Lanthanide-Labeled Clay: A New Method for Tracing Sediment Transport in Karst

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Abstract

Mobile sediment is a fundamental yet poorly characterized aspect of mass transport through karst aquifers. Here the development and field testing of an extremely sensitive particle tracer that may be used to characterize sediment transport in karst aquifers is described. The tracer consists of micron-size montmorillonite particles homoionized to the lanthanide form; after injection and retrieval from a ground water system, the lanthanide ions are chemically stripped from the clay and quantified by high performance liquid chromatography. The tracer meets the following desired criteria: low detection limit; a number of differentiable signatures; inexpensive production and quantification using standard methods; no environmental risks; and hydrodynamic properties similar to the in situ sediment it is designed to trace. The tracer was tested in laboratory batch experiments and field tested in both surface water and ground water systems. In surface water, arrival times of the tracer were similar to those of a conservative water tracer, although a significant amount of material was lost due to settling. Two tracer tests were undertaken in a karst aquifer under different flow conditions. Under normal flow conditions, the time of arrival and peak concentration of the tracer were similar to or preceded that of a conservative water tracer. Under low flow conditions, the particle tracer was not detected, suggesting that in low flow the sediment settles out of suspension and goes into storage.

Introduction

Sediment and sediment surfaces are a fundamental control on the transport and fate of organic contaminants. In porous media aquifers, sediments retard contaminant transport because of sorption and partitioning to immobile solid-phase surfaces. In karst aquifers, in contrast, a wide range of sediments are mobile (Gale 1984; Thrailkill 1989; White and White 1968), and suspended solids may thus act as vectors for contaminant transport. In these systems, settling of contaminated sediment may result in temporary storage of contaminants that may later remobilize during a storm event. Runoff events often result in a temporary but dramatic increase in suspended sediment concentrations in karst springs (Ryan and Meiman 1996). Sediments with a surface origin, in particular, have the potential to introduce hydrophobic contaminants into the karst system (Mahler 1997). The movement of sediment, therefore, may be intimately connected with the movement of sediment-associated contaminants in a conduit flow aquifer. Behavior of the clay-size fraction is of particular interest as this is the size fraction most likely to transport contaminants, because of its high surface area-to-volume ratio (McCarthy and Zachara 1989).

While water flow in karst aquifers can be characterized with readily available solution tracers, little is known about the source and movement of sediment. Anecdotal evidence of sediment discharging at springs is common, in particle sizes ranging from clay to boulders, but sediment source, subsurface residence time, and transport distance have not been characterized (White 1988). Existing sediment tracers are limited in their detectability and flexibility, and karst sediment transport dynamics remain largely a mystery. This paper describes the development and testing of a new tracer technology that uses lanthanide element-labeled clay to characterize transport of the small-size sediment fraction in a karst aquifer.

An ideal sediment tracer should meet several criteria. First, it should have a low detection limit so that it can be used in small quantities and be sensitively identified. Second, it should be available with several differentiable signatures to avoid cross-interference of tracers. Third, it should be simple and inexpensive to produce, detect, and quantify, preferably by standard in-house analytical methods. Fourth, it should be environmentally benign. Finally, it should have physical characteristics similar to the sediment that it is intended to mimic. A variety of particle tracers has been developed in the last 30 years for a variety of uses (Table 1). Each of these tracers has provided some information on sediment movement, but their usefulness in karst aquifers is limited by poor detectability, inappropriate physical characteristics, or requirement of complex or expensive analytical procedures.

Colored lycopodium spores are the only particulate tracers used previously in karst aquifers (e.g., Drew and Smith 1969; Aley and Fletcher 1976; Atkinson et al. 1973). They may be dyed up to five different colors to avoid cross-interference, are nontoxic, and pose no health threat (Davis et al. 1985). They present limitations, however, in their utility for tracing sediment through karst aquifers. First, lycopodium spores are difficult to use: coloring the spores is laborious; there is a high potential for contamination of samples; and detection is done manually under a microscope following filtration and centrifugation (Davis et al. 1985). Second, being composed of

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Table 1
Extant Particle Tracers and Characteristics

Particle Type	Detection Method	Detection Sensitivity	Size	Specific Gravity	Advantages	Disadvantages
Sand labeled with Ir-192 (Sayre and Hubbell 1965)	Scintillation detector	N/A	0.1–1.2 mm	2.65	Radioactivity measured in situ	Environmental/regulatory difficulties
Fluorescent sand (Kennedy and Kouba 1970) (Ingle 1966) (Rathbun et al. 1971)	Manual counting	100 ng/g	0.15–1.3 mm	2.65	Inexpensive Different colors available	Limited to sand-size Paint flakes off Labor-intensive detection
Lycopodium spores (Atkinson et al. 1973)	Manual counting	N/A	30 μm	~1	Six colors available	Single size only Low density
Baker's yeast (Wood and Ehrlich 1978)	Manual counting	N/A	2–3 μm	~1	Appropriate size	Low specific gravity Only one signature available Labor-intensive detection
Fluorescent plastic (Carey 1989)	Filter fluorometry	N/A	3–6 μm	1.4	Different colors available Appropriate size	Low specific gravity
Lanthanide oxides (Krezoski 1989)	Instrumental neutron activation analysis	N/A	N/A	8.35	Sensitive Automated detection	High specific gravity Detection expense
Luminophores (Gerino 1990)	Manual counting	N/A	10–200 μm	N/A		Labor-intensive detection
Plastic microtaggants (Wheatcroft 1991)	Manual counting	N/A	50–180 μm	1.4	Inexpensive	One color, large size Large size Labor-intensive detection
Glass beads (Wheatcroft 1992)	Manual counting	N/A	8–420 μm	2.4	Inexpensive Correct density Several size ranges	Labor-intensive detection
Gold/silver doping (Olmez et al. 1994) (Wheatcroft et al. 1994)	Instrumental neutron activation analysis	0.1–1 ng/g	38–125 μm	Same as sediment	Mimics natural sediment Automated Sensitive detection	INAA costs Limited to two tracers Can't use on carbonate sediment
Carboxylate-modified polystyrene latex (Reimus et al. 1996)	Flow cytometry	N/A	0.3–1 μm	~1		Not yet field tested Low density Flow cytometry not readily available

cellulose, their specific gravity is close to that of water, and they therefore have a tendancy to remain in suspension, better mimicking the behavior of water than that of sediment.

