Tracers and Tracer Testing: Design, Implementation, and Interpretation Methods

G. Michael Shook
Shannon L. Ansley
Allan Wylie

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G. Michael Shook
Shannon L. Ansley
Allan Wylie[a]

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Idaho National Engineering and Environmental Laboratory
Applied Geosciences Department
Idaho Falls, Idaho 83415

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a. Idaho Water Resources Research Institute, University of Idaho

ABSTRACT

Conducting a successful tracer test requires adhering to a set of steps. The steps include identifying appropriate and achievable test goals, identifying tracers with the appropriate properties, and implementing the test as designed. When these steps are taken correctly, a host of tracer test analysis methods are available to the practitioner. This report discusses the individual steps required for a successful tracer test and presents methods for analysis. The report is an overview of tracer technology; the Suggested Reading section offers references to the specifics of test design and interpretation.

ACKNOWLEDGEMENTS

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Tracers and Tracer Testing: Design, Implementation, Tracer Selection, and Interpretation Methods

1. INTRODUCTION AND MOTIVATION

Tracer testing is a powerful method for characterizing the subsurface. Conducting a tracer test is a fairly straightforward procedure, requiring adherence to a specified protocol. As long as one follows the appropriate steps in the correct order, the test has a good chance of success. Failure to follow these steps results in ambiguous test results, at best. Given the cost of conducting tracer tests, and the degree to which one poor test design impacts the perceived utility of tracers, a poor design or implementation is worse than not doing a test at all.

Below are examples of poorly implemented tracer tests in different industries. The purpose of presenting these cases is to show what small piece was overlooked and see what affect it had on test interpretation. The goal of the document is to allow INEEL tracer test practitioners to avoid mistakes made elsewhere and design, conduct and analyze tracer tests successfully.

- A petroleum company in the mid-1980s conducted a partitioning tracer test to estimate residual oil saturation (for enhanced oil recovery projects) in a reservoir. Conservative and partitioning tracers were injected and subsequently monitored for in surrounding production wells; however, no partitioning tracer was ever observed. Subsequent "back of the envelope" calculations showed insufficient tracer was injected to satisfy adsorption in the porous medium. Failure to account for adsorption in calculating mass of tracer required caused the test to be a failure.

- A geothermal company in the 1990s conducted a number of tracer tests in a geothermal field. Fluoroscein was used as the tracer, and the tests were generally considered a success. Further analysis of test results, however, suggested possible problems. A natural tracer, resulting from concentrating chloride in cooling tower water, suggested flow paths (and well connectivity) different than estimated from the fluoroscein results. Recognizing that "fluoroscein's overall conservatism is not well established," they conducted another tracer test with a suite of naphthalene sulfonates. Thermal stability of these compounds is known, but adsorption was not measured. The potential for failure of a second set of tracer tests could have been mitigated by simple laboratory experiments, but was not. The degree of conservativism and geochemistry of the naphthalene sulfonates remains unknown under geothermal conditions (rock type, aqueous chemistry, temperatures, etc.).

- Tracer tests at a DOE laboratory in the 2000s used various organic dyes as tracers. Preliminary tests with the tracers and site soils (to estimate the mass required, retardation, travel times, etc.) were not conducted. Following completion of the field test, however, adsorption isotherms were measured, and up to 80% adsorption of the tracer was observed. Test results could not be analyzed unambiguously.

1.1 Document Organization

This document is designed to identify and discuss the requisite steps necessary to deploy a successful tracer test. The goal is twofold. Recognizing that project management and other decision makers would benefit from an overview of tracer test methodologies, the first part of the document is an overview of tracer test capabilities and requirements. In Section 2 different types of tracer tests are discussed by way of introduction. We discuss tracer test goals in Section 3, and individual steps required to achieve those goals in Sections 4 through 6. Discussion of tracer test costs is beyond the scope of this document; however, discussion of the individual steps should give an indication of test costs.

A second purpose of the document is to present the protocols required to successfully implement a tracer test for test practitioners. In that light, a relatively detailed discussion of interpretation methods is given in Section 7; the practitioner may well wish to review that section before reviewing the preceding sections. Tracer test goals have a direct impact on the methods for test analysis and frequently impact test design and deployment.

The discussion is intended as a summary of tracer test protocol; a detailed discussion of (e.g.) laboratory protocol for the required experiments would make this document burdensome and unwieldy. There exists a vast body of literature describing such issues, and we do not reproduce it here. Section 9 presents suggested readings on each of the topics. These references (and the references contained therein) are adequate to assist in designing and conducting the individual pieces of a tracer test. Definition of terms is given in Section 10, although most variables are defined in the text as well.

It is extremely important for one to be aware that tracer-testing methods continue to evolve, and new interpretation methods are constantly being developed. Therefore, this document may be considered a primer on tracer testing and analysis. Several of the discussions below are intended to give more of a flavor for tracer methods than delineate all possible interpretation methods. New and novel test goals, designs, and interpretation methods are limited only by imagination.

1.2   Overview of Tracer Testing

Tracer testing is simply a means for characterizing the subsurface. In its simplest form, tracer testing can be defined as injecting one or more *tracers*—usually chemical compounds—into the subsurface in order to estimate its flow and storage properties. A tracer test is an indirect method for characterizing aquifer properties. We invariably compare observed behavior with a mathematical (or numerical) model, and infer aquifer properties from the comparison. The quality of any analysis, then, is directly attributable to the accuracy of the model invoked. What phenomena that were assumed second-order in developing the model must in fact be second-order for the analysis to be correct.

Tracer testing has both advantages and disadvantages. Because the method is indirect, test analysis is not unique. That is, different aquifer descriptions can result in a given tracer test result. This is because test analysis results in *volume-averaged properties*, to some extent independent of spatial order. The advantage of tracer testing over other, direct means of characterization (e.g., coring) is that the volume sampled can designed to be at the appropriate scale of interest. Specific properties that can be determined from tracer tests are discussed in Section 2 below.

Execution of a successful tracer test requires adherence to a series of steps, which ensure that the test can answer the questions posed, and that the tracer(s) themselves are appropriate. The level of detail required for each of the steps discussed below depends on the goals of the tracer test itself; however, none of the steps can be completely omitted. The steps can be generally stated as follows (each step is discussed in detail in subsequent sections).

1. *Define Tracer Test Objectives (Section 3)*. Test objectives should be defined as specifically as possible, in order to avoid ambiguity in test design. The objectives impact many other aspects of a tracer test, including the analysis methods used, sampling schedule required, number of tracers used and their properties, etc. The extent to which test objectives can be defined, and the degree to which those objectives are accommodated in design, deployment, and analysis has a direct impact on the likelihood of success.

2. *Tracer Selection and Testing (Section 4)*. This step also includes defining relevant tracer properties based on the test goals. Having defined the required properties, tests are conducted to establish that the tracer candidate actually has those properties under expected deployment conditions.

3. *Implementation Strategy (Section 5)*. This must include explicit description of how the test will be conducted, how much of which tracer(s) will be used, where injected, where sampled, for how long, etc.

4. *Field Implementation (Section 6)*. This is actual deployment of the test design, including the required documentation (field notes, etc.).

5. *Test Interpretation (Section 7)*. Test interpretation can be quantitative, qualitative, and numerical analysis, or any combination, of the test.

The order of these steps is also the chronological order required, as each subsequent step builds on the preceding one. In some cases, subsequent results may require revisiting earlier steps; for example, existing field conditions may require modifications to the test plan.

