# Evaluation of Mass Recovery Impacts on Transport Parameters Using Least-Squares Optimization and Moment Analysis

B. S. Das,\* J. M. Wraith, G. J. Kluitenberg, H. M. Langner, P. J. Shouse, and W. P. Inskeep

## ABSTRACT

Accurate assessment of the fate of contaminants in soil relies on precise estimation of solute transport parameters under field conditions. Traditionally, transport parameters are estimated from measured solute transport data using the least-squares optimization (LSO) technique or the method of moments (MOM). Considerable mismatch between the parameters estimated by these two methods has been reported in the solute transport literature. In this study, the MOM and LSO approaches were examined for estimating pore water velocity (v)and dispersion coefficient (D) from 85 laboratory- and field-measured breakthrough curves (BTCs). The two methods yielded similar estimates of v and D for BTCs with 100% mass recovery. They yielded similar estimates of v for BTCs with incomplete mass recovery. However, estimates of D obtained by the MOM departed significantly from those estimated using LSO for BTCs with incomplete mass recovery. Analyses of truncated BTCs showed that 91% mass recovery resulted in errors of 138 and 57% in D values estimated by the MOM for repacked and undisturbed soil columns, respectively. Corresponding errors in estimated D values were below 5% for the LSO approach. Although it may be possible to normalize or extrapolate the BTC using its zeroth experimental moment to ensure 100% mass recovery, the use of either LSO or MOM would yield a different set of parameters representing a new set of experimental conditions and, therefore, would lead to further complications in obtaining a unique set of transport parameters. This suggests that where the MOM is indispensable, 100% experimental mass balance should be ensured.

Accurate UNDERSTANDING of the fate and transport of contaminants in soil and water bodies has become increasingly important as commonly used chemicals continue to emerge as environmental contaminants (Kolpin et al., 2002). Traditionally, the fate of chemicals in soil is characterized with dynamic solute transport models embodying transport, reaction, and transformation processes. The parameters controlling these processes are estimated by conducting solute displacement experiments in which a target chemical is transported through soil, and its concentration monitored as a function of time or space. The concentration–time response is known as the BTC and the concentration–space response is known as the concentration profile (CP). Two approaches are

Published in Soil Sci. Soc. Am. J. 69:1209–1216 (2005). Soil Physics doi:10.2136/sssaj2004.0255 © Soil Science Society of America 677 S. Segoe Rd., Madison, WI 53711 USA commonly used to analyze a BTC or CP. Transport parameters may be estimated by (i) using nonlinear LSO in conjunction with a solute transport model (e.g., Toride et al., 1995), or (ii) applying the MOM (Aris, 1958; Kubin, 1965; Jury and Sposito, 1985). Both of these methods are described in detail in the solute transport literature (e.g., Toride et al., 1995; Das et al., 2002). Computer codes such as CXTFIT (Toride et al., 1995) are widely used to estimate solute transport parameters in the LSO approach.

In the MOM, the fate of a solute is described in terms of the moments of the BTC or CP, such as the total mass moving through the soil pores (zeroth moment), the mean travel time or mean travel depth (first moment), or the degree of mixing or the variance about the mean travel time or mean travel depth (second central moment) of the solute mass within the porous medium. In addition to its relative simplicity, the MOM is the preferred approach for analyzing field-scale solute transport data and is used as a convenient tool in stochastic analysis of solute transport. Because the MOM does not require a priori assumption of a particular transport model, it becomes the primary tool for describing processes observed with flow through complex and heterogeneous flow geometries, facilitated transport in heterogeneous field soils (Sun et al., 2001), and other cases where selection of a transport model is uncertain or where critical input information is not available. Additionally, it yields a unique set of transport parameters when used as a parameter estimation tool. Because of these characteristics, a substantial number of theoretical studies have been conducted on moment analysis (Nauman, 1981; Valocchi, 1985; Harvey and Gorelick, 1995; Rubin et al., 1997). However, only a few studies have addressed its experimental evaluation or verification.

A common observation with the MOM is that even for simple flow geometries, it often yields parameters that are substantially different from those estimated with the inverse LSO method (Jury and Sposito, 1985; Jacobsen et al., 1992; Kamra et al., 2001; Das et al., 2002). For example, Jacobsen et al. (1992) showed that the curve-fitted dispersion coefficients (D) were always lower than those obtained by the MOM, whereas Kamra et al. (2001) reported both higher and lower values for D estimated with the LSO relative to the MOM method. We estimated the percentage deviations between the MOM- and LSO-estimated D values to range from 5 to 255% in Jacobsen et al. (1992) and from -21 to 53% in Kamra et al. (2001). Explanations for such discrepanc-

B.S. Das, Agricultural and Food Engineering Dep., Indian Institute of Technology, Kharagpur, WB, 721302, India; J.M. Wraith and W.P. Inskeep, Land Resources and Environmental Sciences Dep., Montana State Univ., P.O. Box 173120, Bozeman, MT 59717-3120; G.J. Kluitenberg, Dep. of Agronomy, Kansas State Univ., Manhattan, KS 66506; H.M. Langner, Geology Dep., Univ. of Montana, Missoula, MT, 59812; P.J. Shouse, GEBJ Soil Salinity Lab., Riverside, CA 92507. Received 29 July 2004. \*Corresponding author (bsdas@agfe.iitkgp. ernet.in).

