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"Forced Mass Balance" Technique for Estimating In Situ Transformation Rates of Sorbing Solutes in Groundwater

KIMBERLY J. HAGEMAN,*,† JENNIFER A. FIELD,‡ JONATHAN D. ISTOK§ AND MARTIN H. SCHROTH‖

Department of Chemistry, Department of Environmental and Molecular Toxicology, and Department of Civil, Construction, and Environmental Engineering, Oregon State University, Corvallis, Oregon 97331-7301, and Institute of Terrestrial Ecology, Swiss Federal Institute of Technology (ETH), Zurich, Switzerland

A method for estimating in situ transformation rates of sorbing solutes in groundwater is presented. The method utilizes a novel data processing technique called "forced mass balance" (FMB) to remove the effects of transport processes from reactant and product concentrations measured during single-well, "push−pull" tests. The effectiveness of the FMB technique was evaluated by quantifying errors in derived rates obtained by applying FMB to simulated push−pull test data generated by a numerical model. Results from simulated tests indicated that errors in derived rates increase as the test duration, groundwater velocity, and ratio of reactant to product retardation factors increase. In addition, errors in derived rates increase as the reaction rate constant and aquifer dispersivity decrease. As a demonstration, the FMB technique was used to derive an in situ reductive dechlorination rate for trichlorofluoroethene (TCFE) using data from a field push−pull test. Error analyses indicated that the in situ TCFE transformation rate was underestimated by a factor of 1.1−2. Thus, the FMB technique makes it possible to estimate in situ transformation rates of sorbing solutes and when FMB is coupled with computer modeling to estimate errors in derived in situ rates.

Introduction

Confidence in intrinsic and engineered approaches to groundwater remediation increases when remediation protocols integrate measurements of in situ transformation rates with site characterization, microcosm, and groundwater modeling studies. However, in situ transformation rates are difficult to determine because reactive solute (reactant) concentrations in groundwater are affected by a combination of transformation and transport (advection, dispersion, sorption) processes. A number of methods use spatial differences in reactant and product concentrations to determine in situ transformation rates (*1*−*5*). Spatial differences are determined by collecting data from multiple wells arranged in transects or grids. However, wells are expensive and time-consuming to construct and some of these methods are limited to use with steady-state solute plumes (*3*, *5*, *6*) or plumes containing a nonreactive solute that can serve as an in situ tracer (*3*, *4*).

Temporal differences in reactant and product concentrations measured at a single well can also be used to determine in situ transformation rates. Single-well methods are advantageous in that only one well is needed per test, they are not limited to plumes with special characteristics, and site-scale variability can be assessed by comparing results from different wells at a single site. One approach is to measure reactant concentrations at a single well over time and then use site-specific hydrologic properties in combination with "full inverse" modeling to differentiate changes in reactant concentrations due to transformation from those due to transport processes (*7*). An alternative approach involves determining in situ transformation rates from data collected during single-well "push−pull" tests. Push−pull tests are conducted by injecting ("pushing") an aqueous test solution containing a nonsorbing, nonreactive tracer and one or more reactants into the saturated zone of an aquifer via a monitoring well (*8*). Samples of the test solution/groundwater mixture are then extracted ("pulled") from the same well over time and analyzed for tracer, reactant, and product concentrations.

The in situ transformation rate of an injected reactant is determined by removing the effects of transport processes from measured reactant concentrations using a data processing technique. A data processing technique hereafter referred to as "tracer-normalization" (*9*, *10*) was used to determine in situ transformation rates from push−pull test data for a number of injected reactants, including nitrate (*11*, *12*), acetate (*11*), oxygen (*12*), sulfate (*13*, *14*), and formate (*15*). However, the tracer-normalization technique is limited to use with nonsorbing reactants. Based on the desire to determine in situ reductive dechlorination rates for the sorbing reactant, trichlorofluoroethene (TCFE), Hageman et al. (*15*) developed a data processing technique to remove the effects of transport processes (including sorption) from TCFE concentrations measured during push−pull tests. TCFE, which is sequentially transformed by reductive dechlorination to dichlorofluoroethene (DCFE), chlorofluoroethene (CFE), and fluoroethene (FE) in anaerobic environments is of interest because it can be used as a surrogate for the priority pollutant, trichloroethene (TCE) (*15*, *16*). The data processing technique presented by Hageman et al. (*15*) was developed with the assumption that TCFE and all of its products are transported identically to each other but differently from the tracer. However, in groundwater, TCFE and its products are not necessarily transported identically because differences in their chemical structures result in differing degrees of sorption to aquifer sediments. Since the relationship between accuracy in derived rates and similarity in reactant/product transport behavior has not been evaluated, the utility of the data analysis technique presented by Hageman et al. (*15*) for use in interpreting field push−pull test data is limited.