2. TRACERS AND TRACER TESTS

The extent to which a tracer test characterizes the subsurface relates to the number and type of tracers used. Tracer properties are discussed in detail in Section 4 (Tracer Selection and Testing); however, for the purposes of the following discussion, several definitions are required. A tracer is usually a chemical compound (but energy, viruses, and spores have been used) added to injected fluid to study properties of the subsurface. The tracer should have negligible affect on the transport properties of the injectate (e.g., density and viscosity). A conservative tracer is one that stays entirely in the phase in which it is injected. Anions (e.g., chloride or bromide) are typically—though not always—conservative aqueous phase tracers. Partitioning tracers are compounds that have some affinity for multiple phases, and therefore partition between two or more phases. Examples of partitioning tracers include heavier alcohols (e.g., hexanol), which partition between the aqueous and nonaqueous phase liquid (NAPL) phases, and perfluorocarbons, which partition between the gaseous and NAPL phases. While adsorption can be regarded as partitioning between a mobile and solid phase, it is usually referred to explicitly as an *adsorbing tracer* because of its typically negative connotation. A *reactive tracer* is one that undergoes a proscribed chemical reaction during its use. A plot of tracer concentration versus time at a given well is referred to as a *tracer effluent history* or simply a *tracer history*. It is also known as a tracer breakthrough curve.

Tracer tests take many forms, with different numbers of tracers and different well configurations, different means of introducing tracer and different methods of sampling. We can group tracer test types into the following general categories.

- *Conservative Tracer Tests*. Because a conservative tracer remains in a single phase, only the volume occupied by that phase is being interrogated via tracer tests. One or more conservative tracers are injected, and subsurface properties are inferred from the tracer behavior. Most frequently conducted under single-phase conditions (e.g., below the water table), they are also used in multi-phase applications; for example, to estimate hydraulic conductivity in partially saturated column experiments. Whatever conditions conservative tracers are used under, they provide information relating to its *reference phase*, that is, the phase in which it is soluble.

- *Partitioning Tracer Tests*. In partitioning tracer tests, one or more conservative tracers are injected along with *two or more* partitioning tracers. Because the partitioning tracers partition into other phase(s) that are present, their residence time in the medium is larger relative to the conservative tracer. The difference between the residence times is used to determine the volume of the other phases present. Partitioning tracer tests are very useful in estimating the immobile saturation of a 2nd phase, for example, DNAPL (dense nonaqueous phase liquid) saturation in contaminated aquifers. One application of partitioning tracer tests is to conduct such tests before and after remediation, thereby obtaining independent estimates on performance of the cleanup. The reason that two (or more) partitioning tracers are required is that the degree of separation between conservative and partitioning tracers strongly depends on the amount of the immobile phase (the residual saturation). Since we do not know this (or why run a partitioning tracer test?), several partitioning tracers are used that span a wide range of partition coefficients. This is discussed in more detail in Sections 5 and 7.

- *Other Tracer Methods*. The two tracer methods described above are easily the most frequent application of tracers, but by no means the only ones. Tracer methods that defy categorization involve injecting a suite of tracers and observing differences in their residence times. For example, differences between conservative and adsorbing tracers' effluent history can be attributed to adsorption parameters in the subsurface. If two or more tracers with different diffusion coefficients are injected into fractured media, it is possible to estimate surface area for mass exchange and

tortuosity of the rock matrix. These are two examples of inferring subsurface parameters from differences in tracer behavior. Estimation of these properties is also given in Section 7.

Any one of the tracer test types described above can be conducted with a variety of different well configurations. Single-well tracer tests are usually conducted in a *push-pull* mode, in which tracer is injected and subsequently back-produced. Depending on the nature of the tracers, there is sometimes a *soak* interval between injection (push) and extraction (pull). For example, the first partitioning tracer test conducted relied on the hydrolysis of ethyl acetate to form the tracer suite in situ. That required a finite soak time for the reaction to occur. A similar soak period might be required to characterize biological activity by observing the formation of daughter products over time [e.g., TCE (trichloroethylene) to ethylene]. Single-well tracer tests can also be conducted by creating a circulation cell (to introduce treatment chemicals, for example). In this case, two zones within a wellbore are isolated via packers, and injectate is pumped into one zone and extracted from the other. A circulation cell is established that comprises a portion of the porous medium; the extent of the circulation cell depends on pressure (or head) differences between the two zones, separation distance, and horizontal and vertical permeabilities.

The most popular method of conducting tracer tests, however, involves one or more injection wells and multiple extraction wells. Tracer histories from each extraction well provide information on the injection-extraction well pair. If more than one injection well is used, unique tracers should be used to provide unambiguous results.

Tracer tests can likewise be conducted in a variety of flow conditions, including steady-state flow (either forced or ambient) and transient flow conditions. While numerical methods can be used to interpret test results in any flow condition, analytical interpretation requires steady flow.

Worth special mention is the unique challenge in conducting tracer tests in variably saturated media in general, and the vadose zone in particular. The air phase is frequently the continuous phase initially present, so creating steady-state conditions for liquid phase tracing is difficult. Under ambient conditions, the liquid phase is frequently immobile; a tracer would likewise have zero velocity. Usually, a tracer slug is preceded by several days injection (or infiltration) of clean water, in order to establish a liquid front that can migrate ahead of the tracer. The difficulty in interpreting such a test is correctly stating the initial conditions, which represent some intermediate wetting state. This can be viewed as the intermediate stage of a flooding event, for example. The great difficulty in establishing well-defined conditions for such a test usually requires numerical modeling as part of the interpretation methods.

3.   TRACER TEST GOALS

As stated above, tracer tests are used to characterize subsurface media. Tracers are usually chemical or radioactive compounds that flow in a fluid phase without altering the transport properties of the phase. Note that from this definition, energy (heat), microbes, spores, and viruses can be used as tracers as well. In subsurface applications, the tracer is added to injected (or infiltrating) fluid, and one or more wells in the vicinity are monitored for the presence of the tracer. Spatial and temporal variations in the tracer provide indirect information about the medium through which it flows.

The point to be made is that a tracer test is simply a method used to infer flow properties of a porous or fractured medium; there is no inherent value in a tracer test itself. Therefore, the only goal of a tracer test is to answer a question posed regarding flow and storage properties of a given medium. The correct procession of thought is:

- What properties of a given medium need to be estimated? At what volume?

- Can a tracer test obtain an estimate of this property at that scale?

- Is a tracer test the best method for estimating the property?

Given affirmative responses to the questions above, a tracer test may be designed and implemented. Any discussion of a tracer test goal is in fact a discussion of these three questions.

 The first step in designing a meaningful tracer test is to identify the property or condition to be estimated by tracers. The detail to which the goals of the tracer test can be stated has a profound effect on the probability of success of the test itself. Test goals span the spectrum from purely qualitative to quantitative. The nature of the goals impacts test cost, design, and interpretation. For example, consider the differences in sampling schedule required for two different test goals: (1) Are these two sand bodies in communication? and (2) Under an enforced pressure field, what is the fluid velocity in this aquifer? In Case 1, the presence or absence of the tracer is key, while in Case 2 proper analysis requires the complete tracer breakthrough curve.

Qualitative test objectives typically answer questions regarding fluid sources, recharge/discharge locations, hydraulic connectivity, etc., in a qualitative (yes/no) sense. While of practical utility under certain circumstances, qualitative test goals are harder to define precisely, and therefore difficult to achieve. Answers obtained from qualitative evaluation of tracer tests are usually taken as absolute ("no communication"). The caveats that should be included, such as "…under the flow field imposed, with the transport properties of the tracers used, it appears that…" are invariably omitted, and analysis is potentially misleading. Where the tracer selection protocols discussed below are met, qualitative test goals can be achieved. However, if one or more of the required steps are omitted, test results can be ambiguous, as discussed in more detail below.

