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The Integrated Contaminant Elution and Tracer Test Toolkit, ICET³, for Improved Characterization of Mass Transfer, Attenuation, and Mass Removal

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Abstract

It is evident based on historical data that groundwater contaminant plumes persist at many sites, requiring costly long-term management. High-resolution site-characterization methods are needed to support accurate risk assessments and to select, design, and operate effective remediation operations. Most subsurface characterization methods are generally limited in their ability to provide unambiguous, real-time delineation of specific processes affecting mass-transfer, transformation, and mass removal, and accurate estimation of associated rates. An integrated contaminant elution and tracer test toolkit, comprising a set of local-scale groundwater extraction- and injection tests, was developed to ameliorate the primary limitations associated with standard characterization methods. The test employs extended groundwater extraction to stress the system and induce hydraulic and concentration gradients. Clean water can be injected, which removes the resident aqueous contaminant mass present in the higher-permeability zones and isolates the test zone from the surrounding plume. This ensures that the concentrations and fluxes measured within the isolated area are directly and predominantly influenced by the local mass-transfer and transformation processes controlling mass removal. A suite of standard and novel tracers can be used to delineate specific mass-transfer and attenuation processes that are active at a given site, and to quantify the associated mass-transfer and transformation rates. The conceptual basis for the test is first presented, followed by an illustrative application based on simulations produced with a 3-D mathematical model and a brief case study application.

Keywords

tracer test; attenuation; plume persistence; mass removal; mass discharge; site characterization

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1. Introduction

Groundwater contamination by organic compounds such as chlorinated aliphatics, 1,4-dioxane, MTBE, and poly- and perfluoroalkyl substances (PFAS) continues to be an issue of import for many industrial, commercial, and military facilities. At many of these sites, groundwater contaminant plumes, which are typically hundreds of meters to several kilometers long, pose current or potential risks to human health and/or water resource sustainability. Despite two to three decades of remedial operations at many of these sites, groundwater contamination continues to persist, presenting complex and costly challenges to complete remediation and closure of the sites. It is now recognized that cleanup and closure of many sites with large, complex plumes is impractical within time frames of 50–100 years using current technologies and approaches (e.g., NRC, 2013). This realization has resulted in the examination of cost-effective alternatives for risk reduction and long-term, sustainable management of these sites (NRC, 2013).

The factors and processes that can limit effective contaminant mass removal and contribute to the persistence of groundwater contamination are well known. Primary factors involve mass-removal constraints associated with contaminant residing in poorly-accessible retention domains and/or occurring in phases for which mass transfer is rate limited, i.e., potentially any mass other than matter occurring in groundwater that resides within advection-dominated domains. This mass includes immiscible organic liquid in source zones (NAPL sources) and distributed sources of contaminant such as sorbed-phase mass, dissolved mass residing within lower-permeability units, and mass associated with other potential retention phases (vapor phase, partitioned to NAPL, adsorbed at fluid-fluid interfaces). While most of these factors and their potential impacts are well known, the difficulty faced for effective site characterization and cleanup is delineating and quantifying their relevance for a specific site.

The ability to identify and quantify with reasonable certainty the specific mass-transfer and/or attenuation processes active at a given site is critical for accurate risk assessment, for robust selection and design of remediation systems, and for effective long-term site management. Current standard characterization methods, such as plume-scale analysis of concentration profiles, analysis of concentration profiles associated with sediment cores, and mass-flux fences are generally limited in their ability to provide unambiguous, real-time delineation of specific mass-transfer and attenuation processes and accurate estimation of associated rates. The development of innovative, cost-effective field methods for improved characterization of mass-removal processes has been deemed a critical research need (NRC, 2013; SERDP, 2013).

A standard method used to characterize groundwater contaminant persistence and attenuation is based on the analysis of plume-scale concentration-vs-distance profiles determined along the longitudinal axis of the plume (e.g., Newell et al., 2002). An alternative approach employing mass-flux fences is based on measurement of contaminant mass fluxes at two or more control planes oriented perpendicular to the mean plume trajectory. The mass flux can be measured using a network of multi-level samplers or flux meters (e.g., Borden et al., 1997; King et al., 1999; Basu et al., 2006) or by use of

contaminant pumping tests (e.g., Bockelmann et al., 2001). As has been well established, these approaches are often subject to considerable uncertainty due to a number of factors (e.g., Barker et al., 2000; Newell et al., 2002; Chapelle et al., 2007). First, the methods provide measures of aggregate behavior, i.e., the combined contribution of all processes and factors contributing to mass transfer and attenuation. Because the individual processes are not explicitly delineated, the rate coefficients obtained from analysis of these data are composite (lumped) parameters. This limits their usefulness for predicting how the system will respond to changes in conditions such as induced by modification of well-field configuration or operation for hydraulic-based remediation systems or introduction of a reagent to enhance contaminant mass transfer or transformation (Brusseau, 1998; Chapelle et al., 2007). This, in turn, limits their utility for accurately assessing persistence, or for evaluating the impact of efforts to enhance mass removal. A second significant limitation is the impact of preferential-flow phenomena. Contaminant present in groundwater flowing in the higher-permeability domains typically provides the predominant contribution to concentrations measured with groundwater sampling or flux meter devices. This advective, preferential-flow component can in some cases obscure the concentration signals associated with rate-limited mass-transfer processes such as diffusion from lower-permeability domains (often termed “back diffusion”) and desorption.