**Abbreviations:** ADE, advection dispersion equation; BTC, breakthrough curve; CP, concentration profile; LSO, least-squares optimization; MOM, method of moments; MRF, mass recovery fraction; PFBA, pentafluorobenzoic acid.

ies include (i) equal weighting is given to all observed points in the concentration response curve in the LSO method, while the MOM is biased toward concentrations which appear at later times (for BTCs) or deeper soil layers (for CPs) (Fahim and Wakao, 1982; Jury and Sposito, 1985); (ii) uncertainty (scatter) in the individual data points in a BTC or CP and lack of high frequency (small sampling interval) measurements for many experimental BTCs; (iii) missing tails and extended tailing of BTCs or CPs preclude accurate estimation of moments; (iv) while the least-squares method provides equal flexibility for all model parameters, the dependence of higher-order moments on lower-order moments leads to propagation of error during parameter estimation; and (v) incorrect model assumption while using the LSO approach may lead to unrealistic model parameters. An extensive evaluation of the efficacy of the MOM in estimating transport parameters using actual datasets has not been provided in the literature. Further, it is often argued that the availability of highquality experimental data would likely eliminate difficulties observed with the application of the MOM, yet the characteristics of a high-quality data set are not well defined. The objective of this study is to examine the MOM for its efficacy to describe solute transport in soils using a range of experimental data, and to provide potential explanations for observed discrepancies between two MOM- and LSO-derived transport parameters, pore water velocity and dispersion coefficient.

#### THEORY

We consider the simplest case of one-dimensional solute transport through a homogenous medium in the presence of steady flow. Assuming linear, equilibrium sorption, the governing advection dispersion equation (ADE) can be written as

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \nu \frac{\partial C}{\partial x}$$
[1]

where *C* is the volume-averaged concentration (M L<sup>-3</sup>), *D* is the dispersion coefficient (L<sup>2</sup> T<sup>-1</sup>), *v* is the pore water velocity (L T<sup>-1</sup>), *x* is distance (L), and *t* is time (T). The retardation factor is defined as  $R = 1 + \rho K_d/\theta$ , where  $\rho$  is the dry bulk density (M L<sup>-3</sup>),  $K_d$  is the solute distribution coefficient (M<sup>-1</sup> L<sup>3</sup>), and  $\theta$  is the volumetric water content (L<sup>3</sup> L<sup>-3</sup>).

The solute BTC at the effluent end of a soil column may be viewed as a probability distribution function. The *n*th absolute moments  $(\mu_n)$  and normalized absolute moments  $\mu_n^*$  for a pulse input may be defined as

$$\mu_n = \int_0^\infty t^n C(L,t) dt \qquad [2]$$

$$\mu_n^* = \mu_n / \mu_0 \tag{3}$$

where C(L,t) is the flux-averaged concentration at the exit

boundary (x = L) at time *t*. The *n*th central moment (n > 1) is defined as

$$m_n = \frac{1}{\mu_0} \int_0^\infty (t - \mu_1^*)^n C(L, t) dt$$
 [4]

Evaluating Eq. [4] for n = 2 yields the expression

$$m_2 = \frac{\mu_2}{\mu_0} - \left(\frac{\mu_1}{\mu_0}\right)^2$$
 [5]

for the second central moment in terms of absolute moments.

The method of Aris (1958) can be used to obtain analytical expressions for the moments  $\mu_1^*$  and  $m_2$  (cf. Valocchi, 1985; Leij and Dane, 1991). For a pulse-type solute input of duration  $t_0$ , the analytical expressions for the moments of the BTC are (Valocchi, 1985; Leij and Dane, 1991)

$$\mu_1^* = \frac{\mu_1}{\mu_0} = \frac{RL}{\nu} + \frac{t_0}{2}$$
 [6]

and

$$m_2 = \frac{2R^2DL}{v^3} + \frac{t_0^2}{12}$$
[7]

Equations [6] and [7] are the analytical results for flux-averaged concentrations valid for a semiinfinite column with a third-type boundary condition. Conventionally, effluent concentrations in a laboratory-scale column experiment are treated as flux-averaged concentrations.