The objective of this work was to develop and evaluate a novel data processing technique, called "forced mass balance" (FMB), for deriving in situ transformation rates from push−pull tests when injected sorbing reactants and their products formed in situ are not transported identically. To

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* Corresponding author phone: (541)737-5431; fax: (541)737-0497; e-mail: kim.hageman@orst.edu. Corresponding author address: 1007 Agriculture and Life Sciences, Oregon State University, Corvallis, OR 97331-7301.

† Department of Chemistry, Oregon State University.

‡ Department of Environmental and Molecular Toxicology, Oregon State University.

§ Department of Civil, Construction, and Environmental Engineering, Oregon State University.

‖ Swiss Federal Institute of Technology (ETH).

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evaluate the technique, an extensive series of push−pull tests was simulated using a numerical model. Derived rates were obtained by applying the FMB technique to the simulated data. The accuracy of a derived rate was determined by comparing it to the rate used as an input in the numerical model. Errors in derived rates were quantified with respect to reactant and product retardation factors, test duration, groundwater velocity, first-order rate constant, and dispersivity. The FMB technique was then applied to data obtained during an actual field push−pull test designed to measure the in situ reductive dechlorination rate of TCFE in TCE-contaminated groundwater.

Experimental Section

Forced Mass Balance (FMB). The FMB data analysis technique was developed with the assumptions that (a) sorption occurs by linear equilibrium partitioning and (b) all potential transformation products are quantified and are unique to the reaction of interest. FMB utilizes four steps to derive in situ transformation rates from push−pull test data. First, total (aqueous plus sorbed) concentrations are calculated for the reactant and each product from their aqueous concentrations measured in push−pull test extraction samples. The total concentration of the sorbing product, A, for example, is calculated from

$$[A]_{\mathrm{aq+s}} = \frac{[A]_{\mathrm{aq}}V_{\mathrm{aq}} + [A]_{\mathrm{s}}M_{\mathrm{s}}}{V_{\mathrm{aq}}} = [A]_{\mathrm{aq}}\left(1 + \frac{K_{\mathrm{om}}\,f_{\mathrm{om}}\rho_{\mathrm{b}}}{n}\right) = [A]_{\mathrm{aq}}R(A) \quad (1)$$

where $[A]_{\mathrm{aq}}$ is the aqueous-phase concentration of A in the extraction sample of volume, V_{aq}; $[A]_{\mathrm{s}}$ is the sorbed-phase concentration of A in the sediment mass, M_{s}, associated with the extraction sample based on aquifer porosity, n; K_{om} is the organic matter/water distribution constant; f_{om} is the fraction of organic matter in aquifer sediments; ρ_{b} is the bulk density of aquifer sediments; and $R(A)$ is the retardation factor of A.

The second step is to calculate a "transport-process" adjustment factor for each extraction sample. Ideally, the adjustment factor indicates the degree to which total concentrations were affected by transport processes (including sorption) during the push−pull test. If the reactant and its products are transported identically, then the sum of their total concentrations (in molar units), Σ, is affected by transport but not by transformation during the test. Thus, for the reaction in which A is sequentially transformed to B and C, the adjustment factor, $\Sigma/\Sigma_{\mathrm{o}}$, associated with a given extraction sample is calculated from

$$\Sigma/\Sigma_{\mathrm{o}} = \frac{[A]_{\mathrm{aq+s}} + [B]_{\mathrm{aq+s}} + [C]_{\mathrm{aq+s}}}{[A]_{\mathrm{aq+s,o}} + [B]_{\mathrm{aq+s,o}} + [C]_{\mathrm{aq+s,o}}} \quad (2)$$

where for example, $[B]_{\mathrm{aq+s}}$ and $[B]_{\mathrm{aq+s,o}}$ are the total concentrations of B (expressed in molar units) in the extraction sample and in the well at the end of the test solution injection, respectively. If the reactant and its products are not transported identically, $\Sigma/\Sigma_{\mathrm{o}}$ estimates the degree to which total concentrations were affected by transport processes during the push−pull test.

