work is that the dilution index is a measure of the aquifer volume occupied by the solute. Here, in support of this claim, it will be shown that (1) this assertion is true for the uniform case, where the volume occupied by the solute is known, and (2) for any case where the dilution increases, so does the dilution index.

Focusing on the discrete case, consider that the initial distribution is uniform in a single block and the final distribution is uniform over the whole domain. The initial value of the dilution index is ΔV and the final is V , verifying the assertion. Let us examine the intervening cases. Consider the transfer of mass from a bin with relatively high mass, P_a , to a bin with relatively low mass, P_b ,

$$P_a > P_b \quad (11)$$

everything else remaining the same. (Such a transfer is, of course, the only way dilution may be achieved through diffusion.) If ΔP is transferred, where

$$0 < \Delta P \leq \frac{P_a - P_b}{2} \quad (12)$$

then it is obvious that this constitutes a definite increase of the degree of dilution or mixing. The question is whether the dilution index increases to reflect this change. Taking the ratio of the new over the old value of the dilution index, we find that indeed this ratio is larger than 1:

$$\frac{E_n}{E_o} = \frac{\{\exp[-(P_a - \Delta P) \ln(P_a - \Delta P) - (P_b + \Delta P) \ln(P_b + \Delta P)]\}}{\{\exp[-P_a \ln(P_a) - P_b \ln(P_b)]\}}^{-1} > 1 \quad (13)$$

as a consequence of the strict concavity of the function $P \ln(P)$. The process of dilution from the initial to the final state is a sequence of transfers such as the above. During each step the actual dilution increases, and so does the value of the dilution index.

Thus it has been demonstrated that the dilution index measures the aquifer volume in the initial and final states, for which the result is known, and it provides the right ordering of states of dilution for the intervening states.

Batch Reactor

The reactor is a bounded and closed container. This case is relatively simple to visualize and work with and thus is particularly useful in illustrating the physical meaning of the dilution index, E , and the reactor ratio, M .

The reactor is divided into n bins or cells of equal size. The actual value of E is given from (6). Consider the distribution that maximizes E . The only physical requirement is that the sum of the P_i coefficients must always be 1,

since the tracer is conservative and the reactor is closed. Thus the problem is to find the values of P_1, P_2, \dots, P_n that maximize

$$\exp \left(- \sum_{k=1}^n P_k \ln (P_k) \right) \quad (14)$$

subject to the constraint

$$\sum_{k=1}^n P_k = 1 \quad (15)$$

From the formal solution of this well-known optimization problem [see *Tribus*, 1969, p. 128] it is demonstrated that the maximum value of E is obtained when the mass is distributed uniformly in all bins, $P_k = 1/n$, for $k = 1, \dots, n$, which means that $E_{\max} = n\Delta V$. Clearly, this solution corresponds to our intuitive notion of what is complete dilution in the case of a batch reactor.

Thus the reactor ratio for a batch reactor is

$$M = \frac{1}{n} \exp \left(- \sum_{k=1}^n P_k \ln (P_k) \right) \quad (16)$$

This number is between 0 and 1 and describes how complete is the actual dilution compared to the maximum dilution.

Let us see some examples:

Example 1. Solute is divided evenly in m bins, i.e., $P_k = 1/m$, for $k = 1, \dots, m$, and $P_k = 0$, for $k = m + 1, \dots, n$. Then

$$E = m\Delta V \quad M = m/n$$

We see that in this case, the dilution index E measures the volume of the bins among which the solute is dispersed. The reactor ratio M is the portion of the reactor occupied by the solute.

Example 2. In this case $P_1 = 1/2$, $P_2 = 1/4$, $P_3 = 1/4$, and the other P_i are zero. Then

$$E = 2.83\Delta V$$

which means that the dilution is more complete than if the solute mass was evenly distributed in two bins but less complete than if it were distributed evenly in three bins. This result makes intuitive sense.

Example 3. $P_1 = 3/4$, $P_2 = 1/8$, $P_3 = 1/8$, and the others are zero. Then

$$E = 2.09\Delta V$$

which means that the dilution is ranked to be less complete than in example 2. This result makes intuitive sense because case 2 can be obtained from case 3 by distributing the mass more uniformly, by removing one quarter of the mass from bin 1 and distributing it uniformly between the other two bins.

In the continuous case the maximum value is obtained when $p(x) = 1/V$ in which case $E_{\max} = V$. Thus the reactor ratio is

$$M = \frac{1}{V} \exp \left(- \int_V p(\mathbf{x}) \ln (p(\mathbf{x})) dV \right) \quad (17)$$

Unbounded Domain

Field applications involve flow domains that contain the whole plume or, at least, most of the plume. For such cases, by considering that boundaries are far away and that concentrations and mass fluxes vanish on the boundary, we may talk about transport in "unbounded" porous media. As time passes, the plume tends to change location and to spread out. In the rest of the paper we will discuss the transport of an ideal tracer in such a formation.

Rate of Increase of Dilution Rate

Consider that the transport satisfies the advection-dispersion equation with variable velocity and dispersion coefficients (equation (1)), and the velocity satisfies the incompressibility condition. Then, if the normalized concentration is $p(\mathbf{x}, t)$, the rate of increase of the logarithm of the dilution index is given by the following general expression (see Appendix B):

$$\frac{d \ln (E)}{dt} = \int_V \frac{\partial \ln p}{\partial x_i} D_{ij} \frac{\partial \ln p}{\partial x_j} p dV \geq 0 \quad (18)$$

This result is key in understanding what controls the rate of dilution of a plume at a point in time. This rate is positive (with the exception of some special cases of little physical significance where it may be zero), indicating that the dilution index always increases. Thus the characteristic volume of the plume increases monotonically with time, in contrast to the second spatial moment which may increase or decrease over time as the plume stretches and contracts. (Only on an average or long-term sense does the second spatial moment increase.)

Perhaps the physical meaning of this expression becomes more obvious in the one-dimensional case:

$$\frac{d \ln (E)}{dt} = \int_{-\infty}^{\infty} \left(\frac{\partial \ln p}{\partial x} \right)^2 D p dx \quad (19)$$

This equation states that the rate increases with the square of the log concentration gradient weighted volumetrically by the mass and the local dispersion coefficient. Thus if a high percentage of mass is in areas of steep concentration gradient, then the dilution increases rapidly. Equation (18) is quite general and demonstrates the critical dependence of the dilution rate on the local dispersion coefficients. The instantaneous rate of increase, $d \ln (E)/dt$, is proportional to the local dispersion coefficients, everything else being the same. Thus no matter how small the local dispersion coefficient, it is essential to include in the analysis of dilution.