### **MATERIALS AND METHODS**

#### **Experimental Data**

The experimental BTCs considered here were collected from miscible displacement experiments of Das (1996), Langner et al. (1999), and Ellsworth et al. (1996). Table 1 summarizes the experimental conditions used in those studies. For the saturated flow experiments (Das, 1996), Naron fine loam was uniformly packed in a stainless-steel flow cell with a length of 30 cm and an i.d. of 6.03 cm. The column was saturated with 0.001 *M* CaSO<sub>4</sub> solution during a period of 3 d. Steady state, saturated flow was maintained by controlling water flux density (q) with precision syringe pumps. Six transport experiments were conducted using six different pore water velocities  $(v = q/\theta)$ : 7.2, 16.8, 33.6, 67.2, 100.8, and 136.8 cm d<sup>-1</sup>. After steady state flow was established, 1.0 to 1.5 pore volumes of tracer solution containing tritiated water  $(2.59 \times 10^3 \text{ Bg mL}^{-1})$ <sup>3</sup>H<sub>2</sub>O) was leached through the soil column. The input solution was then switched back to 0.001 M CaSO<sub>4</sub> solution. Effluent was collected in 20-mL increments using a fraction collector. Effluent concentration (flux-averaged) was measured using scintillation spectrometry.

For the unsaturated flow experiments (Langner et al., 1999), four intact cores of Amsterdam silt loam (15.2-cm diam., 30-cm length) were collected from a grassland site at the A.H. Post Experimental Farm near Bozeman, MT. A series of unsaturated transport experiments was performed with these col-

Table 1. Data sources and experimental conditions under which the measured breakthrough curves (BTCs) were generated.

Data source	No. of BTCs	Water flow	Solutes	Experimental conditions
Das (1996)	6	saturated	tritiated water	laboratory experiment, repacked columns, multiple flow rates
Langner et al. (1999)	7	unsaturated	tritiated water	laboratory experiment, undisturbed columns, variable residence time
	7		pentafluorobenzoic acid	laboratory experiment, undisturbed columns, variable residence time
Ellsworth et al. (1996)	39	unsaturated	chloride, nitrate, bromide	field experiment, BTCs at the 25-cm depth
Ellsworth et al. (1996)	26	unsaturated	chloride, nitrate	field experiment, BTCs at the 65-cm depth

1211

umns by maintaining constant suction at the top and bottom boundaries of the columns (Langner et al., 1999). Multiple BTCs for tritiated water and pentafluorobenzoic acid (PFBA) were collected with each column by varying the upper and lower matric heads, resulting in a range of flow rates and residence times. We selected seven tritiated water BTCs (Columns: I-10, I-24, III-2, III-10, IV-3, IV-5, IV-11) and seven PFBA BTCs (Columns: I-10, I-24, II-3, II-5, IV-3, IV-5, IV-11) from Langner et al. (1999) such that the effluent concentrations at the end of experiments were at least two orders of magnitude smaller than the input concentrations. The pore water velocities for these BTCs ranged from 4.8 to 27.36 cm  $d^{-1}$  and matric heads ranged from -3 to -24 cm of water.

In the field experiment of Ellsworth et al. (1996), solute BTCs were measured at depths of 25 and 65 cm using multilevel solution samplers, following the application of separate chloride (1514 mg  $L^{-1}$ ), nitrate (135.5 mg  $L^{-1}$ ), and bromide (82.2 mg  $L^{-1}$ ) pulses. Transport experiments were conducted in a 2- by 2-m plot by maintaining an overall water flux of 1.3 cm d<sup>-1</sup>. A total of 12 solution samplers were installed in this plot. Approximately 20 mL of solution sample was collected daily at the same time after applying 0.5 m of suction to each solution sampler for a period of 10 min. A total of 27 point samples were collected during 27 d for generating each BTC. Thus, 12 BTCs were measured for each compound for each depth. An additional BTC for each compound was also generated by taking the mean of the 12 measured BTCs at each depth. We used all 39 BTCs from the 25-cm depth and 26 BTCs from the 65-cm depth from their experiment. Because the sampling volume of a solution sampler is not well defined, it is not clear whether measured concentrations should be treated as flux-averaged or volume-averaged (Parker and van Genuchten, 1984). We analyzed all the field-measured BTCs assuming flux-averaged concentrations.

In summary, a total of 85 BTCs were examined. These represent different experimental scenarios of saturated and unsaturated flow regimes, and flow geometries encountered with repacked and undisturbed laboratory columns and field soils. We also include BTCs for PFBA, which is used as an organic tracer compatible with organic solutes. These datasets were selected because of their high intensity time data, and because the BTCs exhibit features characteristic of commonly observed solute transport measurements. A common feature of all these experiments is that the observed BTCs may be modeled with one-dimensional ADEs for which analytical solutions are available (Toride et al., 1993).