The third step is to remove the effects of transport processes (including sorption) from the total concentrations of the reactant by dividing them by $\Sigma/\Sigma_{\mathrm{o}}$. Thus, FMB-adjusted concentrations for A, for example, are calculated from

$$[A]_{\mathrm{FMB}} = \frac{[A]_{\mathrm{aq+s}}}{\Sigma/\Sigma_{\mathrm{o}}} \quad (3)$$

The effects of transport processes will not be removed accurately if the $\Sigma/\Sigma_{\mathrm{o}}$ term contains errors due to differences in reactant/product transport behaviors. The final step is to plot FMB-adjusted concentrations of the reactant versus time and to determine the equation that best describes this curve. If the reaction is first-order and occurs in the aqueous phase only (and not in the sorbed phase), then the equation describing the curve is of the form

$$[A]_{\mathrm{FMB}} = [A]_{\mathrm{FMB,o}} \exp(-kt/R(A)) \quad (4)$$

where $[A]_{\mathrm{FMB,o}}$ is the FMB-adjusted concentration of A in the well at the end of the test solution injection, k is the first-order rate constant describing the rate of change in total concentrations of A due to transformation alone, and t is time. FMB-adjusted concentrations for the transformation products can be calculated with equations analogous to eq 3 and used to assess product distribution ratios; however, transformation rates of intermediate products are not readily determined since they are concurrently being produced and transformed. If the effects of transport processes were not removed accurately from total concentrations during the third step because of differences in reactant/product transport behaviors, k values derived from FMB-adjusted concentrations contain errors.

"Forced mass balance" is an illustrative term for this technique because the sum of FMB-adjusted reactant and product concentrations is conserved. FMB differs from the tracer-normalization technique (*9*, *10*) in that tracer normalization uses the relative concentration of a co-injected tracer, T/T_{o}, as a transport-process adjustment factor. While the technique previously presently by Hageman et al. (*15*) also uses the sum of reactant and product concentrations to obtain transport-process adjustment factors, it differs from FMB in that it utilizes only aqueous concentrations. Since potentially different partitioning behaviors of reactants and products are accounted for in the total (sorbed plus aqueous) concentrations used in the FMB technique, FMB is better suited for use with reactants that are transported differently than their products.

Numerical Simulations. Push−pull tests were simulated to evaluate the performance of the FMB data analysis technique at deriving in situ transformation rates of sorbing reactants from push−pull test data. Simulations were conducted with the fully implicit volume-integrated finite-difference simulator, Subsurface Transport Over Multiple Phases (STOMP) (*17*), which has been tested and validated against published analytical solutions and other numerical codes (*18*). In these simulations, STOMP used a modified Newton−Raphson method to solve the linear one-dimensional form of the advection-dispersion equation (*17*). The computational domain consisted of 400 equally spaced grid blocks (0.05 m × 1 m × 1 m). Initial solute concentrations were zero. Constant head boundary conditions were maintained at nodes 1 and 400. Input parameters for bulk density, ρ_{b}, (2.3 kg/L), and porosity, n, (0.2) were selected based on measurements conducted on aquifer sediments collected at the field site where the actual push−pull test was conducted (see section on applying FMB to a field push−pull test). Except where otherwise specified, the groundwater (pore water) velocity was 0.01 m/day and was selected based on measurements conducted at the field site. Except where otherwise specified, the longitudinal dispersivity was 0.1 m and was selected to represent that estimated by fitting modeled data to field data from the site.

The simulated test solution was injected as a source input into node 200 for 125 min at 2 L/min to replicate the injection procedure used during the field push−pull test. The simulated test solution contained equal concentrations of the nonsorbing nonreactive tracer, T, and the sorbing reactant, A. The tracer, T, was included so that comparisons between