Variability in the advective velocity causes only deformation in the shape of the plume without change of volume and thus has no direct effect on the dilution rate. A purely advective ("piston") transport, assuming that it were physically possible, does not change the dilution. For illustration of the principle, consider purely advective transport in a two-dimensional homogeneous porous medium with a completely permeable circular inclusion. The flow is uniform away from the inclusion, but the streamlines converge in the

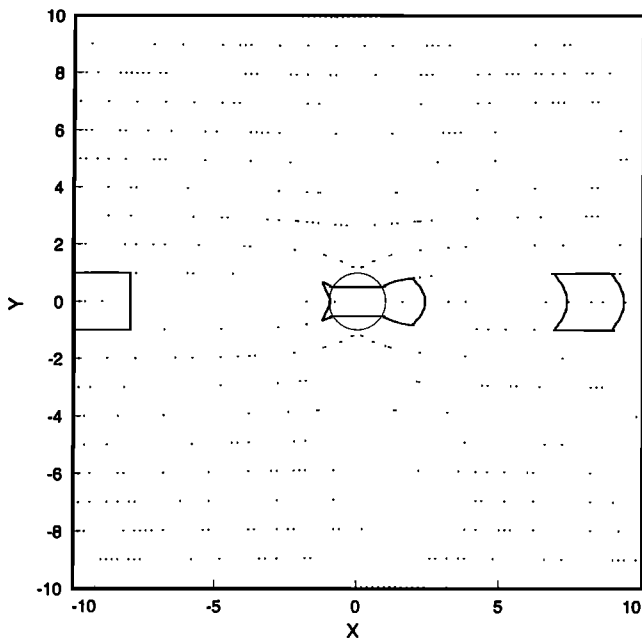


Figure 3. A plume advected through a permeable circular inclusion.

area of no resistance. Figure 3 shows an originally rectangular plume before, during, and after passing through the inclusion. The flow is from left to right. The plume stretches to squeeze through the permeable area and then contracts again while always maintaining exactly the same volume. Note that the plume does not return to its original shape. The net effect of heterogeneity is to increase the degree of irregularity of the plume.

The rate of increase of $\ln E$ depends critically on the shape of the plume. The more stretched and striated a plume, the higher the rate of dilution because mass transfer rates increase with interfacial area. This is expressed in (18) where one can see that the rate depends on the presence of mass over areas of steep gradients. It will also be proved mathematically in the next section, for constant dispersion coefficients, where we will show that a lower bound to this rate is obtained for the regular Gaussian plume with the same spread (second spatial moment) as the spread of the actual plume.

Spatial fluctuations of velocity, such as the ones caused by stratification, tend to make a plume more irregular, and this, in the long term, can increase dramatically the rate of dilution. No matter how small the transverse dispersivity, when multiplied by a steep gradient and applied over a large enough surface it will result in measurable transport rates. Thus the same process that causes "macrodispersion" in the long term increases the dilution rate.

For example, consider horizontal flow in a two-layer system, each layer 1 m thick. The lower layer has conductivity 45 m/d and the upper 15 m/d. Both layers have porosity 0.3, longitudinal dispersivity 0.01 m, and transverse dispersivity 0.001 m, and the head gradient is 0.01. The system is two dimensional as shown in Figure 4. A square tracer pulse of width 0.50 m was injected instantaneously at time 0 and location 0 and then transported with advection and dispersion. Figure 4 shows the tracer plume at 0.01, 1, 2, and 6

days as approximated with a particle-tracing method using 2000 particles. One can see that the plume stretches and deforms due to layering and that the second moment in the longitudinal direction increases almost with time squared. The volume of the tracer plume, however, increases much more slowly. Notice that at early times most of the dilution is due to longitudinal dispersion. As the plume gets longer, the transverse dispersion contributes more to the dilution, and by the time the plume becomes longer than 10 times the thickness of the aquifer the transverse dispersion becomes more important than the longitudinal dispersion. Compare the distribution of the plume at 20, 40, 60, and 80 days (Figure 5) with the distribution that it would have had if the transverse dispersion were exactly zero (Figure 6). If we picture a pulse of another chemical being injected at 6 days after the first chemical, most of the overlapping of the two pulses would take place near the joint between the two layers (Figure 7) and would be the consequence of transverse dispersion.

In many engineering applications, such as enhanced in situ bioremediation, a substrate is injected into a formation through a well screen, and then it is desired to mix it with as large a volume of groundwater as possible. Local dispersion coefficients are low so that "passive" mixing is an extremely slow process. Equation (18) suggests that one can enhance dilution and mixing by moving the flow around in a way that will distort the plume of the injected substrate, thus increasing the rate of dilution increase. Another idea is to control the rate of increase of E by pumping the water into a well, mixing it, and then injecting it back into the formation. Such ideas are exploited in in situ mixing schemes such as dual-screen recirculation wells [MacDonald and Kitanidis, 1993].

Reactor Ratio

How can one define a reactor ratio for the unbounded domain? It is not useful to think of complete mixing in the same way as we did for a finite batch reactor, i.e., as uniform concentration over the whole domain. Nevertheless, at any point in time, one may be able to measure certain characteristics of the plume which constrain the maximum dilution index and allow us to define a reasonable reactor ratio. (This is analogous to the requirement to know the size of the container in the previous example.)

A plume in an aquifer may be described macroscopically through the lower spatial moments which define the total mass, the location of the centroid, and the spreading about the centroid. It is useful to define complete mixing as the concentration that maximizes the dilution index for given first and second moments.

In the continuous case, which is of more practical interest, the normalized probability that maximizes

