

# Time dependence of solute dispersion in aquifers

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**ABSTRACT:** Groundwater contamination is usually modelled using the advection-dispersion equation with a dispersivity that increases with travel distance. An alternative viewpoint is that the dispersivity is travel time dependent. The hydraulic conductivity,  $K$ , varies randomly with position so as to change the local Darcy flux throughout the aquifer. The mean movement of a passive solute is the same as the mean fluid velocity. Its spread, however, is controlled by local variations in fluid flow. Given the statistics of the Darcy flux (derived from the  $K$  statistics), it is possible to predict the macro-scale dispersion that will be experienced by a solute plume moving through the aquifer. A formula for the macro-dispersion coefficient, which is a function of the solute travel time in the aquifer, is presented. The predictions of the theory are then compared with the results of a well-controlled field experiment.

## 0 NOTATION

- a spatial period of velocity fluctuations, L
- $A_0$  differential operator,  $T^{-1}$
- c concentration,  $ML^{-3}$
- D laboratory-scale dispersion tensor,  $L^2T^{-1}$
- K Hydraulic conductivity,  $LT^{-1}$
- l autocorrelation decay length scale, L
- t time, T
- $\bar{t}$  variable of integration, T
- u transformation of c,  $ML^{-3}$
- v groundwater velocity,  $LT^{-1}$
- x position, L
- q Darcy flux,  $LT^{-1}$
- S Fourier transform of  $\Gamma$ ,  $L^5T^{-2}$
- $\alpha$  Fourier transform variable,  $L^{-1}$
- $\theta$  porosity
- $\kappa$  Fourier transform of  $K$ ,  $L^4T^{-1}$
- $\tau$  dimensionless time
- $\Gamma$  Darcy flux fluctuation covariance,  $L^2T^{-2}$
- $\phi$  piezometric head, L
- $\nabla$  del operator,  $L^{-1}$
- $\langle \cdot \rangle$  expectation of  $\cdot$
- $\dot{\cdot}$  fluctuation of  $\cdot$  about its ensemble average
- $\hat{\cdot}$  unit vector derived from  $\cdot$
- $\cdot_i$   $i^{\text{th}}$  component of the vector  $\cdot$
- $\cdot_{ij}$   $ij^{\text{th}}$  component of the tensor  $\cdot$

## 1 INTRODUCTION

Contamination remediation, to be effective, must rely on realistic models of the transport process so that appropriate action may be taken. On the other hand, risk assessment of possible environmental consequences of contamination events likewise requires the predictive capability of accurate models. In the first case, spreading (about the mean position) of the solute may cause large volumes of fluid to be degraded. This volume should be known if a cleanup strategy is to be implemented. In the second case, spreading will result in the presence of low concentrations of solute far ahead of the main signal. Risk assessments must take into account the possibility of hazardous species being present even in low concentrations. It is apparent from these remarks that knowledge of the mean movement of the chemical is not enough; theories should predict spreading as well (Dagan, 1986).

Modelling of solute transport in the laboratory and in the field differs principally in the scales that are of interest. In a laboratory column experiment the scale of interest is usually tens of centimetres to a metre, while in the field scales of the order of perhaps hundreds of me-

res are commonly dealt with in contamination problems. In the laboratory, of course, geotechnical centrifuges can be used to simulate transport through large spatial scales. It has yet to be demonstrated, however, that field-scale variability of hydraulic properties can be faithfully simulated using this technique. More typically, soil properties are determined in laboratory columns, or a field experiment is performed. Often, both laboratory and field approaches will be combined.

One of the major difficulties with aquifer contamination is translating laboratory results to the field scale. In natural settings, heterogeneity of aquifer material is the norm. Typical hydraulic conductivity variations can range by over four orders of magnitude (Bakr, 1976). A question that has received much attention in hydrology in the past 15 years is how this variability should be dealt with. The material presented below is an attempt to describe some of the theoretical advances that have been made, together with some example applications. The main focus will be on transport of a single, non reactive chemical species. Thus, predictions based on the theory will be conservative in that no species will be transported or dispersed more than a tracer. This is a valuable result if a potentially dangerous contaminant is being considered.

## 2 RANDOM VARIABILITY OF FLOW

We begin, not with the solute, but with the groundwater. To specialise matters somewhat, we consider the case of steady groundwater flow.

