The future of applied tracers in hydrogeology

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Introduction

Tracing techniques have a broad application in science and have demonstrated particular usefulness in hydrogeology. Applied tracers, which are defined as non-natural constituents that are intentionally introduced, are especially powerful investigative tools because the tracer application (or source term) is controlled and well characterized. This permits quantification of transport parameters and measurement of subsurface properties in a way often unmatched by standard physical methods. Furthermore, tracer tests directly measure properties in-situ and can be used to investigate very specific processes by selecting tracers with appropriate physicochemical properties. In many cases, tracer test methods offer the most accurate or practical way to measure specific parameters, and in some cases, they are the only reliable investigative technique. Depending on the application, tracer tests can be used to characterize properties representative of large subsurface volumes or investigate small-scale transport phenomena.

Applied tracers have been widely used for centuries to characterize flowpaths and estimate groundwater velocities. In fact, Kass (1998) notes that the Jewish historian Flavius Josephus recorded in approximately 10 A.D. the use of chaff as a tracer to link the spring source of the Jordan River to a nearby pond. Quantitative tracer tests using chloride, fluorescein, and bacteria were first conducted in the large karst regions in Europe in the late 1800s and early 1900s. After World War II, advances in chemical measurement technology permitted quantification of significantly lower tracer breakthrough concentrations and made high-frequency sampling economically feasible. Additionally, these technological advances lead to a significant increase in the diversity of constituents used as tracers.

Historically, applied tracers in hydrogeology have been used mostly to characterize groundwater flow in kart regions. During the 1960s, benchmark studies exploited applied tracers to understand the controls on groundwater recharge (Horton and Hawkins 1965; Zimmerman et al. 1966) and significantly advanced an understanding of the flowpaths of rainfall to the water table. During the past 30 years, applied tracers have been used increasingly to understand solute transport phenomena in porous media and fractured rock aquifers, motivated primarily by environmental concerns related to disposal of radioactive and other wastes. For example, the well-known large-scale tracer experiments conducted at the Borden, Cape Cod, and Macro Dispersion Experiment (MADE) sites in the 1980s (Sudicky 1986; LeBlanc et al. 1991; Boggs et al. 1992, respectively) were designed to compare observed field-scale solute dispersion to macrodispersion predicted by stochastic analysis of independently-measured aquifer heterogeneity. These experiments have resulted in numerous important publications investigating the significance of local geologic heterogeneity, large-scale hydraulic conductivity trends, sorption, and rate-limited processes on solute transport. The results of these tests have also been used to evaluate the performance of numerical contaminant transport models.

Tracing as a hydrogeologic investigative tool has grown significantly, and over the past decade, many new applications of applied tracers have been developed to investigate advanced transport phenomena, including multi-species reactive transport, colloid-facilitated transport, pore-scale mixing, and fracture-matrix control. This increase in tracer research is indicated by the increase in the number of papers. The increase of papers published in *Hydrogeology Journal* and other groundwater-related journals over the past decade that incorporate either an applied tracer technique as part of a broader hydrogeological investigation or specifically develop a new use of applied tracers in hydrogeology. For example, Aggarwal

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(2002) noted a massive increase in papers using tracers, between 1965 and 1970: 650 papers were published in the general hydrology literature that utilized (applied and natural) isotope tracers. His analysis then showed that for the period 1995–2000, over 6,500 papers were published using isotope tracers in groundwater studies alone.

Although a potentially powerful technique, tracer testing also offers unique challenges and limitations. In particular, successful testing is predicated on careful and appropriate design, which generally requires some initial site hydrogeologic information and preliminary transport modeling. In many applications the practical and cost limitations may limit the distance and time scale of experiments, which may then require extrapolation of test results to predict large-scale solute transport and fate. Furthermore, accurate interpretation of tracer test results may be difficult when multiple transport processes are significant and may require sophisticated data interpretation techniques. An important point that is underscored by these challenges is the need to develop focused tracer test training opportunities in university programs and the professional arenas. This is now beginning within the UNESCO and IAEA Joint International Isotopes in Hydrology Program (JIIHP), whose main goal is to infuse hydrological education programs worldwide with (applied and natural) tracer understanding and approaches.