$$\exp \left(- \int_V p(\mathbf{x}) \ln (p(\mathbf{x})) dV \right) \quad (20)$$

subject to the constraints

$$\int_V p(\mathbf{x}) dV = 1 \quad (21)$$

$$\int_V p(\mathbf{x}) x_i dV = \alpha_i \quad (22)$$

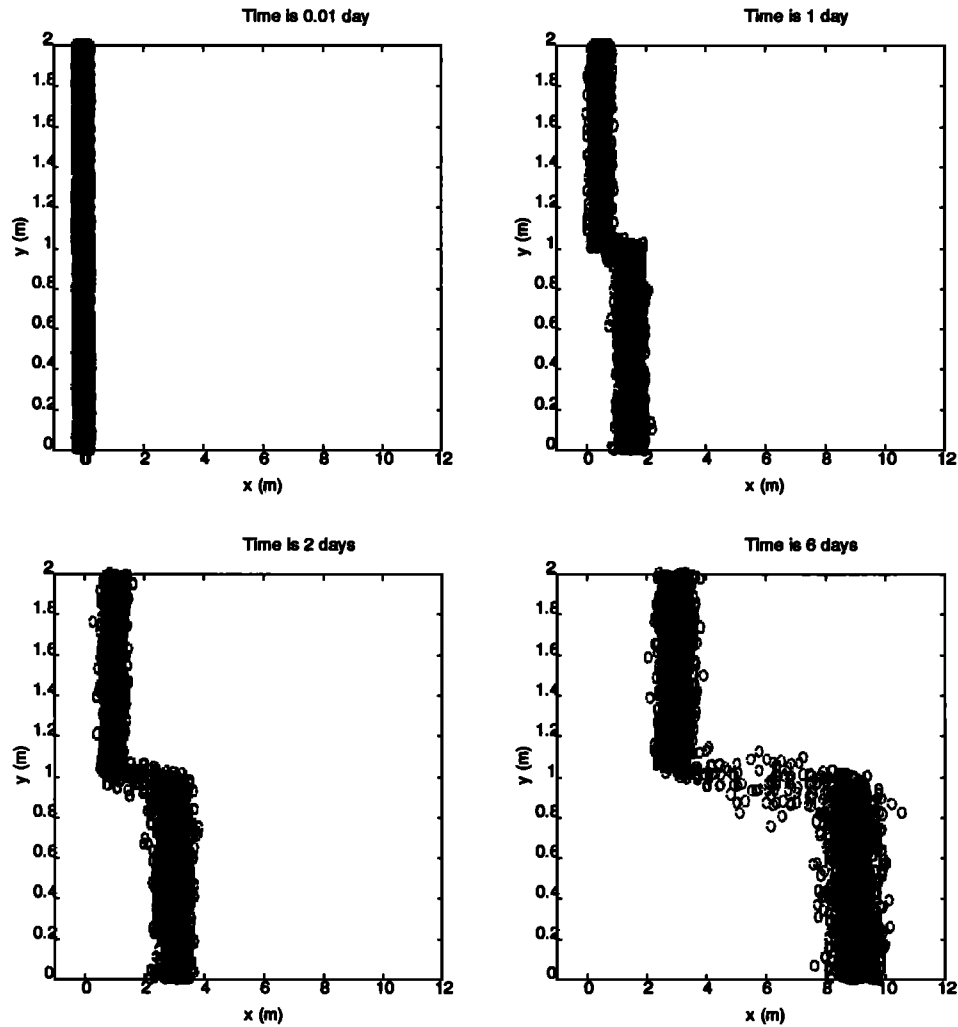


Figure 4. Tracer plume 0.01, 1, 2, and 6 days after release in two-layer system.

$$\int_V p(\mathbf{x})(x_i - a_i)(x_j - a_j) dV = \Delta_{ij} \quad (23)$$

needs to be found. The solution to this mathematical problem has been known for a long time [see *Tribus*, 1969, p. 131], and can also be found in Appendix C using a less conventional but more powerful methodology. It can be expressed, using matrix notation, in a general form that applies for one, two, and three dimensions:

$$p(\mathbf{x}) = (2\pi)^{-n/2} (\det(\Delta))^{-1/2} \exp\left(-\frac{1}{2}(\mathbf{x} - \alpha)^T \Delta^{-1}(\mathbf{x} - \alpha)\right) \quad (24)$$

where α is the vector with the spatial coordinates of the centroid (first spatial moment); Δ is the matrix of the dispersion (second spatial moment); $\det(\Delta)$ and Δ^{-1} are the determinant and inverse of Δ ; and a superscript T means matrix transpose. The maximum value of the dilution index is

$$E_{\max} = (2\pi)^{n/2} \exp(n/2) (\det(\Delta))^{1/2} \quad (25)$$

Notice that E_{\max} depends only on the dispersion tensor, being unaffected by the location of the centroid.

For the sake of easier reference, we will expand the equation for E_{\max} for one, two, and three dimensions:

One-dimensional case

$$E_{\max} = \exp(1/2)(2\pi\Delta)^{1/2} \quad (26)$$

Two-dimensional case

$$E_{\max} = 2\pi \exp(1)(\Delta_{11}\Delta_{22} - \Delta_{12}^2)^{1/2} \quad (27)$$

Three-dimensional case

$$E_{\max} = (2\pi)^{3/2} \exp(3/2)(\Delta_{11}\Delta_{22}\Delta_{33} + \Delta_{12}\Delta_{23}\Delta_{13} + \Delta_{13}\Delta_{12}\Delta_{23} - \Delta_{23}^2\Delta_{11} - \Delta_{13}^2\Delta_{22} - \Delta_{12}^2\Delta_{33})^{1/2} \quad (28)$$

E_{\max} (which is length, area, or volume, depending on the dimension of the domain) can be interpreted as the maximum size of a reactor over which a solute plume of a given extent can be diluted in the unbounded domain case for a plume of given spread (second spatial moment).

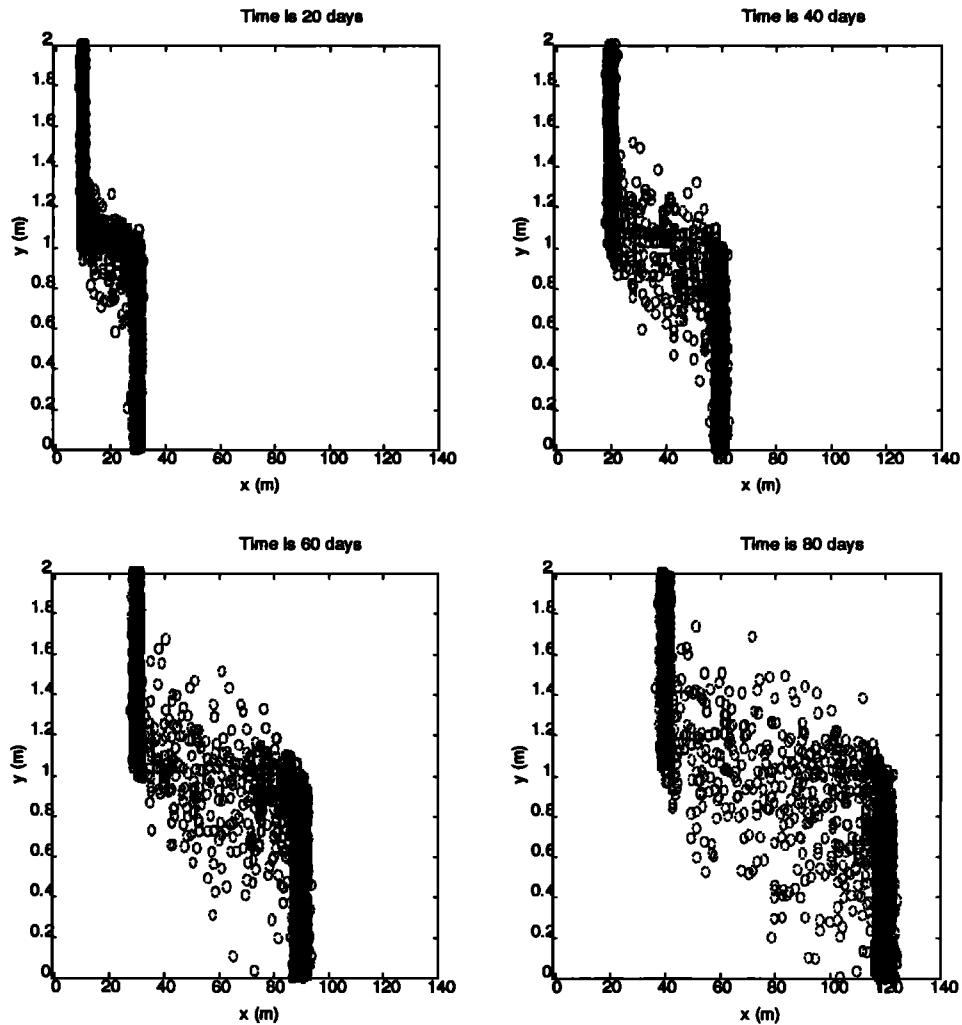


Figure 5. Tracer plume 20, 40, 60, and 80 days after release.