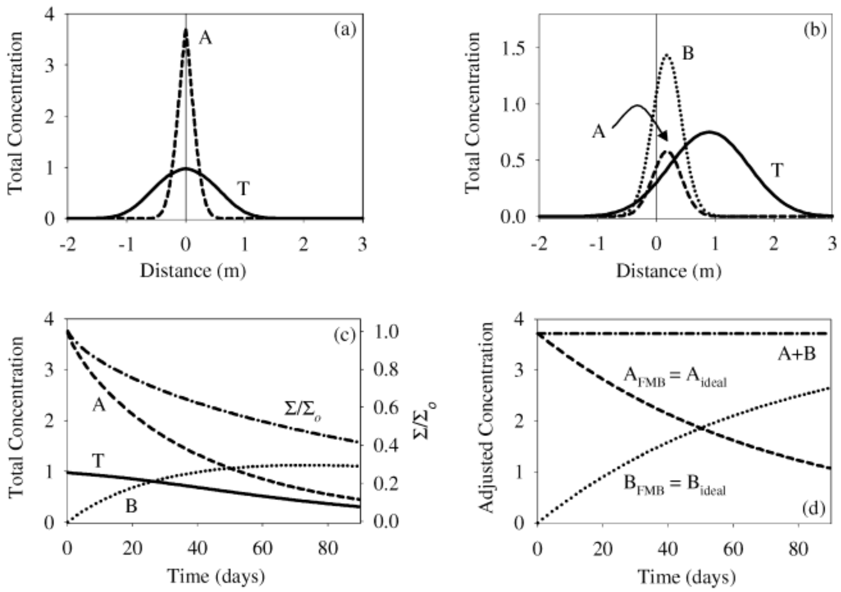

FIGURE 1. Test set I, test 1, $R(A) = R(B) = 5$. (a) Total (aqueous plus sorbed) concentrations of the reactant, A, and the tracer, T, in the simulated aquifer at the end of the test solution injection (125 min). The vertical line (at distance = 0 days) represents the single well. (b) Total concentrations of A, T, and the product, B, at 90 days. (c) Total concentrations of A, B, and T and values for the transport-process adjustment factor, Σ/Σ_o, at the single well. (d) FMB- and ideal transport-adjusted concentrations of A and B at the simulated well.

sorbing and nonsorbing transport behavior could be made. Except where otherwise noted, the input parameter describing the first-order rate constant, *k*, for the transformation of aqueous-phase A to its single product, B, was 0.069 day^{-1} and was selected because it was similar to the transformation rate for TCFE to DCFE observed during the field test. Due to evidence indicating that sorbed-phase reactants are not bioavailable (*19*), only A in the aqueous phase (and not in the sorbed phase) was allowed to undergo transformation. The time step used during the injection phase was 0.05 min. Following the injection phase, solutes were allowed to undergo transport and transformation for 90 days. Time steps were 0.05 days during this phase. To simulate sampling of the test solution/groundwater mixture, aqueous concentrations at the well (node 200) were output once per day. Although concentration versus distance data is not available during an actual field push–pull test, it was output at given times during simulated push–pull tests to aid in understanding the effects of transport behavior on concentrations at the single well. An example input file (*20*) is included in the Supporting Information.

Test set I was designed to determine the accuracy in derived rates obtained using FMB-adjusted concentrations for three illustrative example tests. In all tests, the retardation factor for A, $R(A)$, was 5. The retardation factor for B, $R(B)$, was 5, 1.25, and 20 in the three respective tests. Thus, $R(A)$ was equal to $R(B)$ in the first test, four times greater than $R(B)$ in the second test, and four times less than $R(B)$ in the third test. Test set II was designed to determine the effects of test duration, groundwater velocity, dispersivity, and input *k* on the accuracy of derived rates. For each of these parameters, a series of push–pull tests was simulated in which that single parameter was varied while the others were held constant. Simulations were conducted with $R(A)$ and $R(B)$ set to 5 and 1.25, respectively, and then with $R(A)$ and $R(B)$ set to 5 and 20, respectively. Test set III was designed to determine the effects of retardation factors on the accuracy of derived rates for a broader range of $R(A)$ and $R(B)$ combinations than that used in test set I.

Applying FMB to a Field Push–Pull Test. A field push–pull test was conducted in TCE-contaminated groundwater located at the site of a former chemical manufacturing plant in the San Francisco Bay area where TCE reductive dechlorination has been monitored in recent years (*15*, *21*). The test was conducted in the C-zone, which is characterized by alluvial fan deposits and is located approximately 6–23 m below the ground surface. C-zone groundwater velocities range from 0.01 to 0.08 m/day. The test solution (~250 L) containing TCFE was injected at a rate of ~2 L/min between a pair of inflatable packers designed to isolate a 1-m section of the well screen. Extraction samples were collected once per week for 84 days. Further details about the field site, experimental design, and analytical methods are provided elsewhere (*15*).

A modeling exercise was used to quantitatively evaluate the accuracy of the rate derived from field data using the FMB technique. A series of simulations was conducted using the same input values for ρ_b, *n*, groundwater velocity, and dispersivity used in test sets I and III. The injected test solution contained TCFE instead of the generic sorbing reactant, A. TCFE was allowed to undergo sequential transformation to DCFE and CFE (but not to FE since FE was not detected in field extraction samples) by first-order kinetics in the aqueous phase only. Simulations were conducted with input *k* values ranging from 0.07 to 0.3 day^{-1}. Retardation factors of 2.05, 1.39, and 1.14 were used for TCFE, DCFE, and CFE, respectively, based on calculations using

$$R = 1 + \frac{K_{om} f_{om} \rho_b}{n} \tag{5}$$

The Estimations Programs Interface Suite (*22*) was used to assign K_{om} values of 90.5, 33.5, and 12.2 L/kg to TCFE, DCFE, and CFE, respectively. Values used for f_{om} (0.001), ρ_b (2.3 kg/L), and *n* (0.2) used in eq 5 were selected based on measurements conducted on aquifer sediments collected at the field site. An input *k* value of 0.0017 day^{-1} was selected to describe the transformation of DCFE to CFE based on a best fit analysis between modeled and field data.