However, despite the potential challenges and limitations of tracer approaches, it is believed that applied tracers have a bright future in hydrogeology, both in commonplace site investigations and in fundamental hydrogeological research. The following sections of this essay discuss both specific applied tracer techniques that are likely to become routinely applied tools and possible new sophisticated tracer methods that may be used to uniquely address important future research problems.

Tracers as a common hydrogeologic tool

As noted previously, applied tracers have been used extensively for many years to characterize flowpaths in karst aquifers. However, they will increasingly be considered a standard hydrogeologic characterization tool for other aquifer types, particularly at contaminated sites to obtain basic aquifer characterization information (groundwater velocity, hydraulic connection) and in the development of conceptual site models, calibration of numerical flow and transport models, and assessment of contaminant-related risk. Single-well tracer test methods (Drost et al. 1968; Hall 1993; Brainerd and Robbins 2004) are especially promising because they are simple and inexpensive and can be used to characterize local and spatial variations in groundwater velocities and other hydrogeological properties. Applied tracers will also be used increasingly to evaluate remediation strategies and engineered system performance. For example, tracers can be used to assess in-situ contaminant biodegradation, electron acceptor/donor utilization rates, dilution effects, and zones of influence for enhanced biodegradation techniques (Brusseau et al. 1999; Schürmann et al. 2003; Alter et al. 2003). Because long-term tracer sources are easy and inexpensive to maintain and low concentrations are easily detected for dissolved gas tracers such as helium and sulfur hexafluoride, Sanford and Solomon (1998) suggest their use to evaluate hydraulic capture and to demonstrate contaminant containment. During the past decade, phase-partitioning tracers have been used to quantify subsurface volume and interfacial area of nonaqueous phase liquid (NAPL) (see Rao et al. 2000 and Brusseau et al. 2003 for summaries of these types of techniques); however, the relatively high cost and uncertainties associated with these techniques will likely limit their use to a relatively small percentage of sites.

In many arid areas with large and growing populations, there is growing interest in developing strategies for enhancing recharge of excess surface water to groundwater (either through infiltration ponds or injection wells) in order to increase storage capacity. Applied tracers will be used to characterize critical aquifer and hydraulic characteristics (residence times, flowpaths, permeability changes, etc.) and facilitate efficient management of these operations (Heilweil et al. 2004; Clark et al. 2004). Applied tracer tests will also increasingly be used to assess aquifer vulnerability, particularly as the perception of terrorism-related threats to public water supplies increases. For example, in April 2003, the U.S. Geological Survey conducted a supply wellfield tracer test where unexpectedly short travel times and high tracer concentrations were observed and the drinking water was unintentionally dyed red for nearly a million people in Miami-Dade County, Florida (USA) (see S.S. Papadopulos & Associates 2004). This study has been widely covered by the local media and has generated notable public interest regarding general security of public water supplies (Sierra Club 2004; NBC6 2004). This example shows the potential for tracer tests to communicate water resource concerns and generate public interest; however, it also underscores the challenge of planning and predicting the outcome of a tracer test. Tracers used in aquifer vulnerability assessments will include constituents specifically designed to assess potential bacterial and colloid-facilitated transport (spores, bacteriophages, microspheres, etc.), as well as conventional conservative-type tracers.

While whole watershed tracer applications are yet to be implemented, many studies at the plot and hillslope scale are using applied dye tracers to infer flow pathways and groundwater recharge processes (Flury and Wai 2003; Weiler and Fluehler 2004). For surface water–groundwater interaction studies, applied chemical tracers are proving to be particularly useful for quantifying these linkages. Perhaps the most common anthropogenic tracers at the watershed scale have been 1960s era bomb tritium releases and more recent chlorofluorocarbon emissions. While these are not applied tracers senso stricto (since they were not *intentionally* applied), they do continue to provide useful watershed scale applications for groundwater dating. Tritium/helium-3 ($^{3}H/^{3}He$) and chlorofluorocarbon (CFCs, CFC-11, CFC-12, CFC-113) are now

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regularly used to date the young fraction of groundwater mixtures (Cook et al. 1997).

