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# Deconvolution of a nonparametric transfer function for solute transport in soils

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**Abstract**

Solute transport in soils can be described in terms of solute travel time probability density functions (pdfs). In the past, parameterized functional forms for the travel time pdf have been derived based on models of physical transport processes and the properties of the soil, or have been obtained from observed transport behavior. Alternatively, a nonparametric pdf for a particular soil can be measured experimentally. In general, this measurement requires deconvoluting the pdf, which is mathematically an ill-posed problem. In this paper we perform the deconvolution using a constrained regularization approach. The regularization method uses a basis function representation of the travel time pdf which eliminates numerical problems associated with the standard regularization approach. The method is tested using synthetic and experimental data. Regularized solutions are evaluated using Provencher's (Provencher, 1982a) *F* test statistic along with a visual inspection of their fit to the data. We analyze data from previously published field experiments and the results suggest multimodal travel time pdfs may be appropriate for modeling transport in soils. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

A variety of approaches have been used to model the transport of chemicals through soils. Several review articles (e.g., Addiscott and Wagenet, 1985; Brusseau and Rao, 1990; Jury and Flühler, 1992) provide detailed summaries.

Transport models are usually differentiated based on whether or not they use an explicit description of the physical transport processes occurring in the soil. Limited field testing of both deterministic and stochastic process-based models has been inconclusive. In field soils, physical and chemical nonequilibria, unstable water flow, preferential transport, and spatial variability of soil hydraulic properties all contribute in varying degrees to the overall observed transport. Given the overwhelming difficulty of obtaining a complete description of the process, a fully general description of transport does not seem feasible. Thus the challenge of process-based modeling is in trying to determine which processes are important and which can be ignored. However, it appears that it is not known a priori which processes are important in a given soil (Roth and Jury, 1993).

For some management purposes, it may suffice to use a simpler representation of transport, one that does not require an explicit description of the physics or processes involved. One such approach is the transfer

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function model developed by Jury (1982), which describes the transport of a chemical through a soil in terms of a travel time probability density function (pdf).

### 1.1. Transfer function model of solute transport

Consider the simultaneous release of a large number of conservative, non-reactive solute particles at the surface of a soil under steady water flow. We are interested in the time that is required for the particles to move from the soil surface ($z = 0$) to a depth $z = Z$ in the soil. Because of the tortuous flow channels that exist in soil, the particles will take a variety of pathways to reach that depth and consequently the travel times of the particles will vary. The normalized distribution of all possible travel times constitutes the travel time pdf for the transport volume demarcated by the soil surface and the exit surface at $z = Z$. More formally, the movement of the tracer through the soil can be described by the pdf $f(t)$, where $f(t)\mathrm{d}t$ gives the probability that a solute particle entering the soil surface at time zero will reach the depth $z = Z$ in the time interval $t$ to $t + \mathrm{d}t$ (Jury et al., 1986).

Given the travel time pdf for the transport volume, the principle of superposition is applied to obtain the solute breakthrough at $z = Z$ for any arbitrary input of solute at the surface. The relationship between the input $c_{\text{in}}(t)$, the breakthrough $c(t)$, and the pdf is given by the convolution integral

$$c(t) = \int_0^t c_{\text{in}}(t-\tau)f(\tau)\mathrm{d}\tau \qquad (1)$$

Jury and Roth (1990) discuss the implications of the linearity assumption that is embodied in the use of superposition and the conditions under which this is likely to hold. We limit our discussion to the case of tracer transport in steady water flow because this leads to the most straightforward transfer function model. However, Jury and Roth (1990) discuss methods for extending the transfer function approach to more complicated transport scenarios, including transient water flow and reactive transport. Also, we note that Eq. (1) can be used to predict transport only to the depth $z = Z$. To make predictions to other depths, say $z = L$, it is necessary to adopt a transport process model so that the travel time pdf at $z = L$, $f(t;L)$, can be obtained from $f(t;Z)$ (Jury and Roth, 1990). As discussed above, selecting a process model can be problematic. For our present purposes, we will regard the travel time pdf as a black-box model and will not attempt to extrapolate predictions made at one depth to another. While this does not provide the most general description of transport, it can be useful in practice. For example, because of its impact on groundwater quality, the chemical breakthrough below the root zone is a primary concern in managing agricultural fields. A transfer function model calibrated to this depth can be used to evaluate the effects of various management practices on groundwater quality.

Most studies using transfer function models assume a parameterized functional form for the travel time pdf. In particular, the lognormal distribution has been used (Jury, 1982). However, it is clear that commonly observed transport phenomena (preferential transport, etc.) may not be adequately described by a simple distribution of travel times (White et al., 1986).