The concentration that maximizes the dilution index (equation (24)) is actually the familiar “Gaussian plume solution” that is often computed when analytical methods are used to simulate advective-dispersive transport. In practice, however, actual plumes are not Gaussian, mainly due to spatial variability of advective velocities as well as other deviations from the idealized conditions assumed in analytical solutions.

The analysis leads to the following interesting conclusions for plumes in aquifers away from boundaries:

1. Of all the plumes with the same lower moments, the Gaussian one is characterized by the highest degree of dilution, as measured by the dilution index.

2. The reactor ratio for a plume encountered under field conditions is likely to be considerably less than 1. In such cases the dilution of the plume is not characterized sufficiently by the dispersion, which simply is a measure of plume extent. It is important to provide additionally the reactor ratio which is a macroscopic measure of how complete is the dilution compared to the theoretically maximum dilution.

Advection-Dispersion With Constant Coefficients

Consider transport under the idealized conditions represented by the advection-dispersion equation with constant velocity and dispersion coefficients:

$$\frac{\partial c}{\partial t} + u_i \frac{\partial c}{\partial x_i} = D_{ij} \frac{\partial^2 c}{\partial x_i \partial x_j} \quad (29)$$

where t is time; x_i is the i th coordinate of a Cartesian system; u_i is the constant velocity in the i th direction; and D_{ij} is the ij th component of the constant (local) dispersion tensor. This case is of interest partly because I want to demonstrate the validity of the dilution index and partly because actual conditions in the field are often compared with the conditions envisioned by this simple model.

Under these conditions the dispersion, Δ , increases linearly with time independently of the initial conditions. The time rate of increase of the dispersion tensor is twice the tensor of the dispersion coefficients:

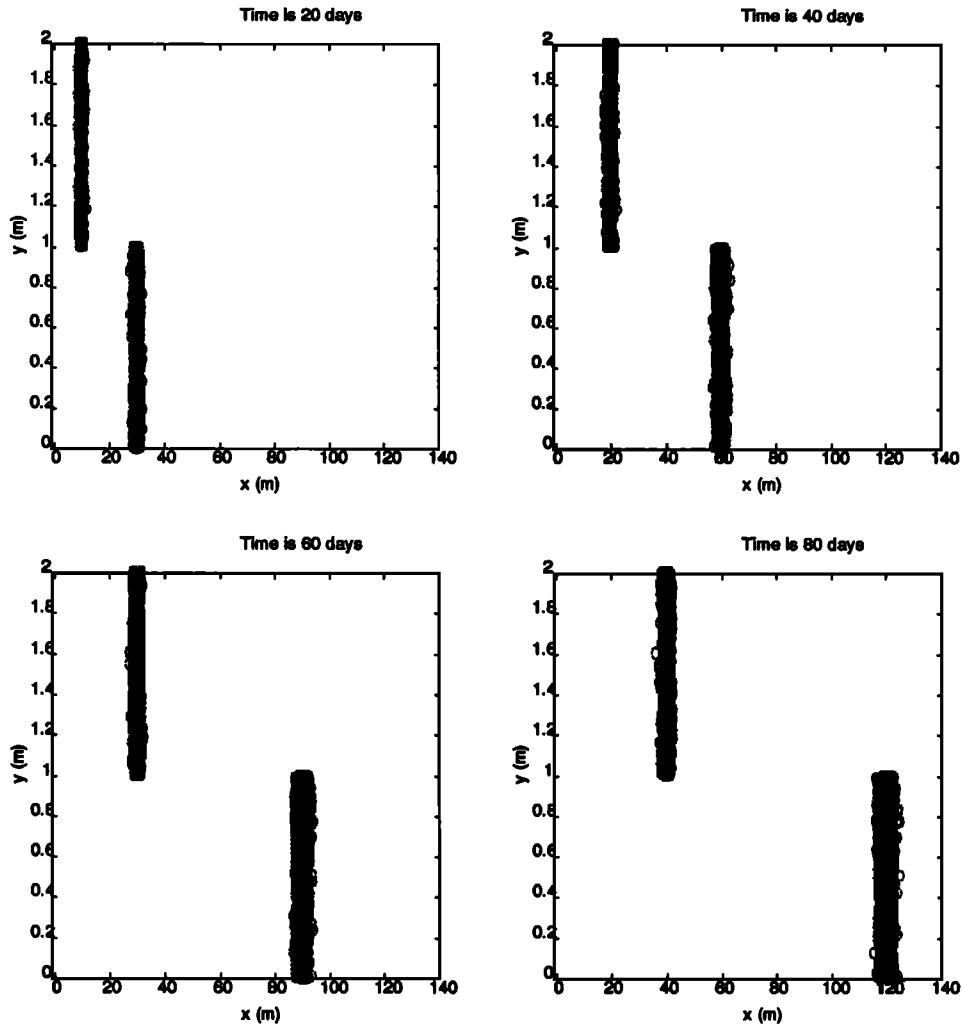


Figure 6. Tracer plume 20, 40, 60, and 80 days, assuming $a_T = 0$.

$$\frac{d\Delta}{dt} = 2\mathbf{D} \quad (30)$$

(This can be shown by applying integration by parts to (29).)

If, for the sake of simplicity, we focus on the example of an instantaneous pulse injection, then it is known that the dispersion is

$$\Delta = 2\mathbf{D}t \quad (31)$$

and the plume is Gaussian. Substituting in (25),

$$E = E_{\max} = (2\pi)^{n/2} \exp(n/2)(\det(2\mathbf{D}))^{1/2} t^{n/2} \quad (32)$$

Thus the dilution index increases with time, t , according to the relation

$$E \sim t^{n/2} \quad (33)$$

where n is the dimension of the domain. This result is as expected because this is how the extent (length, area, volume) of a Gaussian plume increases with time.

The complete solution is that the normalized concentration, assuming instantaneous pulse injection at time $t = 0$ and location $\mathbf{x} = \mathbf{0}$, is

$$p(\mathbf{x}) = (2\pi)^{-n/2} (\det(2\mathbf{D}t))^{-1/2} \cdot \exp\left(-\frac{1}{2}(\mathbf{x} - \mathbf{u}t)^T (2\mathbf{D}t)^{-1} (\mathbf{x} - \mathbf{u}t)\right) \quad (34)$$

The peak concentration is at location $\mathbf{x} = \mathbf{u}t$. Consequently, the peak concentration decreases according to the relation

$$p_{\text{peak}} = (2\pi)^{-n/2} (\det(2\mathbf{D}))^{-1/2} t^{-n/2} \sim t^{-n/2} \quad (35)$$

Thus the dilution index at any time is indeed inversely proportional to the peak concentration, confirming once again that the dilution index is a physically meaningful measure of dilution.