Tracer tests can be designed and interpreted to estimate various average and specific porous media properties. The term *average* in this context implies a volume average; a tracer most frequently provides property estimates averaged over the volume through which the tracer flows. The volume over which properties are averaged is dictated by test duration, sampling locations (distances), and flow field, which are design considerations. The information obtained from tracer testing relates only to the volume interrogated by the tracers, and most information is restricted to flow conditions similar to those imposed during the tracer test. Despite this, conditions conducive to successful tracer testing are not especially restrictive: single or multiple wells can be used, flow boundaries can be open, total tracer recovery need not approach 100%, the flow field may be ambient or forced, and meaningful data can still be extracted from tracer tests. Some specific properties obtainable from tracer tests are discussed below. This is not

meant to be an exhaustive list, as improved interpretation methods continue to expand the information gleaned from tracer testing.

Average medium properties estimated from a tracer test are determined from tracer residence times and include swept pore volume (the volume of the medium contacted by the tracers) and phase volumes or saturations. Total pore volume, as well as phase volumes or saturations, can be determined if the appropriate tracers are used. If multiple extraction wells are used, the spatial distribution of these properties can be estimated from differences in residence times for each injection/extraction well pair. Furthermore, if such tracer tests are run at different times (say, before and after a remediation process), cleanup efficiency of the method can be estimated. Under certain conditions, surface area may be determined from the difference in residence times between conservative and adsorbing tracers. Likewise, tracers with different molecule size and diffusion rates can be used to determine fracture-matrix surface area for mass exchange. Reactivity (or bioactivity) of the medium can be inferred by injecting reactive tracers and observing in situ decay rates.

More specific medium properties are also available from tracer test analysis. For example, streamline geometries (flow and storage capacity) can be extracted from a cumulative tracer recovery history plot. From that plot, the fraction of *fast* or *slow* flow paths is readily apparent, thereby identifying extremes of flow conditions. Use of a numerical model in light of flow geometries from tracer tests can yield estimates of dispersivities and other constitutive relations (relative permeability and capillary pressure versus saturation).

Knowledge (or estimations) of these properties allows us to make more informed decisions. Knowing how much DNAPL is present and how it is distributed in the subsurface gives an idea of volume of water that must be treated during remediation. Geometric distribution of the contaminant has a profound effect on remediation as well. For example, if we knew that most of the contaminant was trapped in a low-velocity portion of the aquifer, containment might be selected over mass removal. Adsorbed contaminant concentration is a strong function of surface area; estimates of surface area can be used to bound possible contamination scenarios. Property estimates are also useful in conceptual models, and help screen possible geologic models. As these models are frequently used in subsequent RI/FS studies, adequate property estimates directly impact all future site activities and processes.

A summary list of properties that can be estimated from tracer test analysis is given in Table 1. We again emphasize that this list is not exhaustive; other quantities may be estimated from tracer testing. The point of this section is to emphasize that tracers merely characterize the subsurface.

Table 1. Summary of subsurface properties identifiable from tracer tests.

1. Fluid velocities
2. Swept pore volume
3. Phase volumes or saturations
4. Surface areas for heat or mass transfer
5. Biological activity (decay constants)
6. Flow geometry distributions
7. Pore geometry distributions
8. Cleanup efficiency
9. Constitutive properties (e.g., hydraulic conductivity and matric potential versus saturation)
10. Phase dispersivities.

4. TRACER SELECTION AND TESTING

Having determined that a tracer test is a suitable method for obtaining answers to the questions at hand, candidate tracer compounds must then be screened for use. Many relevant properties of tracer candidates are available in the literature (e.g., thermal or biological stability, radioactive half-life); others are site-dependant and therefore require further study. Failure to measure the properties discussed below may preclude even qualitative analysis of tracer test results. The reason for this is best illustrated using a simple example. Consider a tracer test whose goal is "to determine if these two sand bodies are in hydraulic communication." A tracer is therefore injected in one of the aquifers, and sampled for in the second; however, unbeknownst to the test operator, the tracer adsorbs onto aquifer sediment. If the tracer is observed in the 2nd aquifer, the test objectives are met. If no tracer is observed, the test objective remains unresolved: the tracer may have completely adsorbed, or the aquifers may not be in communication. The absence of evidence is not evidence of absence.

In order to remove such ambiguity from tracer testing, the following tracer properties must be known or measured. These are summarized in Table 2. These tests are required of all tracer candidates, independent of their type (e.g., conservative, partitioning, etc.).

Table 2. Tracer property requirements.

General Properties (usually from literature and batch experiments)

1. Nontoxic
2. Available and affordable
3. Good solubility for injection, low detection limits
4. Low natural background concentrations
5. Negligible effect on transport properties (density, viscosity, pH, etc.)
6. Stable or well-characterized degradation
   a. Thermal or radioactive decay acceptable
   b. Photo degradation usually unacceptable
   c. Biodegradation acceptable if appropriate for test goals (reactive tracer tests)
7. Well-behaved partitioning over all concentrations
   a. For conservative tracers, no partitioning
   b. For partitioning tracers, constant, reversible partitioning
   c. Adsorption usually unacceptable, unless appropriate for test goals

Site-specific Properties (from column tests with site soil, water, contaminants)

8. Equilibrium partitioning at field rates (i.e., not rate-limited partitioning)
9. No ion exclusion or adsorption
10. No other chemical interaction with site water, soils, etc.
    a. Dissolution/precipitation
    b. Gelation, etc.

4.1   General

Certain tracer requirements are site-independent. That is, the tracers must exhibit these properties in order to be considered a viable candidate. The tracer must be nontoxic, be detectable at low concentrations, be both available and affordable, and have low background concentrations in situ. Background concentrations may be due to natural occurrence or the compounds' historical use. Because tracer compounds exhibit a wide range of behavior (e.g., reversible adsorption, diffusion from dead-end pores), one cannot simply conclude the tracer can be used if it has not been used recently. Elevated background concentrations are detrimental to the tracer's use.

The tracer must also flow with bulk fluid and exhibit stability under test conditions. Tracer stability does not imply the tracer must be inert; it must simply decay in a known fashion. Tracer decay rates must either be known in advance (e.g., radioactive decay), or be a well-characterized function of the aquifer parameters being estimated. For example, if a tracer were known to only decay in the presence of a given microbe (at a fixed rate), its use could characterize the microbe population.

Issues of detection limits, background concentrations, toxicity, and stability all speak directly to the relevant issues of regulatory compliance, sample storage, holding times, and disposal. Specific concerns in these areas are summarized in Table 3.

Table 3.   Regulatory compliance concerns for tracer testing.

1. Toxicity, degradation products, and interactions with preexisting contamination

2. Effects on potable water supplies (i.e., wellhead protection guidelines)

3. Effluent disposal

4. RCRA- or CERCLA-site requirements (i.e., sampling, analysis, waste disposal, and documentation requirements)

5. Air emissions

6. Environmental Checklist approvals before use

4.2   Tracer Phase behavior

The phase behavior required of a given tracer depends on the application. Conservative tracers must have negligibly low solubility in all phases other than the one in which it is injected (or low solubility in others it might encounter). Partitioning tracers must have a constant partition coefficient, as defined by:

$$K_i = \frac{C_{i2}}{C_{i1}} \tag{1}$$

where K_i is the dimensionless partition coefficient of component i, and C_{ij} is the concentration of i in phase j ($j = 1$ is the reference phase, usually the phase in which the tracer is injected). Partition coefficients should be measured in batch experiments at multiple concentrations to ensure that it is a constant over the concentrations expected through the test (i.e., from above the injected concentration to the detection limit). The tracer must also have sufficient solubility in the reference phase such that it is readily mixed.