Tracers in hydrogeologic research

Although transport processes in porous media are reasonably understood, significant fundamental questions remain regarding transport in highly heterogeneous systems and fracture rock aquifers, and this is one of the most promising areas for applied tracers in hydrogeological research. In fact, the topic of the National Ground Water Association (2004) Darcy Lecture focuses specifically on the issue of apparent solute dispersion observed in fracture-rock tracer tests (Shapiro 2004). During the past 30 years, applied tracer tests have dramatically influenced the understanding of solute transport processes in porous media aquifers. In particular, the well-known comprehensive large-scale tracer tests conducted at the Borden, Cape Cod, and the MADE sites provided critical understanding of field-scale dispersion and mixing, and provided a basis of evaluating stochastic analysis of field hydraulic conductivity data, laboratory-scale experiments, and numerical modeling efforts. Cherry (2003) and many others recommend that equivalent-scale tests are needed to understand field-scale dispersion and other transport processes in fractured rock aquifers.

Another particularly exciting area of hydrogeologic research is the application of "intelligent" and other specialized tracers to investigate focused research questions. In particular, the use of nanotechnology is especially promising for characterizing various hydrogeolochemical phenomena. The biomedical industry has already developed numerous applications for nanotechnology in drug delivery that could be readily adapted for hydrogeological research. For example, chemo-selective nano-scale tracers could be constructed specifically to characterize or record in situ geochemical conditions. These types of tracers could be useful for understanding chemically heterogeneous systems and reactive species transport. However, addressing potential environmental, human health, regulatory, and public concerns regarding the use of more exotic tracers, particularly tracers based on nanotechnology, may be challenging (Holmbeck-Pelham et al. 2000; Weiss 2004; Feder 2004). There are numerous other areas where the use of specialized tracers is promising, however, previous work indicates there is particular opportunity in the following specific research areas: colloid- and natural organic matter (NOM)-facilitated transport (McCarthy et al. 1998), microbe mobility (Ryan et al. 1999), pore-scale mixing of conservative and reactive species (Jose and Cirpka 2004), the observed correlation of solute mass transfer timescales to residence times (Haggerty et al. 2004), pH- or redox- dependent species mobility (Kent et al. 2002), and biogeochemical processes in the hyporheic zone (McKnight et al. 2002).

Finally, there is significant potential to increase the general utility and power of applied tracer tests through the development of improved test design/optimization and data interpretation methods. For example, Field (2001, 2003) discusses the limits of simple algebraic expressions for estimating tracer mass recovery and the advantages of test design based on physically appropriate modeling. Notable opportunity exists to develop more sophisticated data interpretation methods to extract additional information from tracer data, such as inverse modeling using three-dimensional tracer concentrations and the use of higher-order temporal moments (Jawitz et al. 2003). Another example is the need to develop more sophisticated methods to better distinguish physical and chemical transport processes, particularly those processes that contribute to "heavy" tailing characteristics of tracer breakthrough curves (Harvey and Garabedian 1991). Fractal tailing behavior of subsurface tracers has also been revealed using new and sophisticated spectral analysis techniques (Kirchner 2000). Many previously developed tracer test techniques may be further strengthened by improving chemical analysis methods. Finally, there is much potential to develop robust techniques to deal with missing or imperfect tracer breakthrough data (Helms 1997), and additional work is needed to develop and evaluate systematic methods, including error propagation and sensitivity analysis, to quantify tracer test uncertainties.

Conclusions

Applied tracers tests are powerful investigative tools, and have a surprisingly long history of application in hydrogeology. They are particularly powerful for investigating solute transport processes because the tracer source term is well characterized and the tracers can be specifically selected based on desired physical and geochemical properties. Although there are important challenges and limitations associated with tracer testing, the significance of these challenges is case-specific and there are many applications where tracer tests clearly provide the most reliable information. Applied tracers will increasingly become a common hydrogeological investigation tool, especially for the characterization and management of contaminated sites. Further, applied tracers will play a critical role in understanding broad fundamental processes, such as recharge and solute dispersion in fractured rock. They also offer significant potential for addressing very focused research questions, particularly with the use of intelligent and specialized tracers for characterizing complex solute transport phenomena. Advances in tracer test design/optimization and data interpretation methods will further increase the power of the technique.