Finally, note that the plot of the logarithm of E against the logarithm of time is a straight line with slope $\frac{1}{2}$, 1, or $\frac{3}{2}$ depending on whether the domain is one, two, or three dimensional and an intercept that is affected by the coefficients of the dispersion tensor:

$$\ln(E) = \left[\frac{n}{2} \ln(2\pi) + \left(\frac{n}{2}\right) + \frac{1}{2} \ln(\det(2\mathbf{D})) \right] + \frac{n}{2} \ln(t) \quad (36)$$

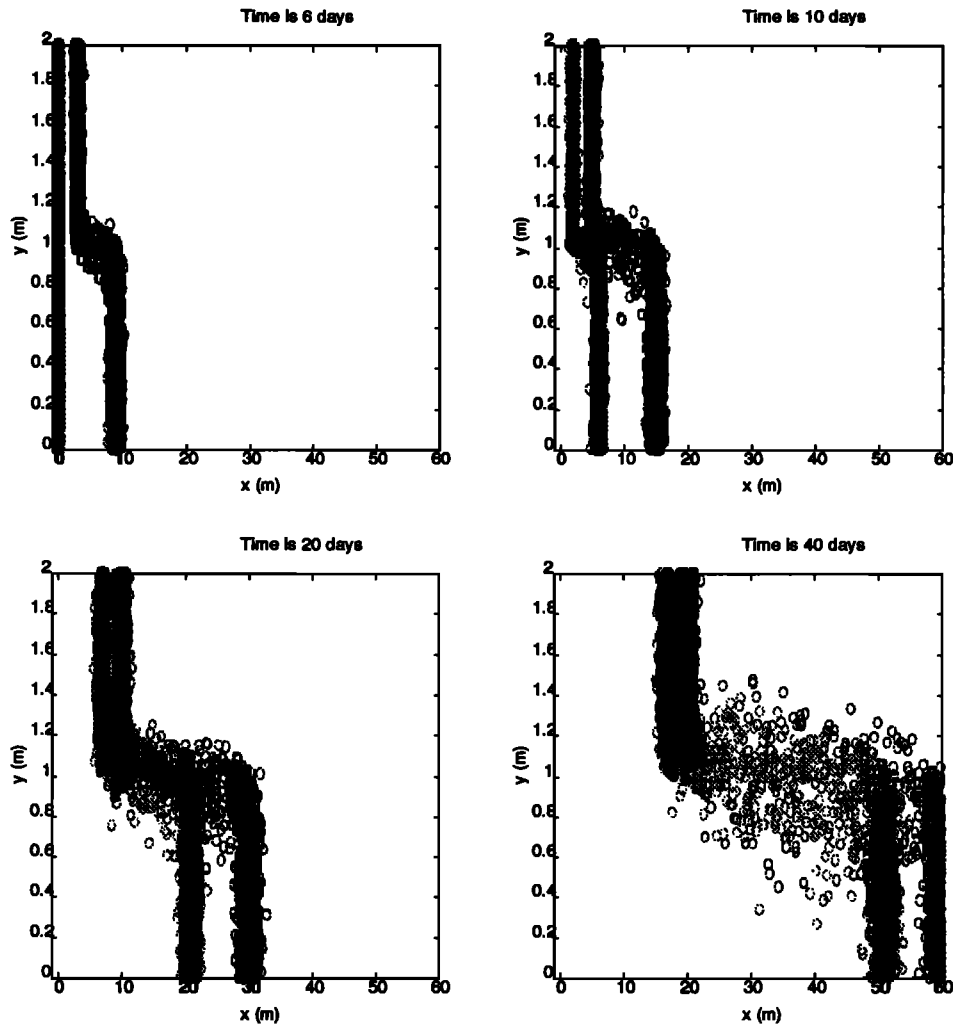


Figure 7. Tracer pulses at 6, 10, 20, and 40 days.

or

$$\frac{d \ln (E)}{d t} = \frac{n}{2} \frac{1}{t} \quad (37)$$

An alternative way to express the same rate for a Gaussian plume is

$$\frac{d \ln (E)}{d t} = D_{ij}(\Delta^{-1})_{ij} = \text{Tr} [\mathbf{D}\Delta^{-1}] \quad (38)$$

where by Δ^{-1} we denote the inverse of the second-moment matrix and Tr means the trace of a square matrix, i.e., the sum of the diagonal elements of the matrix. Thus the rate increases with the magnitude of the local dispersion coefficients and decreases with the size of the plume.

In applications we are interested in the rate with which the dilution index E increases with time because it gives the rate with which concentration levels are reduced. If we have a plume of arbitrary shape in a homogeneous formation, we cannot compute the exact rate of increase of E at the initial time without numerical integrations and we cannot forecast this rate at a later time without solving the advection-

dispersion coefficient. These tasks involve a considerable amount of numerical computations because of the irregularity of the plume shape.

Fortunately, a lower bound to the rate of increase of the logarithm of E can be easily computed by just using the dispersion (second spatial moment) of the plume:

$$\frac{d \ln (E)}{d t} \geq D_{ij}(\Delta^{-1})_{ij} = \text{Tr} [\mathbf{D}\Delta^{-1}] \quad (39)$$

where Δ is the second-moment matrix. The proof of this interesting result is in Appendix D. The bound is tighter if the plume shape approaches the Gaussian.

This lower bound can be used as a rough estimate of the rate of change of the logarithm of the dilution rate without going through the trouble of solving the complete equation. It may be a useful approximation in many applications where there is considerable uncertainty about the exact shape of the plume and the magnitude of the local dispersion coefficients.

For illustration, consider two examples.

Example 1. If $\Delta = 2Dt$ provide an estimate of the rate of increase of the dilution rate:

$$\frac{d \ln (E)}{dt} \geq \text{Tr} [\mathbf{D}\mathbf{D}^{-1}/(2t)] = \frac{n}{2} \frac{1}{t}$$

which is consistent with (37).

Example 2. Consider that the matrix of the dispersion coefficients expressed in square meters per day is

$$\mathbf{D} = \begin{bmatrix} 0.01 & & \\ & 0.001 & \\ & & 0.001 \end{bmatrix}$$

and that the second spatial moment of the plume expressed in square meters is at the present time

$$\Delta_0 = \begin{bmatrix} 2 & 0.2 & 0.2 \\ 0.2 & 1 & 0.1 \\ 0.2 & 0.1 & 1 \end{bmatrix}$$

Find the rate of increase of the dilution index at the present time and also 60 days later.

$$\Delta_0^{-1} = \begin{bmatrix} 0.5189 & -0.0943 & -0.0943 \\ -0.0943 & 1.0273 & -0.0839 \\ -0.0943 & -0.0839 & 1.0273 \end{bmatrix}$$

Thus the present rate is

$$\frac{d \ln (E)}{dt} = 0.0072/d$$

At the present time, the dilution index increases by a factor of 1.0072 per day.