The major difference between the laboratory and field scales is the range of variability of soil hydraulic parameters, the main parameter of interest being the hydraulic conductivity,  $K$ . Although one can, in principle, describe the hydraulic conductivity as a known function of position within the aquifer, in practice this is not possible, nor is it even desirable (Gelhar, 1986). An obvious alternative is to treat  $K$  as being a random variable.  $K$  is then characterised by its low-order statistical moments. Groundwater flux,  $q$ , is given by Darcy's law:

$$q = -K \cdot \nabla \phi. \quad (1)$$

Note that, since  $K$  is random, so are  $\phi$  and  $q$ . A standard method of dealing with (1) is to separate each term in (1) into the appropriate en-

semble average and fluctuation about that average. This decomposition gives (Sposito et al., 1991):

$$K = \langle K \rangle + K', \quad (2)$$

$$\nabla \phi = \langle \nabla \phi \rangle + \nabla \phi' \quad (3)$$

and

$$q = \langle q \rangle + q'. \quad (4)$$

The combination of (2) through (4), together with the assumptions the quantities on the right-hand side of (1) are uncorrelated and that products of perturbations can be ignored (although see Cushman, 1983 and Dagan & Neumann, 1992), gives:

$$q' = \langle q \rangle [\ln(K)]' - \langle K \rangle \nabla \phi', \quad (5)$$

where

$$\langle q \rangle = - \langle K \rangle \langle \nabla \phi \rangle. \quad (6)$$

Equation (5), which is only first order accurate, has been written in terms of  $\ln(K)$  to conform with the observation that  $K$  tends to be log-normally distributed (cf. Bakr et al., 1978).

Now assume the spatial domain is infinite and that  $q$  is wide-sense stationary (Sposito & Barry, 1987), i.e.,  $\langle K \rangle$  is constant and

$$\langle q_i(x,t) q_j(\bar{x}, \bar{t}) \rangle = \Gamma_{ij}(x - \bar{x}, t - \bar{t}), \quad (7)$$

where  $i$  and  $j$  ( $= 1,2,3$ ) represent components. Using (5), the Fourier transform with respect to  $x$  can be found for (7) (Dagan, 1987; Sposito et al., 1991):

$$S_{ij} = [q_i - \hat{\alpha}_i(q; \hat{\alpha})] [q_j - \hat{\alpha}_j(q; \hat{\alpha})] \times \{ \ln \kappa(\alpha, t) [\ln \kappa(-\alpha, 0)] \}^{-1}, \quad (8)$$

where  $\alpha$  is the Fourier transform variable,  $S$  is the Fourier transform of  $\Gamma$  and  $\kappa$  is the Fourier transform of  $K$ . The advantage of (8) is that it approximates the variability of the water flux in terms of the variability of the hydraulic conductivity,  $K$ . It is the former quantity that controls tracer dispersion in the field. In the applications below the possibility of  $S$  varying with time has not been pursued.

## 3 SOLUTE DISPERSION

Solute dispersion observed in an aquifer under

steady flow conditions will be controlled by three factors: (i) molecular diffusion, (ii) boundary conditions, and (iii) variations in the groundwater velocity field. The groundwater velocity is:

$$v = \frac{q}{\theta} \quad (9)$$

Effects of (i) can typically be ignored (but see Matheron & de Marsily, 1980) when compared with (iii). Boundary conditions do not enter when an infinite domain is considered. Thus, below, the effects of (iii) alone are considered.

We have noted already that  $q$  varies due to variability of  $K$ . The porosity,  $\theta$ , varies as well. However, the variability of  $\theta$  (usually normally distributed) is much less than that of  $K$  (Freeze, 1975), and so it can be ignored. Because an average value of  $\theta$  is taken in (9),  $v$  and  $q$  are equal to within a constant, and so the variability in  $v$  is due entirely to  $q$ , whose fluctuations are given statistically by (8).

The governing advection-dispersion equation (ADE) for tracer solute transport in a steady flow field is (e.g., Barry, 1990b):

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \cdot \nabla c) - v \cdot \nabla c, \quad (10)$$

where the components of  $D$  are taken as laboratory-scale constants and  $v$  is the random solute drift velocity. Sposito & Barry (1987) derived an ensemble average equation for  $\langle c \rangle$  using the approach of Van Kampen (1976, 1981). The first step is to divide the differential operator on the right-hand side of (10) into its random and non random components. The non random portion is

$$A_0 = \nabla \cdot (D \cdot \nabla) - \langle v \rangle \cdot \nabla, \quad (11)$$

while  $v' \cdot \nabla$  is the random part. If  $u$  is defined by

$$u = \exp(-A_0 t) c, \quad (12)$$

then (10) can be rewritten as

$$\frac{\partial u}{\partial t} = \exp(-A_0 t) (v' \cdot \nabla) \exp(A_0 t) u. \quad (13)$$