Results and Discussion

Test Set I. Test 1: $R(A) = R(B) = 5$. At the end of the simulated test solution injection (time = 125 min) during which the conservative tracer, T, and the sorbing reactant, A, were coinjected at equal concentrations, the maximum total

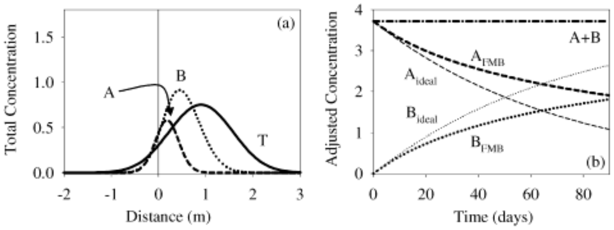

FIGURE 2. Test set I, test 2, $R(A) = 5$, $R(B) = 1.25$. (a) Total concentrations of A, B, and T in the simulated aquifer at 90 days. (b) FMB- and ideal transport-adjusted concentrations at the simulated well.

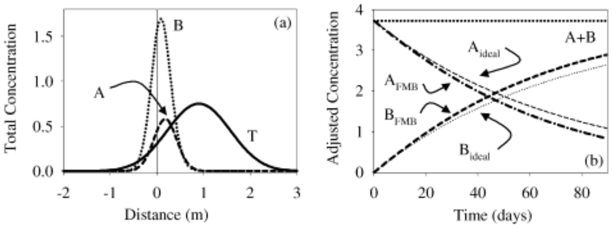

FIGURE 3. Test set I, test 3, $R(A) = 5$, $R(B) = 20$. (a) Total concentrations of A, B, and T in the simulated aquifer at 90 days. (b) FMB- and ideal transport-adjusted concentrations at the simulated well.

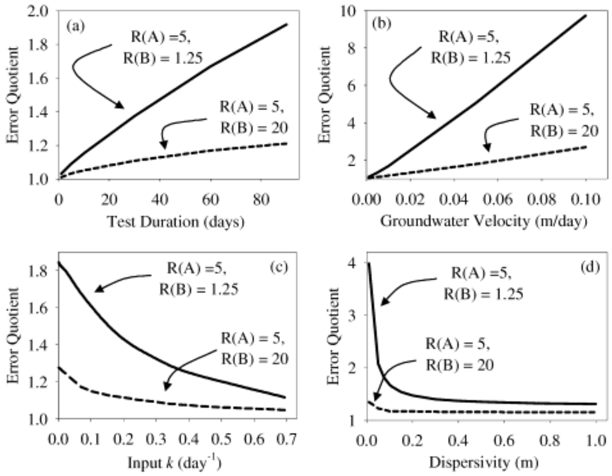

FIGURE 4. Test set II. Error quotients as a function of (a) elapsed test time, (b) ground water velocity, (c) input *k*, and (d) dispersivity.

concentrations of A and T were at the well (distance = 0 m) (Figure 1a). The concentration profile of A was narrower than that of T because it sorbed to aquifer sediments during the injection while T did not sorb. After 90 days of transport and transformation, peaks of A and its product, B (formed in situ), were centered at an equal distance from the well (Figure 1b) but were chromatographically separated from the peak of T. This separation occurred because the transport velocities of A and B were less than that of T. The transport velocity of a solute equals the groundwater velocity divided by the solute's retardation factor (note that the retardation factor of T is 1.) The *k* used as an input in the simulation code for the transformation of A to B could have been back calculated by integrating total concentrations of A and B in the aquifer at any time. However, because concentration measurements are made only at the well during an actual field push−pull test, the challenge was to derive *k* exclusively from the total concentrations found at the simulated well (Figure 1c).