Alternatively, a nonparametric pdf can be measured for a particular soil. With this approach no assumptions are made about the shape of the pdf and any occurring nonideal transport observed in the measurement will be accounted for in the pdf. The nonparametric pdf can be measured by normalizing the observed outflow from the soil following a Dirac-delta function input of solute. In practice, of course, a true Dirac-delta input is never obtained. What is required is an input that sufficiently mimics the behavior of a Dirac-delta input, i.e. a narrow solute pulse uniformly applied to a soil surface such that all of the potential transport pathways are utilized. It would be experimentally simpler if the travel time pdf could be obtained by applying a controlled solute input, measuring the solute breakthrough, and then solving Eq. (1) for $f$. However, this is well known to be an ill-posed problem (e.g., Lavrent'ev et al., 1986), which means small measurement errors may cause large errors in computed pdf.

### 1.2. Deconvolution

Solving Eq. (1) for $f(t)$ is called deconvolution. Deconvolution has been studied in many different contexts, including several hydrologic problems (e.g., Neuman and de Marsily, 1976; Dietrich and

Chapman, 1993; Hinedi et al., 1993; Skaggs and Kabala, 1994). Because the solution of an ill-posed problem can be very sensitive to measurement errors, a solution found by, for example, least-squares will often contain severe oscillations (Neuman and de Marsily, 1976).

One approach to deconvolution is known as regularization (e.g., Lavrent'ev et al., 1986; Provencher, 1982a; Wing, 1991). A solution is found by minimizing a composite objective function consisting of two terms, one which measures the fit of the solution to the experimental data, and the second which measures the smoothness of the solution or, depending on the context, some other property that the solution is known a priori to possess. Requiring that the solution be smooth mitigates the solution's sensitivity to errors and lessens the chance that spurious oscillations will be present.

The purpose of the present work is to investigate the problem of deconvoluting nonparametric solute travel time pdfs from experimental data. We describe a constrained regularization method and test it using synthetic and experimental data.

## 2. Deconvolution of the transfer function

### 2.1. Problem definition

We focus on the inverse problem associated with the transfer function description of solute transport, namely, computing $f(t)$ given an experimental solute application and measured breakthrough at some depth $z = Z$. When the breakthrough curve is measured discretely in time, Eq. (1) may be written as the system of equations

$$c_j \equiv c(t_j) + \xi_j = \int_0^{t_j} c_{\mathrm{in}}(t_j - \tau) f(\tau) \mathrm{d}\tau, \; j = 1, \ldots, N_{\mathrm{obs}} \qquad (2)$$

where $c_j$ is the measured breakthrough concentration at time $t_j$, $c(t_j)$ is the true breakthrough concentration at time $t_j$, $\xi_j$ is a random measurement error associated with $c_j$, and $N_{\mathrm{obs}}$ is the number of breakthrough measurements. We assume that at time $t_{N_{\mathrm{obs}}}$ the entire solute body has passed the depth where the breakthrough is being measured. The deconvolution problem is then defined as solving Eq. (2) for $f(t)$. We next consider a constrained regularization method for obtaining a solution.

### 2.2. Constrained regularization method

As noted earlier, in this standard approach to deconvolution problems a solution is found by minimizing a composite objective function consisting of two terms, the first which measures the fit of the solution to the experimental data and the second which measures the smoothness of the solution. The objective function is minimized subject to constraints that ensure the solution is consistent with any other information available about the solution (e.g., non-negativity).

In applying the regularization method to the current problem, the first step is to introduce the discretized travel time pdf $\mathbf{f}$, with elements $f_k \equiv f(\tau_k), k = 1,\ldots,N_g$, where $N_g$ is the number of grid nodes used in the discretization. The number of nodes $N_g$ can be less than, equal to, or greater than $N_{\mathrm{obs}}$. The computational burden is proportional approximately to $N_g^3$ (Provencher, 1982c; Weese, 1992).

Next we must formulate a linear relation, $\mathbf{c} = \mathbf{Af}$, where $\mathbf{c}$ is the vector of breakthrough measurements with elements $c_j \equiv c(t_j) + \xi_j$, $j = 1,\ldots,N_{\mathrm{obs}}$. Typically this relationship is obtained by applying a quadrature rule to Eq. (2), in which case the elements of $\mathbf{A}$ are the products of quadrature terms and values of $c_{\mathrm{in}}(t_j - \tau_k)$ (see, e.g., Provencher, 1982a). However, it is typical in solute transport experiments that $c_{\mathrm{in}}$ changes rapidly in time, and consequently numerical quadrature may introduce significant error unless an extremely fine discretization is used. The problem is particularly acute when $c_{\mathrm{in}}$ is a step function,