References

Aggarwal P (2002) Isotope hydrology at the International Atomic Energy Agency. Hydrological Proc 16(11):2257–2260

Alter SR, Brusseau ML, Piatt JJ, Ray-Maitra A, Wang J-M, Cain BR (2003) Use of tracer tests to evaluate the impact of enhanced-solubilization flushing on in-situ biodegradation. J Contam Hydrol 64:191–202

Boggs JM, Young SC, Beard LM, Gelhar LW, Rehfeldt KR, Adams EE (1992) Field study of dispersion in a heterogeneous aquifer. 1. Overview and site description. Water Resour Res 28(12):3281–3291

Brainerd RJ, Robbins GA (2004) A tracer dilution method for fracture characterization in bedrock wells. Ground Water 42(5):774–780

Brusseau ML, Piatt JJ, Wang J-M, Hu MQ (1999) A biotracer test for characterizing the in-situ biodegradation potential associated with subsurface systems. In: Brusseau ML, Sabatini DA, Geirke JS, Annable MD (eds) Innovative subsurface remediation: field testing of physical and chemical, and characterization technologies. Oxford University Press, Washington, DC. Am Chem Soc Symp Series 725, Chapter 17, pp 240–264

Brusseau ML, Nelson NT, Costanza-Robinson MS (2003) Partitioning tracer tests for characterizing immiscible-fluid saturations and interfacial areas in the vadose zone. Vadose Zone J 2:138–147

Cherry JA (2003) The role of field experiments in elucidation of dispersion in sandy aquifers. Geol Soc Am Abstr with Programs, 2003 Annual Meeting, Seattle, WA, November 2–5, 2003

Clark JF, Hudson GB, Davisson ML, Woodside G, Herndon R (2004) Geochemical imaging of flow near an artificail recharge facility, Orange County, California. Ground Water 42(2):167–174

Cook PG, Solomon DK (1997) Recent advances in dating young groundwater: chlorofluorocarbons, $^{3}H/^{3}He$ and ^{85}Kr. J Hydrol 191:245–265

Drost W, Klotz D, Koch A, Moser H, Neumaier F, Rauert W (1968) Point dilution methods of investigating ground water flow by means of radioisotope. Water Resour Res 4(1):125–146

Divine CE, McCray JE, Boving T, Blitzer D, Wolf Martin L, Brusseau ML, Blanford W (2004) Partitioning tracer tests as remediation metric: case study at Naval Amphibious Base Little Creek (NABLC), Virginia. Remed J 14(2):7–31

Feder T (2004) Scholars probe nanotechnology's promise and its potential problems. Phys Today, June 2004, pp 30–33

Field MS (2001) Efficient hydrologic tracer-test design for tracer-mass estimation and sample collection frequency, 1. Method development. Environ Geol 42:827–838

Field MS (2003) A review of some tracer-test design equations for tracer-mass estimation and sample-collection frequency. Environ Geol 43:867–881

Flury M, Wai NN (2003) Dyes as tracers for vadose zone hydrology. Rev Geophys 41(1):1002, DOI:10.1029/2001RG000109

Grisak GE, Merritt WF, Williams DW (1977) A fluoride borehole dilution apparatus for groundwater velocity measurements. Can Geotech J 14:554–561

Haggerty R, Harvey C, Von Schwerin C, Meigs L (2004) What controls the apparent timescale of solute mass transfer in aquifers and soils? A comparison of experimental results. Water Resour Res 40(1), DOI:10.1029/2002WR001716

Harvey RW, Garabedian SP (1991) Use of colloid filtration theory in modeling movement of bacteria through a contaminated sandy aquifer. Environ Sci Technol 25(1):178–185

Heilweil VM, Solomon KD, Perkins KS, Ellett KM (2004) Gas-partitioning tracer test to quantify trapped gas during recharge. Ground Water 42(4):589–600

Hall SH (1993) Single well tracer tests in aquifer characterization. Ground Water Monit Remed, Spring, 118–124

Helms AD (1997) Moment estimates for imperfect breakthrough data: theory and application to a field-scale partitioning tracer experiment. ME Thesis, University of Florida

Holmbeck-Pelham SK, Rasmussen TC, Fowler LA (2000) Regulation of injected ground water tracers. Ground Water 38(4): 541–549

Horton JH, Hawkins RH (1965) Flow path of rain from the soil surface to the water table. Soil Sci 100:377–383

