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Analysing the capabilities and limitations of tracer tests in stream–aquifer systems

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Abstract 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. Our methodology applies Monte Carlo uncertainty analysis to assess the ability of the tracer approach to identify the governing transport and reaction processes for a wide range of stream-solute transport and reaction scenarios likely to be encountered in high-gradient streams. Our analyses identified dimensionless factors that define the capabilities and limitations of the tracer approach. These factors provide a framework for comparing and contrasting alternative tracer test designs.

Key words model uncertainty analysis; stream tracer test design

INTRODUCTION

There are a wide range of processes that affect solute transport, redistribution, and reaction in streams. Numerous studies have shown that exchange between the stream and storage zones, coupled with solute reactions, can play an important role in determining the quality of stream waters (Jones & Mulholland, 2000). A significant challenge in stream solute studies is linking these fundamental, small-scale solute-transport and reaction processes with the water quality changes observed over the entire watershed. The stream tracer study has become a widely used tool because it measures processes integrated over a large segment of a stream, providing a whole-stream assessment that is valuable when trying to understand solute transport at the watershed scale.

Conservative-tracer injection studies are commonly used to estimate the physical process parameters that characterize stream-solute dynamics. Investigators have also injected reactive solutes to characterize reactive solute behaviour. However, because of the elevated concentrations of the reactive constituent(s) that result from the reactive-tracer injection, the results from such studies may not be representative of naturally occurring reactions. Here we analysed an alternative to reactive-tracer injection that does not alter the natural levels of the reactive constituents (e.g. Kim *et al.*, 1994; Harvey & 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 transport processes. The reactive-constituent data are combined with a steady-state simulation model to determine the reaction rate describing the net loss of the reactive constituent along the study reach.

Wagner & Harvey (1997, 2000) evaluated the ability of the conservative-tracer injection approach to characterize physical transport processes for a broad range of stream transport characteristics. They found that the success of the stream tracer approach was limited by its ability to characterize the stream–storage exchange process. Moreover, they were able to identify the limits of the stream-tracer approach in terms of the dimensionless Damkohler factor. The goal of this study was to identify any additional limitations that apply when we extend our analysis to the combined conservative and reactive tracer study.

SOLUTE TRANSPORT MODEL

The approach commonly used to analyse stream tracer data is to combine those data with a solute transport model. In the conceptualization of stream-solute transport used in this study, the hydrological 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. The two systems are coupled by a mass transfer mechanism that exchanges solutes between the main channel and the storage zones. Here we focus on reactive loss that occurs only in the storage zones. This assumption is based on the fact that water in the storage zones is in close contact with geochemically and microbially active sediment surfaces. Numerous studies suggest that prolonged contact of channel water with sediment enhances solute reactions (e.g. Kim *et al.*, 1995; Harvey & Fuller, 1998). It is important to note that the methodology presented here can easily be extended to include reactions occurring in the stream channel.

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 is solute concentration in the stream, Q is volumetric flow rate, A is the cross-sectional area of the stream channel, D is the dispersion coefficient, q_L is lateral volumetric inflow, C_L is solute concentration in the lateral inflow, C_s is solute concentration in the storage zone, A_s is cross-sectional area of the storage zone, α is stream-storage exchange coefficient, t is time, and x is distance.

The above equations are used to analyse 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 equations (1) and (2) is used to analyse reactive transport:

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

$$0 = -\alpha\frac{A}{A_s}\left(C_{rs} - C_r\right) - \lambda C_{rs} \tag{4}$$

where C_r is concentration of the reactive solute in the stream, C_{rL} is concentration of the reactive solute in the lateral inflow, C_{rs} is concentration of the reactive solute in the storage zone, and λ is the first-order reaction rate constant describing solute removal in the storage zone.