Sixty days later, the second moment is $\Delta_{60} = \Delta_0 + 2Dt$ or:

$$\begin{bmatrix} 2 & 0.2 & 0.2 \\ 0.2 & 1 & 0.1 \\ 0.2 & 0.1 & 1 \end{bmatrix} + \begin{bmatrix} 0.01 & & \\ & 0.001 & \\ & & 0.001 \end{bmatrix} 60 = \begin{bmatrix} 2.6 & 0.2 & 0.2 \\ 0.2 & 1.06 & 0.1 \\ 0.2 & 0.1 & 1.06 \end{bmatrix}$$

$$\frac{d \ln (E)}{dt} = 0.0059/d$$

which means that the dilution index will be increasing by a factor of 1.0059 per day. Note that as the plume spreads, the dilution index increases at a slower rate.

Summary and Discussion

Considerable confusion can be created by the indiscriminate use of the term "dispersion" to describe both spreading and dilution (or mixing). Spreading is the change of plume shape, as when a plume is distorted in a stratified formation consisting of low- and high-conductivity layers. Dilution is, in a general sense, associated with the change of volume occupied by the plume. A plume in a stratified formation

may be stretching relatively quickly, but its volume increases much more slowly at early times.

In the analysis of field data and in environmental applications, it is often important to make the distinction between spreading and dilution. One of the difficulties associated with studying dilution has been the lack of a good way to quantify the overall dilution state of a plume. The second spatial moment which is occasionally used is a reasonable way to quantify spreading but is ineffectual in describing dilution, except in the idealized case of a Gaussian plume.

The main objective of this work was to introduce a measure of the state of dilution of a plume. It has been demonstrated to be a useful measure of the state of dilution and has been used to improve our understanding of the factors and mechanisms that affect dilution.

The dilution index is a macroscopic or volume-averaged measure of the state of dilution of a system. It is defined through (6) for the discrete case, where the reactor or flow domain is subdivided into a number of bins of equal volume, and through (8) for the continuous case. The dilution index is interpreted physically as the characteristic volume (or area or length for two- and one-dimensional domains) of the plume. Thus the larger the dilution index, the larger the volume of the fluid occupied by the solute. Note that the dilution index is a measure of uniformity in the distribution of mass and provides no information about the total solute mass in the system or the location and spread of the plume.

An important property of the dilution index is that when the distribution of mass becomes more uniform, the index increases. Another important property is that the most complete dilution under a certain set of conditions corresponds to the maximum value of the dilution index under the same conditions. The ratio of the actual dilution index to the maximum value is called the reactor ratio (because it is essentially a ratio of volumes) and is a number between 0 and 1 that signifies how close the system is to complete dilution.

In particular, in the case of a closed container, such as a batch reactor, the most complete dilution corresponds to the case that the distribution is uniform within the container. In the case of a plume in a large formation (where the boundaries are far away) with given mass, centroid, and spread (second spatial moment), the most complete state of dilution is given by the Gaussian distribution of concentration. It is interesting that the Gaussian plume, which is computed from approximate analytical solutions and which has influenced the way we think of plumes, corresponds to an extreme case of diluteness among plumes with the same spread. Plumes found in the field are highly non-Gaussian, indicating a significantly less complete state of dilution.

Note that the dilution index is a snapshot measure of the state of dilution of a solute and applies to both conservative and nonconservative solute.

This work next focused on the case of an ideal tracer in a large formation to study how dilution changes with time. Under general conditions of heterogeneity the following conclusions can be drawn:

1. The rate of increase of the dilution index can never be negative, indicating clearly that the dilution can only increase with time. Of course, this result makes sense intuitively. By contrast, the commonly used second spatial moment of a plume may increase or decrease as the plume stretches or contracts due to heterogeneity.
2. The instantaneous rate of increase of the dilution

depends only on the local dispersion and the shape of the plume. The higher the local dispersion coefficients and the more distorted and striated a plume, the higher the rate of increase.

3. The instantaneous rate of increase of the dilution is unaffected by the advective velocities. Thus if local dispersion were neglected, the dilution would not increase, no matter how nonuniform the velocity. Advection per se may distort a plume but does not change its volume, so it does not change the dilution.

4. In the long term, nonuniformity in the advective velocity increases the dilution rate by increasing the degree of deformation and striation of the plume, i.e., by making the shape of the plume more irregular and increasing the surface area over which the mass transfer due to local dispersion (including molecular diffusion) can occur.

This work also examined the idealized case described by the advection-dispersion equation with constant coefficients. This is the case of uniform flow in a homogeneous aquifer. For a Gaussian plume the rate of increase of the dilution index is given by a simple formula, equation (38), that requires information only about the local dispersion coefficients and the spread (second spatial moment) of the plume. The rate increases with the magnitude of the local dispersion coefficients and decreases with the extent of the plume. If the plume is not Gaussian, the same expression is a lower bound to the dilution rate. This expression is useful as a rough approximation of the rate of dilution at a point in time.

In conclusion, the objective of this work was to develop a physically reasonable way to quantify dilution and to study its properties. Clearly, considerably more work is needed on the subject of dilution and mixing under realistic field conditions and in the context of transformations. This work should include studies of the effects on heterogeneity on rates of dilution and methods to infer the mixing properties of aquifers from field tests.

Appendix A

The E index is obtained for the continuous case by setting $\Delta V = V/n$, where V is the total volume and n is the number of bins, and taking the limit as $n \rightarrow \infty$. Then, $P_k = p(\mathbf{x}_k)\Delta V$.

$$\begin{aligned}
 E &= \lim_{n \rightarrow \infty} \frac{V}{n} \left[\exp \left(- \sum_{k=1}^n P_k \ln (P_k) \right) \right] \\
 &= \lim_{n \rightarrow \infty} \left[\exp \left(- \sum_{k=1}^n p(\mathbf{x}_k)\Delta V \ln (p(\mathbf{x}_k)\Delta V) + \ln \left(\frac{V}{n} \right) \right) \right] \\
 &= \lim_{n \rightarrow \infty} \left[\exp \left(- \sum_{k=1}^n p(\mathbf{x}_k)\Delta V \ln (p(\mathbf{x}_k)) \right) \right. \\
 &\quad \cdot \exp \left(\left(1 - \sum_{k=1}^n p(\mathbf{x}_k)\Delta V \right) \ln \left(\frac{V}{n} \right) \right) \left. \right] \\
 &= \exp \left[- \int_V p(\mathbf{x}) \ln (p(\mathbf{x})) dV \right] \quad (40)
 \end{aligned}$$

because $1 - \sum_{k=1}^n p(\mathbf{x}_k)\Delta V \rightarrow 0$ faster than $\ln(n) \rightarrow \infty$. Note also that although the derivation implicitly assumed that V is finite, the result applies even if we assume that the size of the reactor increases without bound.