Lanthanide tracers have shown great promise as environmental tracers of aerosols, chemical wastes, and herbicide dispersal (Loveland 1989) because of their low cost, nontoxicity, and sensitive detection. Lanthanide oxides mixed with natural fine-grained sediments were used by Krezoski (1989) to measure sediment reworking and transport in the Great Lakes. Lanthanide oxides, however, have a specific gravity several times greater than that of natural sediment, so while they may be serviceable in evaluating bioturbation, they are less useful in studies of transport of suspended sediment.

The lanthanides comprise a group of elements, periodic numbers 57 through 71, which have similar geochemical properties. They have two important chemical characteristics that allow them to be incorporated into the clay lattice: they are all trivalent at earth surface conditions, and they have an ionic radius in eight-fold coordination ranging from 0.87 (Sc^{3+}) to 1.16 (La^{3+}), similar to that of Ca^{2+}. Their low abundance in carbonate rocks enhances their use as tracers in karst aquifers.

The lanthanide ions are readily accepted into the montmorillonite lattice. Bruque et al. (1980) found that the replacement of H^+ by Ln^{3+} was rapid. They also found that the exchange process ceased after 80% of the cation exchange capacity (CEC) was reached when up to a 12 symmetry (S, where one symmetry addition is equal to the CEC of the montmorillonite) solution for saturation, but when an 18 S solution was used, 100% CEC was reached. They attribute this to exchange of the lanthanide ion for Al^{3+} at the higher symmetry addition, and note that it can be achieved at 7 to 10 S if the pH is kept near 5. At $pH > 5$ they found that lanthanide hydroxide precipitated and aluminization occurred at a $pH < 2$. At an optimum pH of 4 to 5, 5 S was sufficient for saturation of the CEC, and with greater S they were able to induce up to 146% saturation of the CEC, probably as a result of precipitation of lanthanide hydroxide.

The lanthanide-labeled clay tracer described here was developed specifically to characterize sediment transport in karst. Lanthanide cations are intercalated into montmorillonite clay, replacing the original interlayer cations. After collection of the sediment sample, the interlamellar lanthanide is removed from the clay lattice by complexation and quantified by simple high performance liquid chromatography (HPLC) techniques. The tracer is detectable at low concentrations, can be synthesized with a number of different signatures, is physically similar to ambient sediment, and is environmentally nonhazardous. The tracer is straightforward to prepare and detect, and its detection is reasonably sensitive. Here we describe the tracer methodology and the results of field trials in surface and ground water.

Materials and Methods

Preparation of the Lanthanide Montmorillonite

Wyoming montmorillonite (SWy-2, University of Missouri-Columbia Source Clay Minerals Repository) was homoionized to the lanthanide form following the method of Bruque et al. (1980). Montmorillonite clay (40 g) was first dispersed in 1 L of water, sonicated for five minutes, then shaken overnight on a wrist shaker. All water used throughout the process was Type III reagent water. Organic matter was oxidized using hot 10% hydrogen peroxide (Paecht-Horowitz and Eirich 1988), and the 0.1 to 1.1 μm fraction (equivalent spherical diameter) was isolated by centrifugation. The organic-free fine fraction was then homoionized to the sodium form by washing twice in 2 N NaCl-0.1 N HCl solution, twice in a 2 N NaCl solution, and then repeatedly in water until the specific conductivity was less than 10 μs. The volume was adjusted with water to make a 1% clay solution by weight, and the clay suspension homoionized to the H-form using Dowex 50-WX-8 resin in the hydrogen form (0.6 mL resin/gram clay) (Aldrich and Buchanan 1958).

The H-montmorillonite was homoionized to the desired lanthanide form by saturating it with the chloride form of the lanthanide element, here either cerium chloride (Sigma), neodymium chloride (Aldrich), or lanthanum chloride (Sigma). A 2 S solution of the lanthanide salt (here S is equivalent to the CEC of the montmorillonite, ~1.2 mEq/g) was added to the clay and shaken for 20 minutes. The clay was isolated by centrifugation, then resuspended in an 8 S solution, agitated, and isolated by centrifugation. The lanthanide montmorillonite was then repeatedly washed with water and centrifuged until the supernatant had a specific conductance of < 10 μs. Before deployment, the clay tracer was equilibrated with water from the sampling site for 24 hours, and the supernatant was examined at regular intervals for dissolved lanthanide. If the tracer was found to be stable in the target solution matrix, the clay solution was then centrifuged, the supernatant removed, and the clay resuspended in the sampling site water to 1% by weight and shaken on a wrist shaker for 30 minutes until dispersed.

The degree of lanthanide saturation was checked by stripping the lanthanide ions from the clay for analysis using 300 millimolar hydroxyisobutyric acid (HIBA) (Aldrich), 10 mM sodium octanesulfonate (Kodak) at pH 3.8 (the same solution used as the HPLC mobile phase): one mL of the 1% by weight clay suspension was diluted 1:1000 with HIBA in a 1.5 mL eppendorf tube, vortexed for 15 seconds, then rotated overnight at 8 rpm. The tubes were centrifuged for five minutes at 14,000 rpm, and 300 μL of the supernatant removed for analysis.

Laboratory Batch Tests

The stability of the lanthanide clay was examined in the laboratory using batch suspensions of Ce-montmorillonite in distilled water, sea water, and solutions covering a range of ionic strength, pH, and calcium concentration (Table 2). Fifteen microliters of the 1% clay suspension was diluted to a total volume of 1000 μL with the desired solution in a 1.5 mL eppendorf tube. The samples were vortexed for 15 seconds and then rotated at 8 rpm. The amount of clay used was determined by computing the quantity required to allow detection of a release of as little as 0.4% of the CEC. For comparison, 1 μL of the 1% by weight clay solution was also diluted to 1000 μL in HIBA. Each sample was run in triplicate. After 48 hours, 500 μL was removed, centrifuged at 14,000 rpm for five minutes, and 300 μL of the supernatant was removed for analysis. After a total of seven days, the remaining 500 μL was centrifuged and the supernatant was removed for analysis.

Lanthanide Detection and Quantification

Lanthanides in the supernatant HIBA solution were separated by isocratic HPLC on a Waters Resolve C_{18} column. The mobile phase was 300 millimolar HIBA, 10 mM sodium octanesulfonate at pH 3.8, at a flow rate of 0.8 mls/min. Detection of the separated lanthanides was by absorbance at 658 nm after post-column complexation by arsenazo III (Millipore Corp. 1989). Multipoint calibration curves were constructed using NBS traceable lanthanide standards (Aldrich); method detection limit for lanthanum, cerium, and neodymium was ~1 ng (~10 μg/L using a 200 μL injection size). Background sediments, extracted using the above procedure, did not interfere with the target lanthanides.