Methods for providing local-scale characterization of attenuation have been developed, with standard approaches based on the analysis of concentration-vs-depth profiles obtained from high-resolution sampling of sediment cores or of groundwater (e.g., Johnson et al., 1989; Ball et al., 1997; Brusseau et al., 1999a; Chapman and Parker, 2005; Brusseau et al., 2007). These concentration profiles reflect the composite impact of all mass-transfer and attenuation processes active at that location. Thus, delineation of specific attenuation processes, and quantification of process-specific rates, is typically influenced by significant ambiguity and uncertainty. This limits their overall utility, similar to the standard plume-scale methods discussed above. In addition, the methods provide data that are produced under natural-gradient conditions—typically demarcated by relatively slow rates of mass transfer and transformation for at least some relevant attenuation processes. This results in two major potential limitations. One, the method may exhibit poor sensitivity to processes that have slower characteristic rates. Second, long, often impractical, monitoring times may be required to accurately characterize these processes. Another, major limitation is caused by the influence of spatial and temporal heterogeneity inherent to sites, i.e., the measurements pertain only to the borehole and its’ close vicinity, and for one snapshot in time. This introduces uncertainty regarding their representativeness, and may require significant cost to overcome.

Induced-gradient contaminant elution tests (CET) or contaminant elution tests for short, also referred to as contaminant pumping tests or mass discharge tests, are another approach for site characterization. CETs have been used to evaluate and quantify mass-removal behavior, characterize the impact of mass-transfer and attenuation processes on contaminant transport, and measure contaminant mass discharge. This test is typically conducted by pumping an extraction well for an extended period and monitoring contaminant concentrations in the discharge. The effluent concentration data are used to produce a contaminant elution curve, which is analyzed to characterize mass-removal behavior. These data can also be used to

determine contaminant mass discharge and to evaluate the potential impact of mass-transfer and attenuation processes.

Whiffen and Bahr (1985) conducted a combined contaminant elution and tracer test within a groundwater contaminant plume at a site in Gloucester Canada to evaluate the potential effectiveness of pump and treat as a remedial option. The test site was approximately 100 m from the source zone, and the primary contaminants investigated were tetrahydrofuran, diethylether, and 1,1,1-trichloroethane. Nonreactive tracers were used to characterize pore-water velocities and dispersivities. Bahr (1989) applied mathematical modeling to the CET data from Whiffen and Bahr to assess the potential impact of rate-limited sorption/desorption on transport. Brusseau (1993a, 1993b) applied a multiprocess mass-transfer model to the same data to delineate and quantify the apparent specific processes controlling mass removal. Thorbjarnarson and Mackay (1997) conducted a combined contaminant elution and tracer test at Rocky Mountain Arsenal in Colorado to characterize contaminant transport behavior during groundwater extraction. The test was conducted within the distal portion of a groundwater contaminant plume (composed primarily of trichloroethene and 1,1,1-trichloroethane), approximately 1 km from the source zones. Sahoo et al. (1998) conducted a variation of a contaminant elution test at the Picatinny Arsenal in New Jersey to characterize the impact of rate-limited sorption and the addition of surfactant on trichloroethene removal. The test was implemented by injecting uncontaminated groundwater and sampling downgradient-monitoring wells, with no extraction wells employed. It was conducted in the center of a groundwater contaminant plume, approximately 350 m from the source zone.

All of the prior noted CET applications were conducted explicitly for systems with no immiscible organic liquid present within the test domain, within the plumes and away from source zones. Brusseau and colleagues conducted combined contaminant elution and tracer tests within a chlorinated-solvent (NAPL) source zone at a site in Tucson, AZ (Nelson and Brusseau, 1996, 1997; Blue et al., 1998; Brusseau et al., 1999a, 2007). The tests were conducted to delineate and quantify the specific processes contributing to the constrained mass removal observed for the pump-and-treat system and the concomitant plume persistence. Trichloroethene is the primary contaminant of concern at the site.

The base CET method suffers from two of the same limitations as the prior methods discussed. One is the confounding influence of the contaminant plume and preferential flow. The CET can be modified to reduce or eliminate this issue by using injection wells to inject clean water, which removes the resident aqueous contaminant mass present in the higher-permeability zones and isolates a portion of the test zone from the surrounding plume. The application of this coupled injection-extraction concept for evaluating the impact of mass-transfer and attenuation processes on transport was employed in most of the studies noted above.

The other limitation for the standard CET is that the observed contaminant elution behavior reflects the aggregate impact of all mass-transfer and attenuation processes influencing contaminant transport for that system. Analysis of such data will return lumped rate coefficients when mass removal is influenced by more than one process but those processes

are not accounted for individually. Delineation of specific processes can be accomplished by employing process-specific tracer tests along with the CET. For example, most of the CET applications noted above used nonreactive tracers to characterize advective-dispersive solute transport. More definitively, a tracer suite can be employed that includes tracers targeted to characterize specific mass-transfer or transformation processes. Examples include tracers to characterize partitioning to NAPL, diffusive mass transfer impacts, and transformation-induced mass loss. The integration of the various available tracer tests with the CET constitutes the integrated contaminant elution and tracer test toolkit (Brusseau, 2017).

