Difluorobenzoates as Nonreactive Tracers in Soil and Ground Water

by Robert S. Bowman and Joseph F. Gibbens

Abstract

Over the past 10 years, several fluorinated derivatives of benzoic acid have proven their usefulness as nonreactive water tracers. In this study, the suitability of four previously untested isomers of difluorobenzoate (DFBA) as saturated- and unsaturated-zone tracers was examined in a series of laboratory and field experiments. Experimental conditions included batch shaking tests with two different soils, laboratory soil column tests under saturated and unsaturated conditions, a three-month aquifer tracer test, and a month-long tracer test in a field soil. Bromide, which is considered nonreactive in most hydrological environments, was included as an index tracer in each experiment. Under every condition, each DFBA isomer showed the same concentration distribution and mass recovery as Br⁻. These and other previously tested fluorobenzoates were ranked according to their suitability as nonreactive soil and ground-water tracers.

Introduction

Water tracers are required to characterize many hydrological properties of soils and aquifers. Examples of such properties include water flow direction and velocity, water flux, solute dispersion, and solute sorption and retardation. Methods to trace water have included injecting chemicals or solid particles into the flow system, tracking thermal pulses, observing geochemical changes over time and distance, and monitoring the distribution of native stable or radioactive isotopes (Davis et al., 1980). The use of added chemical tracers allows source control and generally provides the most accurate estimates of hydrological parameters. While no perfect nonreactive tracer exists, low molecular weight anions (particularly Br⁻) approach this ideal since they undergo little interaction with most natural porous media, are environmentally acceptable, and are readily and economically analyzed (Bowman, 1984a).

Fluorinated benzoic acid derivatives have many of the properties required of nonreactive soil and ground-water tracers (Stetzenbach et al., 1982; Bentley, 1983; McCray et al., 1983; Bowman, 1984a). These acids, with negative-log dissociation constants (pKₐ) less than 4.0, are anionic at neutral to basic pHs, are resistant to chemical and microbial transformations, and are readily analyzed at µg L⁻¹ levels in sub-mL water samples using chromatographic techniques. Use of the fluorobenzoates is warranted when common inorganic anions such as Br⁻, Cl⁻, or NO₃⁻ are not suitable, or when multiple tracers are required.

Of the fluorobenzoates which to date have seen extensive field applications, only the two with aromatic-ring substitution by fluorine (pentafluorobenzoate [PFBA] and 2,6-difluorobenzoate [2,6-DFBA]) have shown long-term resistance to chemical and biological breakdown in the environment (see Previous Work section, below). For field experiments of more than a few weeks' duration, and/or when multiple tracers are required, an expanded suite of proven fluorobenzoates is needed.

The purpose of this work was to evaluate four new ring-substituted difluorobenzoates as soil and ground-water tracers. In addition to the stable and frequently used 2,6-DFBA, five other difluorobenzoate isomers exist and are commercially available. The transport and degradation characteristics of four of these difluorobenzoates were judged in a series of laboratory and multimonth field experiments, under both saturated and unsaturated conditions, by comparing their behavior with that of the well-accepted tracer Br⁻. All eight fluorobenzoates which have seen applications to field problems (Figure 1) were then ranked in terms of their suitability as nonreactive soil and ground-water tracers.

---

4Department of Geoscience and Geophysical Research Center, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801. (J. F. Gibbens is currently at Consolidation Coal Company, Pittsburgh, Pennsylvania 15228.)

Received September 1990, revised March 1991, accepted March 1991.