Note that the differential operators in (13) appearing as arguments of the exponential function have meaning when expanded in series

about  $t = 0$ . Equation (13) can be solved formally because time is the only independent variable. From this formal solution, one can derive an expansion from which an ensemble average equation can be derived. The details of these operations have been detailed elsewhere (Sposito & Barry, 1987). However, the physical interpretation is that  $\partial \langle c \rangle / \partial t$  is approximated as a series in the product of the root-mean-square velocity fluctuations and the time scale over which  $v$  becomes uncorrelated (Van Kampen, 1976; Chu & Sposito, 1980, 1981). The resulting second-order accurate equation for  $\partial \langle c \rangle / \partial t$  is (Sposito & Barry, 1987; Kabala & Sposito, 1991)

$$\frac{\partial \langle c \rangle}{\partial t} = \nabla \cdot (D + F) \cdot \nabla \langle c \rangle - (\langle v \rangle - G) \cdot \nabla \langle c \rangle, \quad (14)$$

where

$$F = \int_0^t \int \frac{S(\alpha, \bar{t})}{\theta^2} \exp(-\alpha \cdot D \cdot \alpha \bar{t}) \cos(\langle v \rangle \cdot \alpha \bar{t}) d\alpha d\bar{t} \quad (15)$$

and

$$G = \int_0^t \int \frac{S(\alpha, \bar{t})}{\theta^2} \exp(-\alpha \cdot D \cdot \alpha \bar{t}) \sin(\langle v \rangle \cdot \alpha \bar{t}) d\alpha d\bar{t}. \quad (16)$$

For steady flow,  $G = 0$  (Sposito et al., 1991). For this case (14) has the form of the usual ADE except that the macrodispersion coefficient is now a function of time. It is interesting to show how various existing macrodispersion coefficients can be derived from (15). A case of some interest is that of a perfectly stratified aquifer with flow along the layers. From (15) or otherwise (Güven & Molz, 1986), with  $S_{11} \propto \delta(\alpha_3 \pm 2\pi/a)$ , the longitudinal macrodispersion coefficient can be determined as:

$$F_{11} \propto \frac{1}{D_{33}} \left[ 1 - \exp\left(\frac{-4\pi^2 D_{33} t}{a^2}\right) \right], \quad (17)$$

where  $a$  is the fluctuation period. Observe from (17) that as  $t \rightarrow 0$ ,  $F_{11} \propto t$ , whereas  $F_{11}$  is constant as  $t \rightarrow \infty$ .

Equation (17) reveals two important features. First, at  $t = 0$ ,  $F_{11} = 0$  so the solute experiences only the laboratory column-scale dispersion. Second, as  $D_{33} \rightarrow 0$ ,  $F_{11}$  becomes unbounded. This means that the transverse,

column-scale dispersion controls the rate at which the asymptotic value of  $F_{11}$  is approached. Without transverse movement of solute either by Fickian or mass transport, the macrodispersivity would grow without bound (Matheron & de Marsily, 1980).

Similar behaviour is observed for other physical situations. In essence, (15) indicates that because  $S$  will decay with increasing spatial and temporal scales, the macrodispersivity will eventually reach some asymptotic value. For example, Dagan (1984) takes the covariance in (8) to be a second-order stationary exponential decay (time-independent). For the two-dimensional case the longitudinal macrodispersivity is

$$F_{11} \propto 1 - \frac{3}{2\tau} - \frac{3\exp(-\tau)}{\tau^2} + \frac{3[1 - \exp(-\tau)]}{\tau^3} \quad (18)$$

where

$$\tau = \frac{\langle v \rangle t}{l} \quad (19)$$

Although (18) is more complex than (17), both expressions reduce to 0 at  $t = 0$ , and increase to a finite asymptotic value. Like (17), (18) shows  $F_{11}$  is linear in  $t$  as  $t \rightarrow 0$ , and is constant for large times.

#### 4 APPLICATION

Roberts & Mackay (1986) report a well-controlled field experiment carried out in Ontario, Canada. A group of solutes was injected into a sandy, unconfined aquifer. Progress of the solutes was monitored via a frequent sampling program over a three-year period. Sudicky (1986) characterised the spatial variability of  $K$  for the site. In particular he estimated the mean, variance and correlation lengths of the  $\ln(K)$  field. Thus, the macrodispersion exhibited by a plume in the aquifer can be compared directly with theoretical predictions.

