Evaluating the Ability of Tracer Tests to Quantify Reactive Solute Transport in Stream-Aquifer Systems

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ABSTRACT

Tracer experiments are valuable tools for characterizing the fate and transport of solutes carried in stream waters; however, the results can have high uncertainty when the technique is not properly implemented. The goal of this study was to identify the limitations that apply when we couple conservative-tracer injection with reactive solute sampling to identify the transport and reaction processes active in a stream. The conservative-tracer injection is used to characterize the physical transport processes of advection, dispersion, ground-water inflow, and stream-storage exchange (the movement of stream water and solute between the active stream channel and storage zones in the channel margins and in the subsurface). The reactive-solute sampling is used to characterize the removal of reactive solute due to geochemical/biotic processes occurring in the storage zones. We apply the methodology of Wagner and Harvey (1997) to evaluate the tracer approach for the wide range of transport and reaction conditions likely encountered in high-gradient streams. The methodology couples solute transport simulation with parameter uncertainty analysis in a Monte Carlo framework to identify those combinations of stream transport and reaction properties that pose limitations to the tracer approach. Our results show that the uncertainty associated with determining the reaction rate constant is strongly related to the reactive loss factor, which is a dimensionless combination of the reaction rate constant, the average solute residence time in the storage zone, the experimental reach length, and the average distance travelled by a stream solute before entering a storage zone. As the reactive loss factor increases, the effect of reactive loss in the storage zones along the study reach increases and the uncertainty in the reaction rate estimate decreases.

INTRODUCTION

There are a wide range of processes that affect solute transport, physical retention, and reactive uptake in stream and shallow ground-water systems. Numerous studies have shown that exchange between stream and storage zones, coupled with solute reactions, can play an important role in determining the quality of stream waters (e.g. Bencala, 1984; Grimm and Fisher, 1984; D’Angelo and others, 1993; Runkel and others, 1996; Harvey and Fuller, 1998). The stream-storage exchange process — the movement of stream water between the active channel and storage zones in the channel margins or in subsurface hyporheic flow paths — serves to increase solute retention time. The increased contact of stream-water solutes with sediment, in turn, stimulates biotic and geochemical processes that affect solute reaction during downstream transport.

Stream-tracer studies are one of the primary tools used to characterize transport and reaction processes. In a stream tracer study, a tracer-labelled solution is injected into the stream. As the tracer body moves downstream, it is affected by the various processes active in the stream system. At some point(s) downstream of the tracer injection site, water samples are collected, providing a record of the tracer’s transport and evolution. The tracer data are then analyzed to describe (in a quantitative fashion) the transport and reaction processes. The approach commonly used is to combine the tracer data with a solute transport simulation model to estimate solute transport parameters for the stream. Conservative-tracer injection studies are commonly used to estimate the physical process parameters.
that characterize stream-solute dynamics (see Stream Solute Workshop, 1990). Investigators have also injected reactive solutes to characterize reactive solute transport (e.g. Bencala and others, 1984, Triska and others, 1993). However, because of the elevated concentrations of the reactive constituent that result from the reactive-tracer injection, the results from such studies may not be representative of the naturally-occurring reactions.

An alternative to reactive-tracer injection is to use a tracer approach that does not alter the natural levels of the reactive constituents, such as the approach used by Kimball and others (1994), Heekyung and others (1995), and Harvey and Fuller (1998). In this approach, a conservative-tracer injection experiment is coupled with synoptic sampling of the reactive constituent. The conservative-tracer data are combined with a transient solute-transport simulation model to characterize the physical processes active in the study reach. The reactive-constituent data are combined with a steady-state simulation model to determine the reaction rate(s) describing the net loss of the reactive constituent along the study reach. The result is a set of models and parameters that can be used to analyze solute transport and reactive loss.

