

Solute dilution at the Borden and Cape Cod groundwater tracer tests

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Abstract. This study presents an analysis of the rate of dilution of a conservative nonreactive tracer in two well-known field experiments: The Borden (Ontario, Canada) experiment and the Cape Cod (Massachusetts) experiment. In evaluating the dilution of injected sodium bromide, in addition to computing the second spatial moments, we have used the dilution index and the reactor ratio. The dilution index is a measure of the formation volume occupied by the solute plume, and the reactor ratio is a shape factor, which measures how stretched and deformed the plume is. Unlike the second moments, which may go up or down during an experiment, the dilution index should increase monotonically. The results for both plumes were quite similar. After an initial period the dilution index increased linearly with time, which is macroscopically equivalent to transport in two-dimensional uniform flow. The reactor ratio was relatively constant during the period of the experiments. Their values, about 0.72 for the Borden test and 0.63 for the Cape Cod test, indicate that the Cape Cod plume was more stretched and deformed than the Borden plume. The maximum concentration, which is an alternative to the dilution index for quantifying dilution, was found to be more erratic and more susceptible to sampling error.

Introduction

Transport of an ideal tracer in a porous medium is commonly described by the advection-dispersion equation. The dispersive process results in spreading of the solute about the center of mass as well as its dilution into a larger volume of water. It is common practice to measure the extent of spreading through the second spatial moments about the center of mass and to quantify the rate of spreading through the macrodispersion coefficients (defined as one half the time rate of change of the second central spatial moments). However, the second moments or the macrodispersion coefficients are not necessarily adequate measures of the degree or rate of dilution of a solute in groundwater. The reason is that in the field, chemical plumes are lumpy and concentration contours are irregular so that dilution must be distinguished and quantified separately from spreading.

Figures 1 and 2 illustrate the difference between dilution and spreading. Figures 1a and 2a depict contour lines of constant bromide concentrations ("isoconcentration lines") on a vertical cross section along the center of the Borden [Roberts and Mackay, 1986] and Cape Cod [Leblanc *et al.*, 1991] tracer plumes at days 381 and 384, respectively, after the tracer injection. The irregular isoconcentration lines must be a consequence of small-scale variations in velocity, probably due to variations in hydraulic conductivity. High-concentration spots appear in areas of lower concentration, and peak values are slightly displaced toward the rear part of the plumes. Figures 1b and 2b are the same cross sections as Figures 1a and 2a, but the isoconcentration lines have been reconstructed using a Gaussian mass distribution with the measured mass, center of mass, and spatial second mo-

ments. Whereas the actual and the regularized plumes have the same macroscopic characteristics of total mass, centroid location, and second moments, the actual plumes are less diluted than the regularized ones. For example, notice the significant difference of peak concentrations in each plume (146 versus 104 and 47.3 versus 18.2 mg/L, respectively). It appears also that the regularized plumes occupy a larger aquifer volume than the actual ones. This example demonstrates the need to supply information additional to the second central moment in order to quantify the degree of solute dilution of actual plumes, such as the ones shown in Figures 1a and 2a.

In practice, there arise many applications where we need to make better predictions of solute dilution. For example, to judge compliance with environmental regulations, it is critical to assess the rate of decrease of the maximum concentration in a contaminant plume. Dilution of chemicals is also an important concept in predicting reaction rates, such as when different soluble chemicals need to mix in a formation for reactions to take place. This is the case for some in situ bioremediation schemes, such as the pulsed injection of chemicals for enhancing the cometabolism of organic contaminants [Roberts *et al.*, 1990].

To quantify dilution, the following two measures have been proposed: The dilution index is a measure of the volume that is occupied by the chemical, and the reactor ratio is a dimensionless shape factor of the concentration distribution [Kitanidis, 1994]. The dilution index and the reactor ratio can supplement the spatial moments by providing information regarding the overall volume into which a chemical has been dissolved. This study applies the dilution index concept to quantify the overall dilution of the nonreactive tracer bromide (Br^-) at two natural gradient groundwater tracer tests: Borden, Ontario, and Cape Cod, Massachusetts [Roberts and Mackay, 1986; Mackay *et al.*, 1986;