Discussion open until July 1, 1992.
Previous Work

The fluorobenzoates o-TFMBa, m-TFMBa, 2,6-DFBA, and PFBA have recently been used as water tracers in a variety of hydrologic environments. (All acronyms, structures, and chemical names are presented in Figure 1.) Bowman and Rice (1986a, 1986b) used these fluorobenzoates to follow the downward movement of individual slugs of irrigation water in flood-irrigated agricultural fields in central Arizona. The pH of the soils in these studies was in the range of 7.5 to 8.0, and their organic carbon contents were less than 1%. PFBA, 2,6-DFBA, and o-TFMBa were used to determine surface-origination points of subsurface discharge resulting from rainfall on a forested hillslope at the Bear Brook Watershed in east-central Maine (Hornberger et al., 1990; G. M. Hornberger, 1990, personal communication). The pH of the ground water at the MADE site ranged from 4.3 to 5.2. Stensrud et al. (1990) characterized aquifer heterogeneity in fractured dolomite in southeastern New Mexico by injecting o-TFMBa, m-TFMBa, and PFBA into separate wells and monitoring their arrivals at a pumping well. The ground water at the site was highly saline (electrical conductivity of 140 mS cm⁻¹) and had a pH of 7.3. Adams et al. (1989) have investigated these and other fluorobenzoates as water tracers in geothermal systems. Generally low thermal stabilities limit the usefulness of fluorobenzoates in such environments, however.

The present study was designed to expand the suite of fluorobenzoate tracers proven stable in a variety of hydrologic environments.

Materials and Methods
Fluorobenzoate Properties and Chromatographic Analysis

The eight fluorobenzoates listed in Table 1 were obtained from Aldrich Chemical Co., Inc. (Milwaukee, Wisconsin). Chemical purities were 97% or greater according to the manufacturer; the compounds were used without further purification. The acid dissociation constants for these compounds were determined for 0.01 M solutions using base titration, as described by Nelson and Kemp (1981). Fluorobenzoate diffusion coefficients were estimated from their molecular structures using the Hayduk and Laudie method (Tucker and Nelken, 1982). A high-performance liquid chromatographic (HPLC) analysis to simultaneously quantify 2,3-, 2,5-, 3,4-, and 3,5-DFBA, as well as Br⁻, NO₂⁻, NO₃⁻, and Cl⁻, was developed by modifying a procedure described by Bowman (1984b). The 2,4-DFBA isomer was not evaluated in this study due to initial interference problems when it was analyzed in the presence of 2,5-DFBA. The instrumentation consisted of a Model 501 pump, Model U6K injector, Model 481 variable-wavelength UV detector, and Model 745 data module, all from Waters Chromatography Division, Millipore Corp. (Milford, Massachusetts). The 4.6-mm by 250-mm stainless steel analytical column was packed with 5-µm Spherisorb SAX by Regis Chemical Co. (Morton Grove, Illinois). The mobile phase was 30 mM KH₂PO₄ buffer, pH adjusted to 2.85 with H₃PO₄, with 20% acetonitrile (v/v) as an organic modifier. The flow rate was 1.0 mL min⁻¹. Detection wavelength was 205 nm.

Batch Soil Equilibration Tests

Batch soil equilibrations were conducted to evaluate the stability and sorption characteristics of the DFBA isomers. Two soils chosen on the basis of their differing chemical and physical properties were used. Bluepoint fine sand (Typic Torripsamments) is from a floodplain deposit in central New Mexico and has a cation exchange capacity (CEC) of 0.0018 mol cation (Na⁺) kg⁻¹, an organic carbon fraction of 0.0002, and a pH (1:1 aqueous extract) of 7.5. Beardon silty clay loam (Aeric Kalciaquolls) is an agricultural soil from the vicinity of Grand Forks, North Dakota. It has a CEC of 0.32 mol cation (Na⁺) kg⁻¹, an organic carbon fraction of 0.035, and a pH (1:1 aqueous extract) of 7.2. Twenty-gram
samples of <2-mm soil were placed in 50-mL polypropylene centrifuge tubes. Twenty mL of an aqueous solution of Br⁻; 2,3--; 2,5--; 3,4--; and 3,5-DFBA was added to the tube. Two aqueous solutions were used. One contained 10 mg L⁻¹ Br⁻ and 5 mg L⁻¹ of each difluorobenzoate, while the other contained 100 mg L⁻¹ Br⁻ and 50 mg L⁻¹ of each difluorobenzoate. Each combination was prepared in triplicate for each of the two soils, as were appropriate blanks with and without soil. The tubes were capped, stored in the dark at a room temperature of 24° ± 2°C, and shaken daily. Periodically, the tubes were centrifuged and 0.15-ML sub-samples of the supernatant solutions were collected for HPLC analysis. The soil was then resuspended and the tubes again placed in storage. The equilibration tests were continued for 85 days.