Here we extend the work of Wagner and Harvey (1997) to analyze tracer test design for the combined conservative/reactive tracer approach described above. Wagner and Harvey evaluated the ability of the conservative-tracer injection study to characterize the physical transport processes of advection, dispersion, dilution from ground-water inflow, and stream-storage exchange. They evaluated a variety of different tracer test designs for a broad range of stream transport characteristics and found that the success of a tracer study is limited by its ability to quantify the stream-storage exchange process. The goal of this study was to identify any additional limitations that might apply when we attempt to use the conservative/reactive tracer approach to identify both the transport and the reaction processes.

**METHODOLOGY**

The approach used in this study follows that developed by Wagner and Harvey (1997). The methodology is based on the concept of global parameter uncertainty analysis, which combines solute transport simulation with parameter uncertainty analysis in a Monte Carlo framework. Simply stated, the methodology considers the wide range of transport conditions likely to be encountered in the field and identifies the conditions under which tracer experiments will be successful, that is, the conditions under which solute transport processes can be reliably identified.

**Modeling Stream Solute Transport**

In the conceptualization of stream-solute transport used in this study, the hydrologic regime is divided into two coupled systems: a system of flowing water in the main stream channel (where advection, dispersion, and groundwater inflow processes are active) and a system of storage zones at the margins of the stream channel or in the subsurface (fig. 1). The two systems are coupled by a mass transfer mechanism that exchanges solutes between the main channel and the storage zones. It is only in the storage zones that reactive loss occurs. The assumption that reactive loss occurs only in the storage zones is based on the fact that biological and geochemical reactions are expected to take place much faster in contact with sediment, due to

![Figure 1. Schematic representing stream-solute transport and reaction system: advection and dispersion, stream-storage exchange, groundwater inflow, and reactive loss in storage zones.](image-url)
geochemical coatings and microbes on sediments that catalyze the reactions (for example, Harvey and Fuller, 1998). It should be noted that although this study is limited to the conditions described above, the methodology is flexible and can be adapted to handle any solute transport and reaction scenario for which a mathematical model can be developed.

The mathematical model for one-dimensional advective-dispersive transport with inflow and storage-zone exchange is

\[
\frac{\partial C}{\partial t} = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left( AD \frac{\partial C}{\partial x} \right) + \frac{q_L}{A} (C_L - C) + \alpha (C_s - C) \tag{1}
\]

\[
\frac{\partial C_s}{\partial t} = -\alpha \frac{A}{A_s} (C_s - C) \tag{2}
\]

where

- \( C \) solute concentration in the stream (mg L\(^{-1}\)),
- \( Q \) volumetric flow rate (m\(^3\) s\(^{-1}\)),
- \( A \) cross-sectional area of stream channel (m\(^2\)),
- \( D \) dispersion coefficient (m\(^2\) s\(^{-1}\)),
- \( q_L \) lateral volumetric ground-water inflow rate (per length) (m\(^3\) s\(^{-1}\) m\(^{-1}\)),
- \( C_L \) solute concentration in the lateral inflow (mg L\(^{-1}\)),
- \( C_s \) solute concentration in the storage zone (mg L\(^{-1}\)),
- \( A_s \) cross-sectional area of the storage zone (m\(^2\)),
- \( \alpha \) stream-storage exchange coefficient (s\(^{-1}\)),
- \( t \) time (s),
- \( x \) distance (m).

To simulate solute transport using (1) and (2) the process parameters must be specified. Since direct measurement of these parameters is difficult or impossible, they must be determined by fitting the model described by equations (1) and (2) to the data collected as part of the tracer study. We advocate using techniques of optimization and statistics to estimate the parameters that best reproduce the tracer data and to determine the reliability of the parameter estimates (for example, Wagner and Gorelick, 1986; Wagner and Harvey, 1996).