The various components of the ICET³ have been used to varying degrees in individual applications for some time. A strength of the integrated toolkit is the synergism attained from the concurrent implementation of the individual components. Despite the several benefits and advantages of the method, it has apparently yet to become widely applied. The objective of this work is to present the concept and elements of the integrated CET toolkit approach. Application of specific test components will be illustrated with a case study. Implementation and data-analysis aspects will be covered briefly.

2. Applications for the ICET³

The integrated contaminant elution and tracer test toolkit (ICET³) method is an integration of aquifer-perturbation and tracer-test methods, coupled with the use of standard and novel tracers to target specific individual mass-transfer and attenuation processes (Figure 1). It employs extended groundwater extraction to stress the system and induce and increase hydraulic and concentration gradients. In many cases, this serves to enhance the sensitivity of the method by perturbing extant magnitudes and rates of mass transfer and transformation. This also reduces the time required for obtaining quality measurements, and thus increases the ability to obtain measurements in reasonable timeframes. Injection wells can be employed for injection of clean water, which ensures that the concentrations and fluxes measured within the isolated are directly and predominantly influenced by the local mass-transfer and transformation processes controlling mass removal. The suite of tracers is selected to allow characterization of specific processes, and quantification of associated rate coefficients.

The test interrogates a much larger volume compared to borehole-based methods, reducing uncertainty associated with spatial variability. The spatial domain interrogated by the test can be scaled according to site conditions and test objectives, which allows for cost-effective optimization of the test. The test can be conducted multiple times to characterize the impact of natural temporal variability or that of human-induced perturbations.

During the ICET³ test, groundwater samples are collected periodically from the extraction well (and monitoring wells if desired), and analyzed for the target constituents (contaminants of concern, tracers, nutrients, transformation products). The constituent concentrations are used to produce elution curves for the contaminants and breakthrough curves (comprising both arrival and elution waves) for the tracers (Figure 2). These curves provide the foundation data sets for the various applications of the method. It should be

noted that groundwater levels can be monitored during the test to provide data for characterization of aquifer hydraulic properties.

2.1 Characterize mass removal and contaminant persistence

A primary application for the standard and integrated CET is its use for characterization of mass-removal behavior. Generally, it constitutes the most effective method for such characterization. The contaminant elution curves are inspected to determine the type of behavior exhibited. Specifically, the elution-curve profiles are examined for specific landmarks such as the presence and extent of steady-state (relatively uniform concentrations) and asymptotic (slow rate of decrease to low concentrations) stages, as well as distinct changes in slope. The observed behavior is interpreted in conjunction with the site conceptual model to evaluate mass-removal scenarios and help identify the one most likely representative of the extant system. This information is used to evaluate the potential impact of rate-limited mass-transfer or transformation processes on contaminant transport and fate.

Several examples of possible contaminant elution-curve profiles are shown in Figure 3. Five distinct types of behavior are represented: (I) high-concentration steady state, (II) low-concentration steady state, (III) high-concentration asymptotic, (IV) low-concentration asymptotic, and (V) multi-stage. Each type of behavior is associated with a specific type or types of mass-removal condition, which is mediated by the amount of the contaminant present, its hydraulic accessibility (distribution of the contaminant, hydraulic properties of the system), and the potential for contaminant transformation. For example, Type I and II behavior would be anticipated for systems in which a large mass of non-dissolved-phase contaminant is distributed relatively uniformly within the domain and mass transfer is significantly rate limited, or the mass is located within a fraction of the domain and the measured concentrations are influenced by significant dilution, or some combination thereof. The distinction between Type I and II would relate to site conditions and the specific nature of the non-dissolved-phase mass and/or rates of transformation. Type I would be expected, for example, for situations wherein NAPL sources are present, whereas Type II may be prevalent for systems with distributed-contaminant phases such as dissolved mass present in lower-permeability domains or sorbed mass (and no NAPL). Alternatively, both Type I and II may represent a site with substantial non-dissolved-phase mass distributed in similar manner, with the difference in steady-state concentrations reflecting the impact of relatively high rates of transformation for Type II. Type IV behavior may connote that nearly all contaminant present is hydraulically accessible, and is present in limited quantities and/or influenced by relatively rapid rates of transformation. For example, contaminant that is present primarily as dissolved mass in the higher-permeability domains of the system. Type III behavior may represent a system similar to Type I, but for which mass-transfer constraints are not as extreme. Multistage elution profiles may occur for systems wherein contaminant mass is distributed in multiple domains for which characteristic times of mass transfer are distinctly different (Type V).

Mathematical modeling can be used to assist in the analysis and interpretation of CET data. When interpreting elution-curve data, it is critical to deconvolute the impact of the regional plume from the local processes influencing mass transfer and attenuation. In addition, it is

important to recognize that the observed behavior is an aggregation of all factors and processes influencing mass removal. Data analysis and interpretation should always be reflective of this reality. This leads to the next application, delineation of specific processes.

2.2 Delineate specific mass-transfer and attenuation processes

As discussed in the preceding subsection, CET data can be used to evaluate the impact of mass-transfer and attenuation processes on mass removal. This analysis can be extended to identify specific operative processes. In this regard, interpretation of the test results is relatively straightforward for a system in which a single mass-transfer or attenuation process is predominant. However, for many systems, contaminant transport and mass removal is influenced by multiple processes. In such cases, a suite of tracers can be used to help delineate and characterize specific processes and their respective impact on mass removal.