Other tracer properties required depend on the application. For example, chemically reactive tracers can be used to estimate bioactivity in the subsurface. Because the reactions are a function of other chemical species (e.g., an electron donor), its spatial distribution, and time, reaction rates in the field are seldom identical to those in laboratory batch experiments. Nevertheless, laboratory measurements are

required to ensure that the appropriate mass of tracer is injected for the approximate conditions expected, test duration, etc. The same holds for measuring mineral content or adsorption sites using adsorbing tracers. Adsorption isotherms must be measured in the laboratory, with adsorption being measured as a function of what we wish to estimate in the field (e.g., carbon content). An adsorbing tracer test can subsequently be used to estimate that property in the field. The problems that are faced with designing such a test are two-fold. First, laboratory rates are invariably different that those observed in the field. This can be due to mineral weathering, changes in redox states, or other variables. Second, and perhaps more significantly, the models that are used cannot capture all nuances of field behavior and yet remain tractable. For that reason, we must consider these properties to be "effective" properties, and state, for example, that "the the medium *acts* as though it contains 5% organic carbon by volume." Note that in order to identify the correct tracer for either reactive or adsorbing tracer tests, some idea of prevailing conditions in the aquifer itself, the volume of aquifer being tested, and the time over which the test is conducted must be considered.

Adsorption and bioactivity tend to be site-specific as well. For example, fluorescein has been used successfully in tracing karst aquifers, yet it is a poor candidate in sand aquifers with high organic content. For this and various other reasons, site-specific tracer tests are required in addition to the more general ones discussed above.

4.3   Site-Specific Tests

Having identified a tracer candidate that successfully meets the criteria summarized above, a set of site-specific tests is required. These tests ensure that site conditions are properly accounted for in tracer selection. They are designed to examine chemical interactions between site soil, water, contaminants, and prospective tracer candidates, and therefore require experiments using site soil(s), site water (or a chemically equivalent proxy thereof), and site contaminants. Specific issues are briefly discussed below, and are also summarized in Table 2.

- *Ion exclusion*. Depending on the surface charge on soils, ions in solution may be excluded from some portion of the pore volume. Anion exclusion is the more common occurrence, with exclusion fractions reaching as high as 10% of the pore volume. It is crucial to ensure tracers are neither accelerated, via exclusion, nor retarded, via adsorption or partitioning, unintentionally.

- *Adsorption*. As noted above, soil composition may alter the utility of a given tracer candidate. For this reason, additional adsorption experiments are required using site soil, water, and contaminant.

- *Geochemical incompatibility*. This is a fairly broad concern, which is intended to describe the potential for adverse chemical reactions between site water and contaminants and the proposed tracer, including precipitation, viscosity effects, undesired chemical reactions, etc.

In addition to the concerns listed above, it is usually important to demonstrate that phase partitioning, etc., are not rate-limited under conditions of injection. For this reason, the site-specific tests discussed above are best run in column (dynamic) experiments using site soil and water, tracer candidates, and site contaminants, at injection rates that mimic flow velocities expected at the field scale.

5. IMPLEMENTATION STRATEGY

With test goals established and tracers screened and selected, the test deployment can be designed. The set of design parameters are summarized in Table 4, and discussed below. It should be emphasized that the methods used for test analysis also have a bearing on the design, frequently impacting the number of tracers used, test duration, and sampling. It is therefore crucial that the implementation strategy be considered with the proposed test analysis methods in mind.

Table 4. Tracer test design issues.

1. Number and type of tracers needed
2. Mass of tracer required (dilution, mixing, etc.)
3. Flow field
    a. Ambient or forced
    b. Steady state or transient
4. Test Duration (aquifer volume sampled)
5. Tracer Introduction
    a. Injection/Infiltration locations, depths
    b. Use of packers for horizon isolation
6. Effluent Treatment
7. Sampling and Analysis
    a. Sample frequency
    b. Sample preservation
    c. Analysis methods
8. Documentation of steps taken and data obtained

Outcome: Test Plan

Question: Does this design achieve test goals?

Number and Types of Tracers Needed. In partitioning tracer tests, a suite of partitioning tracers is usually needed for quantitative analysis. The reason for this is that the retardation of the partition tracer (relative to the conservative tracer) is a function of the amount of the immobile phase present, S_r, which is an unknown. Too little partitioning results in little or no separation in the tracer histories; too much prolongs the test unnecessarily. As a rule of thumb, tracers should be selected on the basis of a partition coefficient, K_i, such that the following inequalities hold:

$$0.2 \le \frac{S_r K_i}{1 - S_r} \le 3.$$

The rationale for these limits is based on tracer residence times, and is postponed to Section 7 below. Since the residual saturation is unknown, several different tracers with a suitable distribution in partition coefficient should be used.

Mass of Tracer Required. Based on expected dilution, decay/degradation, residence time, detection limits, and other factors, the mass of tracer required can be calculated or estimated. Note that dilution may be from mixing caused by heterogeneity (dispersion) or by the sheer volume of the medium being tested. Some knowledge of the medium is required, or values must be estimated.

Flow Field. Tracer testing may be conducted under conditions of transient (e.g., infiltration) or steady-state flow, depending on—as usual—test goals. If steady-state flow is required, how long before introducing the tracer should injection/extraction operations occur to establish steady conditions? Where is (are) the best location(s) for injection/extraction to achieve test goals? How many wells? For a given flow field, how much tracer is expected to be captured, and over what time period? What are the effects of far-field conditions? As before, some educated guesses or estimates are required.

Test Duration. Depending on the volume of aquifer to be tested with tracers, the flow rate imposed, and transport characteristics of the tracers, the required length of the test can be estimated. The product of volumetric flow rate, q, and time, t, gives an approximation to the pore volume of the aquifer tested ($V_p = qt$). Given some idea of the delay in transport of the tracer, caused by adsorption or partitioning, an estimate of required test duration can be made. Again, some estimates of aquifer properties are required.

Tracer Introduction. How is the tracer introduced? For steady-state flow, the tracer is usually mixed in a small volume of injectate and injected as rapidly as possible (a spike of tracer) to simplify test analysis. How many tracers should be used?

Effluent Treatment. A frequently overlooked or minimized concern is effluent treatment. How much fluid will be produced during the tracer test? What is the chemical makeup? How is it best treated? Are there environmental or regulatory issues that need to be addressed before conducting the test?

Sampling and Analysis. Proper sample collection and handling represent key factors in any tracer test. If the samples are not collected and preserved properly, a well-designed tracer test will certainly fail. Several factors that require careful consideration include the sample collection frequency, the sampling locations, the sampling method, sample preservation, and QA required (which is frequently dictated by the regulatory oversight and tracer test goals). Field personnel should be made aware of the test goals and sample plan, to minimize sampling errors or sample mishandling. A Sampling and Analysis Plan should be an explicit portion of the Tracer Test Plan.

Background samples should be collected before running any field tracer test to determine the concentration of all potential tracers and the basic groundwater chemistry. The choice of tracers will partially depend on background concentrations of potential tracers and potential interfering compounds.

    Frequency and Duration–The appropriate sample collection frequency should be determined during the design phase. This frequency should adequately define the tracer history to enable interpretation of the results and should be determined on a site-specific basis. If the tracer test is qualitative, a simple *presence or absence* sample may be all that is required. In this instance, sampling may be conducted by suspending sorptive compounds in a well. On the other hand, if the test is quantitative, adequately describing the tracer history requires more frequent grab samples, generally at varying time intervals. Sampling frequency should be highest when at least one tracer's concentration is changing rapidly. Preliminary modeling or other calculations should be used to estimate when sampling should start, sample frequency during the test, and duration of the sampling campaign. Failure to collect samples over the appropriate time period may compromise test integrity.

    Location–The sampling locations should be identified based on the test goals during the preliminary design phase. Locations should be selected to maximize the interpretability of the

test. Sampling locations are frequently based on results of numerical modeling during test design, which introduces some bias into the sampling program. This can be overcome to some extent by modifying the sampling program as the test proceeds and conceptual models are refined.