#### **Data Analysis**

Accurate estimation of moments from elution curves is difficult because the upper limit of the integral in Eq. [2] is infinity, and particularly because of the small concentration values leading to measurement uncertainty at long times (Rony and Funk, 1971). Rony and Funk (1971) introduced the concept of partial normal moments to describe moments of an experimental BTC which extends from time t = 0 to a finite cutoff time  $t_c$ . For practical purposes in the case of complete BTCs, one may safely assume zero concentration (less than the detection limit of the instrument) beyond time  $t_c$ . With this assumption, partial moments will approximate the true moments of the BTC, and thus any of the integration approaches may be used to estimate moments.

Equation [2] also shows that higher-order moments grow rapidly in proportion with the *n*th power of time, indicating that the estimation errors for moments would grow with the order of the moment. Das et al. (2002) showed that the estimation of higher order moments depends on the accuracy with which the lower order moments are estimated. In our analysis, we use only the first three moments (zeroth, first, and second) and we consider that the estimation errors are not substantial. High sampling resolution (close proximity) in our datasets also minimizes such errors. An additional difficulty in the estimation of moments from experimental data stems from the greater weighting at larger times (i.e., the multiplication of  $t^n$  with *C* in Eq. [2]) in integration schemes. This is particularly critical for higher-order moments. To overcome such difficulties, a number of different approaches have been proposed, but each modified approach appears to also have shortcomings. For example, in the weighted moment method (Østergaard and Michelsen, 1969),

$$\mu_n = \int_0^\infty t^n C(L,t) e^{-pt} dt \qquad [8]$$

moments are estimated by including an exponentially decaying function,  $e^{-pt}$ , in the argument of the integral in Eq. [2]. Such a step essentially transforms the governing differential equation to include a first-order production process, thereby changing the primary model assumption. Thus, we do not consider Eq. [8] appropriate for estimating experimental moments, and hence we adopted the partial moment scheme of Rony and Funk (1971) for estimating experimental moments.

Two different integration schemes are reported for estimating experimental moments from measured BTCs (Haas, 1996): the trapezoidal rule,

$$u_n = \frac{\sum_{i=2}^n 0.5(t_i^n C_i + t_{i-1}^n C_{i-1})(t_i - t_{i-1})}{\sum_{i=2}^n 0.5(C_i + C_{i-1})(t_i - t_{i-1})}$$
[9]

and the inertia method,

ŀ

$$\mu_n = \frac{\sum_{i=2}^n \left(\frac{t_i + t_{i-1}}{2}\right)^n \left(\frac{C_i + C_{i-1}}{2}\right) (t_i - t_{i-1})}{\sum_{i=2}^n \left(\frac{C_i + C_{i-1}}{2}\right) (t_i - t_{i-1})}$$
[10]

The trapezoidal rule is commonly used (Misra and Mishra, 1977; Jacobsen et al., 1992) and is an unbiased (Haas, 1996) integration scheme for estimating moments from experimental data. Using synthetic data sets, Haas (1996) showed that the inertia method is more biased than the trapezoidal method. We estimated the first three moments of the BTCs ( $\mu_0$ ,  $\mu_1$ , and  $\mu_2$ ) using both of these numerical integration schemes. The results were then substituted into Eq. [3] and [5] to obtain estimates of  $\mu_1^*$  and  $m_2$ . Transport parameters were estimated by rearranging Eq. [6] and [7], and assuming R = 1, to give

and

$$v = L/(\mu_1^* - t_0/2)$$
[11]

$$D = \frac{v^3}{2L} \left( m_2 - \frac{t_0^2}{12} \right)$$
 [12]

We emphasize that all solutes considered in this study were treated as conservative and nonreactive tracers (i.e., R = 1) in Eq. [11] and [12], notwithstanding the fact that limited adsorption may be observed for tritiated water, and anion exclusion may occur for ionic solutes such as PFBA and the three used in the field experiments (Ellsworth et al., 1996; Langner et al., 1999).

The solute transport program CXTFIT (Toride et al., 1995) was used to estimate parameters from the 85 different BTCs by the LSO method. CXTFIT requires at least one parameter as a known quantity in addition to the observed BTC. Gener-

ally, pore water velocity is measured during transport experiments and hence is provided as a known parameter for CXTFIT analysis. In our analyses, we set R = 1 to test the ability of both MOM and LSO approaches to estimate v. Thus, we estimated transport parameters v and D using a local equilibrium transport model by both LSO and MOM approaches for each of the 85 measured BTC datasets.