The above equations are used to analyze the data from a conservative-tracer injection. Measurements of a reactive solute can be combined with this physical transport analysis to determine a rate constant describing the removal of the reactive solute in the storage zones. The following steady-state form of (1) and (2) is used

\[
0 = -\frac{Q}{A} \frac{\partial C}{\partial x} + \frac{1}{A} \frac{\partial}{\partial x} \left( AD \frac{\partial C}{\partial x} \right) + \frac{q_L}{A} (C_{rL} - C_r) + \alpha (C_{rs} - C_r) \tag{3}
\]

\[
0 = -\alpha \frac{A}{A_s} (C_{rs} - C_r) - \lambda_s C_{rs} \tag{4}
\]

where all parameters remain the same as in (1) and (2) with the following exceptions

- \( C_r \) concentration of the reactive solute in the stream (mg L\(^{-1}\)),
- \( C_{rL} \) concentration of the reactive solute in the lateral inflow (mg L\(^{-1}\)),
- \( C_{rs} \) concentration of the reactive solute in the storage zone (mg L\(^{-1}\)),
- \( \lambda_s \) first-order reaction rate constant describing solute removal in the storage zone (s\(^{-1}\)).

Because the physical transport parameters are determined from modeling the conservative-tracer injection, only the rate constant, \( \lambda_s \), remains to be determined. This is done by modeling the reactive solute data using (3) and (4) with the physical transport parameters determined from the conservative-tracer data. Again, we advocate the use of formal inverse methods for this task.

### Evaluating Parameter Reliability

The complexity of stream-solute transport can make it difficult to reliably determine the solute transport and reaction parameters. Parameter uncertainty analysis provides a quantitative measure of the reliability of parameters estimated from tracer data and forms the basis of the methodology for evaluating and comparing alternative tracer experi-
ment designs. The underlying assumption here is that a tracer experiment is successful if the solute transport and reaction parameters can be reliably determined. Here we calculate parameter reliability using the first-order approximation to the parameter estimate covariance matrix, $V_p$

$$V_p = (J^t V_c^{-1} J)^{-1}$$

where
- $V_p$: covariance matrix that defines the uncertainty in the parameter estimates, an $n \times n$ matrix where $n$ is the number of parameters.
- $V_c$: covariance matrix that defines the uncertainty in the concentration data, an $m \times m$ matrix where $m$ is the number of concentration data.
- $J$: jacobian, the matrix of sensitivities of modeled concentrations with respect to changes in the model parameters, an $m \times n$ matrix.

The parameter estimate covariance matrix can be used to identify the parameters that are well (or poorly) estimated. In this study we use the coefficient of variation as the ultimate measure of a parameter’s reliability

$$cov(p_i) = \frac{sd(p_i)}{p_i}$$

where
- $p_i$: process parameter $i$,
- $cov(p_i)$: coefficient of variation for process $i$,
- $sd(p_i)$: standard deviation of $p_i$, which is defined as the square root of the $i^{th}$ diagonal element of $V_p$.

The coefficient of variation is a unitless measure that defines the standard deviation as a fraction of the parameter value. We use this measure in our analyses because it allows us to compare results across all parameter types, regardless of the magnitudes or dimensions of the parameters.

**Monte Carlo Analysis of Stream Tracer Test Design**

The methodology applied here uses Monte Carlo analysis to account for the wide range of transport characteristics that can be encountered in the field. In brief, the methodology proceeds as follows. On the basis of prior information, we generate many realizations of the solute transport and reaction parameters needed to define (1) - (4), with each realization representing a possible “model” of the true stream solute transport and reaction system. We then define a tracer-test design (that is, a combination of a conservative-tracer injection and sampling strategy and a reactive-solute sampling strategy). Next, a Monte Carlo parameter uncertainty analysis is performed to analyze parameter reliability for each parameter realization for the tracer-test design considered. The result is a suite of parameter uncertainties that are used to analyze the capabilities and limitations of the tracer approach over the spectrum of possible transport and reaction conditions. A detailed description of the methodology can be found in Wagner and Harvey (1997).