**Laboratory Column Tests**

The transport characteristics of the four DFBA isomers were compared to those of Br⁻ in laboratory saturated and unsaturated flow experiments. Duplicate PVC tubes (75-cm long by 10.2-cm I.D.), fitted with end caps, screens, and outflow valves, were packed with Bluepoint soil to a bulk density of 1.6 Mg m⁻³. After saturating with tap water from the bottom, a constant ponded depth of 50 mm was established on the surface using a Mariotte siphon. The flow through each column was regulated at 1.0 mL min⁻¹ using the outflow valve. After several days of leaching, the flow rates and water contents stabilized, resulting in pore volumes (PVs) of 2.41 L and 2.26 L for columns 1 and 2, respectively. At this point, tap water input ceased, and a 3.0-PV slug containing 100 mg L⁻¹ Br⁻, 50 mg L⁻¹ of each difluorobenzoate in tap water was introduced under a constant ponded depth of 50 mm. After all of the slug had infiltrated, leaching with tap water resumed at the same ponded depth. Effluent samples were collected at 0.2-PV intervals after slug addition and analyzed via HPLC.

Following this saturated flow study, each column was fitted with a surface-water distribution system. Water was applied at the rate of 0.5 mL min⁻¹ and the columns were allowed to desaturate. When the outflow rate equalled the inflow rate, PVs had stabilized at 1.41 L and 1.29 L for columns 1 and 2, respectively. Since the column outlets were at atmospheric pressure, the water contents increased with depth, and a saturated zone existed in the lower portion of each column. A 2.0-PV slug of Br⁻ (100 mg L⁻¹) and the difluorobenzoates (50 mg L⁻¹ each) was added at the same flow rate. Leaching with tap water resumed after infiltration of the slug. Effluent samples were again collected at 0.2-PV intervals and analyzed.

**Aquifer Tracer Test**

The stability and sorptive properties of the difluorobenzoates were compared to those of Br⁻ in a sandy alluvial aquifer. An experimental well field was established on the floodplain of the Rio Salado in the Sevilleta Wildlife Refuge, 32 km north of Socorro, New Mexico. The aquifer consists of medium to coarse sand with cobbles, overlain by 8-10 cm of fine-grained eolian sand. A complete description of the subsurface geology is provided by Stephens and Knowlton (1986). The depth from the surface to low-permeability shale and clay layers is about 19 m. The depth to the phreatic water surface was about 3.2 m at the time the site was instrumented. Due to the ephemeral nature of Rio Salado discharge, the water-table elevation, as well as the direction and velocity of ground-water flow, are seasonally variable.

Two 5.0-cm I.D. PVC-cased wells were installed to a depth of 8.3 m below land surface. Each casing had a 1.6-m slotted screen interval at the bottom. The lateral separation of the wells was 3.1 m. A 20-L slug containing 1000 mg L⁻¹ Br⁻ and 150 mg L⁻¹ of each difluorobenzoate was injected into Well #1. Well #2 was pumped at a rate of approximately 56 L min⁻¹ for seven hours to draw the slug out of the bore of Well #1 and into the aquifer. The slug was left in the aquifer for 90 days, at which time Well #1 was pumped at a rate of approximately 56 L min⁻¹ for 12 hours. Samples of the discharge were collected every five minutes. The discharge samples were analyzed for Br⁻ and the difluorobenzoates.