# **RESULTS AND DISCUSSION**

# **Estimation of Moments from Experimental Data**

In Fig. 1, we show typical solute BTCs from the transport experiments considered in this study. Figure 1A shows tritiated water BTCs for repacked and undisturbed soil columns. Fifteen of the 20 BTCs from the laboratory experiments had >95% mass recovery and were collected using very small sampling intervals. In contrast, BTCs from the field experiment (Fig. 1B) had more irregular shapes and mass recoveries ranged from 41 to 156%. Breakthrough curves with missing tails, wide sampling intervals, scatter in concentration measurements, and uncertain applied solute mass may result in inaccurate derived transport parameters using both the MOM and LSO approaches. We address some of these issues in the following sections.

Experimental moments of all the 85 BTCs were estimated using the trapezoidal rule and the inertia method. Although the difference in the estimated moments by these two methods increases with the order of the moments (data not shown), and slightly larger moment estimates with the inertia method were consistently observed from our datasets, our analysis showed no substantial differences when using these two estimation methods. Comparison of transport parameters estimated using both



Fig. 1. Measured solute breakthrough curves (BTCs) obtained from (A) laboratory and (B) field miscible displacement experiments, illustrating a range in typical solute transport behaviors and measurement characteristics. Symbols show observed BTCs, and the solid lines were generated by optimizing pore water velocity (v) and dispersion coefficient (D) using CXTFIT (Toride et al., 1995). PFBA = pentafluorobenzoic acid.

moment estimation approaches and subsequent comparison with those obtained using CXTFIT further showed no advantage of one integration approach over the other. We conclude that either of these methods may be used for estimating moments from experimental data as long as high resolution (close proximity) solute concentration histories are available. All results presented hereafter were obtained using the trapezoidal integration scheme.

### Estimated Pore Water Velocity and Dispersion Coefficients

Pore water velocities estimated by the MOM and LSO approaches from the laboratory column data sets were very close to the v values calculated from the steady state water flux densities. However, a range of v was observed for the field data, although a single flow rate was used in the field transport experiments. We chose to optimize v by keeping  $\hat{R} = 1$  because a major goal of this study was to examine the MOM for its efficacy to estimate the pore water velocity from measured BTCs. For the field experiment, the means of the pore water velocities obtained by the MOM were 2.33 and 3.89 cm  $d^{-1}$  for the 25- and 65-cm depths, respectively. The means of the pore water velocities obtained by LSO were 2.39 cm  $d^{-1}$  and 3.26 cm  $d^{-1}$  for the 25- and 65-cm depths, respectively. The measured pore water velocity for this field experiment was  $3.53 \text{ cm } \text{d}^{-1}$ .

Figure 2 shows a comparison between the parameters estimated by the MOM and LSO for 85 BTCs. Both the MOM and LSO yielded similar pore water velocities while dispersion coefficients spread along the 1:1 line showing all three possible outcomes: MOM-estimated dispersion coefficients similar to, greater than, or less than LSO-estimated values. For the LSO analysis, coefficients of determination  $(r^2)$  ranged from 0.71 to 0.999 and exceeded 0.90 for more than 75% of the 85 data sets. For the purpose of making comparisons, corresponding values of v and D were combined to obtain a single parameter, the solute dispersivitiv, defined as  $\lambda = D/v$ . Linear regression between dispersivities estimated by MOM and LSO showed that the MOM-estimated dispersivities were consistently lower than those obtained by least-squares optimization ( $\lambda_{MOM} = 0.79 \lambda_{LSO}$ ;  $r^2 =$ 0.94, n = 85). The following discussion explores a possible explanation for this discrepancy.

We evaluated correlation between parameters estimated by the MOM and LSO methods and observed that the percentage deviation in the dispersion coefficients [100 ( $D_{\rm LSO} - D_{\rm MOM}$ )/ $D_{\rm LSO}$ ] was closely correlated ( $r^2 = 0.8$ , n = 85) with the percentage error in mass recovery fraction (MRF). Because we considered only conservative solutes in Fig. 3, the expected MRF may be assumed unity. Thus, the expression [100 (1 - MRF)] shown in the abscissa of Fig. 3 indicates the extent of mass balance error, that is, the percentage deviation between observed and expected mass recoveries for a given BTC. The expressions shown in the ordinate in Fig. 3 may be considered measures of deviation between MOM- and LSO-estimated parameters. Figure 3A clearly indicates that the deviation between MOM-estimated



Fig. 2. Comparison of solute transport parameters: (A) pore water velocity (v) and (B) dispersion coefficient (D) obtained by leastsquares optimization (LSO) using CXTFIT (Toride et al., 1995) and by the method of moments (MOM), for 85 measured solute breakthrough curves. PFBA = pentafluorobenzoic acid.