Both bromide and chloride were injected as tracers, and the evolution of the tracer plume has been analysed in various studies (Freyberg, 1986; Barry et al., 1988; Barry & Sposito, 1990; Graham & McLaughlin, 1991; Rajaram & Gelhar, 1991). In Fig. 1, estimates of the longitudinal variance of the solute plume are plotted, along with the theoretical predictions based on the model of Dagan (1988) (cf. Barry, 1990a). The experimental values include approximate confidence intervals calcu-

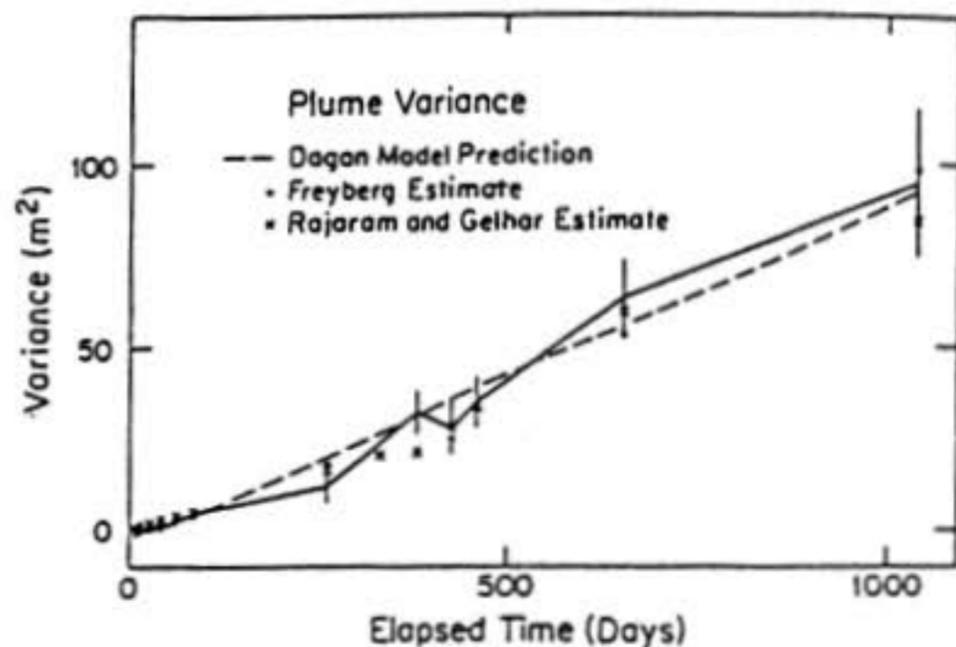


Figure 1. Comparison of Borden tracer plume variance estimates calculated by Freyberg (1986) (open circles), Rajaram & Gelhar (1988) (crosses), Barry & Sposito (1990) (solid line, with confidence interval estimates), and a theoretical prediction of Dagan (1988) (dashes).

lated using jackknifing (cf. Barry, 1991). The theory and field experiment data clearly agree well.

#### 5 CONCLUDING REMARKS

For tracer solutes, theory based on a local scale stochastic ADE has been shown to predict well with experimentally determined plume variance. Equation (14), however, implies that for any initial condition, a Gaussian plume will result. In practice, aquifers are not infinite domains and the groundwater velocity exhibits seasonal variations. Further, the question of appropriate averaging length and time scales over which solute concentrations should be averaged is open since the concentration in (14) is an ensemble average (cf. Dagan, 1984).

A difficulty with the approach presented here is that it does not include information that may be collected on an on-going basis as part of a site investigation. Obviously, such data should be used if it is available. If a combined water flow and transport model can faithfully replicate measured head,  $K$  and concentration values at a given time, then future predictions will be subject to less uncertainty. In contrast, equations like (17) and (18) predict the dispersivity based solely on the information available at some initial time. Head or  $K$  data collected at the site will act to reduce the uncertainty in statistical description of  $K$ , i.e., the covariance in (8) will be modified. Such data can then be used to reduce the concentration variance

measured at other locations. It can also be used to predict where future data should be collected so that the concentration uncertainty can be further reduced (e.g., Graham & McLaughlin, 1989).

Finally, the question of reactive solute transport has not been addressed. Although some theory has been reported (e.g., Kabala & Sposito, 1991), little is known about the most appropriate statistical description of reaction parameters such as retardation factors. One possibility is to assume that both  $K$  and local solute retardation are both correlated with a soil property like clay content.

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