This method was developed to rapidly analyze only the five lightest lanthanide elements with good detectability. The background lanthanide content, however, may require the use of heavier lanthanides. An alternate method, using a gradient elution, can detect all of the lanthanide elements in a single run, with detection limits of 5 to 50 μg/L (Millipore Corp. 1989). The gradient method is slower, however, because of the equilibration time between gradient runs.

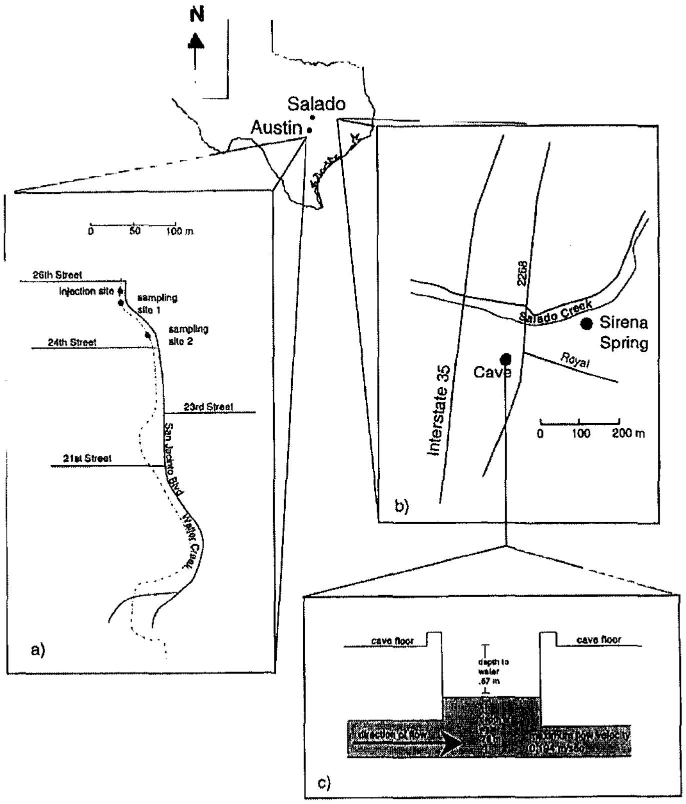

Figure 1. Locations of the surface water (a) and ground water (b) traces. Also shown is a schematic diagram of the well inside the cave (Salado, Texas) (c). Water depth and flow velocity shown are for conditions in November 1996.

Table 2
Chemistry of Solutions Used to Test Stability of Ce-montmorillonite in Batch Experiments.

$CaCl_2$ (pH=6.5, I=0.026)	pH (I=0.026)
0.5 mM	5.5
1.0 mM	6.5
5.0 mM	7.5

I (pH=6.5)
0.0159 (1 mM $NaNO_3$)
0.0262 (10 mM $NaNO_3$)
0.1210 (100 mM $NaNO_3$)

All solutions were buffered to the desired pH with sodium phosphate salts. Ionic strength (I) was held constant in the pH and $CaCl_2$ solutions at I=0.026 with the addition of $NaNO_3$.

Field Tracer Tests

One surface and two subsurface field tracer tests were completed and evaluated. For the surface water experiment, neodymium-labeled montmorillonite was tested in Waller Creek, a small urban creek in Austin, Texas (Figure 1). A stretch of approximately 65 m was chosen through which the water flowed without pooling, with sample stations established at 15 m and 65 m downstream of the injection site. To determine discharge and travel times to the two sampling stations, a dilute salt tracer was released one hour prior to the clay tracer and dilution measured by conductance. The clay tracer was 105 mL of 1% Nd-montmorillonite. Because of the small size of the creek, 60 mL samples were collected at the near sampling station and 1 L samples were collected at the far sampling station by grab-sampling. The sample stations were both at locations where all the creek flow was directed over a lip of rock into a single homogeneous stream; the samples were collected by holding the sample bottle under the middle of this stream. The clay fraction was isolated in the laboratory by syringe filtration of the 60 mL samples through a 25 mm diameter, 0.22 µm nylon filter and by vacuum filtration of the 1 L samples through a 47 mm diameter, 0.22 µm nylon filter.

The subsurface sediment traces were carried out at Sirena Spring in Salado, Texas, part of the northernmost set of major springs in the Edwards (Balcones Fault Zone) aquifer of central Texas (Figure 1). Prior water tracing had confirmed that Sirena Spring is hydraulically connected via a subsurface conduit to an upgradient uncased well in a cave 219 m southwest of the spring. The water level in the well is 1.7 to 2.7 m higher in elevation than the spring, depending on the season.

For the first trace, 900 mL of a 1% by weight suspension of Ce-montmorillonite was flushed into the open well. This was followed 75 minutes later with 50 mL of rhodamine WT as a water tracer and 6 kg of powdered silica as a nonlabeled sediment tracer. (Rhodamine WT was used in lieu of NaCl for the subsurface traces, as it is one of the most commonly used tracers in karst terrain.) The second trace was performed at the same location; therefore, Nd-montmorillonite was used to avoid any possible cross-interference with the previous trace. For this trace, injection of 1100 mL of a 1% by weight suspension of Nd-montmorillonite was followed 75 minutes later by the injection of 30 mL of rhodamine WT. Powdered silica was not used for the second trace. For both subsurface traces, each sample of ~2.5 L was collected through the intake hose of a peristaltic pump which was inserted down into the limestone crevice from which the spring issues; the samples were field-filtered directly onto 47 mm diameter, 0.22 µm nylon filter membranes.

After filtration, loaded filters were placed in 1.5 ml acid-washed eppendorf tubes containing 0.5 mL of the HPLC mobile phase, and the eppendorf tubes were turned on a rotater overnight at 8 rpm. The tubes were then centrifuged at 14,000 rpm for 10 minutes to isolate the stripped clay, and 300 µL of the supernatant was pipetted off for analysis by HPLC. The optical solution tracers were quantified directly by filter fluorometry.