Various types of tracers can be used, each to target a specific transport, mass-transfer, or transformation process:

1. **Conservative tracer-** a conservative tracer, one that is not subject to sorption, other retention processes, or transformation reactions (i.e., an analogue to water) is used to characterize advective-dispersive transport, residence times, and flow heterogeneity. This standard tracer approach has been widely employed for site characterization. Additionally, multiple conservative tracers, with different molecular weights (i.e., diffusion coefficients), can be used to characterize specifically the occurrence of diffusive mass transfer (back diffusion) and its impact on contaminant transport (Brusseau, 1993; Maloszewski and Zuber, 1993; Nelson and Brusseau, 2003). Specifically, for a system influenced by a diffusive mass-transfer process, the rates of mass transfer will differ for solutes with different diffusion coefficients. Thus, tracers with different diffusion coefficients should exhibit dissimilar transport behavior (e.g., different amounts of spreading, different extents of tailing) for a given set of conditions. This is illustrated in Figure 2.
2. **Sorptive/retention tracers-** tracers can be used to characterize the impact of retention on transport. One example are tracers that are sorbed by the sediment to evaluate the impact of sorption and retardation on transport and mass transfer. Other examples include tracers selected to probe other potential retention processes, such as partitioning to NAPL, to fluid-fluid interfaces, and to trapped air phases. Related tracer-test methods involve the use of partitioning tracers to characterize the presence and quantity of NAPL present in source zones, water content in vadose zones, and the magnitude of fluid-fluid interface (e.g., Nelson and Brusseau, 1996; Annable et al., 1998a, 1998b; Deeds et al., 1999; Cain et al., 2000; Keller and Brusseau, 2003).
3. **Biotransformation tracer-** susceptible to biotransformation, but is not affected by abiotic transformation. This type of tracer is used to characterize the specific impact of biotransformation processes. Tracer tests conducted with biodegradable tracers have been used successfully to characterize the impact of biotransformation processes (Istok et al., 1997; Brusseau et al., 1999b; Alter et

al., 2003; Sandrin et al., 2004). Products of biotransformation can be monitored along with the target tracer to provide additional data.

4. **Abiotic transformation tracer**- susceptible to abiotic transformation, but is not affected by biotransformation. This tracer type is used to characterize the specific impact of natural abiotic transformation processes, such as mineral-induced reduction. Products of abiotic transformation can be monitored along with the target tracer to provide additional data. Note that tracers can be selected to characterize speciation changes for inorganics due to abiotic (or biotic for biotransformation) processes.

It should be noted that the tracers discussed above generally refer to surrogates for contaminants of concern at a site. Of course, actual contaminants of interest can be used as tracers in these tests as well, which has often been done at research sites. However, such use at typical contaminated sites is often precluded.

The use of this integrated tracer suite provides a means to identify the contributions of individual processes to mass removal, including back diffusion, desorption, biotransformation, and abiotic transformation. The use of injected tracers allows accurate determination of mass recoveries and associated magnitudes and rates of mass-transfer and transformation. Thus, the test can provide improved, quantitative determination of the specific contributions of individual processes to overall mass removal and persistence.

2.3 Quantitative analysis and determination of rate coefficients

It should be stressed that the qualitative analysis discussed above is just as important as quantitative analysis. As discussed, most field sites will entail conditions wherein multiple processes contribute to mass removal. The qualitative analysis supported by the test allows delineation of specific attenuation processes, and thus enhances the accuracy of the rate coefficients determined from quantitative analysis.

One method used to obtain rate coefficients is based on fitting selected functions to the contaminant/tracer elution curve. These functions range from a simple first-order decay function (e.g., Newell et al., 2002) to power-law functions, for which the power-law magnitude has been correlated to specific mass-transfer behavior (e.g., Haggerty et al., 2000; Luo et al., 2007). Another method of analysis is based on temporal-moment analysis (e.g., Leij and Dane, 1992; Das and Kluitenberg, 1996; Srivastava et al., 2004; Das et al., 2005; Luo et al., 2006). Standard methods are available for application of function and moment analysis to elution and breakthrough curves.

A major advantage of using function or moment analysis is that it does not require the use of mathematical transport modeling, and does not require the attendant input data that are potentially costly and time-consuming to obtain. A major disadvantage of these methods of analysis is that the rate coefficients obtained are aggregate (lumped) parameters, representing the contribution of all processes that influenced the transport of that constituent. However, the design of the ICET³ test, with its use of a suite of tracers, can minimize this limitation. For example, analysis of nonreactive tracer data will provide specific

characterization of diffusive mass-transfer rate coefficients. Similarly, the rate coefficient determined for the abiotic tracer data will reflect the impact of abiotic-related attenuation.

Another potential limitation for data analysis is associated with data truncation (incomplete elution curves), which can increase uncertainty of the estimated parameters. Methods to account for the impact of data truncation on parameter estimation are available (e.g., Skopp, 1984; Das and Kluitenberg, 1996; Luo et al., 2006). In addition, the use of flow-interruption or stop-flow tests can help compensate for data truncation and other issues (Brusseau et al., 1989, 1997).