FMB-adjusted concentrations of A and B (Figure 1d) were calculated by dividing their total concentrations by corresponding Σ/Σ_o values (Figure 1c) (eq 3). Ideally, the FMB technique removes the effects of transport processes (including sorption) from total concentrations. To test the effectiveness of the FMB technique, "ideal" transport-adjusted concentrations of A and B were calculated (Figure 1d). Ideal concentrations are those that would occur if the reaction were taking place in the absence of transport processes (e.g. in a batch reactor). Ideal (batch reactor) concentrations of A were calculated at each time point used in the simulation from

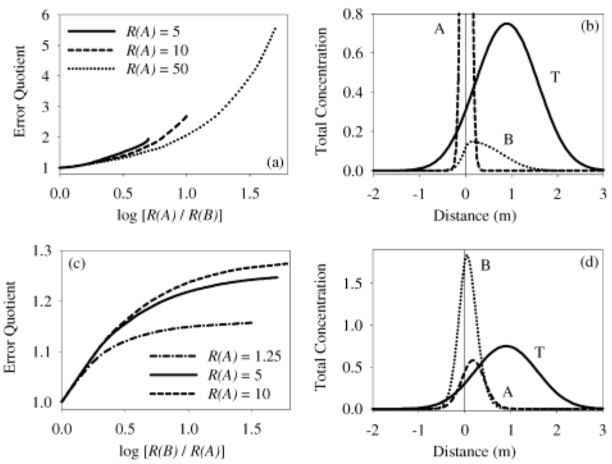

FIGURE 5. Test set III. (a) Error quotients as they relate to retardation factor when $R(A) > R(B)$. (b) Total concentrations of A, B, and T in the simulated aquifer at 90 days when $R(A) = 50$ and $R(B) = 1$. (c) Error quotients as they relate to retardation factor when $R(A) < R(B)$. (d) Total concentrations of A, B, and T in the simulated aquifer at 90 days when $R(A) = 5$ and $R(B) = 250$.

$$[A]_{\text{ideal}} = [A]_{\text{aq+s,o}} \exp(-kt/R(A)) \tag{6}$$

The value for *k* used in eq 6 was equal to the input *k* used in the simulations. $R(A)$ was included in the denominator of the exponential term because when transformation is only permitted in the aqueous phase, the effective rate constant equals *k* divided by the retardation factor of the reactant. Ideal transport-adjusted concentrations of B were calculated at each time point as the difference between the initial concentration of A and the ideal concentration of A at that time point. FMB- and ideal transport-adjusted concentrations of A and B were identical during this test (Figure 1d), indicating that the FMB technique successfully removed the effects of transport processes from total concentrations. The conclusion that the FMB technique can be used to determine accurate in situ transformation rates when the reactant and product are transported identically was further supported by results from other simulated tests in which values of $R(A)$ and $R(B)$ were equal (data not shown).

Test 2: $R(A) = 5$, $R(B) = 1.25$. The concentration profiles of T and A at the end of the test 2 injection phase (data not shown) were identical to those observed at the end of the test 1 injection phase (Figure 1a). Furthermore, the peak areas of A and B at 90 days (Figure 2a) were identical to those observed at 90 days during test 1 (Figure 1b) because the effective rate constant, $k/R(A)$, was identical during the two tests. However, in test 2, peaks for A, B, and T were chromatographically separated from each other since each solute had a unique transport velocity. Because B was transported further downgradient during test 2 than during test 1, its total concentration at the well at 90 days was lower in test 2 than in test 1. As a result, the ratio of the total concentrations of A to B at the well at 90 days was higher in test 2 than in test 1. Since this ratio is proportional to the FMB-adjusted concentration of A (eqs 2−3), FMB-adjusted concentrations of A were higher in test 2 (Figure 2b) than in test 1 (Figure 1d) and deviated from their ideal transport-