Results

Tracer Stability and Detection

After seven days, only one of the 30 batch suspensions (Table 2) had released any detectable lanthanide. The exception was one of the three 48-hour suspensions in sea water, which released an amount of cerium representing 11.6% of the montmorillonite CEC (0.59 mg Ce/L solution or 3.95 mg Ce/g clay); however, the remaining two samples of that triplicate set and all three of the seven-day samples showed no release of cerium. We suspect that the cerium detected in the one sample was the result of the inadvertent injection of a small amount of the clay itself into the HPLC, where the cerium was released immediately upon mixing with the HIBA mobile phase. However, triplicate samples of cerium-montmorillonite suspended in deionized distilled water initially appeared to be less stable than those in the batch suspensions described in Table 2. Cerium was detected in supernatant from all three of the 48-hour deionized distilled water suspensions and two of the three seven-day suspensions; the amount detected averaged 2.9% +/- 1.0 (standard error, hereafter referred to as SE) of the CEC of the montmorillonite (0.15 +/- 0.05 (SE) mg Ce/L solution or 0.99 +/- 0.33 (SE) mg Ce/g clay). We suspected that the apparent release of cerium was caused by poor flocculation of the clay in distilled water, resulting in a small amount of clay being brought back into suspension during the removal of the supernatant and its subsequent injection into the HPLC. Therefore, the experiment was repeated for the distilled water samples, taking care not to disturb the clay after centrifugation; this time cerium was detected in the supernatant from only one of the 48-hour and one of the seven-day samples, suggesting that the lanthanide-clay was indeed stable in all the solutions including distilled water. The stability of lanthanide clay as a tracer was further confirmed by HPLC analysis of supernatant from a one-year-old 1% neodymium-montmorillonite suspension in creek water, in which no neodymium was detected.

Method efficiency was determined in the laboratory using three 1% by weight suspensions of montmorillonite, each homoionized to a different lanthanide form: lanthanum, cerium, or neodymium. The clay suspensions were diluted 1:1000 with HIBA to release lanthanide ions; HPLC detection was performed on an injection of 200 µL of the extract. The extract from the La-montmorillonite contained lanthanum representing 124% of the CEC (0.43 mg La/L of solution or 0.93 mEq La/g clay). The extract from the Ce-montmorillonite (the clay used in the batch experiment) contained cerium representing 89% of the CEC of the clay (0.35 mg cerium/L solution 0.67 mEq Ce/g clay). The Nd-montmorillonite extract contained neodymium representing 82% of the clay CEC (0.29 mg Nd/L solution or 0.61 mEq Nd/g clay).

The final method efficiency and maximum dilution during a particle trace in the field is a function of the suspended solid concentration, the volume of water filtered, the volume of extract, the extraction efficiency, and the HPLC injection size. Given the extraction efficiencies filtering a 2 L water sample, treating the solids obtained with 0.5 mL HIBA, and injecting 200 μL of the extract for analysis, the lanthanide-montmorillonite can be detected at a concentration of about 30 ng La-montmorillonite/L sample, 33 ng Ce-montmorillonite/L sample, or 40 ng Nd-montmorillonite/L sample. This corresponds, during a field trace, to dilution on the order of 10^9 of 1 L of 1% clay suspension. The dilution factor can be improved by filtering a larger volume of solution or by injecting a larger volume into the HPLC.

Surface Water Sediment Tracing

Preliminary analysis of the natural suspended and bedload sediment at Waller Creek, the site of the surface water field test, showed no detectable lanthanide elements or species that might react with the HPLC mobile phase to give a false positive. Breakthrough curves for the sediment tracer (Nd-montmorillonite) and conservative water tracer (NaCl) are shown in Figure 2. Based on dilution of the conservative NaCl tracer, the computed discharge of the creek was 6.3 L/sec ± 0.3 L/sec (SE). Using this discharge and integrating over the sampling interval, 224 mg of Nd-montmorillonite was transported past the sampling site 15 m downstream of the injection point, representing 21% of the total injected. Sixty-five m downstream from the injection point, 34 mg of Nd-montmorillonite traversed the second sampling site, corresponding to 3% of the total injected. Thus, 79% of the sediment tracer settled out of suspension in the first 15 m of the creek, and an additional 18% settled out in the 50 m between the two sample sites. The peak concentration of 0.49 mg/L of Nd-clay was collected one minute 10 seconds after injection at the near sample site; therefore, the clay was diluted by a factor of 2 × 10^4 after 15 m of transport. At the far sample site, the peak concentration of 8 × 10^{-3} mg/L of Nd-clay was collected 15 minutes after injection, a dilution factor of 1.3 × 10^6 after 65 m of transport.

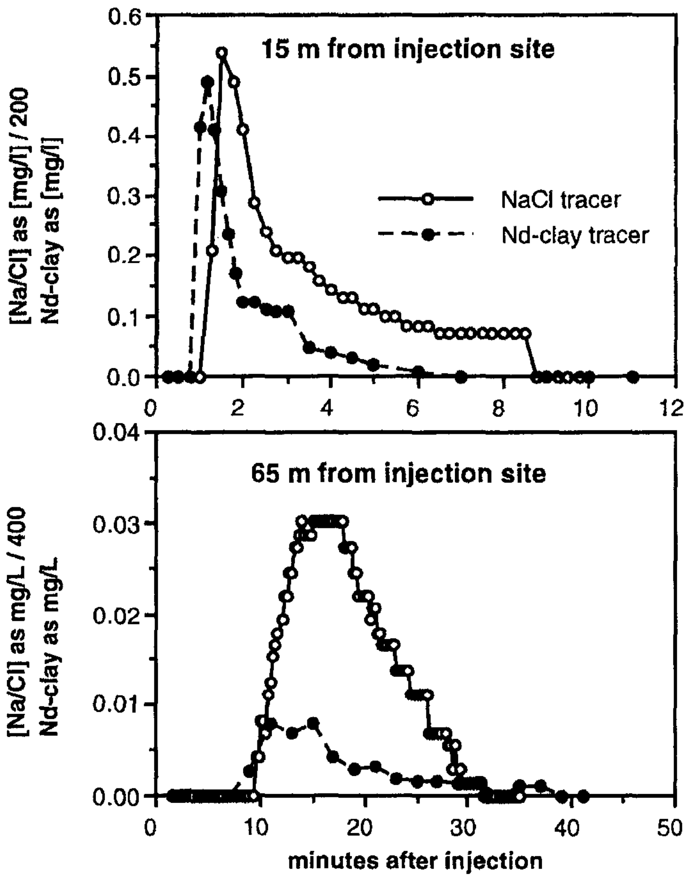

Figure 2. Breakthrough curves for the surface water tracing test, showing results for both the conservative water tracer (NaCl) and particle tracer (Nd-montmorillonite).