Sample Collection–The tried-and-true sampling technique is to pump three wellbore volumes and then collect the samples. This technique increases the amount of time required to collect each sample and complicates wastewater disposal problems. New sample collection methods involve low-flow sampling, which minimizes both the sampling time and the volume of wastewater.

Often, the 3D flow field is of interest, and collecting samples is important at different horizons to describe how aquifer properties vary horizontally and with depth. Multilevel samplers have been developed in the last 20 years that provide information on the vertical distribution of tracer. Various commercial multilevel samplers are now available.

Sample Preservation–Different tracers will require different preservation techniques. Failing to preserve the sample properly or failing to analyze the sample before the holding time is exceeded can render the tracer test useless. The appropriate preservation technique, maximum holding times, etc., are test-dependent, but should be incorporated in test design and sampling and analysis procedures.

Documentation. Maintaining accurate field notes is also crucial to test integrity. These notes document site conditions and include the specific steps taken during the test, especially any excursions from the test design. Field notes are often also a source of test results, and are always crucial to understanding test analysis.

This discussion reveals the need for knowledge or estimates of many aquifer properties in test design. This is an interesting Catch-22; if we knew this information, we wouldn't need to conduct a tracer test! Moreover, many of the questions posed above involve optimizing the design (e.g., number and location of injection/extraction, flow rates, etc.). For these reasons, a numerical model is an excellent design tool. Once the tracer test goal is settled on, the suite of tracers selected, and site-specific information collected, several numerical experiments can be conducted to refine the tracer test design. This is done by using different distributions of reasonable properties (aquifer and contaminant) and modeling the test. Used in this manner, a numerical model can establish bounds on fluid velocities, tracer dilution, test duration, tracer history at various sampling locations, sampling requirements and frequencies, etc. Based on the results of this analysis, one can select the design that yields the highest probability of achieving test goals. If the results from the numerical experiment are inconclusive (and they often are), field observations can be compared to numerical predictions, and conceptual models calibrated.

The final product from the test design is a Tracer Test Plan. This document is the guidance document for conducting the tracer test. As such, it must address all aspects of deploying a test, and be followed in the field so that analysis of the test results is possible and test goals achieved.

6. FIELD IMPLEMENTATION

Table 5 summarizes the steps required to implement a tracer test in the field. Deploying a tracer test essentially requires following the test design steps discussed above, with a single additional concern. The well drilling technique, well design, and completion materials can also impact tracer tests. All aspects of well drilling and construction should be reviewed for possible adverse impact on tracer tests, whether one is evaluating the suitability of an existing well or designing a new well for use in a tracer test. Use of an existing well that is inappropriately drilled or completed for the purpose of the test is false economy and may lead to incorrect test interpretation.

Table 5 Field Implementation Issues.

1. Tracer/well interaction

    a) Well drilling, construction, completion, and materials

    b) Well development

2. Establishing the flow field

3. Introduction of tracer

4. Sample and analysis

5. Field documentation

    - Site conditions during test

    - Operations during test

    - Deviations from Test Plan

6.1 Well Drilling and Completions

Several texts adequately describe well drilling techniques, and we will not outline the various techniques here. However, tracer testing imposes several unique requirements on wells that need discussion.

Drilling fluids. Many drilling fluids contain material with high sorptive capacity (e.g., bentonite), which would clearly interfere with tracer transport. Other drilling fluids (e.g., air) may introduce trace atmospheric contaminants such as fluorocarbons. Drilling fluids also invade the aquifer and may lead to plugging. Specifics regarding the drilling program must be reviewed in light of a given set of proposed tracer compounds.

Well development. All drilling techniques damage the formation, so all wells need to be aggressively developed after construction. Occasionally, field personnel neglect this vital step, and drill cuttings are left in the aquifer to impede flow into the well. Cuttings may posses high sorbtive capacity and alter tracer concentrations observed in the well. Chemical treatment can likewise interfere with tracers; the chemicals can alter the pH and redox state near the well.

Well completions. Both tracer sampling wells and injection wells should be designed to minimize the volume of dead water in the well. This serves to minimize the volume of purge water collected during sampling and the volume of tracer required to displace water in the well. Where possible, wells with small casing diameters should be used, or zones of the well isolated with packers. Completion intervals are likewise critical; using an existing well completed at the wrong depth can lead to incorrect conclusions regarding flow.

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Well completion material. Casing material must be chemically inert with respect to the suite of tracers selected for the test. For example, organic tracers cannot be used in PVC-cased wells. The filter-pack must also be inert with respect to the tracer suite.

6.2   Establishing the Flow Field and Injecting Tracer

The flow field must be established in accordance with the test design. This may result in field operations being conducted for some extended period before introducing tracer. Generally, tracer is injected in as short a time as possible (a *spike* of tracer), but because groundwater velocity is generally low and tracer residence time relatively large, tracer injection may occur over the course of hours and still be considered spike injection.

Minimizing dead water in the injection well decreases dilution of the tracer mix (a *cocktail*) and minimizes the tracer injection and mixing time. Use of small-diameter wells and/or isolation of zones with packers helps optimize tracer injection.

When the tracer cocktail is introduced into the well, it needs to be mixed with the existing water to ensure an even tracer concentration. If the well is shallow, the mixing apparatus could be simply a plunger. However, if the well is deep or the injection zone is isolated with packers, a mixing pump should be employed. The tracer is subsequently forced out into the formation by continued injection of a chase fluid. Depending on the flow conditions required (e.g., steady state versus transient), this chase fluid injection may last the life of the tracer test.

6.3   Sampling

Maintaining and documenting the integrity of samples collected during a tracer test are crucial steps to ensure that test results are accurate, unbiased, and defensible. Specific issues that must be addressed include sample holding times, sample preservation requirements, and potential for cross-contamination during both sampling and analysis. Chain of custody requirements include sample identification and tracking, maintaining custody to ensure samples have not been tampered with, and thorough documentation of field activities to demonstrate that sample integrity was not compromised. Sample analysis requirements include documentation of laboratory procedures to ensure that sample integrity was not compromised during analysis. The procedures followed in the field should be taken from the Sample and Analysis section of the Tracer Test Plan.

6.4   Documentation

Field notes are an important source of information regarding the test implementation. Notes should reflect site conditions during the test, especially including information that impacts test results (e.g., weather conditions that impact sample handling). Field notes should also include any excursions from the test plan. Some excursions are to be expected. For example, actual sample times may differ from those specified in the test plan. This may or may not be an issue; nevertheless, such discrepancies must be documented. This type of information is crucial to test interpretation.

7. TEST INTERPRETATION METHODS

A host of analysis methods are available. These can be generally categorized as qualitative, quantitative, and numerical methods, as described below.

7.1 Qualitative Methods

Qualitative methods are usually yes/no analyses: either tracer was seen at Point B or it was not. Under certain conditions, this analysis is the appropriate level of detail; however, it can be misleading if tracer properties are not adequately measured. The example given in Section 4 above summarizes the potential for misinterpretation: did the tracer adsorb, or are the aquifers not hydraulically connected? Test analysis is usually unambiguous only if the tracer is observed at the sample point that answers the test goals affirmatively. A negative result is ambiguous unless all transport properties of the tracers have been measured.

Other possibilities for misinterpretation exist. A given pressure field may result in flow paths that do not lead to a given extraction well (despite the fact that the flow paths exist). If a tracer partitions among phases, it may not be tracing the flow paths because of buoyancy effects. If dilution is too large, the concentrations at extraction wells may be below the detection limit. In some sense, these are *false negatives* that lead to erroneous conclusions. That tracer is not observed at a given point merely means that, for the conditions and tracers used, the tracer did not flow there at sufficient concentration—*not that no flow path exists*. These problems are not specific to qualitative analysis, as separation of tracer from bulk transport leads to an erroneous interpretation. The important point to be made is that all tracer properties must be measured adequately, even if "only" a qualitative analysis is to be made. As mentioned previously, test conclusions are generally restricted to the field conditions imposed (e.g., velocity or pressure field) during the test.