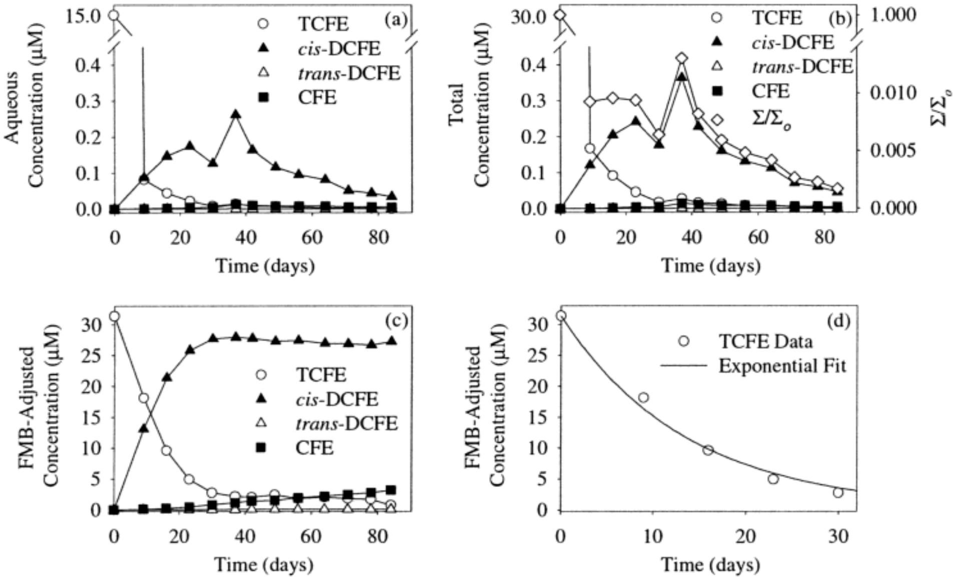

FIGURE 6. (a) Aqueous measured concentrations of TCFE and its products, indicating concentration changes due to transformation and transport processes, (b) total concentrations calculated from aqueous measured concentrations and values for the transport-process adjustment factor, Σ/Σ_o, (c) FMB-adjusted concentrations, indicating concentration changes due to transformation only, and (d) the plot of the best-fit exponential equation from which the derived rate was obtained.

adjusted concentrations (Figure 2b). Likewise, FMB-adjusted concentrations of B were lower in test 2 than in test 1 and also deviated from their ideal concentrations. The deviation of FMB-adjusted concentrations of A from ideal concentrations caused the *k* derived from FMB-adjusted concentrations (0.041 day^{-1}) to be smaller than the input *k* (0.069 day^{-1}). Thus, the error quotient, or the ratio of the derived *k* to the input *k*, was $0.069/0.041 = 1.7$. Results from this simulated test indicate that in situ transformation rates estimated from field test data may be a factor of 2 smaller than actual rates when field conditions are similar to those used in this simulation.

Test 3: $R(A) = 5$, $R(B) = 20$. The concentration profiles of T and A at the end of the test 3 injection phase (data not shown) were identical to those at the end of the test 1 injection phase (Figure 1a). Furthermore, the peak areas of A and B at 90 days (Figure 3a) were identical to those observed at 90 days during test 1 (Figure 1b) because the effective rate constant, $k/R(A)$, was identical during the two tests. The peaks of A, B, and T were again separated from each other chromatographically; however, in this case, the B peak was located closer to the well than the A peak. The chromatographic separation of A and B peaks during this test caused the FMB concentrations of A and B to deviate from their ideal transport-adjusted concentrations (Figure 3b). However, since the B peak was located closer to the well than the A peak, FMB-adjusted concentrations of A were smaller than ideal concentrations of A and FMB-adjusted concentrations of B were larger than ideal concentrations of B. As a result, the *k* derived from FMB-adjusted concentrations of A (0.082 day^{-1}) was larger than the input *k* (0.069 day^{-1}), and the error quotient was $0.082/0.069 = 1.2$. In this case, the error quotient was defined as the derived *k* to the input *k* so that it would not have to be expressed as a fraction. The error quotient obtained in test 3 was smaller than that obtained in test 2 because the degree to which A and B were chromatographically separated was less in test 3 than in test 2. Results from this simulated test indicate that in situ transformation rates estimated from field test data may be high by a factor of less than 1.5 when field conditions are similar to those used in this simulation.

Test Set II. The effects of test duration, groundwater velocity, input *k*, and dispersivity on the accuracy of derived rates were determined for cases in which $R(A)$ and $R(B)$ were 5 and 1.25, respectively, and 5 and 20, respectively. From this point forward, the error quotient is defined as the ratio (input *k*)/(derived *k*) for all cases in which $R(A)$ is greater than $R(B)$ and the ratio (derived *k*)/(input *k)* for all cases in which $R(A)$ is less than $R(B)$. Error quotients increased as test duration (Figure 4a) or groundwater velocity (Figure 4b) increased since increases in these parameters led to increases in the chromatographic separation of A and B. Error quotients decreased as the input *k* increased (Figure 4c) because faster rates allowed more of the conversion of A to B to occur before chromatographic separation became significant. Error quotients also decreased with increasing dispersivity (Figure 4d) because dispersivity affected the peak widths of A and B. As A and B peaks became more narrow (i.e. as dispersivity decreased), the overlap of the two peaks decreased and the ratio of the total concentrations of A to B at the well increasingly deviated from what it would have been if A and B were transported identically.

Test Set III. The effect of retardation factors on the accuracy of derived rates was assessed from test set III simulations. For cases in which $R(A)$ was greater than $R(B)$, error quotients became increasingly larger as the ratio of $R(A)$ to $R(B)$ increased for any given $R(A)$ value (Figure 5a). Again, chromatographic separation was responsible for error in derived rates. For example, the chromatographic separation of A and B was significantly greater when $R(A)$ and $R(B)$ were 50 and 1, respectively, (Figure 5b) than when they were 5 and 1.25, respectively (Figure 2a). Error quotients increased as $R(A)$ decreased for a given $R(A)$ to $R(B)$ ratio (Figure 5a) because differences in transport velocities between A and B increased as $R(A)$ decreased for a given $R(A)$ to $R(B)$ ratio.