Appendix B

This appendix develops a general equation to compute the rate of change of the dilution of an ideal tracer in an unbounded domain.

The transport is described by the advection-dispersion equation with variable coefficients:

$$\frac{\partial p}{\partial t} + \frac{\partial (u_i p)}{\partial x_i} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial p}{\partial x_j} \right) \quad (41)$$

where $p(x_i, t)$ is the concentration normalized by the mass; t is time; x_i is the i th coordinate of a Cartesian system; u_i is the velocity in the i th direction; and D_{ij} is the ij th component of the constant dispersion tensor. The velocity is variable but satisfies the incompressibility condition:

$$\frac{\partial u_i}{\partial x_i} = 0 \quad (42)$$

The dilution index is

$$E = \exp \left(- \int_V p(\mathbf{x}, t) \ln (p(\mathbf{x}, t)) dV \right) \quad (43)$$

where the integration is over the unbounded domain, V . From this equation

$$\begin{aligned}
 \frac{d \ln (E)}{dt} &= - \int_V \frac{\partial p}{\partial t} \ln (p) dV - \int_V \frac{\partial p}{\partial t} dV \\
 &= - \int_V \frac{\partial p}{\partial t} \ln (p) dV - \frac{\partial}{\partial t} \left(\int_V p dV \right) \\
 &= - \int_V \frac{\partial p}{\partial t} \ln (p) dV \quad (44)
 \end{aligned}$$

Next we substitute $\partial p/\partial t$ from the advection-dispersion equation

$$\frac{d \ln (E)}{dt} = - \int_V \left[- \frac{\partial (u_i p)}{\partial x_i} + \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial p}{\partial x_j} \right) \right] \ln (p) dV \quad (45)$$

and then proceed to apply integration by parts. We will consider the following boundary conditions: At large distances the normalized concentration and its gradients decay to zero exponentially so that on the envelope, S , of the total domain,

$$p = 0 \quad (46)$$

$$u_i p \ln (p) = 0 \quad (47)$$

$$u_i p = 0 \quad (48)$$

$$D_{ij} \frac{\partial p}{\partial x_j} \ln (p) = 0 \quad (49)$$

Then, by applying integration by parts and the divergence theorem of calculus, we find

$$\begin{aligned}
\int_V \frac{\partial(u_i p)}{\partial x_i} \ln(p) dV &= \int_V \frac{\partial(u_i p \ln(p))}{\partial x_i} dV \\
- \int_V u_i \frac{\partial p}{\partial x_i} dV &= \int_S u_i p \ln(p) dS_i - \int_V u_i \frac{\partial p}{\partial x_i} dV \\
&= - \int_V u_i \frac{\partial p}{\partial x_i} dV = - \int_V \frac{\partial(u_i p)}{\partial x_i} dV + \int_V p \frac{\partial u_i}{\partial x_i} dV \\
&= - \int_S u_i p dS_i = 0 \tag{50}
\end{aligned}$$

Thus we see that the advective velocity does not affect the instantaneous rate of increase of the dilution rate.

$$\begin{aligned}
- \int_V \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial p}{\partial x_j} \right) \ln(p) dV \\
&= - \int_V \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial p}{\partial x_j} \ln(p) \right) dV + \int_V \frac{1}{p} \frac{\partial p}{\partial x_i} D_{ij} \frac{\partial p}{\partial x_j} dV \\
&= - \int_S D_{ij} \frac{\partial p}{\partial x_j} \ln(p) dS_i + \int_V \frac{1}{p} \frac{\partial p}{\partial x_i} D_{ij} \frac{\partial p}{\partial x_j} dV \\
&= \int_V \frac{1}{p} \frac{\partial p}{\partial x_i} D_{ij} \frac{\partial p}{\partial x_j} dV \tag{51}
\end{aligned}$$

Thus we finally find that

$$\frac{d \ln(E)}{dt} = \int_V \frac{1}{p} \frac{\partial p}{\partial x_i} D_{ij} \frac{\partial p}{\partial x_j} dV \tag{52}$$

or

$$\frac{d \ln(E)}{dt} = \int_V \frac{\partial \ln p}{\partial x_i} D_{ij} \frac{\partial \ln p}{\partial x_j} p dV \tag{53}$$

Because the dispersion-coefficient matrix D_{ij} is nonnegative definite, the quadratic form $(\partial \ln p / \partial x_i) D_{ij} (\partial \ln p / \partial x_j)$ cannot be negative. Thus

$$\frac{d \ln(E)}{dt} \geq 0 \tag{54}$$

Thus the dilution of a conservative tracer in an unbounded domain without sources or sinks cannot decrease. In fact, with the exception of special cases, D_{ij} is positive definite, in which case

$$\frac{d \ln(E)}{dt} > 0 \tag{55}$$

which means that the dilution increases monotonically.

Appendix C

For the sake of simplicity, we will consider the one-dimensional case. We consider an unbounded reactor. The

centroid, α , and the dispersion, Δ , of the plume are considered given. To find the most complete mixing, the objective here is to find through variational calculus the function that minimizes

$$\int_{-\infty}^{\infty} p \ln(p) dx \tag{56}$$

subject to

$$\int_{-\infty}^{\infty} p(x) dx = 1 \tag{57}$$

$$\int_{-\infty}^{\infty} p(x)x dx = \alpha \tag{58}$$

$$\int_{-\infty}^{\infty} p(x)x^2 dx = \Delta \tag{59}$$

Let p be the function that is the true solution and let $\eta(x)$ be any function which simply satisfies the homogeneous form of the constraints:

$$\int_{-\infty}^{\infty} \eta(x) dx = 0 \tag{60}$$

$$\int_{-\infty}^{\infty} \eta(x)x dx = 0 \tag{61}$$

$$\int_{-\infty}^{\infty} \eta(x)x^2 dx = 0 \tag{62}$$

Then, for any scalar ε , the function $p(x) + \varepsilon \eta(x)$ automatically satisfies the constraints. The integral

$$I(\varepsilon) = \int_{-\infty}^{\infty} (p(x) + \varepsilon \eta(x)) \ln(p(x) + \varepsilon \eta(x)) dx \tag{63}$$

is a function of ε that must take its minimum value when $\varepsilon = 0$; otherwise, the solution is not a unique minimum locally. Thus $dI/d\varepsilon = 0$ at $\varepsilon = 0$.

$$\int_{-\infty}^{\infty} [\eta(x) + \eta(x) \ln(p(x))] dx = 0 \tag{64}$$

or, after simplification,

$$\int_{-\infty}^{\infty} \eta(x) \ln(p(x)) dx = 0 \tag{65}$$

Because η is arbitrary other than that it satisfies equations (60)–(62), the coefficient, $\ln(p(x))$, must be selected so that the integral is indeed 0. The only terms allowed are the ones that will automatically make the integral 0 by virtue of the constraints (60)–(62):

$$\ln(p(x)) = C_0 + C_1 x + C_2 x^2 \tag{66}$$

From

$$p(x) = \exp(C_0 + C_1 x + C_2 x^2) \tag{67}$$

and the three constraints (57)–(59) we find that the only solution is

$$C_0 = \ln \left(\frac{1}{(2\pi)^{1/2}} \right) - \frac{\alpha^2}{2\Delta} \quad C_1 = \frac{\alpha}{\Delta} \quad C_2 = -\frac{1}{2\Delta}, \quad (68)$$

so that

$$p(x) = \frac{1}{(2\pi\Delta)^{1/2}} \exp \left(-\frac{(x - a)^2}{2\Delta} \right) \quad (69)$$

The extension to the multidimensional case is straightforward, following exactly the same methodology.