The shape of both the particle and water tracer breakthrough curves is similar (Figure 2). The sudden drop-off in NaCl concentration at nine minutes is an artifact of the specific conductance detection system. Both tracers peaked quickly and dropped off only slightly less quickly, and both show a slight leveling off before continuing to decrease back to baseline. Dispersion of both tracers, based on the length of time required to return to baseline, is similar. At the far sample site, both tracers arrived at approximately the same time; it appears that the peak in particle tracer concentration may have preceded the peak in the water tracer concentration, although it is difficult to compare the peaks given the slight drop in concentration of the particle tracer at 13 minutes. Arrival time of the water tracer centroid, however, exceeded that of the particle tracer by 40%.

Subsurface Sediment Tracing

Two subsurface sediment and water traces were performed: the first on December 12, 1995, and the second on May 9, 1996. During this period central Texas was experiencing a drought, which began in the autumn of 1995. From November 1, 1995 to May 31, 1996 there was no significant rainfall. Consequently, the gauged discharge at the spring outlet decreased from 27 L/sec to 14 L/sec between the two traces, and the maximum velocity in the flow conduit in the cave, as measured with a flowmeter over the entire vertical interval of the conduit intersecting the well bore, decreased from 0.18 m/s to 0.14 m/s. In the summer of 1994, in contrast, spring flow was gauged at 95 L/sec and maximum conduit velocity was gauged at 0.44 m/s.

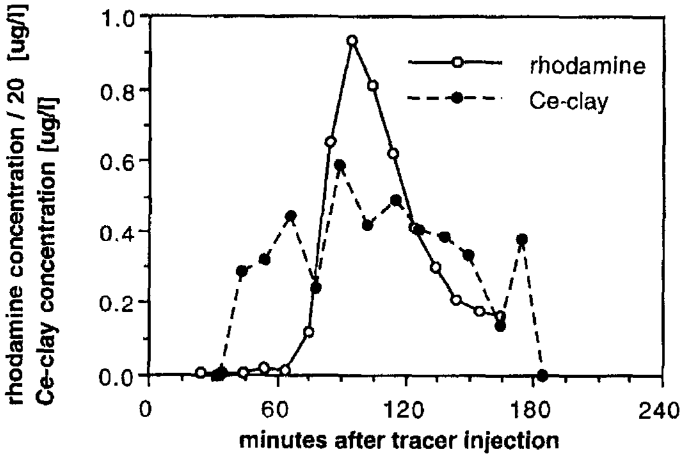

Figure 3. Breakthrough curves for the December 1995 subsurface tracing test, showing results for both water tracer (rhodamine WT) and particle tracer (Ce-montmorillonite).

The breakthrough curves for the first subsurface trace are shown in Figure 3. The Ce-montmorillonite and rhodamine first appeared at 43 and 54 minutes after injection, with peak concentrations at 89 and 94 minutes after injection, respectively. The powdered silica, introduced as an additional particle tracer, was visible in the centrifuge tubes from samples collected 89 and 99 minutes after its injection (corresponding to 164 and 174 minutes after injection of the Ce-clay). Although the natural suspended sediment contained no detectable lanthanide elements, powdered silica, when eluted in HIBA and analyzed by HPLC, was found to produce a broad peak that interfered with the detection of cerium. The arrival of the bulk of the powdered silica may account for the apparent increase in cerium concentration just before its return to baseline.

Rhodamine recovery for the first trace was approximately 2.5% of the rhodamine injected, based on gauged spring discharge of 27 L/sec and integration under the breakthrough curve. Of the Ce-montmorillonite injected into the cave conduit, 83.5 mg was recovered (0.9%). Thus, the total particle tracer recovered was 37% of the total water tracer recovered. The peak concentration of Ce-montmorillonite (0.6 μg Ce-montmorillonite/L of water), collected 89 minutes after its injection, represents a dilution of 1.7×10^7.

During the second tracer test, the rhodamine first appeared 101 minutes after injection and peaked 131 minutes after injection, 37 minutes (or 40%) later than rhodamine peak travel time for the first trace performed five months earlier. The Nd-montmorillonite sediment tracer was not detected.

Discussion

Tracer Stability

The results of the laboratory batch experiments demonstrate that the lanthanide clay tracer is stable in solutions covering a range of pH, ionic strength, and calcium concentration (Table 2). The apparent release of a small amount of lanthanide in the distilled water solutions was likely caused by incomplete clay flocculation resulting in the inadvertent injection of a lanthanide clay particle into the HPLC. This eventuality presents no problem to the sediment tracer user: as any lanthanide clay particles collected in the field are stripped with HIBA and the resulting extract injected into the HPLC, the unintentional injection of a clay particle will not affect the results of the analysis.

Saturation of the montmorillonite with the lanthanides was at least 82% of the CEC for neodymium, 89% of the CEC for cerium, and 124% of the CEC for lanthanum. The over-saturation for lanthanum may have been a result of precipitation of lanthanum hydroxide caused by use of a higher S solution than necessary, as experienced by Bruque et al. (1980). The user of the lanthanide clay tracer should determine the saturation of his or her lanthanide clay before using the tracer, so that the amount of clay recovered from the field trace can be determined.

After preparation of the tracer, the initial wash of the lanthanide clay with water from the sampling site always resulted in the release of a small amount of lanthanide ion. However, after the initial washing, lanthanide ion was not removed by subsequent immersion in the sample site water, suggesting that there is a small percentage of the lanthanide that is mobile due to exchange with calcium in solution, but the stability constant favors the lanthanide elements. It may be that while most of the lanthanide ion replaces cations in the montmorillonite lattice, a small portion is adsorbed to the outer surface of the clay. This surface-adsorbed lanthanide is then available for exchange with calcium, or complexation by carbonate ion in solution (Wood 1990). The ratio of the dissolved to surface-adsorbed species ($[\mathrm{REE}]_{\mathrm{diss}}/[\mathrm{REE}]_{\mathrm{ads}}$) can be determined as described by Erel and Morgan (1991); for this experimental system ($[\mathrm{REE}]_{\mathrm{diss}}/[\mathrm{REE}]_{\mathrm{ads}}$) is approximately 10^{-6}. Thus, the amount of lanthanide that may be released due to this phenomenon is insignificant from the point of view of a sediment tracer.