**Prior Parameter Information**

As outlined above, the first step in the analysis is to define the prior parameter information. Here we analyzed the ability of the tracer approach to identify transport and reaction processes for the range of conditions representative of high-gradient streams. These streams have widely varying physical transport properties. Stream discharge and velocity, ground-water inflow, dispersion, and stream-storage exchange properties can vary by orders of magnitude from one system to another. In addition, the reaction properties of the system can vary significantly depending on the biological and geochemical characteristics of the stream-storage system and the solute, and on the amount of interaction between the solute and the subsurface hyporheic flow paths. Here we define the ranges of transport and reaction parameters on the basis of parameter values that have been reported in the literature. The parameter ranges are listed in Table 1. Note that the ranges for the physical transport parameters are identical to those used in Wagner and Harvey (1997).

Once the parameter ranges have been defined, the next step is to generate many realiza-
tions of the stream transport and reaction parameters. For the analyses presented here we generated 1,000 sets of transport and reaction parameters. The parameters were generated using the same approach as Wagner and Harvey (1997). In brief, the parameters were randomly selected assuming they varied uniformly and independently between their lower and upper levels. The only exceptions were stream discharge and cross-sectional area which were constrained to be consistent with the physics of open-channel flow.

### The Basic Tracer Test

There are many variables that must be considered when designing a tracer study, such as the length of the reach over which the study is performed, the duration of the conservative-tracer injection, the frequency of sampling of the conservative tracer, and the sampling plan for the reactive constituent in the stream. In order to compare results across the wide range of transport and reaction conditions considered, we have adopted the standardized design variables used by Wagner and Harvey (1997). For every case analyzed, the experiment was assumed to take place over a 150-m reach of stream. For the conservative-tracer injection, we assume a continuous injection with sampling of the tracer rise, plateau, and fall. It was further assumed that the conservative-tracer injection would give a plateau concentration at the sampling site that was 25 times the background concentration, and that stream water would be sampled in 30-second intervals. For the reactive constituent, it was assumed that 15 samples would be collected at evenly spaced intervals along the stream reach. It also was assumed that the reactive-constituent concentration entering the study reach was 10 times the background concentration in ground-water inflow. Finally, for both conservative and reactive constituents, it was assumed that the concentration data errors, which define $V_c$ in (5), have standard deviations equal to 15 percent of the true concentration values. In later sections we will investigate the sensitivity of the results to changes in study reach length, which we found to be the most important design variable.

Using the design variables described above, we assessed the ability of the tracer study approach to estimate solute transport and reaction parameters. For each of the 1,000 transport and reaction scenarios described in Table 1, the parameter covariance (5) was calculated. The suite of 1,000 covariance matrices provides the basis for assessing the capabilities and limitations of the tracer approach.

### RESULTS

#### Identifying The Physical Transport Parameters

As noted earlier, there are six unknown parameters in (1) - (4) that must be estimated based on tracer data: the physical transport parameters ($A$, $D$, $q_L$, $A_s$, and $\alpha$) and the reactive-loss rate parameter ($\lambda_s$). Previous work by Wagner and Harvey (1997) provides a comprehensive analysis of the ability of conservative-tracer injection studies to estimate the physical transport parameters. That study showed that the success of a tracer test is limited by our ability to estimate the stream-storage exchange parameters ($A_s$ and $\alpha$), and that the limitations can be defined using the experimental Damköhler number

$$DaI = \frac{\alpha(1 + A/A_s)L}{v}$$  \hspace{1cm} (7)  

where $A$, $A_s$, and $\alpha$ are as defined earlier and $v$ average stream water velocity (m/s),

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q$ (m$^3$/s)</td>
<td>0.005 - 0.2</td>
</tr>
<tr>
<td>$q_L$ (m$^3$/s m)</td>
<td>0.0 - 0.0001</td>
</tr>
<tr>
<td>$A$ (m$^2$)</td>
<td>0.02 - 0.6</td>
</tr>
<tr>
<td>$D$ (m$^2$/s)</td>
<td>0.025 - 0.8</td>
</tr>
<tr>
<td>$A_s$ (m$^2$)</td>
<td>0.01 - 2.0</td>
</tr>
<tr>
<td>$\alpha$ (1/s)</td>
<td>0.000005 - 0.001</td>
</tr>
<tr>
<td>$\lambda_s$ (1/s)</td>
<td>0.000001 - 0.01</td>
</tr>
<tr>
<td>$C_L$ (mg/L)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
The length of the study reach (m).