When applied in the context of a tracer study, the solute transport model defined by equations (1)–(4) is run repeatedly to determine the model parameter values that best reproduce the data collected during the tracer study. Although this approach can be very useful, the results can have high uncertainty when the tracer test is not properly designed (Wagner & Harvey, 1997, 2000). Uncertainty analysis provides a rational framework for determining the information (or lack of information) about solute transport processes contained in tracer data. Moreover, uncertainty analysis can be used to aid the design of tracer studies, i.e. to evaluate the capabilities and limitations of a particular tracer test design before that design is implemented.

METHODOLOGY

The methodology applied in this study uses uncertainty analysis in a Monte Carlo framework to evaluate and compare alternative tracer test designs for a wide range of stream transport scenarios. In brief, the methodology proceeds as follows. First, we generate many realizations of the solute transport and reaction parameters needed to define equations (1)–(4), with each realization representing a "model" of a stream solute transport and reaction system. We then define a tracer test design; that is, we select 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 analyse parameter reliability for each parameter realization for the tracer test design under consideration. The result is a suite of parameter uncertainties that are used to analyse 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 & Harvey (1997).

The first step of the Monte Carlo uncertainty analysis is to define the stream-solute transport and reaction scenarios to be considered. The subset of streams considered in this study—high-gradient streams—have transport and reaction properties that can vary over orders of magnitude from one stream to another. Here we define the ranges of transport and reaction scenarios on the basis of parameter values that have been reported in the literature. The parameter ranges are listed in Table 1. Based on these parameter ranges, 1000 sets of transport and reaction parameters were generated as follows. First values of discharge, Q, inflow, q_L, stream slope and stream width were randomly generated assuming they were (logarithmically) uniformly distributed between the values listed in Table 1. Next, the associated value of stream cross-sectional area, A, was determined using Manning's equation, which means that the values of

Table 1 Parameter ranges for high-gradient stream analysis.

Parameter	Range	Mean	Standard deviation
Q (m^3 s^{-1})	0.005–0.2	0.11	0.05
q_L (m^3 s^{-1} m)	0.0–0.0001	0.03	0.02
A (m^2)	0.02–0.6	0.20	0.09
D (m^2 s^{-1})	0.025–0.8	0.40	0.22
A_s (m^2)	0.01–2.0	0.22	0.29
α (1 s^{-1})	0.000005–0.001	0.0005	0.0003
λ (1 s^{-1})	0.00001–0.01	0.001	0.002
C_L (mg l^{-1})	1.0		
Slope (m m^{-1})	0.01–0.15		
Width (m)	0.5–5.0		

discharge are physically consistent with a strong positive correlation between discharge and area. The remaining parameters, D, A_s, α and λ were generated assuming they were independent and (logarithmically) uniformly distributed according to the limits given in Table 1. The result is 1000 unique stream-solute transport and reaction "systems" that encompass the wide range of discharge, velocity, storage and reaction scenarios likely to be encountered in high-gradient streams..

The design of a tracer test involves the selection of numerous design parameters, such as the study reach length and the tracer injection and sampling strategies. To facilitate the comparison of results across the wide range of transport and reaction conditions considered, standardized design variables similar to those used by Wagner & Harvey (1997) were adopted. These include: a 600-m study reach length; a continuously injected conservative tracer with sampling of the tracer rise, plateau, and fall; a tracer plateau concentration 25-times the background concentration; and tracer sampling at 30-s intervals. In addition, we assume there are 30 reactive constituent samples collected at regular intervals along the study reach. Using this design, we analysed the capabilities and limitations of the tracer approach for the 1000 stream-solute transport and reaction systems described in Table 1. We performed 1000 uncertainty analyses to identify the parameters that are well (or poorly) estimated. In this study, we used the coefficient of variation—the standard deviation of the parameter estimate divided by the parameter value—as the measure of a parameter's reliability. The coefficient of variation is a unit less measure that allows us to compare results across all parameter types, regardless of the magnitudes or dimensions of the parameters.