7.2 Quantitative Analysis

Quantitative methods for tracer test analysis rely on steady-state flow conditions and require the calculation of the tracer's mean residence time in the subsurface. Inasmuch as this calculation is used throughout this section, it is reviewed below.

The mean residence time of a tracer, $\bar{t}$, is also known as the first temporal moment of the tracer. It is the time-weighted average of a tracer history and is easily calculated from the tracer history itself. Defining C as the dimensionless concentration of tracer and t_s as the time over which the tracer was injected (sometimes referred to as "slug size"), we define the mean residence time (Levenspiel 1962) as:

$$\bar{t} = \frac{\int_0^\infty Ctdt}{\int_0^\infty Cdt} - \frac{t_s}{2} \tag{2}$$

The integrals given above can be calculated in various ways. If the data are smooth, a curve can be fit to the data, and integrated analytically. Usually, however, the integration is approximated numerically in a spreadsheet.

Single-Phase or Conservative Tracers. For a given, steady-state flow field with a volumetric injection rate q, the tracer mean residence time is used to calculate the pore volume, V_p, swept by the tracer:

$$V_p = q \cdot \bar{t} \qquad (3)$$

The equation above works well in column studies and other systems in which all tracer mass is captured by a single well. If more than one extraction well is used with a single injector, Equation (3) is modified to account for the allocation of flow as (Pope et al. 1994):

$$V_p = \frac{m}{M} q \cdot \bar{t} \qquad (4)$$

where m/M is the fraction of tracer mass recovered at the specified extraction well, and q is the total volumetric injection rate. Either Equation (3) or (4) is used if the medium being studied is single phase or if the tracer is soluble in only one phase. In the case of partial saturation, however, the volume swept by the tracer is not the complete pore volume; it is the saturated pore volume (pore volume times phase saturation).

Two Phase, Partitioning Tracers. As noted in Section 2 above, conservative tracers and partitioning tracers are injected simultaneously, and differences in their residence time are used to determine the saturation of the immobile phase. The immobile phase is frequently a NAPL; we will assume that is the case below. The tracers are injected in an aqueous phase below the water table, or in the vapor phase above. We can calculate the tracers' residence times from Equation (2). Defining the mean residence time of a conservative tracer as t_1 and the partitioning tracer as t_2, we can calculate the average residual saturation, S_r, as (Jin et al. 1995):

$$S_r = \frac{\bar{t}_2 - \bar{t}_1}{(K_2 - 1)\bar{t}_1 + \bar{t}_2} \quad . \qquad (5)$$

The swept pore volume can be found from either Equation (6) or (7). Note that this is the entire swept volume (i.e., occupied by NAPL and water or air).

$$V_p = \frac{q\bar{t}_1}{1 - S_r} \qquad (6)$$

$$V_p = \frac{q\bar{t}_2}{1 - S_r(1 - K_2)} \quad . \qquad (7)$$

Extrapolating the Tracer History. Due to economic considerations, a tracer test is frequently terminated before the tracer concentrations fall below the detection limit. Because mean residence time is a time-weighted average, failing to include late time data can seriously underpredict swept volumes (pore volume and saturation). This is especially true when estimating small values of residual saturation (from a partitioning tracer test, for example); a majority of the information is in the tail of the tracer history curve. One method to obtain the information in the tail is to extrapolate the tracer history using an integrable function. An example is given below.

If a plot of logC versus time is linear, the tracer history is declining exponentially. For times greater than t_b (where t_b is in the exponential decline portion), the tracer concentration can be represented mathematically as (Pope et al. 1994):

$$C = C_b e^{-\frac{(t - t_b)}{a}} \qquad (8)$$

1/a is the slope of the straight-line portion of the curve. The moment calculation given in Equation (2) above can then be broken down into two parts:

$$\bar{t} = \frac{\int_0^{t_b} Ctdt + \int_{t_b}^{\infty} Ctdt}{\int_0^{t_b} Cdt + \int_{t_b}^{\infty} Cdt} - \frac{t_s}{2} \tag{9}$$

The 2nd integral in both numerator and denominator in Equation (9) are integrated easily, and the first moment of the tracer can be written as:

$$\bar{t} = \frac{\int_0^{t_b} Ctdt + a(a + t_b)C_b}{\int_0^{t_b} Cdt + aC_b} - \frac{t_s}{2} \quad . \tag{10}$$

Functions other than exponential decline may be useful as well. The goal is to extrapolate the tracer history to better estimate the first moment.

Partition Coefficient Requirements. Another dilemma encountered in partitioning tracer test design involves actually selecting the correct tracer. A tracer that partitions too strongly into the immobile phase prolongs test duration unnecessarily; too little partitioning makes discerning the differences in mean residence times difficult. It has been shown that errors can be minimized by appropriate selection of tracers based on their partition coefficient. The retardation factor, R, is defined as the ratio of partitioning tracer mean residence time to that of the non-partitioning tracer:

$$R = \frac{\bar{t}_2}{\bar{t}_1} \quad . \tag{11}$$

Maintaining R>1.2 results in relative errors of 10% or less (e.g., 0.02 +/- 0.002) (Dwarakanath et al. 1999). Equating Equations (6) and (7) above and using Equation (11) and the constraint of R>1.2 give an estimate of partition coefficient requirements:

$$0.2 \le \frac{S_r K_i}{1 - S_r} \le 3.0 \quad . \tag{12}$$

The inequalities given in Equation (12) are useful in determining suitable tracer compounds, yet point to a fundamental problem in test design. Since we do not know the residual saturation, we cannot a priori determine the partition coefficient necessary. The only solution is to inject a suite of partitioning tracers that have a sufficiently wide range of partition coefficients. In that way, should the residual saturation be large, the tracers with lower K values are useful, and the test can be terminated earlier. If the saturation is low, the low K value tracers will not exhibit sufficient retardation to be useful, but the others would. Tracers with partition coefficients on the order of 100 are sometimes necessary.

Characterization of Surfaces. One application of tracer testing not yet field-tested is measurement of surface areas using adsorbing tracers. The method essentially requires a tracer whose adsorption isotherm can be expressed on a specific surface (area/volume) basis. For example, if a mineral formed only on a fracture face at some known or measured density, and a tracer was identified that adsorbed on that mineral, measuring the fracture-matrix interfacial area is straightforward. A similar method could, in

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theory, be applied to estimating organic or clay content in an aquifer. The method can be described in the following fashion.

Writing the conservation equation for the adsorbing tracer and assuming incompressible fluid gives the following expression:

$$\frac{\partial C_w}{\partial t} + \frac{\vec{u}_w}{\varphi} \frac{\varphi \rho_w}{\left[\varphi \rho_w + (1-\varphi)\rho_s \frac{\partial C_s}{\partial C_w}\right]} \vec{\nabla} C_w = 0 \quad . \tag{13}$$

Equation (13) is a hyperbolic equation; the method of characteristics can be used to show the velocity of the tracer, v_T, given by:

$$v_T = \frac{\vec{u}_w}{\varphi} \frac{\left[\varphi \rho_w\right]}{\varphi \rho_w + (1-\varphi)\rho_s \frac{\partial C_s}{\partial C_w}} = \vec{v}_w \frac{1}{1 + \left[\frac{(1-\varphi)\rho_s \frac{\partial C_s}{\partial C_w}}{\varphi \rho_w}\right]} = \vec{v}_w \frac{1}{1 + D} \quad . \tag{14}$$

A conservative tracer moves at bulk fluid velocity (v_w). Differences in the velocity, and therefore residence times, of a conservative versus the adsorbing tracer is attributable to the retardation factor, D, given in Equation (14). If the adsorption isotherm is measured, the expression for D can be inverted to give specific surface area. Mean residence time of the conservative tracer gives pore volume, which is used to convert specific surface area to total area.