and LSO-estimated pore water velocities shows little dependence on the percentage error in MRF. However, Fig. 3B shows that the deviation between MOM-estimated and LSO-estimated dispersion coefficients is linearly related to the mass balance error. As expected, the data points for repacked and undisturbed laboratory leaching experiments are closest to the (0,0) coordinate. For these two data sets the mass recoveries were nearly unity. We recognize that the above result is not coincidental. The dispersion coefficient is estimated from the second moment, and inspection of Eq. [5] shows that the second moment is inversely proportional to the square of the zeroth moment, which is proportional to the MRF. Using synthetic data, Das et al. (2002) showed that mo-



Fig. 3. Impact of the mass recovery fraction (MRF) on the relative difference in (A) pore water velocity (v) and (B) dispersion coefficient (D) estimated by the least-squares optimization (LSO) and the method of moments (MOM) approaches for 85 measured solute breakthrough curves. The subscripts indicate the estimation method (LSO or MOM) for the respective parameters. PFBA = pentafluorobenzoic acid.

ment estimates are less sensitive to random error than to truncated BTCs. It was shown that errors in the first five absolute moments were less than 3% for a maximum random error of 45%. On the other hand, a 30% error in mass recovery caused by BTC truncation resulted in errors as large as 80% in the first five absolute moments. To further verify this result, we examined 39 BTCs observed from the surface 25 cm soil of Ellsworth et al. (1996) by normalizing each concentration value with the zeroth moment of its corresponding BTC. For incomplete BTCs, concentrations in the tailing end of each such BTCs were log-transformed, and a straight line was fit to the resulting values. The straight line was extended to the abscissa to generate a smooth and complete BTC. Both moment analysis and least-squares optimization were performed for the resulting BTCs. An excellent match between both methods of parameter estimation may be seen in Fig. 4. Thus, incomplete mass recovery resulting from truncation error appears to be a major source of error for the estimation of higherorder moments and, consequently, the calculated transport parameters. The LSO approach also yielded different estimates for v and D when BTCs with normalized and extrapolated concentrations, and 100% mass recovery were used for estimating these parameters. These results suggest that the frequently observed incomplete mass recovery in field-scale leaching experiments must be avoided. Alternatively, the MOM approach should be applied with caution if incomplete mass recovery is observed.

# Mass Recovery Error Impacts on Estimated Dispersion Coefficient

To evaluate the impact of mass recovery error arising from incomplete (truncated) BTCs on the derived mo-



Fig. 4. Comparison of solute transport parameters pore water velocity (v) and dispersion coefficient (D) for surface soils (25-cm depth) of Ellsworth et al. (1996), obtained by least-squares optimization (LSO) using CXTFIT (Toride et al., 1995) and by the method of moments (MOM), after each of 39 solute BTCs were scaled by their respective zeroth moment.

ments and on estimates of D obtained from these moments, we may examine the dependence of D on the second normalized central moment  $m_2$ . Combining Eq. [5] and [7] and using R = 1 gives

$$m_2 = \frac{\mu_2}{\mu_0} - \left(\frac{\mu_1}{\mu_0}\right)^2 = \frac{2DL}{\nu^3} + \frac{t_0^2}{12}$$
[13]

Figure 3A shows that the effect of mass recovery error on the estimation of v is negligible and v is uniquely related to  $\mu_1/\mu_0$  (Eq. [6]). Thus, it may be assumed that the error caused by incomplete mass recovery does not influence the ratio  $\mu_1/\mu_0$  and v. Equation [13] would then suggest that the error in D will be caused by errors in  $\mu_0$  and  $\mu_2$ . Hence, we assume that  $\mu_2/\mu_0$  is the true second moment and therefore yields the correct value for D when mass recovery is 100%, whereas BTCs with incomplete mass recovery yield the apparent values  $\mu'_2/\mu'_0$ and D'. Therefore, assuming that mass recovery error does not influence the ratio  $\mu_1/\mu_0$ , Eq. [13] may be rewritten for incomplete mass recovery as

$$m_2' = \frac{\mu_2'}{\mu_0'} - \left(\frac{\mu_1}{\mu_0}\right)^2 = \frac{2D'L}{v^3} + \frac{t_0^2}{12}$$
[14]

Subtracting Eq. [14] from Eq. [13] and dividing the result by a rearranged form of Eq. [13] yields

$$\frac{D-D'}{D} = \frac{\frac{\mu_2}{\mu_0} - \frac{\mu'_2}{\mu'_0}}{\frac{\mu_2}{\mu_0} - \left(\frac{\mu_1}{\mu_0}\right)^2 - \frac{t_0^2}{12}}$$
[15]

which provides a useful form for computing relative error in the dispersion coefficient from the true and apparent moments. To graphically illustrate this result,