The other method used to quantitatively analyze ICET³ test data and to obtain rate coefficients is based on the application of reactive transport modeling. It must be stressed that it is critical to use a process-discrete (distributed-parameter) approach to modeling, wherein each transport, mass-transfer, and attenuation process is explicitly and separately represented. As has been well established, the use of simplified, lumped-process models provides generally poor results for systems with multiple processes affecting migration and attenuation (e.g., Brusseau, 1998; Chapelle et al., 2007). The use of process-discrete modeling improves the determination of accurate process-specific rate coefficients. The primary disadvantage of using complex, process-specific transport models is the significant data input requirements. However, implementation of an ICET study is an effective way to obtain much of the required input data.

Quality assurance and quality control procedures should be implemented for assessing overall robustness of the test data. This would include identification of possible outliers and potential impacts of sampling or analytical artifacts. The relatively high temporal resolution of the ICET test is an advantage for conducting such assessments. The process-specific information gleaned from the tests is another advantage.

2.4 Other Applications

Contaminant mass flux or discharge (CMD) has become an alternate or supplemental metric for use in characterizing risk and evaluating the performance of remedial operations. Multiple methods are available to measure CMD, with the CET one such approach. The CET method has been used for example to measure CMD before and after a large-scale in-situ chemical oxidation project conducted at a federal Superfund site in Tucson to evaluate remedial operation performance (Brusseau et al., 2011a).

The mass of contaminant present at the time of characterization and remediation, referred to herein as resident contaminant mass, is a critical parameter for assessing risk and evaluating remediation efforts for contaminated sites. Unfortunately, accurate determination of resident mass is generally problematic at most sites, with the standard characterization method (high-resolution coring) being typically cost-prohibitive to employ. However, resident mass can be estimated by fitting simple mass-depletion functions to measured CET data. For example, mass-depletion functions have been applied to CMD data obtained from CETs conducted within NAPL source zones (Brusseau et al., 2013a; Johnston et al., 2013).

The CET is ideal for evaluating the potential effectiveness of hydraulic-based remediation methods. For example, solutions of reagent(s) (e.g., surfactants, oxidants, electron acceptors, electron donors) associated with a remediation technology under consideration can be injected to test effectiveness. Essentially, these are implemented as pilot tests of the proposed technology. The data can be analyzed as has been discussed for the CET applications to enhance knowledge gained from the pilot tests.

3. Implementation

The design of the test and the selection of components employed will depend upon the objectives of the test and site conditions. The specific configuration of the well field, the operational pumping rates, and the length of the test are primary design variables. Multiple additional factors need to be considered to ensure successful implementation. Mathematical modeling can be conducted to assist in the design of the tests, and is particularly recommended for more complex systems.

3.1 Well-field configuration

The standard well-field configuration for contaminant elution and tracer tests comprises a single injection-extraction dipole (Figure 4). Another, widely used variation consists of multiple injection and extraction wells arranged separately in two parallel lines. Either approach can provide isolation of the central region of the test domain, but data collected from the extraction well(s) remains influenced by the surrounding plume. This is a significant limitation for some applications because the extraction well provides critical data for analysis of transport and attenuation.

Recently, Guo and Brusseau (2017) evaluated alternative well-field configurations to improve isolation of the extraction well from the plume for these tests. Two alternative configurations were tested and compared to the standard dipole (Figure 4, B and C). The results demonstrated that the nested couplet configuration established isolation of the inner extraction well from the surrounding plume. Hence, it appears useful for applications in which isolation from the plume is desired. However, such isolation is not desired for other applications, including those characterizing mass removal associated with the plume itself.

A tandem vertical circulation well system can be used within the isolated zone in place of the standard injection-extraction wells to eliminate the need for extracting large volumes of groundwater to the surface and subsequent treatment. This can be done for example using the approach presented by Goltz et al. (2009), who used the system to measure mass flux. This approach may be advantageous for sites with limited capability to treat contaminated groundwater, or where regulatory limits preclude injection. Implementation of ICET tests with such a configuration would require in-well treatment of contaminants to maintain clean-water injection, and tracer removal or specific accounting for tracer reinjection.

3.2 Additional test components

In addition to this baseline design, additional components can be implemented, including:

- i. **Vertical discretization of sampling.** The extraction and monitoring wells can be fitted with vertically discrete sampling devices to characterize vertical variability. The use of multiple monitoring wells interspersed within the target domain provides characterization of areal spatial variability.
- ii. **Stop-flow tests** can be conducted to enhance characterization of rate-limited phenomena. These tests, developed by Brusseau and colleagues (Brusseau et al., 1989, 1997), have since been widely used to characterize mass-transfer processes. For example, potential concentration rebound can be monitored within the isolated zone to specifically evaluate the impact and rates of back diffusion and desorption. Brogan and Gailey (1995) presented a method to estimate field-scale mass-transfer rate parameters based on analyzing concentrations of a resident contaminant obtained during the recovery phase of a groundwater pumping test. The method was successfully demonstrated using mathematical modeling simulations for a system with rate-limited sorption as the mass-transfer limitation.
- iii. **Push-pull tests** can be conducted within the isolated zone of the test domain to provide additional smaller-scale characterization of specific processes. These tests, wherein solutions are injected into the aquifer and then extracted after a given “reaction period” (e.g., Drever and McKee, 1980; Istok et al., 1997; Hansen et al., 2016), have been used for example to characterize attenuation, particularly biotransformation, processes and to measure attenuation rates. These tests have been demonstrated to provide robust characterization of transformation processes under certain conditions. They are also used to characterize hydrodynamic transport behavior and the impact of retention processes on transport.