$$c_{\mathrm{in}}(t) = \begin{cases} C_0 & 0 \le t \le T_0 \\ 0 & t > T_0 \end{cases} \qquad (3)$$

and experience has shown that the required discretization can make the computational costs of the methodology prohibitive. Provencher (1982a) suggests the following alternative approach that avoids these difficulties. The travel time pdf is approximated

$$f(\tau) \approx \bar{f}(\tau) = \sum_{k=1}^{N_g} f_k \Omega_k(\tau) \qquad (4)$$

where $\Omega_k$ is a convenient basis function and $f_k$ is defined as before. Substituting Eq. (4) into Eq. (2) gives

$$c_j = \int_0^{t_j} c_{\mathrm{in}}(t_j - \tau) \sum_{k=1}^{N_g} f_k \Omega_k(\tau) \mathrm{d}\tau, \; j = , \ldots, N_{\mathrm{obs}} \qquad (5)$$

or equivalently $\mathbf{c} = \mathbf{Af}$ with

$$A_{jk} = \int_0^{t_j} c_{\mathrm{in}}(t_j - \tau)\Omega_k(\tau)\mathrm{d}\tau \tag{6}$$

When the input is given by Eq. (3)

$$A_{jk} = C_0 \int_{a(t_j)}^{t_j} \Omega_k(\tau)\mathrm{d}\tau \tag{7}$$

where

$$a(t_j) = \begin{cases} 0 & t_j \le T_0 \\ t_j - T_0 & t_j > T_0 \end{cases} \tag{8}$$

We use the linear basis functions

$$\Omega_k(\tau) = \begin{cases} 0 & \tau < \tau_k - 1 \\ (\tau - \tau_{k-1})/(\tau_k - \tau_{k-1}) & \tau_{k-1} \le \tau \le \tau_k \\ (\tau_{k+1} - \tau)/(\tau_{k+1} - \tau_k) & \tau_k \le \tau \le \tau_{k+1} \\ 0 & \tau > \tau_{k+1} \end{cases},$$

$$k = 1, \ldots, N_g, \tag{9}$$

and analytically evaluating $A_{jk}$ in Eq. (7) is then straightforward.

Having obtained the required relationship $\mathbf{c} = \mathbf{Af}$, the regularized pdf $\mathbf{f}_{\mathrm{reg}}(\tau;\alpha)$ is defined as the solution to the minimization problem

$$\min\ V(\alpha) = \|\mathbf{c} - \mathbf{Af}\|^2 + \alpha^2\|\mathbf{Hf}\|^2 \tag{10}$$

subject to

$$\mathbf{f} \ge \mathbf{0} \tag{11}$$

$$\mathbf{a}'\mathbf{f} = 1 \tag{12}$$

where $\|\cdot\|$ is the Euclidean norm. The first term on the right-hand side of Eq. (10) is the familiar least-squares objective function which measures the solution's fit to the data. The second term imposes a smoothness requirement, where the smoothness of the solution is quantified by its second derivative. Thus the $(N_g + 2) \times N_g$ matrix $\mathbf{H}$ computes the second divided differences of $\mathbf{f}$

$$\mathbf{H} = \Delta^{-2} \begin{bmatrix} 1 & & & & \\ -2 & 1 & & & \\ 1 & -2 & 1 & & \\ & \ddots & \ddots & \ddots & \\ & & 1 & -2 & 1 \\ & & & 1 & -2 \\ & & & & 1 \end{bmatrix}$$

where $\Delta = \tau_{k+1} - \tau_k$ is the grid spacing used in discretizing $f$ (for simplicity the spacing is taken to be uniform). The first and last two rows of $\mathbf{H}$ are obtained by assuming two additional nodes beyond the edges of the solution grid and setting them equal to zero. This has the effect of making the regularized pdf tend toward zero at its edges.

The constraints Eq. (11) and Eq. (12) ensure $\mathbf{f}_{\mathrm{reg}}$ is physically plausible. The first constraint specifies the travel time pdf is non-negative. The second specifies the integral of the pdf is unity, where $\mathbf{a}'$ is a row vector that approximates the integral of the solution. We use the trapezoidal rule to approximate the integral, meaning the elements of $\mathbf{a}'$ are $a_1 = a_{N_g} = 0.5\Delta$ and $a_k = \Delta$, $k = 2,\ldots,N_g - 1$.

The regularization parameter $\alpha$ determines the relative weight given the two terms in the objective function and finding its optimal value is a critical aspect of the regularization methodology. We include the argument $\alpha$ in $\mathbf{f}_{\mathrm{reg}}(\tau;\alpha)$ to emphasize the dependence of the solution on the regularization parameter. When $\alpha$ is too small, the solution is overly sensitive to errors in the data; when $\alpha$ is too large the solution is dominated by the regularization operator and is artificially smooth.