Jawitz JW, Annable MD, Demmy GG, Rao PSC (2003) Estimating nonaqueous phase liquid spatial variability using partitioning tracer higher temporal moments. Water Resour Res 39(7): SBH1–19

Jose SC, Cirpka OA (2004) Measurement of mixing-controlled reactive transport in homogeneous porous media and its prediction from conservative tracer test data. Environ Sci Technol 38(7):2089–2096

Kass W (1998) Tracing technique in geohydrology. Balkema, Rotterdam, The Netherlands, 581 pp

Kent DB, Davis JA, Anderson LCD, Rea BA, Coston JA (2002) Effect of adsorbed metal ions on the transport of Zn- and Ni-EDTA complexes in a sand and gravel aquifer. Geochim Cosmochim Acta 66(17):3017–3036

Kirchner JW, Feng XH, Neal C (2000) Fractal stream chemistry and its implications for contaminant transport in catchments. Nature 403:524–527

LeBlanc DR, Garabedian SP, Hess KM Gelhar LW, Quadri RD, Stollenwork KG, Wood WW (1991) Large-scale natural gradient tracer test in sand and gravel, Cape Cod, Massachusetts, 1. Experimental design and observed tracer movement. Water Resour Res 27(5):895–910

McCarthy JF, Sanford WE, Stafford PL (1998) Lanthanide field tracers demonstrate enhanced transport of transuranic radionuclides by natural organic matter. Environ Sci Technol 32(24):3901–3906

McKnight DM, Hornberger GM, Bencala KE, Boyer EW (2002) In-stream sorption of fulvic acid in an acidic stream: a stream-scale transport experiment. Water Resour Res 38:10.1029

NBC6 (2004) The red dye test: environmentalists say drinking water is at risk. Accessed online May 20, 2004 at http://www.nbc6.net/ecowatch/3267475/detail.html

Rao PSC, Annable MD, Kim H (2000) NAPL source zone characterization and remediation technology performance assessment: recent developments and applications of tracer techniques. J Contam Hydrol 45:63–78

Rasmussen TC, Baldwin RH, Dowd JF, Williams AG (2000) Tracers vs. pressure wave velocities through unsaturated saprolite. Soil Sci Soc Am J 64:75–85

Ryan JN, Elimelech M, Ard RA, Harvey RW, Johnson PR (1999) Bacteriophage PRD1 and silica colloid transport and recovery in an iron oxide-coated sand aquifer. Environ Sci Technol 33(1):63–73

Shapiro AM (2004) Recent advances in characterizing ground water flow and chemical transport in fractured rock: from cores to kilometers. National Ground Water Association 2004 Darcy Lecture, Colorado School of Mines, Golden, CO, March 5, 2004

Sanford WE, Shropshire RG, Solomon DK (1996) Dissolved gas tracers in groundwater: simplified injection, sampling, and analysis. Water Resour Res 32(6):1635–1642

Sanford WE, Solomon DK (1998) Site characterization and containment assessment with dissolved gases. J Environ Eng 124(6):572–574

Schürmann A, Schroth MH, Saurer M, Bernasconi SM, Zeyer J (2003) Nitrate-consuming processes in a petroleum-contaminated aquifer quantified using push-pull tests combined with ^{15}N isotope and acetylene-inhibition methods. J Contam Hydrol 66:59–77

Sierra Club (2004) Everglades: protecting the wetlands, preserving Florida's drinking water. Accessed online on August 23, 2004 at http://www.sierraclub.org/communities/fl/everglades.asp

S S Papadopulos & Associates, Inc. (2004) Evaluation of tracer tests conducted at the Northwest Wellfield, Miami-Dade County, Florida

Sudicky EA (1986) A natural gradient experiment on solute transport in a sand aquifer: spatial variability of hydraulic conductivity and its role in the dispersion process. Water Resour Res 22(13):2069–2082

Weiler M, Fluehler H (2004) Inferring flow types from dye patterns in macroporous soils. Geoderma 120:137–153

Weiss R (2004) Tiny, mighty science: nanotechnology raises hopes–as well as fears–of long-term damage. The Washington Post National Weekly Edition, April 5–11, 2004, pp 6–8

Zimmermann U, Munnich KO, Roether W, Kruetz W, Schubach K, Siegel O (1966) Tracers determine movement of soil moisture and evapotranspiration. Science 152(3720):346–347

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