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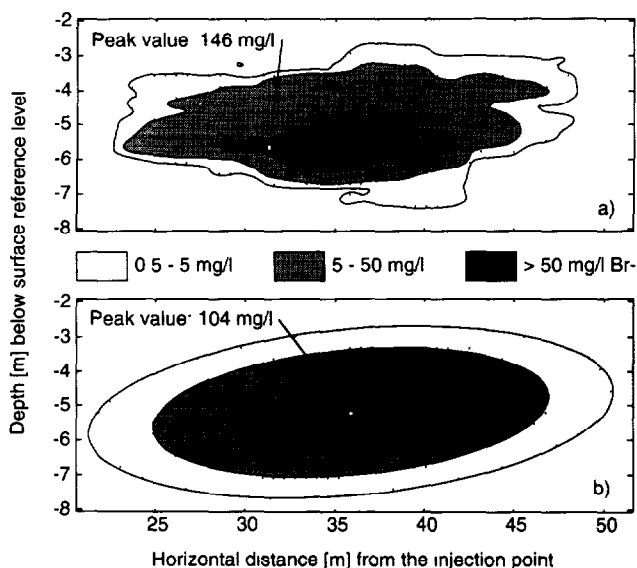


Figure 1. Borden experiment, day 381: Vertical cross sections along the center of the tracer plume. (a) Actual irregular bromide isoconcentration lines, from interpolation of data. (b) Isoconcentration lines of Gaussian plume inferred from the second spatial moments.

Leblanc *et al.*, 1991; Garabedian *et al.*, 1991]. Table 1 summarizes the main site characteristics and experimental setup for these tests. Measuring the mass distribution in a plume requires a large body of information. The Borden and Cape Cod experiments provide such a database and present an opportunity to evaluate dilution in the field.

Methods

Dilution Index and Reactor Ratio

The "dilution index" (or "dilution volume") E is a quantity that measures the overall degree of dilution of a tracer in a system [Kitanidis, 1994]. The dilution index is

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

where $P_k(t)$ is the ratio of the solute mass in an elementary volume ΔV of the system to the total mass of solute in the system at time t , and m is the total number of elementary volumes in the system. The dilution index is a macroscopic measure of the space (volume, area, or length) occupied by the solute.

In a continuous mode, obtained by taking the limit of very small ΔV , (1) is expressed as

$$E(t) = \exp \left(- \int_V p(\mathbf{x}, t) \ln p(\mathbf{x}, t) dV \right) \quad (2)$$

where $p(\mathbf{x}, t)$ is the normalized concentration at location \mathbf{x} and time t defined by

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

where V is the total volume of the domain and $\int_V c(\mathbf{x}, t) dV$ is the total mass.

In a closed system, optimal dilution is obtained when the solute is distributed uniformly throughout the system, i.e., with the same mass in every elementary volume ΔV . In that case E reaches its maximum E_{\max} obtained from (1) by setting $P_k = 1/m$,

$$E_{\max} = \Delta V \exp (-mP_k \ln (P_k)) = m\Delta V = V \quad (4)$$

Notice that in this special case, the maximum value of the dilution index is equal to the volume of the system.

The reactor ratio M is defined as

$$M = E/E_{\max} \quad (5)$$

The reactor ratio is a dimensionless number between 0 and 1 that describes how complete the actual dilution is compared to the theoretical maximum.

In an unbounded domain, the maximum dilution of a solute plume is not defined in relation to the size of the system, which is very large, but in relation to the maximum value of the dilution index E_{\max} for a given spatial second moment. By maximizing the dilution index (2) for given first and second spatial moments,

$$E_{\max} = (2\pi)^{n/2} \exp (n/2) (\det (\Delta))^{1/2} \quad (6)$$

where n is the dimension of the domain of the solute plume (1, 2, or 3) and Δ is the second-moment tensor. The concentration that maximizes the dilution index (2) is the "Gaussian plume solution" that is computed when analytical methods are used to simulate advective-dispersive transport of a point injection in a large domain with uniform flow. Thus E_{\max} is E for the case of a Gaussian plume with the same second spatial central moments as the actual plume.