Provencher (1982a) obtains a value for $\alpha$ using Fisher's $F$-distribution (variance ratio distribution) in a procedure similar to that used for hypothesis testing in linear regression. With $V(\alpha)$ defined in Eq. (10), $\alpha$ is found using the test statistic

$$F(\alpha) = \frac{(V(\alpha) - V_0)/N_0}{V_0/(N_{\mathrm{obs}} - N_0)} \tag{13}$$

where $V_0 \equiv V(0)$ is computed with $\alpha$ equal or close to zero and $N_0$ is the number of degrees of freedom associated with $V_0$ (see Provencher, 1982a). The statistic $F$ increases monotonically with increasing $\alpha$ and is evaluated using the $F$-distribution with $N_0$ degrees of freedom in the numerator and $N_{\mathrm{obs}} - N_0$ degrees of freedom in the denominator. The idea is to assess the increase in $V$ that is attributable to the regularizer as $\alpha$ is made larger. When $F \gtrsim F_{0.1}$, where $F_{0.1}$ is the value of $F$ such that 10% of the distribution lies to the left of $F_{0.1}$, the regularizer is exerting only a minimal influence on the solution and there is a high likelihood that $\mathbf{f}_{\mathrm{reg}}$ is overly sensitive to data errors. Conversely, if $F \gtrsim F_{0.9}$, the regularizer is strongly influencing the solution and it is likely that

$\mathbf{f}_{\mathbf{reg}}$ is artificially smooth. Provencher therefore recommends that $\alpha$ be chosen such that $F_{0.1} \lesssim F \lesssim F_{0.9}$. See Golub et al., (1979), Weese (1992), and Hansen (1992) for discussion of alternative methods for determining $\alpha$.

However, it is widely recognized (e.g., Provencher, 1982c; Neuman and de Marsily, 1976) that subjective judgement is also important in selecting an optimal value for $\alpha$. Knowledge and intuition about the characteristics that the solution should possess need to be taken into consideration. In our problem, the number of peaks in $\mathbf{f}_{\mathbf{reg}}$ is of interest because a travel time pdf with more than a single peak indicates that the observed transport differs from that conceptualized by either the classical convective–dispersive model or the convective lognormal transfer function model. In this sense deconvoluting the travel time pdf is diagnostic, allowing one to identify, for example, whether or not preferential transport is occurring. If a regularized travel time pdf found using the $F$-distribution criterion contains multiple peaks, a salient question is whether the data can be described adequately by a simpler pdf, i.e. one with fewer peaks. Provencher suggests addressing such questions by computing additional regularized solutions that are constrained to have a fixed number of extrema. These modality constraints are implemented by putting additional inequality constraints on the objective function Eq. (10) (see Provencher, 1982a). Provencher argues that if a solution found with fewer peaks has a test statistic $F_{0.1} \lesssim F \lesssim F_{0.9}$, it is a strong indication that the simpler solution is sufficient to describe the data and is the preferred solution based on the principle of parsimony. On the other hand, if $F \lesssim F_{0.1}$ or $F \gtrsim F_{0.9}$, it is an indication that the more complex solution is required to adequately describe the data.

In this paper, we compute regularized solutions using the computer program CONTIN developed by S.W. Provencher (Provencher, 1982a, b and c). The minimization problem Eq. (10) is solved for a series of $\alpha$ values, and the $\mathbf{f}_{\mathbf{reg}}$ with $F$ statistic nearest $F_{0.5}$ is taken to be the regularized solution. In simulations with noisy synthetic data, we found that these solutions occasionally contained spurious peaks that were not present in the actual pdf. Consequently, we use the following procedure (Provencher, 1982c). A solution is found initially using the $F$-distribution criterion as described above. If this pdf contains peaks or oscillations that are suspect, the same value of $\alpha$ is used to compute solutions constrained to be uni- and bimodal with the peak value(s) located at the $\tau_k$ where maxima of $\mathbf{f}_{\mathbf{reg}}$ are observed in the initial solution. Occasionally these new solutions contain long flat sections (sections where $f_k \approx f_{k+1} \approx f_{k+2} \approx \ldots$). These sections are usually assumed to be numerical artifacts (Provencher, 1982c), so when they arise $\alpha$ is increased until the flat spots are eliminated and the resulting pdfs are taken to be the peak-constrained regularized solutions. Finally, the $F$ statistics of the peak-constrained pdfs are compared with that of the original and this information, along with a visual inspection of how well each pdf reproduces the data, is used to determine which pdf is the best solution.