The results of this study mirror those of Wagner and Harvey (1997). In general, uncertainty associated with $A_s$ and $\alpha$ reaches a minimum when $Da_I$ is on the order of 0.1-1.0, and uncertainty increases when $Da_I$ decreases below or increases above this value. This relationship is shown in Figure 2, which plots the experimental Damkohler number $Da_I$ versus the coefficient of variation for the storage-zone cross-sectional area $A_s$ (a similar relationship is found for $\alpha$). This relationship can be explained based on the degree of interaction between the solute and storage zones. When $Da_I$ is small (due to high $v$, small $\alpha$ and $A/As$, and(or) small $L$) parameter uncertainties are high because only a small amount of tracer interacts with the storage zones along the study reach. In this case, the effect of stream-storage exchange is small and cannot be identified. When $Da_I$ is large, solute exchange rates are high relative to advective movement, and tracer dispersion caused by stream-storage exchange reaches an equilibrium condition. In this case, uncertainty is high because the effect of exchange cannot be separated from that of dispersion.

Identifying The Reactive Loss Parameter

The experimental Damkohler number is useful for assessing the limitations of the stream tracer approach. We would like to identify a similarly useful expression for determining the limitations on estimating the reaction rate constant, $\lambda_s$. Here we test the dimensionless parameter grouping suggested by Harvey and Fuller (1998) that we call the reactive loss factor (RLF)

$$RLF = \frac{\lambda_s t_s L}{L_s}$$

where $\lambda_s$ and $L$ are as defined earlier and

$$t_s = A_s/\alpha A$$, average residence time of water in storage zones,

$$L_s = v/\alpha$$, average distance travelled by a parcel of water before entering a storage zone.

The reactive loss factor (8) is a measure of the effect of the reactive loss process along the study reach. When $RLF$ is small, there is little loss of the reactive constituent within the experimental reach. This occurs when the reaction rate, $\lambda_s$, is small, the residence time in the storage zones, $t_s$, is small, and(or) the turnover length, $L_s$, is large relative to the experimental reach length, $L$. As $RLF$ increases (due to increasing $\lambda_s$, increasing $t_s$, or decreasing $L_s$) the effect of reactive loss becomes more pronounced.

Figure 3 is a plot of $RLF$ versus the coefficient of variation for $\lambda_s$. This plot highlights two important characteristics of the conservative/reactive tracer approach. First, for the conditions analyzed here, the tracer approach is consistently unable to reliably determine the reaction rate constant $\lambda_s$. Across the entire range of transport and reaction conditions analyzed, the coefficient of variation of $\lambda_s$ reaches a minimum of approximately 1, which we consider to be an unacceptably high level of uncertainty. (Although somewhat arbitrary, we believe a parameter is reliably estimated only if its coefficient of variation is considerably less than 1. This choice is based on the concept of a 95 percent confidence interval for a normally distributed random variable. For example, a parameter with a coefficient of variation equal to 0.1 will have a 95 percent confidence interval that is approximately plus or minus 20 percent of the parameter value.) We will show later how the design variables used in this base case can be changed to improve parameter estimate reliability.

The second characteristic highlighted in Figure 3 is the relationship between the reactive loss
factor and the coefficient of variation of $\lambda_s$. For the lower-range values of RLF, there appears to be a strong relationship between increasing RLF and decreasing uncertainty in $\lambda_s$. For the upper-range values, however, this relationship disappears. We believe this can be explained by the linkage between the physical and reaction transport processes and the need to identify the physical transport processes (specifically the stream-storage exchange process) before the reaction rate constant can be determined. Recall that the conceptual model (fig. 1) used here assumes that reactive loss occurs only in the storage zones. Further, the amount of reactive loss — that is, the imprint of the reactive loss process — along the study reach is dependent on both the degree of interaction between the solute and the storage zones and the magnitude of the reaction rate constant. Although the reactive loss factor RLF accounts for both, it does not account for the fact that the stream-storage exchange process is not always reliably determined. It appears that when the exchange parameters' uncertainty is very high, the reaction rate constant cannot be reliably determined, even when the RLF is large.