A major potential limitation of the push-pull method is increased uncertainty due to poor tracer recovery in some cases. One case occurs for systems wherein the rates of attenuation are relatively slow compared to the hydraulic residence times (i.e., sites with relatively large groundwater velocities). For this case, a significant fraction of the injected solution may migrate outside of the zone of recapture during the non-pumping phase, and thus would not be extracted during the “pull” phase. This would lead to significant loss of tracer, and result in greater uncertainty in estimated parameters, as shown by the results of field tests (Burbery et al., 2004). This issue would need to be considered for application with an ongoing ICET. Small-volume, vertically discrete push-pull tests can be conducted using multilevel sampling devices located within the isolated zone to provide high-resolution characterization of processes in the vertical dimension, while at the same time reducing the influence of potential mass-loss issues. This can be done for example using the method presented by Knecht et al. (2011). Tests can be conducted at different locations within the test zone to characterize areal spatial variability.

3.3 Additional implementation factors and potential constraints

It is critical to consider all factors that may influence or limit implementation of the tests, as well as the potential impacts of the tests on the subsurface system. Generally, the greatest

potential impact is the possible alteration of subsurface conditions with the injection of clean water. For example, electron acceptors other than oxygen are predominant in many groundwater contaminant plumes. Introducing oxygenated water may significantly alter redox conditions, thereby affecting redox-sensitive reactions and associated reactants and products. Similarly, differences in pH between the injected water and resident groundwater may affect pH-sensitive conditions. Microbial-community profile, ionic composition, and temperature are other factors to consider. Therefore, it is imperative that the biogeochemical properties of the injected water be matched to the target subsurface system. This can often be accomplished by using resident groundwater as the source for injected water, subject to appropriate procedures to maintain representativeness while meeting the requirements for the test.

The effective range of tracer detection is an important factor to consider in tracer selection. This is influenced by the analytical method(s) available and associated quantitative detection limits, as well as potential impacts of the environmental matrix (e.g., presence of background concentrations of the selected tracer or interferences). Ideally, the conditions will support a detection range of several logs to better characterize transport behavior. In addition, the detection range would span lower concentration ranges such that high injection concentrations are not required, which will minimize solution-density contrasts and other potential undesirable impacts.

It is also desirable that the tracers employed have minimal impact on the subsurface system, except as specifically targeted. For example, the tracers should not affect the sorption of resident contaminants, nor induce mobilization of NAPL present. In addition, the tracers should not contribute to long-term groundwater contamination. Another condition for implementing the test is on-site capacity to treat the volumes of contaminated groundwater extracted during the test.

As noted above, one advantage of the ICET method is the much larger measurement volume compared to standard borehole-based methods. In addition, the measured domain is a design variable that can be tailored to site conditions and test objectives through the dimensions of the well field, as well as the use of interspersed monitoring wells. And, vertical spatial variability can be characterized with use of vertically discrete sampling as noted. The typical configuration would produce areal measurement domains of roughly several 10s to a few 1000s of m², and can be matched to mesh sizes used for field-scale mathematical modeling. However, due the nature of the tests, smaller-scale heterogeneity is not captured. Sediment coring or push-pull tests can be implemented to supplement the ICET if so desired.

4. Illustrative Applications

4.1 Simulated example test

A simulated ICET test is presented to illustrate the types of data that would be collected, as well as to present an example of timeframes required to complete the test. The properties of the domain were selected to be generally representative of an alluvial aquifer system, with values for some parameters patterned after information generated from our prior studies conducted at the Tucson International Airport Area (TIAA) Superfund site (Zhang and

Brusseau, 1999). The flow model used in this work was MODFLOW, the three-dimensional (3D) finite-difference numerical model developed by the U.S. Geological Survey (McDonald and Harbaugh, 1988; Harbaugh et al., 2000). The 3D solute transport model MT3D with TVD solver (Zheng, 1990) was used to simulate solute transport. Groundwater Vista (GV; version 6.85) (Rumbaugh and Rumbaugh, 2007) and Groundwater Modeling System (GMS, version 7.1) (EMRL, 2005) were used as graphical user interfaces.

The model domain was 625 square meters. The domain was divided into a regular orthogonal grid consisting of 100 rows and 100 columns with grid space $0.25\text{-m} \times 0.25\text{-m}$. The grid size was set to ensure numerical accuracy for the given simulation conditions. The thickness of the domain was 10 m, which was split into 10 layers with 1 m thickness for each layer. The test area where the injection-extraction well systems were set up was $5\text{-m} \times 3\text{-m}$.

A random field generator (Gutjahr, 1989) was used to derive realizations of K for the aquifer unit of the domain. It was assumed that the permeability of the sand was lognormally distributed with mean $\langle \ln K \rangle$ and variance σ_Y^2 . The simulations were conducted in a domain with permeability heterogeneity of arithmetic mean value of K equal to 10 m/d and σ_Y^2 as 5. Specified head boundaries were used along right and left borders of the model, with natural gradient 0.01 under confined conditions inducing groundwater flow from the left to right side. Longitudinal dispersivity was set to 0.05 m based on standard grid-Peclet number criteria, and transverse, and vertical dispersivities were set to 0.005, and 0.0005 m, respectively. A porosity of 0.3 and bulk density of 1.73 g/cm^3 were used.