RESULTS

The governing transport model, equations (1)–(4), contains nine unknown parameters. However tracer experiments normally include sampling controls that can be used to reduce the number of parameters that must be estimated. One form of control is to measure in-stream and subsurface solute concentrations under background conditions to determine C_L and C_{rL}. Another form of control is to use gauging techniques to determine Q at the upstream end of the study reach. For the tracer approach analysed here, we assume these controls are in place, leaving six parameters to be estimated: the physical transport parameters (A, D, q_L, A_s, and α) and the reactive-loss rate parameter (λ). Previous work by Wagner & Harvey (1997) provides an in-depth analysis of the capabilities and limitations of the conservative-tracer injection study. They showed that there are limitations to a tracer test's ability to estimate the stream–storage exchange parameters (A_s and α), and that those limitations can be defined using the experimental Damkohler number, DaI:

$$DaI = \frac{\alpha(1 + A/A_s)L}{v} \qquad (5)$$

where v is average stream water velocity and L is experimental reach length. The results of this study mirror those presented in Wagner & Harvey. In general, parameter uncertainty reaches a minimum when DaI is on the order of 0.1–1.0, and uncertainty increases as DaI decreases below or increases above this range. This relationship can be explained in terms of the increasing amount of stream–storage exchange as DaI increases. When DaI is small, only a small amount of tracer interacts with the storage zones along the study reach, resulting in a stream–storage exchange effect that is small and difficult to identify through tracer data. When DaI is large, tracer dispersion caused by stream–storage exchange reaches an equilibrium condition. In this case, the effect of exchange is difficult to identify because it cannot be separated from that of dispersion.

The experimental Damkohler number is useful for identifying the limitations when attempting to determine the stream–storage exchange properties. We would like to identify similar expressions for determining the limitations on estimating lateral inflow, q_L, and the reaction rate constant, λ. Lateral inflow is an important process because it represents a source of water and solute that, in areas of contamination, could be a long-term source of stream water pollution. We can relate the inflow estimate uncertainty to the dimensionless inflow factor, IF:

$$IF = q_L \times L/Q \qquad (6)$$

Figure 1 shows the coefficient of variation of q_L versus IF for the 1000 stream-transport scenarios analysed in the Monte Carlo uncertainty analysis. The strong correlation evident in this figure can be explained in terms of the dilution that occurs due to lateral inflow over the study reach. During a tracer test with continuous tracer injection, the tracer concentrations plateau at the sampling sites. The information for estimating q_L is found in the plateau data. As we move downstream from the injection site, the plateau concentrations decrease. Figure 1 tells us that the reliability of the inflow estimate improves as the site-to-site difference in plateau concentrations increases. The improved reliability occurs because the larger plateau difference allows us to more easily separate the effect of inflow from the data error and variability.

The ultimate goal of the combined conservative-reactive solute tracer test is to characterize the reactive loss of contaminants along the study reach. To do this we must be able to reliably determine the reactive-loss parameter, λ. Here we use the reactive loss factor, RLF (see Harvey & Fuller, 1998; Wagner & Harvey, 1999):

$$RLF = \frac{\lambda t_s L}{L_s} \qquad (7)$$

where t_s is average residence time of water in storage zones, $t_s = A_s/\alpha A$; and L_s is the

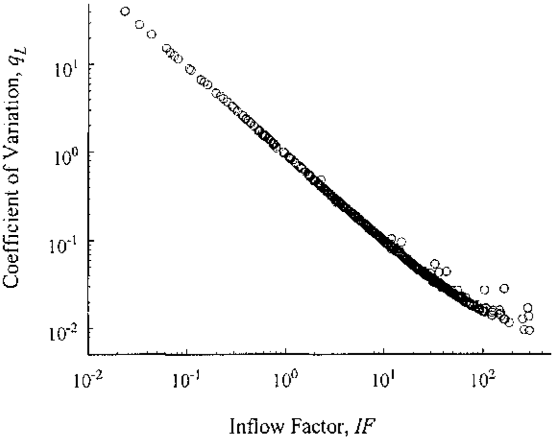

Fig. 1 Plot of coefficient of variation *vs* inflow factor for lateral inflow parameter, q_L.