**IMPROVING THE TRACER TEST DESIGN**

The above analysis focused on the ability of the tracer approach to characterize reactive loss in the storage zones. The results show that, for the basic tracer test design used in our analyses, it is not possible to obtain a reliable estimate of the reaction rate constant $\lambda_s$. However, we know that there is a strong tendency for decreasing uncertainty in $\lambda_s$ with increasing reactive loss factor, and that this relationship holds only when the storage-exchange parameters are reliably estimated. We also know that in order to reliably characterize stream-storage exchange, the experimental Damkohler number should be on the order of 0.1-1.0. The obvious question to ask is: Can we alter the tracer test design to improve the reliability with which $\lambda_s$ is estimated?

The one defining property of $Dal$ and $RLF$ that we can control when designing a stream tracer study is the experimental reach length $L$. This suggests that the choice of the experimental reach length could be an important factor in determining whether the reaction rate constant can be reliably estimated. To investigate the influence of the reach length on $\lambda_s$ uncertainty, we selected a single parameter realization and performed a series of parameter uncertainty analyses, with reach length varied from 150 m (the base case) to 1,000 m. Furthermore, in order to normalize the results, we assumed that the same number (15) of reactive-constituent measurements would be collected in each analysis. The results of this sensitivity analysis are presented in Figure 4.

**Figure 3.** Plot of coefficient of variation vs. reactive loss factor for reaction rate constant $\lambda_s$.

**Figure 4.** Plot of $\lambda_s$ coefficient of variation vs. reactive loss factor. The data correspond to reach lengths of 150 m, 300 m, 600 m, and 1000 m.
The data plotted in Figure 4 show a strong dependency between the uncertainty associated with $\lambda_s$ and the RLF value. It is important to note that in these analyses, the only factor changed was the experimental reach length. As RLF increases (due to the increase in the reach length $L$), the coefficient of variation of $\lambda_s$ decreases. This suggests that the RLF may be useful for designing tracer studies by providing guidance for selecting the appropriate experimental reach length. However, because the data in Figure 4 are based on a single parameter realization, additional research is required to determine if these results can be transferred for use in stream systems with different transport and reaction properties. Moreover, we know that the reliable estimation of the reaction rate constant is dependent on reliably estimating the stream-storage exchange parameters, which in turn is dependent on having the appropriate $Dal$ value. We also know that the only means we have of varying $Dal$ when designing a stream tracer study is by varying the experimental reach length, just as we did to get the data plotted in Figure 4. Therefore it will be very important when designing a stream tracer study to consider the effects of varying experimental reach length on both $Dal$ and RLF.

SUMMARY

We analyzed the capabilities and limitations of the stream tracer approach that combines conservative-tracer injection with measurement of a reactive constituent in a stream. The methodology used Monte Carlo parameter uncertainty analysis to evaluate and compare tracer test efficiencies over the spectrum of transport and reaction scenarios that are likely to be encountered in the field. Our analyses found that determining the reaction rate constant is dependent on two factors: (1) the reactive loss factor, RLF, is sufficiently large; and (2) the experimental Damkohler number, $Dal$, is in the range that provides reliable estimates of the stream-storage exchange parameters.

We demonstrated how the reaction rate constant can be reliably estimated by increasing the experimental reach length, which increases the reactive loss factor, RLF. However, this analysis was limited to a single realization of the solute transport and reaction parameters. Research is ongoing to determine how (if) the reactive loss factor might be used to select the reach length that provides a reliable estimate of the reactive loss parameter, and to better understand the trade-offs encountered when designing the conservative-tracer injection (based on $Dal$) and the synoptic sampling of the reactive solute (based on RLF).

REFERENCES


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