## 3. Synthetic experiments

We assume in these simulations that solute transport is described by the convection–dispersion equation, or equivalently, that the true travel time pdf is (Jury and Roth, 1990)

$$f(t)=\frac{Z}{2\sqrt{\pi D t^3}}\exp\left[-\frac{(Z-vt)^2}{4Dt}\right] \tag{14}$$

where $v[LT^{-1}]$ is the pore water velocity and $D[L^2T^{-1}]$ is the dispersion coefficient. Note that we make this assumption only so we have a "true solution" with which to compare our numerical results and that the deconvolution method used here does not require any knowledge of the actual transport processes or functional form of the pdf.

With input function Eq. (3) and $T_0$ = 1 day, $C_0$ = 1 meq $L^{-1}$, $v$ = 1 cm day$^{-1}$, and $D$ = 5 cm$^2$ day$^{-1}$, Eq. (1) is used to calculate $N_{obs}$ = 34 error-free breakthrough measurements, $c(t_j)$, $j$ = 1,...,34, at depth $z$ = $Z$ = 30 cm. To create a synthetic data set, normally distributed random deviates are added to the true observations according to

$$c_j=c(t_j)+\xi_j \tag{15}$$

where $c_j$ is the synthetic concentration measurement at time $t_j$, $\xi_j=\epsilon_j\sigma$, $\epsilon_j$ is a standard normal random deviate ($\epsilon_j \sim N(0,1)$), and $\sigma = 0.001$ meq $L^{-1}$. To avoid negative concentrations, $c_j$ is taken to be zero when $c(t_j) + \xi_j <$ 0. The resulting data are shown as open squares in Fig. 1(a), along with the true breakthrough curve (dashed line). Using this data set, we deconvolute the travel time pdf using the constrained regularization method. The regularized solutions are found with $N_g = 50$ and $\Delta = 2.45$ days, and the results are given along with the true pdf in Fig. 1(b). The true pdf is shown as a dashed line, the pdf obtained without modality constraints is shown as a solid line ($\alpha = 3.45\ 10^{-2}$ days$^3$ meq L$^{-1}$), and the unimodal pdf is shown as a dotted line ($\alpha = 12.0$ days$^3$ meq L$^{-1}$). The unimodal pdf is a reasonable solution, deviating only slightly from the true solution, whereas the pdf without modality constraints is clearly overly sensitive to errors in the descending arm of the breakthrough data.

Next we consider an example with $D = 0$ (piston flow). Here, the true travel time pdf is the Dirac-delta function $\delta(t - Z/v)$. We chose $Z/v = 5$ days, $T_0 = 5$ days, $C_0 = 1$ meq $L^{-1}$ and use the same procedures as before with $\sigma = .01$ meq L$^{-1}$ to generate the synthetic data (Fig. 2(a)). The resulting pdf ($N_g = 50$, $\Delta = 0.2$ days, $\alpha = 2.78\ 10^{-2}$ days$^3$ meq L$^{-1}$, no modality constraints) is shown in Fig. 2(b). The solution provides reasonable resolution of the delta function.

Based on the synthetic examples, the regularization methodology appears to be a reasonable approach to deconvoluting solute travel time pdfs. We next use the method to analyze field data.

## 4. Analysis of field experiments

### 4.1. Van de Pol (1974) experiment

Van de Pol (1974) describes an experiment conducted on a layered soil consisting of 15–20 cm of clay overlying 50–60 cm of silty clay overlying sandy loam and sand. After attaining steady-state flow conditions, the plot was irrigated with a chloride solution for 36 days followed by 51 days of leaching

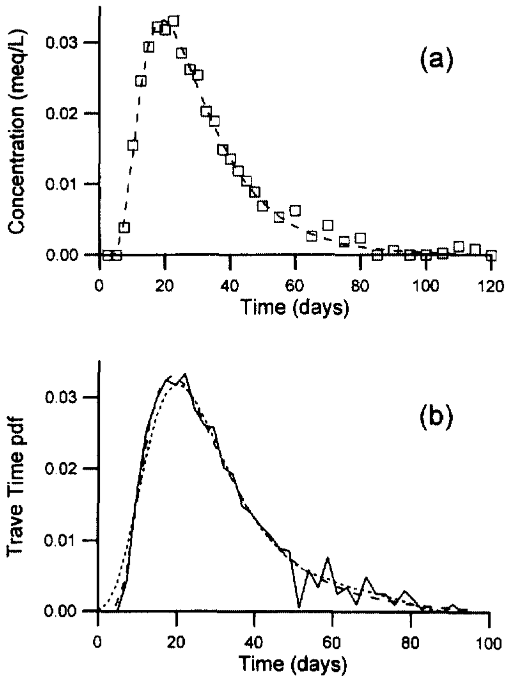


Fig. 1. Computed travel time pdfs using synthetic transport data for $Z = 30$ cm. (a) The breakthrough "measurements" are shown as open squares and the true breakthrough curve is indicated with a dashed line; (b) the true travel time pdf is shown as a dashed line, the regularized solution computed without modality constraints is shown as a solid line, and the unimodal regularized solution is shown as a dotted line.