The extreme efficiency of hydroxyisobutyric acid (HIBA) in complexing lanthanide ions (Elchuk and Cassidy 1979) is the key to the success of this sediment tracer. HIBA is used both to strip the lanthanides from the clay lattice and as the HPLC mobile phase. The HIBA complexed intercalated lanthanides representing more than 80% of the CEC of the montmorillonite, resulting in a low detection limit. Because the HIBA can be added to the sampling filters on-site, the supernatant removed within 24 hours, and directly injected into the HPLC, analysis is quick and simple. The direct complexation of the target elements into the HPLC eluent results in a clean chromatographic baseline and no need for cleanup, matrix matching, or dilution. The HIBA also complexes calcium from solution, however, which elutes in a broad peak at 24 minutes during HPLC (Mahler, unpublished data). We advise flushing the HPLC system for an appropriate amount of time between samples to avoid interference between the late-eluting calcium peak and the following sample. We experienced no interference with ferric iron.

Field Sediment Traces

The results of the surface water trace show that the lanthanide clay tracer can be used to obtain the standard transport parameters generally sought in hydrologic studies, such as travel time for leading edge, peak concentration, centroid, and trailing edge (Table 3). Interestingly, the arrival times of all portions of the particle tracer curve except the trailing edge preceded those of the "conservative"

Table 3
Concentration-Time Curve Data for Water and Particle Tracers in Waller Creek, Austin, Texas

	Elapsed Time (minutes)			
	Leading Edge	Peak	Centroid	Trailing Edge
Station 1				
NaCl	1.25	1.50	2.37	8.75
Nd-clay	1.00	1.00	1.55	11.00
Station 2				
NaCl	9.50	16.25	22.00	31.50
Nd-clay	9.00	15.00	15.50	37.00
	Travel Times (minutes)			
	Leading Edge	**Peak**	**Centroid**	**Trailing Edge**
NaCl	8.25	14.75	19.6	22.75
Nd-clay	8.00	14.00	13.9	26.00

Elapsed times are computed as the difference between arrival times of the different breakthrough curve parameters at sampling stations. Stations 1 and 2 are 15 and 65 m downstream from the injection site, respectively.

solution tracer. Similarly, the arrival and peak of the lanthanide clay tracer preceded that of rhodamine dye during the first subsurface trace through the karst system at Salado. The early arrival of particulates as compared to water tracers has been observed by researchers using baker's yeast (Wood and Ehrlich 1978) and lycopodium spores (Buchtela et al. 1968; Drew 1968; Atkinson et al. 1973). Wood showed that the arrival of baker's yeast preceded that of both bromide and iodide because neither solution tracer was truly conservative, as both were retarded by sorption. The early arrival of lycodium spores remains unexplained (Atkinson et al. 1973). It is possible that during the subsurface tracer test at Salado, the arrival of the rhodamine peak was delayed due to adsorption, although it is unlikely that this was the case with the NaCl in the surface water trace. Whatever the cause, the lag between arrival of the particle and solution tracers in both the surface and subsurface traces underlines the importance of determining true sediment transport velocities in the field with a sediment tracer.

The subsurface sediment trace offers some insight into both subsurface conduit geometry and particle transport in this karst aquifer. The low recovery of both the solution and particle tracers during the first trace (2.5% and 0.93%, respectively) suggests that Sirena Spring may not be the main discharge point for the ground water flowing through the well where the tracers were injected. There are 20 or more flowing springs in the area, although Sirena is the largest, and there is a significant contribution to baseflow along this reach of Salado Creek (Dahl 1990). However, all outlets, even those that are poorly connected, may be of interest at any site, particularly when contaminant transport is concerned. Comparison of direct-line travel time as computed from downhole velocity and actual solution tracer travel time confirms that the geometry of the conduit passing through the well must change significantly en route to Sirena Spring. In December 1995, the computed direct-line travel time was 19 minutes and the actual travel time for peak appearance of the rhodamine dye was 89 minutes; in May 1996, the computed direct-line travel time had increased to 22.5 minutes, and the peak appearance of the rhodamine dye occurred at 130 minutes. Despite the decrease in velocity from December 1995 to May 1996, some water was still traveling from the well to Sirena Spring, as evidenced by detection of the water tracer, yet the particle tracer was not detected. This suggests that by May 1996, the hydrologic conditions had changed to the point where the particle tracer was no longer transported to this outlet. The contrasting results of the two subsurface traces demonstrate the importance of using an actual sediment tracer to determine behavior of particulates in the subsurface: use of a particle tracer can ascertain under what hydraulic conditions sediment (and any associated contaminants) is transported through a karst system, and under what conditions sediment goes into storage or is diverted to other outlets.

Lanthanide Clays as Particle Tracers

Field tests in both surface and ground water systems show that lanthanide-labeled clays are serviceable particle tracers. Tracer breakthrough curves (Figures 2 and 3) show reasonable agreement with those of a conservative water tracer both in terms of time of first appearance and peak concentration; the early arrival of the particle tracer relative to the water tracer in both surface and subsurface traces highlights the importance of using an actual particle tracer to determine sediment transport times rather than relying on water tracing data. The degree to which lanthanide-labeled clay fulfills the criteria for a sediment tracer in karst is discussed here.

First, detection of the lanthanide clay particle tracer is quite sensitive. Dilution of the Ce-montmorillonite of the lowest concentration sample detected at Sirena Spring (0.14 ug Ce-clay/L water) was 7.1×10^7, based on 3 L of spring water per filter. The detection limit with the HPLC system, using isocratic flow and single pressure regulation of the post-column reagent, was approximately 1 ng lanthanide ion. As described earlier, this detection limit corresponds to approximately 30 to 40 ng of lanthanide clay/L of water collected, depending on which lanthanide tracer is used, and is approximately an order of magnitude less than the detection limit of the solution tracer rhodamine WT. Cassidy (1988) reported HPLC detection of 0.1 to 0.5 ng lanthanide ion using gradient elution and two-stage regulation. Using a system such as he describes, detection of La-montmorillonites could be improved by an order of magnitude.

Lanthanide clay tracers can be produced with several differentiable signatures. There are 13 common lanthanide elements plus lanthanum itself, making a total of 14 possible tracers. The existence of several differentiable tracers allows the simultaneous use of different lanthanide clay particle tracers at different locations within the watershed, or repeated injection of different lanthanide clay tracers at the same location without worry of cross-interference with previous traces.