The maximum index is

$$E_{\max} = \exp (1/2)(2\pi\Delta)^{1/2} \quad (70)$$

Note that E_{\max} can be interpreted as the size of the reactor.

The reactor ratio is

$$M = \frac{\exp [-\int_V p(x) \ln (p(x)) dx]}{\exp (1/2)(2\pi\Delta)^{1/2}} \quad (71)$$

which can be interpreted as the ratio of the reactor where there is solute to the maximum size of the reactor given the available information.

Appendix D

Here, we will derive a lower bound to $d \ln (E)/dt$ for spatially constant dispersion coefficients.

We will first derive the bound for the one-dimensional case:

$$\frac{d \ln (E)}{dt} = \int_{-\infty}^{\infty} \left(\frac{\partial \ln p}{\partial x} \right)^2 D p dx \quad (72)$$

From

$$\frac{\partial}{\partial x} ((x - \alpha)p(x)) = p(x) + (x - \alpha) \frac{\partial p}{\partial x} \quad (73)$$

$$[(x - \alpha)p(x)]_{-\infty}^{\infty} = \int_{-\infty}^{\infty} p(x) dx + \int_{-\infty}^{\infty} (x - \alpha) \frac{\partial p}{\partial x} dx \quad (74)$$

or

$$0 = 1 + \int_{-\infty}^{\infty} (x - \alpha) \frac{\partial \ln p}{\partial x} p dx \quad (75)$$

or

$$1 = \left\{ \int_{-\infty}^{\infty} (x - \alpha) \frac{\partial \ln p}{\partial x} p dx \right\}^2 \leq \left\{ \int_{-\infty}^{\infty} (x - \alpha)^2 p dx \right\} \cdot \left\{ \int_{-\infty}^{\infty} \left(\frac{\partial \ln p}{\partial x} \right)^2 p dx \right\} = \frac{\Delta}{D} \left\{ \int_{-\infty}^{\infty} \left(\frac{\partial \ln p}{\partial x} \right)^2 D p dx \right\} \quad (76)$$

where we made use of the Cauchy-Schwartz inequality for integrals. Thus

$$\frac{d \ln (E)}{dt} \geq \frac{D}{\Delta} \quad (77)$$

where D is the dispersion coefficient and Δ is the second spatial moment. The lower bound corresponds to the rate of a Gaussian plume with the same second spatial moment. (Compare with (38). Another way to prove this statement is to note that the inequality reduces to equality only if $(\partial \ln p/\partial x)/(x - \alpha)$ is a constant, or $\ln p \sim (x - \alpha)^2$, which happens only for the Gaussian plume.)

The derivation for the multidimensional case is more complicated. We want to find a bound to

$$\frac{d \ln (E)}{dt} = \int_V \frac{\partial \ln p}{\partial x_i} D_{ij} \frac{\partial \ln p}{\partial x_j} p dV = D_{ij} F_{ij} \quad (78)$$

where

$$F_{ij} = \int_V \frac{\partial \ln p}{\partial x_i} \frac{\partial \ln p}{\partial x_j} p dV \quad (79)$$

We start with

$$\frac{\partial}{\partial x_j} ((x_i - \alpha_i)p(x)) = \delta_{ij}p(x) + (x_i - \alpha_i) \frac{\partial p}{\partial x_j} \quad (80)$$

for $i, j = 1, \dots, n$, where

$$\begin{aligned} \delta_{ij} &= 1 & i &= j \\ \delta_{ij} &= 0 & \text{otherwise} \end{aligned} \quad (81)$$

Then, integrating both sides over the whole domain,

$$\begin{aligned} \int_V \frac{\partial}{\partial x_j} ((x_i - \alpha_i)p(x)) dV \\ = \int_V \delta_{ij}p(x) dV + \int_V (x_i - \alpha_i) \frac{\partial p}{\partial x_j} dV \end{aligned} \quad (82)$$

From application of the divergence theorem and because p decays exponentially at large distances, the left-hand side vanishes and we can rewrite the equation as follows

$$-\delta_{ij} = \int_V (x_i - \alpha_i) \frac{\partial \ln p}{\partial x_j} p dV \quad (83)$$

This equation holds for every value of i and j .

Next, for two arbitrarily chosen n -dimensional vectors (which do not depend on the spatial location) λ_i and μ_i , the matrix form of the Cauchy-Schwartz inequality gives

$$\begin{aligned} \left\{ \lambda_i \left(\int_V (x_i - \alpha_i)(x_j - \alpha_j) p dV \right) \lambda_j \right\} \\ \cdot \left\{ \mu_k \left(\int_V \frac{\partial \ln p}{\partial x_k} \frac{\partial \ln p}{\partial x_l} p dV \right) \mu_l \right\} \geq \{ \lambda_m \delta_{mn} \mu_n \}^2 \end{aligned} \quad (84)$$

Next, using the definition of the second spatial moment Δ and of F and simplifying,

$$\{ \lambda_i \Delta_{ij} \lambda_j \} \{ \mu_k F_{kl} \mu_l \} \geq \{ \lambda_m \mu_m \}^2 \quad (85)$$

Assuming that F is invertible (practically always F is a positive definite matrix), we select μ as the product of the inverse of F times λ :

$$\mu_i = (F^{-1})_{ij}\lambda_j \quad (86)$$

Then

$$\{\lambda_i \Delta_{ij} \lambda_j\} \{\lambda_k (F^{-1})_{kl} \lambda_l\} \geq \{\lambda_k (F^{-1})_{kl} \lambda_l\}^2 \quad (87)$$

or

$$\lambda_i (\Delta - F^{-1})_{ij} \lambda_j \geq 0 \quad (88)$$

Since this relation holds for any λ , it follows that matrix $\Delta - F^{-1}$ is a nonnegative matrix or Δ is "larger" than matrix F^{-1} which means that

$$\lambda_i (\Delta^{-1} - F)_{ij} \lambda_j \leq 0 \quad (89)$$

$$(\Delta^{-1} - F)_{ij} D_{ij} \leq 0 \quad (90)$$

Thus

$$\frac{d \ln(E)}{dt} = D_{ij} F_{ij} \leq (\Delta^{-1})_{ij} D_{ij} \quad (91)$$

We derived a lower bound to the rate of increase of the logarithm of the dilution index. The inequality becomes an equality when the plume has a Gaussian shape.

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