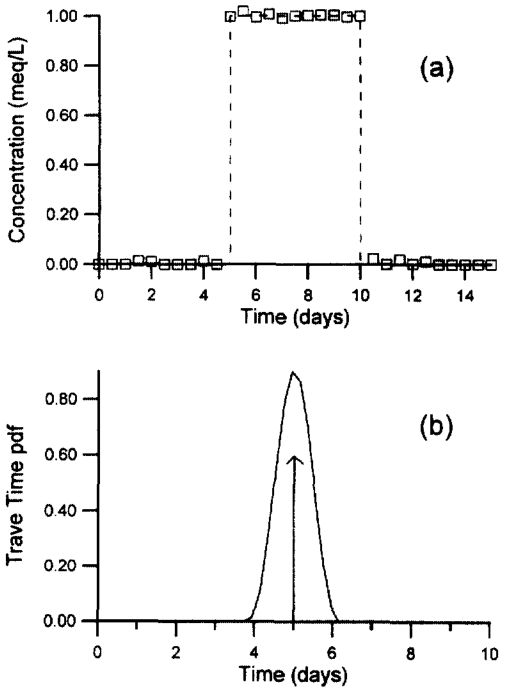


Fig. 2. Computed travel time pdf when the true pdf is a delta function. (a) The synthetic breakthrough measurements (open squares) and the true breakthrough curve (dashed line); (b) the true pdf (Dirac-delta function at time $t = 5$ days) and the regularized solution (solid line). The computed pdf provides reasonable resolution of the delta function.

with regular irrigation water. Soil solution samples were taken at various depths and times.

Using the breakthrough data at $Z = 15$ cm, we calculate the travel time pdfs. Fig. 3(a) shows regularized solutions with $\Delta = 0.4$ days and $N_g = 50$. The pdf shown in the inset of Fig. 3(a) is obtained without modality constraints and $\alpha = 2.55$ days$^3$ meq L$^{-1}$. The $x$-axis in the inset spans the range [0,20], whereas the main plot spans [0,14]. The pdf in the inset contains three peaks, although the small peak near time $t = 19$ days is difficult to see in this figure. The main plot in Fig. 3(a) is obtained when the regularized solution is constrained to have two peaks located where the two largest maxima are observed in the inset. The same solution grid and regularization parameter ($\alpha = 2.55$ days$^3$ meq L$^{-1}$) is used, but the plot is truncated at time $t = 14$ days. In going from three to two peaks, the value of $F$ changes only from $F_{0.658}$ to $F_{0.660}$, indicating that the third peak is not required by the data and may be regarded as an artifact. Fig. 3(c) shows the regularized solution constrained to be unimodal with $\alpha = 43.2$. The location of the peak is systematically varied, with the final location being that which produces the smallest $V$. The test statistic for the unimodal solution is $F_{1.0}$, indicating it is likely that the influence of the regularizer is too strong.

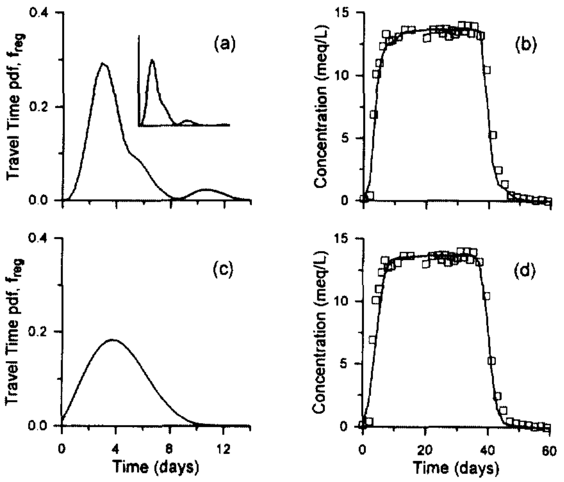


Fig. 3. Regularized travel time pdfs computed for the Van de Pol data at $Z = 5$ cm. (a) The main plot shows the computed pdf constrained to have two peaks and the inset shows the computed pdf without modality constraints; (b) the fit of the breakthrough predicted by the computed two-peaked pdf to the measured data; (c) the computed pdf constrained to have one peak; and (d) the fit of the breakthrough predicted by the one-peaked pdf.