A major advantage of the lanthanide clay tracer is its straightforward preparation and rapid and automated detection by HPLC. Preparation of the tracers requires only the repeated saturation and washing of the clay first with NaCl and then with the desired lanthanide salt. The tracer can be prepared using standard laboratory equipment and chemicals. The lanthanide salts themselves are easily obtained and are cost-competitive with standard fluorescent water tracers (Loveland 1989). Sample preparation is minimal, involving only the treatment of nylon or membrane filters with HIBA and centrifugation. Automation of the HPLC system makes detection quick, reproducible, and far less tedious than detection by manual counting, as is necessary for fluorescent sand, lycopodium spores, yeast, luminophores, plastic microtaggants, and glass beads. HPLC also requires less time than detection by neutron activation analysis (Loveland 1989); results are obtainable within 24 hours of running the tracer test. Additionally, HPLC, unlike INAA or laser cytometry, is a standard laboratory procedure, and set-up of HPLC instrumentation, which has a wide range of uses, is comparatively inexpensive.

Lanthanide clays have a distinct advantage over other, more exotic particles in that they are the same size and density as the clay size fraction of sediment, whose behavior they are designed to mimic. Although several of the synthetic particle tracers are in the appropriate size range (1 to 5 μm), they lack the appropriate specific gravity.

Finally, lanthanide-labeled clays have the benefit of being environmentally benign at the concentrations necessary for sediment tracing, that is, 10 ng to 1 microgram lanthanide ion per gram of ambient sediment. Rare earth elements are found in trace quantities in many soils and sediments, often far exceeding, in fact, the maximum concentration desired for tracing in a lanthanide-free environment. The use of lanthanide clay tracers in systems carrying sediments naturally high in lanthanide concentrations will be limited to the lanthanide elements with low background levels. Overall, rare earth elements have been found to be most abundant in granites and basalts, less abundant in shales, and least abundant in carbonates (Haskin et al. 1966).

The user of lanthanide clay as a particle tracer should perform background analyses before performing the trace. Even in carbonate terrane, care should be taken to fully characterize and account for any background lanthanide concentration. Any tracers that will be used in conjunction with the lanthanide clay should be treated with HIBA and analyzed by HPLC to determine possible analytical interference. HPLC analyses to determine background interference from both the source water and additional tracers should have a duration several times that of the expected appearance time of the lanthanide peaks, as late-eluting peaks from other constituents may interfere with subsequent lanthanide analyses. Furthermore, the tracer user will need an estimate of the suspended sediment content of the system being traced. In turbid water, the amount of La-montmorillonite that can be collected per sample will be limited by the amount of other sediment in suspension. A 47 mm diameter, 0.22 μm filter can capture approximately 50 mg of sediment before it clogs, less if the clay or algal content is high. Therefore, in water with a concentration of total suspended solids greater than approximately 20 mg/L, it may be more useful to consider the detection sensitivity in terms of ng La-montmorillonite/kg ambient suspended sediment. The amount of tracer injected should be determined accordingly.

Implications

Particle tracing with lanthanide clay may have a variety of uses in karst terrain. It could be used to determine the source of sediment in a system, or to determine sediment residence times as a function of flow conditions. The number of differentiable signatures available will prove extremely useful in ground water tracing as it allows several traces over both spatial and temporal domains without cross-interference. Field results from sediment tracer tests will assist in calibration of contaminant transport models, which require estimation of particle velocity, concentration, and source area, among other parameters.

Although lanthanide clay was designed for sediment tracing in karst systems, it may prove useful in other environments, particularly if used in conjunction with other particle tracers to compare the transport behavior of different types (size and density) of particles. For example, the behavior of lanthanide clay could be compared to that of synthetic microspheres, such as those used by Reimus et al. (1996), in fractured aquifers. Although the particles are in the same size range, lanthanide clay is a mineral, while the carboxylate-modified polystyrene latex microspheres may behave more like organic colloids. In bioturbation studies, the redistribution of lanthanide clay particles could be compared to that of gold-doped particles (Olmez et al. 1994) in the silt- and sand-size range to determine the effect of particle size on extent and rate of sediment mixing.

Conclusions

Lanthanide-labeled clay is an ideal particle tracer for tracing sediment through karst aquifers. Cost of production is similar to that of standard fluorescent water dyes and requires only standard laboratory equipment. Detection limits are extremely low. Sample analysis is straightforward and automated; using HPLC, results are available within 24 hours of the tracer test. The tracer can be made with up to 14 differentiable signatures, potentially eliminating cross-interference in the field over both time and space. Finally, the tracer presents no environmental hazards at the concentrations needed.

Field tests of the lanthanide clay tracer in both surface and subsurface flow systems revealed tracer behavior that was generally similar to, but not identical to, that of a water tracer, highlighting the importance of using an actual sediment tracer to determine sediment transport parameters. More important, during two subsurface tracer tests undertaken in contrasting hydrologic conditions, the water tracer was detected during both tests, but the particle tracer was detected only during the test with higher flow. These results demonstrate the utility of a sediment tracer for determining the conditions under which particulates are transported and those under which they go into storage.

Lanthanide clay may prove to be useful in the study of sediment transport in other environments in addition to karst, such as in fractured aquifers or on the marine floor. It may also be used in conjunction with particle tracers with contrasting characteristics to examine the differences in transport behavior exhibited by different types of naturally occurring particles.

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References

Aldrich, D.G., and J.R. Buchanan. 1958. Anomalies in techniques for preparing H-Bentonites. *Soil Science Society of America Proceedings* 22, 281–285.

Aley, T., and M.W. Fletcher. 1976. Water tracer's cookbook. *Journal of the Missouri Speleological Survey* 16. no. 3: 32 p.

Atkinson, T.C., D.I. Smith, J.J. Lavis, and R.J. Whitaker. 1973. Experiments in tracing underground waters in limestones. *Journal of Hydrology* 19, no. 4: 323–349.

Bruque, S., T. Mozas, and A. Rodriguez. 1980. Factors influencing retention of lanthanide ions by montmorillonite. *Clay Minerals* 15, no. 4: 413–420.

Buchtela, K., J. Mairhofer, V. Maurin, T. Papadimitropoulous, and J. Zotl. 1968. Comparative investigations into recent methods of tracing subterranean water. *National Speleological Society Bulletin* 30, 55–74.