Flow Geometry Distributions. If the porous (or fractured) medium is viewed conceptually as a set of (many) streamtubes of varied length, porosity, permeability, etc., then estimations of pore space and flow path distributions are readily made from tracer tests. Incremental pore volume and fluid velocities are functions of the streamtubes' relative volume and resistance to flow. Resistance to flow is a complicated function of the streamtube's length, permeability, and porosity. While absolute flow resistance is difficult to determine, the relative resistance is directly obtainable from tracer tests.

We define *flow capacity*, F, as the relative, incremental fluid velocity of a given flowpath, and *storage capacity*, C, as its incremental pore volume. In truth, these are discrete properties (C_i and F_i) of individual fractures. However, the true properties can be estimated as continuous functions from tracer tests, as follows (Shook, 2003).

$$C_i = \frac{\sum_{i=1,}^{\#frac} \varphi_i \lambda_i}{\overline{\varphi L}} \cong \frac{\int_0^t c\tau d\tau}{\int_0^\infty ctdt} = C(t) \tag{15}$$

$$F_i = \frac{\sum_{i=1,}^{\#frac} k_i / \lambda_i}{\overline{k}/L} \cong \frac{\int_0^t cd\tau}{\int_0^\infty cdt} = F(t) \quad . \tag{16}$$

As before, these are simple integrals to evaluate from the tracer history. They are used to construct a F-C diagram. The F-C presentation can be used to identify fast, average, or slow flow paths, and the fluid capacity of each. Just by looking at an F-C diagram, one can observe (for example) that "50% of the flow

(F) comes from 10% of the pore volume" (some fast flow paths). Estimating flow and storage geometry in this fashion (or any other) facilitates engineering decisions on transport issues. The single drawback to F-C diagrams is that the spatial distribution of the streamtubes cannot be determined. However, conventional measures of heterogeneity, including the Lorenz coefficient, L_c and the Dykstra-Parsons coefficient, V_{DP}, can be determined from the F-C diagram (Lake 1989). These parameters are frequently used in generating geostatistical reproductions of the porous medium.

Matrix Diffusion Parameters. Tracers can also be used to estimate how much contaminant might diffuse into the rock matrix at a fractured site by determining matrix diffusion coefficients. Two or more tracers with differing aqueous diffusion coefficients are introduced into the aquifer, and differences in tracer history are used to estimate the matrix diffusion. Feenstra et al. (1984) provide the following equation for non-sorbing tracers:

$$C(r,t) = C_o \operatorname{erfc}\left(\frac{\pi\varphi\sqrt{D'}\cdot(r^2 - r_o^2)}{2q\sqrt{t - \frac{\pi b(r^2 - r_o^2)}{q}}} \right), \qquad t > \frac{\pi b(r^2 - r_o^2)}{q} \tag{17a}$$

$$C(r,t) = 0, \qquad t < \frac{\pi b(r^2 - r_o^2)}{q} \tag{17b}$$

where

t = time
b = fracture half-aperture
φ = matrix porosity
D' = effective matrix diffusion coefficient
q = half-fracture flow rate
r_o = radius of the injection well
r = radial distance from the injection well
C = concentration of tracer in the fracture
C_o = injection concentration.

By measuring or estimating fracture aperture and porosity, and controlling injection rate, the expression above can be inverted to provide estimates of the effective diffusion coefficient, D'. Both the error function and the complementary error function are found on standard spreadsheet applications, and an "Optimize" macro can be invoked to return the value of D' that best matches the concentration history. Curve matching (type-curves) could also be used to estimate D' from a tracer test.

Estimating Effective Decay Rate Coefficients. In situ values of effective first-order rate coefficients can also be estimated from single well tracer tests. There are various approaches that account for different boundary conditions, push-pull phases with and without a soak period, etc. The simplest method is discussed below.

Snodgrass et al. (1998) assume instantaneous injection of a uniform slug of water containing a conservative tracer and a decaying tracer, and subsequent extraction without a soak period. Under those assumed conditions, and even in the presence of dispersion, normalized concentrations of the

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conservative tracer versus the decaying tracer are a result of the effective decay rate, λ_a, in the aquifer. Because injection is assumed to occur instantaneously, time refers to the residence time in the aquifer ($t = 0$ is the instantaneous injection), and the decay rate follows directly from plotting the following tracer history relationships (C_c refers to the conservative tracer concentration, C_d to the decaying tracer):

$$\ln\left(\frac{C_d(t=0)}{C_c(t=0)}\right) - \ln\left(\frac{C_d(t)}{C_c(t)}\right) = -\lambda_a t \ . \tag{18}$$

The effective decay rate of the reactive tracer can then be compared with measured rates, and the population of a biological community, for example, can be determined.

7.3   Numerical Methods

Use of numerical models has become a standard method of interpreting tracer tests. Known as *history matching,* for obvious reasons, the purpose is to simulate the test (injection and extraction operations, tracer details, boundary conditions, etc.) and match the tracer histories at each well by modifying the porous medium properties. A successful history match implies that the properties in the model are correct. Of course, *successful* is a subjective term, and the problem itself is mathematically ill posed. Nevertheless, it is a useful and insightful exercise under many conditions. A key point that is essential in interpreting numerical results is the importance of understanding the assumptions and limitations associated with the model itself.

History matching is done either manually or with inverse models. A manual history match is where the analyst runs a forward model (e.g., fate and transport model), compares simulated results with tracer histories, and then manually changes input parameters to the model. Inverse modeling does the same, but the parameter estimates are updated automatically in response to calculated sensitivity of simulated response to changes in the parameter. Both methods require a large number of forward model runs. One advantage of automatic history matching programs is they provide statistics that describe the level of confidence one might have in the parameters estimated, including parameter uncertainty and sensitivity and error propagation. These statistics are useful in determining the extent to which tracer test objectives are met.

8. SUMMARY

This document identifies and discusses the steps that promote a successful tracer test. We make no attempt to present the details of each of these steps, believing that the document would then become unwieldy and not used. Rather, we outline the steps required and offer a set of recommended readings in Section 9 below. The individual steps that were outlined and discussed are as follows:

- *Define Tracer Test Objectives (Section 3)*. Test objectives should be defined as specifically as possible, in order to avoid ambiguity in test design. Test objectives impact many other aspects of a tracer test, including the analysis methods used, sampling schedule required, number of tracers used, and their properties, etc. The extent to which test objectives can be defined, and the degree to which those objectives are accommodated in design, deployment, and analysis has a direct impact on the likelihood of success.

- *Tracer Selection and Testing (Section 4)*. This step also includes defining relevant tracer properties based on the test goals. Having defined the required properties, tests are conducted to establish that the tracer candidate actually has those properties under expected deployment conditions.

- *Implementation Strategy (Section 5)*. This must include explicit description of how the test will be conducted, how much of which tracer(s) will be used, where injected, where sampled, for how long, etc.

- *Field Implementation (Section 6)*. This is actual deployment of the test design, including the required documentation (field notes, etc.).

- *Test Interpretation (Section 7)*. Test interpretation is quantitative, qualitative, and numerical, or any combination, thereof.

The table below summarizes the individual steps required for successful tracer test and analysis, and can be used as a checklist by the practitioner.

Table 6. Checklist A—Required steps for planning and executing a successful tracer test.

1. Define the test goals

   a. List the properties of a given medium that need to be estimated.

   b. Can a tracer test obtain an estimate of these properties?

   c. Is the scale at which the properties can be estimated via tracer tests appropriate?

   d. Is a tracer test the best method for estimating the properties?

   e. Are tracer test answers qualitative or quantitative in nature?