**Vadose Zone Tracer Test**

The stability and sorptive properties of the difluorobenzoates were evaluated in a field experiment under unsaturated conditions. As part of another study, a 10-m by 10-m test plot was established in an alluvial outwash deposit on the campus of the New Mexico Institute of Mining and Technology. The stratigraphic profile beneath the site is heterogeneous, and consists of interbedded clays, sands, gravels, and cobbles. The plot was heavily instrumented with soil solution samplers, tensiometers, and neutron probe access tubes to depths of up to 8 m. A drip irrigation system having emitters on a 0.5-m by 0.5-m grid was controlled by a timer to provide steady water application and maintain unsaturated conditions. The site geology and instrumentation are described in detail by Parsons (1988) and Gibbens (1989).

A constant water input of 7.75 cm day⁻¹ was applied to the plot. After two months, neutron probe data indicated a nonvarying water content profile to a depth of 8 m, and the tensiometers indicated an average hydraulic gradient of -1.03 to a depth of 5 m. The average volumetric water content to the 3.2-m depth was 0.20, equal to about 50% of saturation. Under these steady-state water flow conditions, a slug containing Br⁻ (135 mg L⁻¹) and the difluorobenzoates (15 mg L⁻¹ each) was applied for 24 hours via the irrigation system to a 2.5-m by 10-m strip of the plot. Soil solution samples were taken for 25 days using five porous cup samplers located at depths from 1.0 to 3.2 m below the drip lines. The soil solution samples were analyzed for Br⁻ and the difluorobenzoates.

**Results and Discussion**

**Fluorobenzoate Properties and Chromatographic Analysis**

The acid dissociation constants for eight fluorobenzoates are presented in Table 1. The pKₐs range from 2.7 to 3.8, with the difluorobenzoates having values between 3.0 and 3.8. All of the fluorobenzoates thus are more than 99% ionized (anionic) at pHs greater than 5.8.
A chromatogram of a Bluepoint soil extract spiked with 25 ng of each of the four difluorobenzoate isomers and Br\(^{-}\) is presented in Figure 2. The elution of the difluorobenzoates is in the order of decreasing pK\(_{a}\), as expected for a pure ion-exchange reaction on the chromatographic column. Table 1 lists the detection limits for the difluorobenzoates under the given analytical conditions.

**Batch Soil Equilibration Tests**

Results of the batch equilibrations with Bluepoint and Beardon soils are presented in Figure 3. Data are plotted in terms of relative concentration (concentration of the compound divided by its initial concentration prior to soil addition) versus time. For both soils, each difluorobenzoate and Br\(^{-}\) showed no decrease in concentration during the 85 days of the experiment. Thus, none of the difluorobenzoates were subject to any sorption or degradation under these conditions. The data shown are for the equilibrations with the higher initial concentrations; data for the lower initial concentrations were similar.

**Laboratory Column Tests**

Results of the laboratory column leaching studies are presented in Figure 4. For each column under each set of conditions, solute breakthrough curves (BTCs) for the four difluorobenzoates were indistinguishable from that of Br\(^{-}\). Tracer retardation factors, estimated from the number of PEs at which the relative concentration equaled 0.5, ranged from 0.94 to 0.99 for the duplicate columns under the two
sets of conditions (saturated or unsaturated). These retardation factors indicate a slight amount of anion exclusion by the sandy column material. In any individual experiment, the retardation factor for Br- and each difluoro benzoate was the same.

Table 2 shows that effluent recoveries for each difluorobenzoate and Br- equaled 100 ± 2%. No loss of tracer mass was evident during passage through the columns, indicating that degradative processes were negligible in this soil material during the 10-day duration of each experiment.