Two injection wells were used with flow rate of $1\text{ m}^3/\text{d}$ for each well, and one extraction well located between the injection wells was used with extraction rate of $2\text{ m}^3/\text{d}$. The injection and extraction wells were screened through the entire thickness of the domain. The initial tracer concentration was zero for the entire domain, the tracers were injected via the upgradient injection well and clean water was injected via the downgradient injection well. Four different tracers were used. The first two are non-reactive tracers (NRT) with diffusion coefficients of 0.0076 and $0.00076\text{ m}^2/\text{d}$, respectively. The third is a sorptive tracer with a diffusion coefficient of $0.0076\text{ m}^2/\text{d}$ and distribution coefficient (K_d) of 0.35 mL/g , resulting in a retardation factor of 3. For this example, sorption is assumed to be linear and rate limited. First order kinetics was applied with the mass transfer (desorption) rate coefficient set at 15 d^{-1} . The fourth tracer was a transformation tracer and the transformation process was simulated by first order irreversible kinetics, with the aqueous-phase rate constant set at 0.04 d^{-1} . The tracers were injected continuously for 10 days followed by 100 days of monitoring. The properties of the resident contaminant were set to represent a conservative constituent (no sorption or decay), to allow illustration of the impact of physical heterogeneity and back diffusion on mass removal. The entire domain was contaminated with an initial concentration set to 1 g/m^3 . Temporal data were collected in high resolution from the extraction well for the simulations.

The elution curve for the resident contaminant and breakthrough curves for the tracers produced using the time continuous concentrations are presented in Figure 2A. Different

transport behavior, with different amounts of spreading and tailing, are observed for the two nonreactive tracers with different diffusion coefficients. This observed difference signifies the impact of diffusive mass transfer on transport. The breakthrough of the sorptive tracer occurs later compared to the curves for the non-reactive tracers because of the impact of retardation. The concentrations for the transformation tracer are much lower as a result of degradation. Long tailing is observed in the elution curve for the resident contaminant, which is attributed to the influences of the surrounding plume and back diffusion. These different behaviors reflected in the breakthrough/elution curves are the result of the contributions of individual processes to transport. It is often very useful to examine breakthrough curve and elution data in a semilog format to better evaluate potential mass-transfer limitations and the impact of flow heterogeneities (Figure 2B).

The effective pore volume (PV) of the test domain was 45 m³, and approximately 0.22 PV of tracer solution was injected. By the end of the simulation, approximately 5 PV of groundwater was extracted. The impacts of different processes on transport were readily apparent after ~60 days, equivalent to approximately 3 PV of groundwater being extracted. Increases to the pumping rates would shorten the overall experiment time. These results illustrate that ICET tests can be conducted in reasonable time frames.

4.2 Application at the Tucson International Airport Area Superfund site

Brusseau and colleagues conducted an extensive study of source-zone remediation efforts and associated groundwater contaminant-plume behavior for a chlorinated-solvent contaminated site in AZ undergoing pump-and-treat remediation. The site that was the focus of the study is part of the Tucson International Airport Area (TIAA) federal Superfund site in southern Arizona. A large, multiple-source plume of trichloroethene and 1,1-dichloroethene exists in the upper portion of the regional aquifer, which in the past was the primary source of potable water for the Tucson metropolitan area. Administratively, the TIAA site is separated into two major zones, the North and South sections. The study site is located within the South section. Three primary NAPL-contaminated source zones have been delineated in the South section. The major hydrogeologic units in the area of the site have been designated as (in descending order with depth): the Unsaturated Zone, the Upper Aquifer, an Aquitard Unit, and the Lower Aquifer. The Unsaturated Zone extends from the land surface to the regional groundwater surface, which is located 30 to 40 m below ground surface (BGS). The Upper Aquifer extends from the regional groundwater surface to a depth of approximately 54 to 66 m BGS, where it is underlain by the Aquitard Unit. The Upper Aquifer consists of sand and gravel lenses/layers separated in some areas by clayey sediment ranging from 1 m to greater than 7 m in thickness. The contaminants are limited primarily to the upper 6-m thick portion of the Upper Aquifer. Concentrations of trichloroethene in groundwater ranged from less than 100 to approximately 12,000 µg/L within the study site. The DCE concentrations are approximately ten times lower than the TCE concentrations.

Multiple methods, including induced-gradient contaminant elution tests, multiple-solute tracer tests, high-resolution sediment coring and vertical groundwater sampling, analysis of historic pump-and-treat operations data, laboratory experiments, and mathematical modeling, were used to characterize the relative impacts of plume-scale back diffusion,

plume-scale sorption/desorption, and dissolution of organic liquid trapped in the source zones on contaminant mass removal and plume persistence (Nelson and Brusseau, 1996, 1997; Blue et al., 1998; Brusseau et al., 1999a; Zhang and Brusseau, 1999; Johnson et al., 2003a, 2003b, 2009; Nelson and Brusseau, 2003; Sandrin et al., 2004; Brusseau et al., 2007, 2011a, 2011b, 2013a, 2014).