Carey, D.A. 1989. Fluorometric detection of tracer particles used to study animal-particle dynamics. *Limnol. Oceanogr.* 34, no. 3: 630–635.

Cassidy, R.M. 1988. Determination of rare-earth elements in rocks by liquid chromatography. *Chemical Geology* 67, no. 3/4: 185–195.

Dahl, S.L. 1990. Hydrogeology and stream interactions of the Edwards Aquifer in the Salado Creek Basin, Bell and Williamson counties, central Texas. M.S. thesis, Dept. of Geology, Baylor University, Waco, Texas.

Davis, S.N., D.J. Campbell, H.W. Bentley, and T.J. Flynn. 1985. *Ground-Water Tracers*. Ada, Oklahoma: U.S. Environmental Protection Agency.

Drew, D.P. 1968. A review of the available methods for tracing underground waters. *Proc. Br. Speleol. Assoc.* 6, no. 1: 1–20.

Drew, D.P. and D.I. Smith. 1969. Techniques for the tracing of subterranean drainage. *Br. Geomorphol. Res. Group Tech. Bulletin* 2, 36 pp.

Elchuk, S., and R. M. Cassidy. 1979. Separation of the lanthanides on high-efficiency bonded phases and conventional ion-exchange resins. *Analytical Chemistry* 51, no. 9: 1434–1438.

Erel, Y., and J.J. Morgan. 1991. The effect of surface reactions on the relative abundances of trace metals in deep-sea water. *Geochimica et Cosmochimica Acta* 55, no. 7: 1807–1813.

Gale, S.J. 1984. The hydraulics of conduit flow in carbonate aquifers. *Journal of Hydrology* 70, no. 1–4: 309–327.

Gerino, M. 1990. The effects of bioturbation on particle redistribution in Mediterranean coastal sediment: Preliminary results. *Hydrobiologia* 207, no. 1–3: 251–258.

Haskin, L.A., F.A. Frey, R.A. Schmitt, and R.H. Smith. 1966. Meteoric, solar, and terrestrial rare earth distributions. In *Physics and Chemistry of the Earth*, ed. L.H. Ahrens, F. Press, S. K. Runcorn, and H. C. Urey, 169–321. Oxford: Pergamon Press.

Ingle Jr., J.C. 1966. *The Movement of Beach Sand. Developments in Sedimentology.* vol. 5. New York: Elsevier.

Kennedy, V.C., and D.L. Kouba. 1970. Fluorescent Sand as a Tracer of Fluvial Sediment. U.S. Geological Survey Professional Paper 562–E.

Krezoski, J.R. 1989. Sediment reworking and transport in eastern Lake Superior: In situ rare earth element tracer studies. *Journal of Great Lakes Research* 15, no. 1: 26–33.

Loveland, W. 1989. Environmental sciences. In *Lanthanide Probes in Life, Chemical and Earth Sciences: Theory and Practice*, ed. J.-C.G. Bünzli and G.R. Choppin, 391–411. Amsterdam: Elsevier.

Mahler, B. 1997. Sediment Transport in a Karst Aquifer. Ph.D. dissertation, Dept. of Geological Sciences, University of Texas at Austin, Austin.

McCarthy, J.F., and J.M. Zachara. 1989. Subsurface transport of contaminants. *Environ. Sci. Technol.* 23, no. 5: 496–502.

Millipore Corp. 1989. *Waters Ion Chromatography Cookbook.* Bedford, Massachusetts: Millipore Corp.

Olmez, I., F.X. Pink, and R.A. Wheatcroft. 1994. New particle-labeling technique for use in biological and physical transport studies. *Environ. Sci. Technol.* 28, no. 8: 1487–1490.

Paecht-Horowitz, M., and F.R. Eirich. 1988. The polymerization of amino acid adenylates on sodium-montmorillonite with preadsorbed polypeptides. *Origins of Life and Evolution of the Biosphere* 18, no. 4: 359–387.

Rathbun, R.E., V.C. Kennedy, and J.K. Culbertson. 1971. Transport and dispersion of fluorescent tracer particles for the flat-bed condition, Rio Grande conveyance channel, near Bernardo, New Mexico. U.S. Geological Survey Professional Paper PO 562-I.

Reimus, P.W., B.A. Robinson, H.E. Nuttall, and R. Kale. 1996. Simultaneous transport of synthetic colloids and a nonsorbing solute through single saturated natural fractures. In *Proceedings of the 18th International Symposium on the Scientific Basis for Nuclear Waste Management, Part 1,* 363-370. Pittsburgh, Pennsylvania: Materials Research Society.

Ryan, M., and J. Meiman. 1996. An examination of short-term variations in water quality at a karst spring in Kentucky. *Ground Water* 34, no. 1: 23–30.

Sayre, W.W., and D.W. Hubbell. 1965. Transport and dispersion of labeled bed material, North Loup River, Nebraska. U.S. Geological Survey Professional Paper PO 0433-C.

Thrailkill, J. 1989. Shallow conduit-flow carbonate aquifers: Conceptual models and parameter evaluation. In *Recent Advances in Ground-Water Hydrology*, ed. J.E. Moore, A.A. Zaporozed, S.C. Csallany, and T.C. Varney, 153–159. St. Paul, Minnesota: American Institute of Hydrology.

Wheatcroft, R.A. 1991. Conservative tracer study of horizontal sediment mixing rates in a bathyal basin, California borderland. *Journal of Marine Research* 49, no. 3: 565–588.

Wheatcroft, R.A. 1992. Experimental tests for particle size-dependent bioturbation in the deep ocean. *Limnol. Oceanogr.* 37, no. 1: 90–104.

Wheatcroft, R.A., I. Olmez, and F.X. Pink. 1994. Particle bioturbation in Massachusetts Bay: Preliminary results using a new deliberate tracer technique. *Journal of Marine Research* 52, 1129–1150.

White, E.L., and W.B. White. 1968. Dynamics of sediment transport in limestone caves. *National Speleological Society Bulletin* 30, 115–129.

White, W.B. 1988. *Geomorphology and Hydrology of Karst Terrains.* New York: Oxford University Press.

Wood, S.A. 1990. The aqueous geochemistry of the rare-earth elements and yttrium. *Chemical Geology* 82, no. 1/2: 159–186.

Wood, W.W., and G.G. Ehrlich. 1978. Use of baker's yeast to trace microbial movement in ground water. *Ground Water* 16, no. 6: 398–403.