2. Select appropriate tracer(s) based on test goals and test design

   a. Determine number and types of tracers

   b. Determine tracer properties

      (1) Is tracer(s) conservative (low/negligible solubility in all but 1 of the phases)?

      (2) Does tracer(s) partition?

         (a) Is the partition coefficient constant? (Partition coefficients should be measured in batch experiments at multiple reference concentrations.)

         (b) Is the partitioning reversible? Should it be?

      (3) Is the tracer reactive or sorbing? Has that behavior been measured under appropriate conditions, so observed behavior can be attributed to field conditions?

      (4) Are there other interactions between the tracer(s) and soils, water, pre-existing contaminants?

      (5) Have other concerns been evaluated regarding the tracer(s) such as toxicity, detectability at low concentrations (detection limits), availability and affordability, does the tracer(s) flow with the bulk fluid, is it stable under the test conditions and in the test environment?

   c. Determine site-specific tracer compatibility

      (1) Have batch tests been conducted? (see partition coefficient above)

      (2) Have column (dynamic) tests been conducted for adsorption, ion exclusion, geochemical compatibility tests using site soil, water, contaminants, and tracer candidates, at injection rates that mimic flow velocities expected at the field site?

      (3) Have site-specific use histories of selected tracers been investigated?

      (4) Have site-specific background tracer concentrations been measured?

3. Design the tracer test

   a. Employ numerical model(s) to help design the test and conduct sensitivity analyses.

   b. Will test be conducted under forced gradient or ambient flow conditions?

   c. Determine the expected number and types of tracer(s) to be used.

   d. How much tracer mass will be required to overcome dilution, decay/degradation, residence time, sorption, etc.?

   e. Where and how will the tracer(s) be injected?

   f. Where and how will receptor location(s) be sampled?

    g. How long will sampling at the receptor(s) continue after injection?

    h. Are receptor effluent managed according to applicable environmental regulations

    i.   Are sampling methods and locations, sample preservation methods, and sample collection frequencies compatible with test goals, test design and tracer properties?

    j.   Are all test goals, design parameters, and sampling details documented in the Test Plan according to applicable requirements?

    k. Are test goals and test design compatible with the existing well field configuration (receptor locations) and well completions (depths and materials)?

    l.   If new wells are drilled, are drilling fluids, well completions (depths and materials), and well development methods compatible with test goals and test design?

4. Implement the field test

    a. All field activities should follow the Test Plan guidelines.

       (1) Changes to the Test Plan guidelines should not compromise the test goals or quality control requirements.

    b. All field activities must be documented according to applicable quality control requirements.

    c. Applicable quality control and quality assurance measures must be maintained.

5. Interpret the test data

    a. Use qualitative methods, if applicable

       (1) All tracer properties must be measured adequately

    b. Use quantitative methods, if applicable

       (2) Conservative tracers

       (3) Partitioning tracers

          (a) Extrapolating tracer history

          (b) Partition coefficient requirements

       (4) Characterization of surfaces or mineral content

       (5) Flow geometry distributions

       (6) Matrix diffusion parameters

    c.   Use Numerical methods, if applicable

9. SUGGESTED READINGS AND REFERENCES FOR DESIGNING AND IMPLEMENTING TRACER TESTS

The references listed below provide an introduction to the research literature on tracer testing, tracer properties, data analysis methods, and other associated topics. Although this list is not an exhaustive compilation of all tracer literature, it is a starting point for more detailed searches for applicable material within the references of the citations below. Significant advances and contributions in tracer research have been made by foreign scientists; however, international references are not included unless they have been published in English.

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10. DEFINITIONS

Adsorption. The attraction and adhesion of a chemical compound from solution to the solid surfaces with which it is in contact.

Batch experiments. An experiment, or series of experiments conducted in the absence of flow, i.e., a static experiment.

Boundary conditions. The solution of groundwater flow and transport equations requires specification of *boundary conditions* that constrain the problem. Typically, the boundary conditions are (a) head/concentration is known for surfaces bounding the flow region (Dirichlet conditions), (b) flow/concentration is known across surfaces bounding the region (Neuman conditions), and (c) some combination of Dirichlet and Neuman.

Breakthrough curve. Effluent concentration history.

Cleanup efficiency. Mass of contaminant removed divided by the mass of contaminant originally present.

Column experiments. An experiment, or series of experiments, in which a container is filled with aquifer material and aquifer water (or the chemical equivalent of aquifer water) and fluids are continually added on one side of the container and extracted on the other side of the container, i.e., a dynamic experiment.

Conservative tracer. A tracer that has affinity for only one phase (the one in which it dissolves), neither partitioning into other phases nor adsorbing. Conservative tracers *trace* the flow of a single phase.

Detection limit. The lowest concentration that can be reliably measured by a particular analytical technique.

Diffusion. The process by which both ionic and molecular species dissolved in water move from areas of higher concentration to areas of lower concentration.

Dispersion. The phenomenon by which a solute in flowing groundwater mixes with in situ fluids through mechanical mixing in pores, variations in fluid velocity, and heterogeneity.

Fate and transport model. A numerical model that solves mass conservation equations for contaminants and usually allows transport via advection, dispersion and diffusion, adsorption, and decay.

First temporal moment of a tracer. The mean residence time of a tracer in a given volume (reactor vessel, porous medium, etc.).

Flow path. Imaginary line that traces the path that a particle of groundwater would follow as it flows through an aquifer, also known as a streamline.

Forced-flow conditions. Situation in which one alters the ambient flow field to force flow into a more desirable configuration. Usually, flow is changed by injecting and/or extracting water in new locations.

Forward model. Running a fate and transport model with all input values known or assumed.

Hydraulic conductivity. A measure of the capacity of a medium to allow fluid flow. Fluid velocity (volumetric flux) is proportional to hydraulic conductivity and the imposed pressure (or head) gradient from Darcy's Law. Hydraulic conductivity, K, is related to permeability, k, by:

$$K = \frac{k\rho g}{\mu}$$

where ρ is density, g is gravity, and μ is viscosity, usually taken as water phase properties at 20ºC.

Injectate. Fluid injected into the subsurface.

Inverse model. A numerical model in which some of the input parameters are considered unknown and automatically adjusted to match field measurements. Generally, the term relates to sophisticated computer programs using the Gauss-Marquardt-Levenberg method of parameter estimation.

Matrix diffusion. The process by which chemicals will enter a low-permeability rock matrix from the fractures, and is a function of surface area available, tortuosity, and diffusion coefficients of the chemicals.

Partition coefficient. A constant of proportionality relating the equilibrium concentration of a chemical in two phases.

Partitioning tracer. A tracer that has affinity for more than one phase.

Permeability. The property or capacity of a porous rock, sediment, or soil for transmitting a fluid; see *hydraulic conductivity*.

Residual saturation. The saturation of a phase (volume of phase / pore volume) below which the phase will not flow.

Retardation. A general term for the many processes in porous media that result in the velocity of a solute being lower than the phase velocity, including reversible adsorption, cation exchange, etc.

Sensitivity studies. A series of forward model runs, conducted in an attempt to explore the uncertainty in input parameters.

Streamline geometries. Measure of the distribution in flow paths (streamlines), including relative flow velocity, lengths, etc.

Swept pore volume. The pore volume in a porous medium through which a fluid flows (sweeps) under a given flow field. The swept volume can change if the flow field changes.

Thermal stability. A measure of the stability of a chemical (rate of decay or lack thereof) as a function of temperature.

Tortuosity. Sinuousity of the actual flow path in porous medium, defined as the actual length of a groundwater flow path divided by the straight-line distance between the ends of the flow path.