An example of the multi-solute tracer-test results is presented in Figure 5. Figure 5a shows the breakthrough curves obtained for two non-reactive tracers, with different diffusion coefficients. The breakthrough curve for the larger solute (with a smaller diffusion coefficient) exhibits greater spreading. This reflects the impact of diffusive mass transfer between the higher-permeability aquifer and the adjacent low-permeability clay unit. The results of this test supported process delineation and parameterization of the mathematical model used for simulations of contaminant transport.

An example of a NAPL-partitioning tracer test conducted at the site is presented in Figure 5b. The breakthrough curve for the tracer that can partition to NAPL (but that is not sorbed by the sediment) is observed to be delayed compared to the non-reactive tracer. This indicates the presence of NAPL within the test domain. These data were analyzed to determine a NAPL saturation value. This value was used for conducting a mass balance on contamination present at the site versus the mass removed with pump and treat, and to support mathematical modeling.

An example of a contaminant elution profile obtained from the ICET tests conducted at one of the source zones at the site is presented in Figure 5c. It is observed that the data exhibit Type I behavior, with pseudo steady state concentrations at relatively high values. Information obtained from the ICET tests and other characterization efforts was used to support development of a mathematical model to simulate flow and transport. An example of using the model to obtain a value for the NAPL dissolution rate coefficient is shown in the Figure. As noted previously, conducting such a modeling analysis necessitates understanding the processes influencing mass removal if one is to obtain robust results. In this case, the model accounted for all three factors contributing to constrained mass removal (NAPL dissolution, back diffusion, and desorption). Application of a simplified model, accounting solely for NAPL dissolution, would result in determination of an incorrect mass-transfer coefficient.

The results of the integrated studies indicated that all three mass-transfer processes were influencing mass removal and plume persistence, with organic-liquid dissolution the primary factor. In addition, the results showed that contaminant concentrations were generally higher within the laterally extensive lower-permeability units compared to the more permeable units, indicating that pump and treat was ineffective at flushing the lower-permeability units. Assessment of the historic integrated plume-scale contaminant mass discharge, along with the results of mathematical modeling, indicated that the plume would persist for many decades even with the isolation or removal of the source zones, primarily due to back diffusion of contaminant associated with the lower-permeability units (Brusseau et al., 2007).

The information obtained from the ICET tests was integral in the comprehensive assessment of mass removal and plume persistence for the site. The test results allowed delineation of the specific processes contributing to observed behavior. They also provided data for model parameterization to support the mathematical modeling. As a result of the ICET and associated work, the site conceptual model was revised and additional remediation strategies were implemented, focusing on source-zone treatment.

5. Conclusion

The integrated contaminant elution and tracer test toolkit was presented as an improved method for characterizing mass-removal behavior and delineating the underlying mass-transfer and attenuation processes that impact the transport, fate, and remediation of contaminants in complex, heterogeneous subsurface environments. Application of this toolkit will support delineation of the specific processes that are active at a given site, and quantification of the associated mass-transfer and transformation rates. The method will improve our understanding of the impact of site-specific processes on plume persistence. In addition, the test will produce information and parameter values that can be used to enhance the accuracy of mathematical models for predicting plume behavior under a range of conditions, including active pump and treat, enhanced attenuation, and monitored natural attenuation.

This information can be used to improve the site conceptual model, support robust risk assessments, and promote cost-effective long-term management of the large, complex groundwater contaminant plumes present at many sites. In addition, it should be noted that while the current work was focused on saturated-zone systems, the method can also be employed for vadose-zone characterization (Brusseau et al., 2013b). The method can be integrated with other site-characterization tools to produce the most robust, cost-effective site information possible.

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Highlights

- An integrated contaminant elution and tracer test method is presented
- Conceptual framework and illustrative applications of the method are presented
- The method is anticipated to improve characterization of contaminant mass removal and persistence

Figure 1.
Illustrative schematic of the ICET³ concept.

Figure 2.
Results of simulated contaminant elution and tracer test; NRT = nonreactive tracer, CET = contaminant elution test data (i.e., resident contaminant).

Figure 3.

Representative types of behavior for contaminant elution curves. (I) high-concentration steady state, (II) low-concentration steady state, (III) high-concentration asymptotic, (IV) low-concentration asymptotic, and (V) multi-stage.

Figure 4. Schematic of example well-field configurations for the ICET³ test. A) standard single dipole, B) dual dipole, C) nested dipoles. Note that the flowlines presented are idealized, representing an ideal homogeneous system. Figure from Guo and Brusseau (2017).

Figure 5.

- Illustrative results of multi-solute non-reactive tracer test conducted at the TIAA site. The aqueous diffusion coefficients are 0.075 and 0.006 cm²/h for bromide and HPCD (hydroxypropyl-beta-cyclodextrin), respectively. From Nelson et al., 2003.
- Illustrative results of a NAPL-partitioning tracer test conducted at the TIAA site. Relative concentration for the NAPL-partitioning tracer (PT), SF₆, is plotted on the left vertical axis, while the relative concentration for the nonreactive tracer, bromide, is plotted on the right vertical axis. From Nelson and Brusseau, 1996.
- Illustrative results of a contaminant elution test conducted at the TIAA site. The extraction well was pumped continuously for 60 days. Simulations produced using different Sherwood Number values, where $Sh = k_{la} \cdot d^2 / D$, and k_{la} is the first-order dissolution rate coefficient, d is the mean grain diameter, and D is the aqueous diffusion coefficient. Adapted from Blue et al., 1998.