Fig. 5. Experimental breakthrough curves collected from a (A) repacked and (B) undisturbed soil column under laboratory conditions. The vertical lines show the points truncated to generate BTCs with incomplete mass recoveries. The arrow in the bottom panel (B) shows the point of truncation corresponding to 100% mass recovery.

we estimated (D - D')/D as a function of errors in MRFs resulting from incomplete tritiated water BTCs for two different transport conditions (repacked and undisturbed soil columns). The BTC for the repacked soil column was taken from Experiment IV (v = 67.2 cm  $d^{-1}$ ) of Das (1996) and that for the undisturbed soil column was taken from Experiment I-24 (v = 4.8 cm d<sup>-1</sup>) of Langner et al. (1999). Fifteen incomplete BTCs were generated by truncating each of the measured BTCs as shown in Fig. 5. The BTCs represented concentrations sampled at close sampling interval (5 and 1% of the mean resident times for Experiment IV and Experiment I-24, respectively) precluding the likelihood of errors due to large sampling intervals. Dispersion coefficients were estimated from each of these BTCs using the MOM and the LSO approaches. The pore water velocities were kept constant during these estimations in both of the approaches to be consistent with the derivation of Eq. [15]. We also chose to treat the pulse duration as a known value in the LSO approach, although there is an option to optimize the pulse duration in the optimization program CXTFIT.

Evaluation of Eq. [15] also requires that *D* must be estimated from BTCs having mass recovery of 100%. Mass recoveries for the measured BTCs were 99.8% for the repacked soil column and 100.9% for the undisturbed soil column. We assumed that the measured BTC with 99.8% of mass recovery for the repacked soil column yields true values of *D*. For the undisturbed soil column, we truncated the BTC by removing the last 33 data points (indicated by the arrow in Fig. 5B) to obtain a BTC that yielded 100% mass recovery. Thus, this truncated BTC with 100% mass recovery was used to estimate true *D* for the undisturbed soil column. The true *D* values obtained by MOM were 29.76 cm<sup>2</sup> d<sup>-1</sup> and 10.32 cm<sup>2</sup> d<sup>-1</sup> for the repacked and undisturbed soil



Fig. 6. Percentage errors in estimated dispersion coefficients, using the least-squares method (filled squares) and the method of moments (filled triangles), are plotted as a function of percentage error in mass recovery fraction for transport of tritiated water through a (A) repacked and (B) undisturbed soil column.

columns, respectively. The LSO approach yielded true D values of 37.08 cm<sup>2</sup> d<sup>-1</sup> and 6.24 cm<sup>2</sup> d<sup>-1</sup> for the repacked and undisturbed soil columns, respectively. Corresponding mass recoveries were 99.8 and 100%.

Figure 6 shows that error in estimated D values increased with increasing error in mass recovery, but the errors in D estimates were significantly smaller for the LSO method than for the MOM. For example, mass recovery of 91% (9% error in mass recovery) resulted in errors of 138 and 57% in D values estimated by the MOM for the truncated BTCs of the repacked and undisturbed soil columns, respectively. Corresponding errors in estimated D values were below 5% for the LSO approach. The difference in estimated errors (138 vs. 57%) using two different experimental conditions for the same value of mass recovery error suggests that the experimental conditions influence the magnitude of errors for a particular parameter estimate and, therefore, it is not possible to identify an unequivocal acceptable limit for the mass recovery that would correspond to an allowable error in the parameter estimate in any transport experiment. However, considering that the errors in Destimates were <5% in the LSO approach for a mass recovery of <10%, we suggest that 10% error in mass recovery may be allowable in a laboratory-scale transport experiment if the parameters are estimated using the LSO approach.

### **SUMMARY**

The MOM and the LSO approaches were critically examined for estimating solute transport parameters. The parameters v and D were estimated from 85 laboratory- and field-measured BTCs using the MOM and the conventional LSO method. Results showed that these two procedures yielded similar parameter estimates for BTCs with 100% mass recovery. For BTCs with incomplete mass recovery, dispersion coefficients estimated

by the MOM departed significantly from those estimated using the LSO method, while the two approaches yielded similar estimates of pore water velocity. Numerical calculations using BTCs obtained from repacked and undisturbed soil columns showed that truncation error, which leads to incomplete mass recovery, has a significant impact on the estimation of D. In general, the MOM yielded larger errors in D estimates than the LSO method. Finally, we showed that, although it may be operationally possible to extrapolate a BTC and normalize it using its zeroth experimental moment to ensure 100% mass recovery, the use of either LSO or MOM yields a different set of parameters than for the untransformed BTC, leading to further complications in estimating unique transport parameters. This emphasizes that where the MOM is applied, 100% mass balance should be ensured.