In evaluating the computed pdfs, it is useful to also visually inspect their fit to the data by comparing the modeled breakthrough $\mathbf{c}_{\mathbf{reg}} = \mathbf{Af}_{\mathbf{reg}}$, with the observed breakthrough. Fig. 3(b) shows the fit for the bimodal pdf and Fig. 3(d) the fit for the unimodal pdf. Not shown is the result for the pdf in the inset of Fig. 3(a), which is nearly identical to the result for the bimodal pdf. The fits in Fig. 3(b) and 3(d) are similar. In Fig. 3(b), $\mathbf{c}_{\mathbf{reg}}$ closely matches the ascending portion of the data, as well as the tailing of the breakthrough. The curve in Fig. 3(d) is a somewhat better representation of the descending arm of the data, but is a poorer representation of the ascending arm. Based on the test statistics and the visual inspection, we conclude that the bimodal pdf in Fig. 3(a) is the best solution for depth $Z = 15$ cm.

The regularized pdfs for $Z = 49$ cm are given in Fig. 4. The solution without modality constraints ($\Delta = 1.8$ days, $N_g = 50$, $\alpha = 908$ days$^3$ meq L$^{-1}$) contains two peaks and is shown in Fig. 4(a). The pdf constrained to be unimodal is shown in Fig. 4(c) (same solution grid and regularization parameter). The test statistic for this solution is $F_{.732}$, compared with $F_{.506}$ for the solution in Fig. 4(a). This suggests the second peak in Fig. 4(a) is not required by the data. In Fig. 4(b) and (d), the data fits for the two solutions are shown to be very similar. We conclude that the

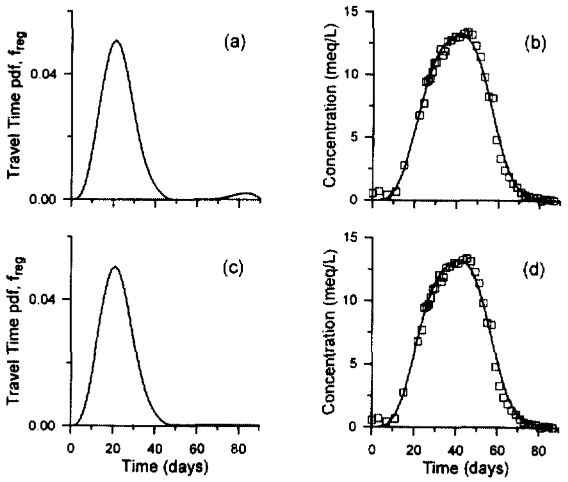


Fig. 4. Regularized travel time pdfs for the Van de Pol data at $Z = 49$ cm. (a) The computed pdf without modality constraints and (b) the fit of its predicted breakthrough to the observed data; (c) the computed pdf constrained to have one peak and (d) the fit of its predicted breakthrough to the observed data.

unimodal regularized solution represents the best possible solution.

### 4.2. Butters and Jury (1989) experiment

Butters and Jury (1989) applied a narrow bromide pulse to a loamy sand field and leached it with regular irrigation water under steady-state flow conditions. Soil solution samples were taken at various depths and times. The independent variable in this case is net applied water (NAW), which is proportional to time during steady water flow.

The regularized solution without peak constraints for $Z$ = 90 cm is shown in Fig. 5(a) ($N_g$ = 50, $\Delta$ = 2.25 cm, $\alpha$ = 28.7 cm$^3$ meq L$^{-1}$). The pdf is not very smooth and contains peaks near $NAW$ = 11, 22, and 45 cm. When the solution is constrained to have only two peaks with $\alpha$ = 28.7 cm$^3$ meq L$^{-1}$, the small peak at $NAW$ = 22 cm is eliminated while the rest of the solution remains virtually unchanged (solid line, Fig. 5(c)). Constraining the solution to have two peaks changes the test statistic from $F_{.174}$ to $F_{.180}$. When constrained to have only one peak with $\alpha$ = 202 cm$^3$ meq L$^{-1}$ (dashed line, Fig. 5(c)), the test statistic jumps to $F_{1.0}$, suggesting the regularizer is too strong n this case.

Fig. 5(b) and (d) show the fit of the pdfs to the data. All are reasonable representations of the data, although the unimodal regularized solution underestimates the large peak concentration. The bimodal regularized solution appears to be the best choice of the three solutions.