For the hypothetical case of homogeneous conditions, with constant velocity and dispersion coefficients and instantaneous point injection, the plume is Gaussian and the second (central) moment increases linearly with time:

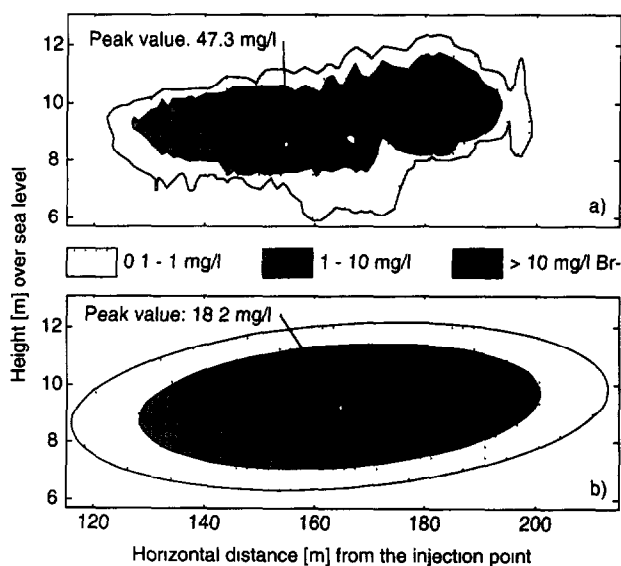


Figure 2. Cape Cod experiment, day 384: Vertical cross sections along the center of the tracer plume. (a) Actual irregular bromide isoconcentrations lines, from interpolation. (b) Isoconcentration lines of Gaussian plume inferred from the second spatial moments.

Table 1. Groundwater Tracer Tests at the Borden and Cape Cod Sites. Site Characteristics and Experimental Settings

	Borden, Ontario, Canada	Cape Cod, Massachusetts
Aquifer geology	glaciofluvial and glaciolacustrine stratified sands and silts	fluvio-glacial outwash, stratified sands and gravels
Hydraulic conductivity (range, mean)	5×10^{-7} to 2×10^{-4} , 9.75×10^{-5} m/s.	$(0.7-1.7 \times 10^{-3})^*$, 1.3×10^{-3} m/s.
Porosity (range, mean)	(0.31-0.35)*, 0.33	0.36-0.42, 0.39.
Groundwater flow velocity	0.091 m/d	0.42 m/d
Dispersivity A_L, A_H, A_V	0.36-0.5, 0.039-0.05, 0.0022 m	0.96, 0.018, 0.0015 m.
Types of tracer used	bromide, chloride, bromoform, carbon tetrachloride, perchloroethylene, 1,2-dichlorobenzene, hexachloroethane.	bromide, lithium, molybdate, and fluoride, as LiBr, LiF, and Li_2MoO_4
Solution volume and Br^- mass	12 m ³ , 3870 g	7.6 m ³ , 4900 g
Injection system	nine wells slotted between -2.0 and -3.6 m below a surface reference level	three wells screened between 1.2 and 2.4 m below the water table
Date and rate of tracer injection	August 23, 1982, 13.5 L/min	July 18-19, 1985, 7.45 L/min
Whole plume sampling after injection	at days 1, 9, 16, 29, 43, 63, 85, 133, 259, 335, 381, 429, 462, 647, and 1038	at days 13, 33, 55, 83, 111, 139, 174, 203, 237, 273, 315, 349, 384, 426, 461, and 511.

Data from Roberts and Mackay [1986] and Rajaram and Gelhar [1991] for the Borden experiment, and from Leblanc et al [1991] and Garabedian et al. [1991] for the Cape Cod experiment.

*Values in parentheses are estimated from published data.

$$\Delta = 2D_t \tag{7}$$

where **D** is the tensor of the dispersion coefficients. Using (7) in (6), we obtain the following relation:

$$E = (2\pi)^{n/2} \exp(n/2) (\det(2D))^{1/2} t^{n/2} \tag{8}$$

Thus if the medium behaves as a homogeneous one, *E* increases proportionally to $t^{n/2}$ and should be represented by a straight line in a $\ln(E)$ versus $\ln(t)$ plot, with a slope of $n/2$. The peak solute concentrations in the plume should decrease proportionally to $t^{-n/2}$. Furthermore, the rate of increase of $\ln(E)$ is

$$\frac{d \ln(E)}{dt} = \frac{n}{2} \frac{1}{t} \tag{9}$$

It is emphasized that (7), (8), and (9) are for the hypothetical case of instantaneous point injection in a uniform flow field and will be useful for comparison purposes. Equations (1), (2), and (5) are general and apply for a plume of any shape.