### REFERENCES

- Aris, R. 1958. On the dispersion of linear kinematic waves. Proc. R. Soc. London. Ser. A 245:268–277.
- Das, B.S. 1996. Nonequilibrium sorption and degradation of organic solutes in soil. Ph.D. thesis. Kansas State Univ., Manhattan, KS.
- Das, B.S., R.S. Govindaraju, G.J. Kluitenberg, A. Valocchi, and J.M. Wraith. 2002. Time moment analysis and solute transport studies in soil. p. 239–279. *In* R. Govindaraju (ed.) Stochastic methods in subsurface contaminant hydrology. American Society of Civil Engineers, Reston, VA.
- Ellsworth, T.R., P.J. Shouse, T.H. Skaggs, J.A. Jobes, and J. Fargerlund. 1996. Solute transport in unsaturated soil: Experimental design, parameter estimation, and model discrimination. Soil Sci. Soc. Am. J. 60:397–407.
- Fahim, M.A., and S. Wakao. 1982. Parameter estimation from tracer response measurements. Chem. Eng. J. 25:1–8.
- Haas, C.N. 1996. Moment analysis of tracer experiments. J. Environ. Eng. 122:1121–1123.
- Harvey, F.C., and S.M. Gorelick. 1995. Temporal moment-generating equations: Modeling transport and mass transfer in heterogeneous aquifers. Water Resour. Res. 31:1895–1911.
- Jacobsen, O.H., F.J. Leij, and M.Th. van Genuchten. 1992. Parameter determination for chloride and tritium transport in undisturbed lysimeters during steady flow. Nord. Hydrol. 23:89–104.
- Jury, W.A., and G. Sposito. 1985. Field calibration and validation of solute transport models for the unsaturated zone. Soil Sci. Soc. Am. J. 49:1331–1341.
- Kamra, S.K., B. Lennartz, M.Th. Van Genuchten, and P. Widmoser. 2001. Evaluating nonequilibrium solute transport in soil columns. J. Contam. Hydrol. 48:189–212.
- Kolpin, D., E. Furlong, M. Meyer, E.M. Thurman, S. Zaugg, L. Barber, and H. Buxton. 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance. Environ. Sci. Technol. 36:1202–1211.
- Kubin, M. 1965. Beitrag zur theorie der chromatographie. Collection Czechoslov. Chem. Commun. 30:1104–1118.
- Langner, H.W., H.M. Gaber, J.M. Wraith, B. Huwe, and W.P. Inskeep. 1999. Preferential flow through intact soil cores: Effects of matric head. Soil Sci. Soc. Am. J. 63:1591–1598.
- Leij, F.J., and J.H. Dane. 1991. Solute transport in a two-layer medium investigated with time moments. Soil Sci. Soc. Am. J. 55:1529–1535.
- Misra, C., and B.K. Mishra. 1977. Miscible displacement of nitrate and chloride under field conditions. Soil Sci. Soc. Am. J. 41:496–499.
- Nauman, E.B. 1981. Invited review: Residence time distributions and micromixing. Chem. Eng. Commun. 8:53–131.
- Østergaard, K., and M.L. Michelsen. 1969. On the use of the imperfect tracer pulse method for determination of hold-up and axial mixing. Can. J. Chem. Eng. 47:107–112.
- Parker, J.C., and M.Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments. Bull. 84–3. Virginia Agric. Exp. Stn., Blacksburg, VA.

# 1216

- Rony, P.R., and J.E. Funk. 1971. Retention time and the first time moment in elution chromatography. III. General conclusions. J. Chromat. Sci. 9:215–219.
- Rubin, Y., M.A. Cushey, and A. Wilson. 1997. The moments of the breakthrough curves of instantaneously and kinetically sorbing solutes in heterogeneous geologic media: Predictions and parameter inference from field measurements. Water Resour. Res. 33:2465– 2481.
- Sun, N., N. Sun, M. Elimelech, and J.N. Ryan. 2001. Sensitivity analysis and parameter identifiability for colloid transport in geochemically heterogeneous porous media. Water Resour. Res. 37(2):209–222.
- Toride, N., F.J. Leij, and M.Th. van Genuchten. 1993. A comprehensive set of analytical solutions for nonequilibrium solute transport with first-order decay and zero-order production. Water Resour. Res. 29:2167–2182.
- Toride, N., F.J. Leij, and M.Th. Van Genuchten. 1995. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments. Res. Rep. No. 137. U.S. Salinity Lab., USDA-ARS, Riverside, CA.
- Valocchi, A.J. 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. Water Resour. Res. 21:808–820.