Fig. 6 shows the results for $Z$ = 300 cm. The breakthrough data contains a small pulse arriving near $NAW$ = 6 cm, followed by the remainder of the solute. Fig. 6(a) shows the regularized pdf without modality constraints ($\alpha$ = 160 cm$^3$meq L$^{-1}$, $F = F_{.218}$), and Fig. 6(c) shows the pdfs constrained to have two peaks (solid line, $\alpha$ = 4.25 10$^3$ cm$^3$ meq L$^{-1}$, $F = F_{.993}$) and one peak (dashed line, $\alpha$ = 1.12 10$^3$ cm$^3$ meq L$^{-1}$, $F = F_{1.0}$). The fits of all pdfs are shown in Fig. 6(b) and (d). The peak-constrained solutions have high test statistics and do not fit the early arriving data as well as the unconstrained solution. We conclude that the pdf without modality constraints is the best regularized solution.

## 5. Summary and conclusions

Deconvoluting the solute travel time pdf is an ill-posed problem and consequently the solution is

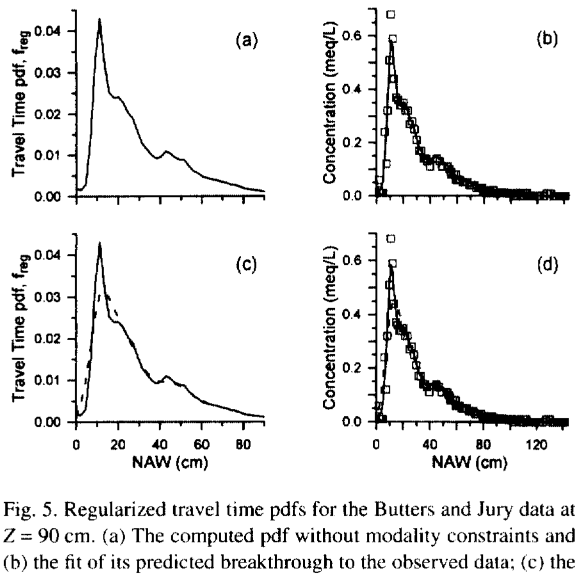


Fig. 5. Regularized travel time pdfs for the Butters and Jury data at $Z$ = 90 cm. (a) The computed pdf without modality constraints and (b) the fit of its predicted breakthrough to the observed data; (c) the computed pdfs constrained to have one (dashed line) and two (solid line) peaks and (d) the fit of their predicted breakthroughs to the observed data.

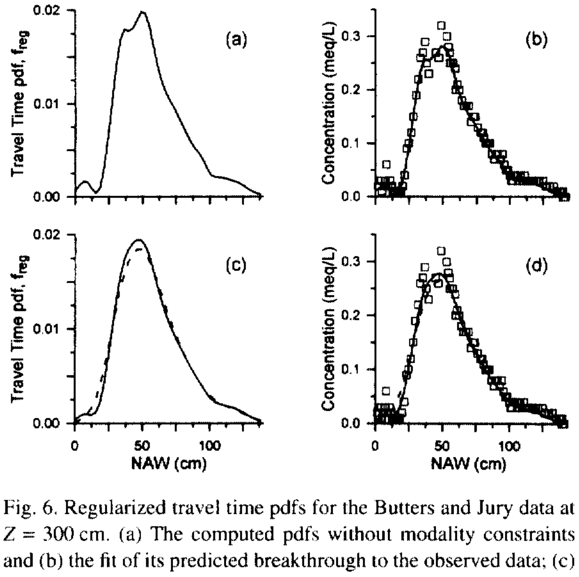


Fig. 6. Regularized travel time pdfs for the Butters and Jury data at $Z$ = 300 cm. (a) The computed pdfs without modality constraints and (b) the fit of its predicted breakthrough to the observed data; (c) the computed pdfs constrained to have one (dashed line) and two (solid line) peaks and (d) the fit of their predicted breakthroughs to the observed data.

sensitive to data errors. Using synthetic and experimental data, we performed the deconvolution employing a constrained regularization methodology. We conclude:

1. To apply the regularization methodology, the transport model must be written as a linear function of the discretized travel time pdf, **f**. The standard approach for obtaining this relationship is to apply a quadrature rule to Eq. (2). However, when $c_{in}$ is a step function, the discretization introduces error and can cause computational difficulties. These problems were avoided by using a basis function representation of $f$ to obtain the required linear relationship.
2. The regularized pdfs were assessed using Provencher's test statistic along with a visual inspection of their fit to the breakthrough data. In two of the four experimental data sets analyzed, a bimodal pdf was required to describe the observed transport. In a third, a bi- or trimodal pdf was required. The need for a multi-modal pdf suggests that the simple travel time distributions indicated by both the classical convection–dispersion model and the convective lognormal transfer function model may be inadequate and that a parameterized bimodal pdf (e.g., Utermann et al. (1990)) may be appropriate for modeling transport in some soils.

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