Spatial Moments Calculation

Spatial moments estimates are needed for determination of the maximum value of the dilution index E_{max} (equation (6)). The spatial moments are calculated by numerical evaluation of the following integrals:

$$M_{ijk}(t) = \iiint_{-\infty}^{+\infty} \eta c(x, y, z, t) x^i y^j z^k dx dy dz \tag{10}$$

where $M_{ijk}(t)$ is an (*i, j, k*)th spatial moment, η is the porosity, $c(x, y, z, t)$ is the concentration, *x, y, and z* are the spatial coordinates, and *t* is the time. Physically, the zeroth moment M_{000} is equal to the mass of tracer in solution. The first moments ($M_{100}, M_{010}, M_{001}$) normalized by the mass in solution define the coordinate location of the center of mass (x_c, y_c, z_c). The second moments ($M_{200}, M_{110}, M_{101}, M_{020}, M_{011},$ and M_{002}) about the center of mass, normalized by M_{000} , define the spatial second central moment (or covariance) tensor. The rate of increase of the principal components S_i of this covariance tensor over time

allows the calculation of coefficients of macrodispersion in its principal directions.

$$D_i^m = \frac{1}{2} \frac{dS_i}{dt} \tag{11}$$

See Freyberg [1986] and Garabedian et al. [1991] for numerical approximation of the spatial moments and calculation of the dispersion coefficients.

Interpolation Scheme

The estimation of the dilution index and the spatial moments requires the evaluation of integrals from values available at the observation points. The field data at the Borden and Cape Cod sites were collected on an irregular grid. The common approach is to first interpolate the data onto a fine regular three-dimensional grid and then to evaluate the integrals using a numerical quadrature method. The interpolation is the most problematic step in the estimation of the integrals. As also pointed out by Barry and Sposito [1990] and Rajaram and Gelhar [1991], the interpolation scheme should avoid excessive smoothing of the data. This requirement is particularly important in computing the dilution index because excessive smoothing will result in overestimation of the dilution in the aquifer.

Despite the importance of interpolation, there is no method that is universally accepted. For interpolation of the Borden data, Freyberg [1986] projected all values from the multiport boreholes to a horizontal plane, to sum up the concentration over the vertical direction:

$$C_z(x, y, t) = \int_{-\infty}^{+\infty} C(x, y, z, t) dz \tag{12}$$

He then interpolated the data onto a square grid from the four nearest neighboring data points by weighting inversely to the distance, or in some cases the squared distance, between the node and the data point, with the sum of the

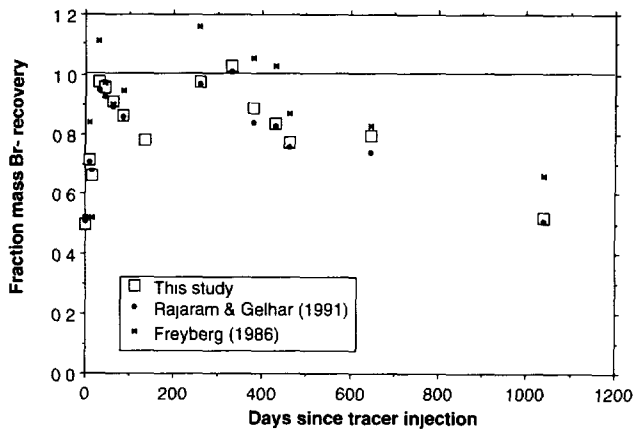


Figure 3. Fraction of mass accounted for in bromide data for the Borden tracer test.

weighting factors equal to 1. Thus this method does not compute moments in the vertical direction.

Barry and Sposito [1990] explored the use of a large number of high-order interpolation schemes for the Borden plume data in order to determine the spatial moments of the plume. For each sampling period they optimized a scheme by cross validation on the actual data. Barry *et al.* [1988] analyzed the two-dimensional (vertically averaged) moments.

Rajaram and Gelhar [1991] for the Borden plume and Garabedian *et al.* [1991] for the Cape Cod plume used a scheme based on linear interpolation on a triangular grid constructed between the multilevel samplers in the horizontal plane and an integration over the vertical direction, using trapezoidal rule quadrature. This technique may involve less smoothing of the data.