For cases in which $R(A)$ was less than $R(B)$, error quotients began to level off after an initial increase as the ratio of $R(B)$ to $R(A)$ increased for any given $R(A)$ value (Figure 5c). Maximum error quotients were small relative to those observed when $R(A)$ was greater than $R(B)$ because the chromatographic separation of A and B was minimal during all cases in which $R(A)$ was less than $R(B)$. For example, A and B did not undergo significant chromatographic separation even when $R(A)$ and $R(B)$ were 5 and 250, respectively (Figure 5d). Error quotients increased as $R(A)$ increased for a given $R(A)$ to $R(B)$ ratio (Figure 5c). This trend cannot be attributed to differences in transport velocities between A and B since they increased as $R(A)$ decreased for a given $R(A)$

to $R(B)$ ratio. Thus, R must have played a different, more important role in affecting errors when $R(A)$ was less than $R(B)$. One explanation is that errors increase with increasing $R(A)$ because R influences the effective rate constant (k/R) and the effective dispersivity (dispersivity/R), which both influence error (test set II).

Field Application

Aqueous concentrations of TCFE and its transformation products, DCFE (*cis*- and *trans*-), CFE, and FE were measured in extraction samples collected during a field push−pull test (see Experimental Section) (Figure 6a). Aqueous concentrations shown at time zero equal those in the injection solution. Total (aqueous plus sorbed) concentrations (Figure 6b) for each solute except FE, which was not detected, were calculated from their aqueous concentrations using equations analogous to eq 1 and the R, K_{om}, f_{om}, ρ_b, and n values cited in the Experimental Section. FMB-adjusted concentrations were calculated for each solute (Figure 6c) by dividing their total concentrations by corresponding Σ/Σ_o values (Figure 6b). Nonlinear least-squares analysis was then used to obtain the exponential equation in the form of eq 4 that best describes the FMB-adjusted concentrations of TCFE between days 0 and 30 (Figure 6d). The best-fit exponential equation

$$[\mathrm{TCFE}]_{\mathrm{FMB}} = 31\ \mu\mathrm{M}\ \exp(-0.15\ \mathrm{day}^{-1}\ t/2.05) \qquad (7)$$

indicates that the k derived from field data is 0.15 day^{-1}.

Error estimates from the sensitivity analysis performed in test sets I−III were then used to qualitatively assess the accuracy of the k derived from field data. First, it is likely that the k derived from field data is underestimated relative to the actual in situ k since the retardation factor of TCFE is greater than that of its products. In addition, the magnitude of the error is likely to be less than a factor of 2 since data from the first 30 days of the test were used to estimate k (Figure 4a), the groundwater velocity was ∼0.01 m/day (Figure 4b); k was ∼0.15 day^{-1} (Figure 4c), and the dispersivity was ∼0.1 m (Figure 4d). The derived k is also expected to be in error by a factor of less than two than since the log $R(TCFE)/R(DCFE)$ value was 0.17 (Figure 5a).

FMB does not require the use of computer modeling to obtain in situ transformation rates from field data. However, a series of push−pull tests was simulated with a test solution containing TCFE to quantitatively evaluate the accuracy of the k derived from field data. Simulations were conducted with a range of input k values (0.07−0.26 day^{-1}) that bracketed the value for the k derived from field data. The FMB technique was then used to derive k values from the simulation data. The empirical relationship between the input k values and the values for k derived from simulation data for the transformation of TCFE to DCFE was

$$\text{input } k = 1.1 \text{ derived } k + 0.0080 \qquad (8)$$

which indicates that the k values derived from field data were underestimated by a factor of 1.1, or 10%. If this error quotient is applied to the k value derived from field data, the estimated in situ k becomes 0.17 day^{-1}. Thus, the errors in rates for the transformation of TCFE to DCFE obtained from field data collected at this site are not considered significant.

The potential effects of nonequilibrium sorption, aquifer property heterogeneities, and reaction rate heterogeneity on derived rates were not evaluated in this study. These issues will be investigated in future research projects. Nonetheless, to the best of our knowledge, the FMB technique makes it possible to estimate in situ transformation rates of sorbing solutes from push−pull test data for the first time. Moreover, errors in rates derived using the FMB technique can be quantified by coupling the technique to computer modeling.

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Supporting Information Available

Example input file for use with the numerical model, STOMP (*20*). This material is available free of charge via the Internet at http://pubs.acs.org.

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