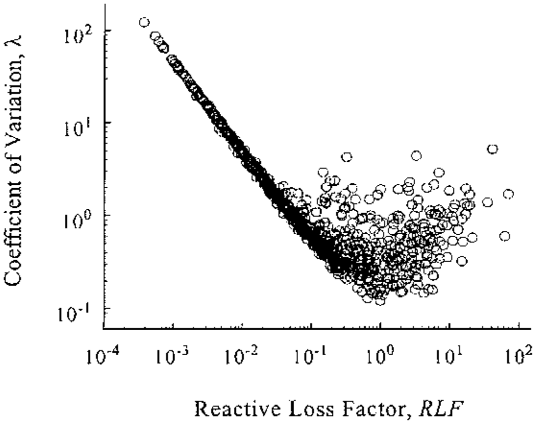

Fig. 2 Plot of coefficient of variation *vs* reactive loss factor for reaction rate constant, λ.

average distance travelled by a parcel of water before entering a storage zone, $L_s = v/\alpha$. The reactive loss factor measures the effect of the reactive loss process. When *RLF* is small there is little loss of the reactive constituent over the study reach. As *RLF* increases the effect of reactive loss becomes more pronounced. Figure 2 is a plot of *RLF* versus the coefficient of variation for λ. This figure displays a strong relationship between *RLF* and the reliability with which λ can be estimated. As *RLF* increases there is a strong trend of decrease in the coefficient of variation. For approximately 15% of the parameter realizations, however, this relationship disappears. In addition, Fig. 2 suggests that in general the tracer approach has difficulty in reliably estimating λ, with approximately 50% of the realizations having a coefficient of variation greater than 1.0.

The results presented above provide three dimensionless factors that can be used when designing a tracer study. However, the use of these dimensionless factors is complicated by the paradox of design: the parameters needed to define *DaI*, *IF* and *RLF* are in fact the parameters to be estimated through the tracer data. The one defining property that we can control when designing a tracer study is the experimental reach length, *L*. To investigate the influence of reach length on λ uncertainty, we performed three additional Monte Carlo uncertainty analyses with $L = 150$, 300 and 1000 m. The data from these three additional analyses display the same trend and pattern as found in Fig. 2. Those data that fall on the trending line in Fig. 2 remain on that line for each reach length, with λ uncertainty decreasing with increasing *L*. For those data that fall off the trending line, they individually show a strong relationship between *RLF* and λ uncertainty that in general mirrors the slope of the main body of data.

CONCLUSIONS

Our study used parameter uncertainty analysis to evaluate the ability of the tracer study to identify the solute transport and reaction processes active in a stream. We have shown that the inflow factor, *IF*, and reactive loss factor, *RLF*, are indicative of the tracer test's ability to reliably identify the inflow and reaction processes. Figures 1 and 2 suggest that *IF* and *RLF* must be on the order of 1.0 or greater for the tracer test to provide reliable estimates of inflow and reaction rate. We believe that these factors (along with the experimental Damkohler number, *DaI*) are useful for designing tracer studies, although this step is complicated by the fact that the parameters needed to define *DaI*, *IF*, and *RLF* are in fact the parameters to be estimated by the tracer data. We refer to this problem as the paradox of experimental design, which is encountered throughout the environmental sciences. Overcoming the paradox requires obtaining preliminary information about the transport and reaction properties of the stream under study. This could come from earlier tracer experiments at the site of interest, from information obtained at "similar" sites, or from readily available information that is known to be correlated to one or more of the unknown parameters. An example of this approach to tracer test design can be found in Harvey & Wagner (2000). Research is ongoing to further improve our understanding of the limitations of the stream tracer approach, and to better understand the trade-offs encountered when designing the conservative tracer injection (based on *DaI* and *IF*) and the synoptic sampling of the reactive solute (based on *RLF*).

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