For this study, values were interpolated on a regular three-dimensional mesh with spacing $\Delta x \times \Delta y \times \Delta z = 1.0 \times 1.0 \times 0.15$ m, using a modification of the procedure applied by Rajaram and Gelhar [1991] and Garabedian *et al.* [1991]. Our approach involves the following steps:

1. It is assumed that concentration outside of the measurement region is zero: Even when top, bottom, or peripheral locations of the sampling network recorded concentrations significantly higher than the background value (0.5 mg/L), fictitious sampling points with zero concentration values were created beyond these locations for closing the interpolation domain. First, where concentrations at the top or the bottom port of a MLS (multilevel sampler) are ≥ 0.5 mg/L, a fictitious port with a zero concentration value is added above or below, respectively, this port at a distance equal to the vertical port spacing. Second, where a peripheral MLS records a bromide concentration greater than 0.5 mg/L, a fictitious MLS location with zero values at each port is added beyond it at a distance equal to the MLS spacing (in a row of MLS) or to the next row of samplers.

2. Over the vertical direction, at each MLS, the data are linearly interpolated from the port sampling levels to values on each of the planes of grid nodes. This way, on each plane of grid nodes, we obtain through interpolation concentration values at the locations where this plane crosses an MLS line.

3. On the top horizontal plane of grid nodes, for each node three locations are chosen where the plane crosses an

MLS from which to interpolate linearly the concentration; the same interpolation scheme is applied to all planes below.

The first step is similar to the procedure described by Rajaram and Gelhar [1991]. The addition of zero concentration values beyond available sampling locations where the plume is truncated by the measurement network is based on the assumption that the monitoring network covers the area of the plume. Although this is a good assumption in the majority of cases, at certain sampling dates of the Borden plume (e.g., days 85, 647, and 1038) and at a few sampling dates of the Cape Cod plume (e.g., days 13, 33, and 511), significant parts of the tracer plumes were apparently not sampled.

During the third step, which is interpolation of the concentrations on each grid node on the x - y plane, an iterative process was used to select the three MLS locations which fulfill the following conditions: (1) one of the MLS locations is the closest one to the grid node; (2) the three MLS locations form a triangle that includes the grid node and that does not include any other MLS location; and (3) the distance separating the grid node from the most remote vertex of the MLS triangle is minimized. However, in order to avoid interpolation over too long a distance, an MLS where this distance from the node is greater than twice the mean distance between MLS locations was not taken into account. When a grid node could not be enclosed in a triangle of MLS locations, the node concentration was assumed to be zero.

Results

Spatial Moments Estimation

The results from the Borden and Cape Cod experiments that will be presented in this work are all estimated from data interpolated, as already mentioned, onto a grid with sizes $\Delta x \times \Delta y \times \Delta z = 1.0 \times 1.0 \times 0.15$ m. Estimates of the spatial moments were used for calculating E_{\max} and the reactor ratio (equations (6) and (5)). The computed zeroth and second moments are shown in Figures 3–6. Because the method used for interpolating on a regular grid is like the technique described by Rajaram and Gelhar [1991] and Garabedian *et al.* [1991], our spatial moments estimates are

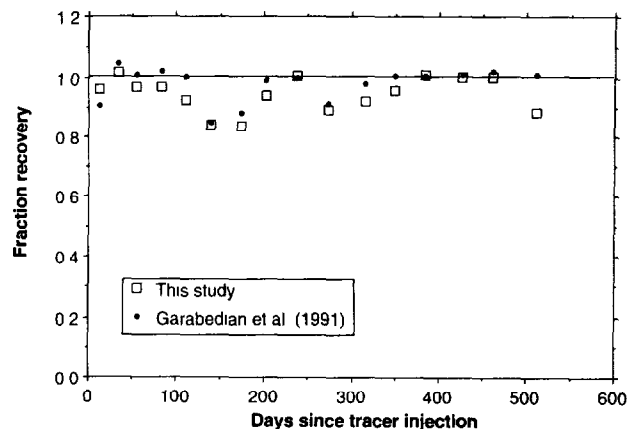


Figure 4. Fraction of mass accounted for in bromide data of the Cape Cod tracer test.