Aquifer Tracer Test

Figure 5 shows the results of the drift-and-pumpback aquifer tracer test. Although there was more variation among difluorobenzoate and Br- concentrations than in the laboratory studies, the concentration distributions were nonetheless very similar. In particular, the “bumps” in the pumpback curve were tracked similarly by all five chemicals. The mean value of the difference between the concentration of each difluorobenzoate and Br- over all sampling times did not differ significantly from zero at the 95% confidence level.

Difluorobenzoate recoveries ranged from 102 to 112%, while Br- recovery was 106% (Table 2). The recovery of any individual tracer was within two standard deviations of the mean recovery for all of the tracers. The deviations from 100% recovery were small, given the large slug dilution in this study, which resulted in maximum relative concentrations in the pumped water of less than 0.01 (Figure 5). Slight variations in the pumping rate during the seven-hour sampling period may also have contributed to a calculated recovery which differed from 100%.

Vadose Zone Tracer Test

Breakthrough curves for the tracers at the five solution samplers are shown in Figure 6. Soil heterogeneity and layering at the field site resulted in different-shaped BTCs and different mean tracer velocities at the different sampling locations. For any one sampler, the difluorobenzoate BTCs were similar to that for Br-, and the mean value of the difference between the concentration of each difluorobenzoate and Br- over all sampling times did not differ significantly from zero at the 95% confidence level.

The mass recovery for each tracer at each sampling location is presented in Table 2. Recoveries were calculated assuming a uniform water flux and uniform tracer application over the entire treated area. Mean tracer recoveries at

Table 2. Tracer Recoveries (%) in Laboratory and Field Tests

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Laboratory column tests</th>
<th>Aquifer tracer test</th>
<th>Vadose zone tracer test</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-DFBA</td>
<td>100</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>2,5-DFBA</td>
<td>99</td>
<td>101</td>
<td>99</td>
</tr>
<tr>
<td>3,4-DFBA</td>
<td>101</td>
<td>100</td>
<td>102</td>
</tr>
<tr>
<td>3,5-DFBA</td>
<td>101</td>
<td>99</td>
<td>101</td>
</tr>
<tr>
<td>Br</td>
<td>100</td>
<td>101</td>
<td>101</td>
</tr>
<tr>
<td>Mean</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.84</td>
<td>0.84</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Fig. 4. Breakthrough curves for the four DFBA isomers and Br- in columns of Bluepoint sand under saturated and unsaturated conditions. Symbols represent 2,3-DFBA (<>); 2,5-DFBA (▲); 3,4-DFBA (○); and 3,5-DFBA (□). The solid line connects the Br- data points.

Fig. 5. Concentration distributions for the four DFBA isomers and Br- during the pumpback phase of the aquifer tracer test. Symbols represent 2,3-DFBA (<>); 2,5-DFBA (▲); 3,4-DFBA (○); and 3,5-DFBA (□). The solid line connects the Br- data points.
Based upon this research and that of others cited in the Previous Works section, the fluorobenzoates can be ranked in the following order of reliability as stable, nonreactive anionic tracers: PFBA > 2,6-DFBA > 2,3-DFBA = 2,5-DFBA = 3,4-DFBA = 3,5-DFBA > o-TFMBA > m-TFMBA. All of these fluorobenzoates show transport properties indistinguishable from those of Br⁻ (Bowman, 1984a; results presented herein). PFBA and 2,6-DFBA are the fluorobenzoates of choice since they have performed well in the widest variety of environments. Based upon the present work, the other four difluorobenzoate isomers appear to have equivalent stabilities and transport characteristics. Both TFMBA isomers have shown transformation losses in multimonth field experiments, with the o-TFMBA isomer perhaps exhibiting somewhat greater persistence (Bowman and Rice, 1986a, b).

In addition to its stability, a tracer's detection limit, price, and availability will influence whether it is the ultimate choice for a given investigation. All eight of the above tracers, plus Br⁻, could be used together if necessary and quantified simultaneously in water samples via HPLC. For multitracer experiments requiring a smaller suite of tracers, the fluorobenzoates of choice will include those least subject to analytical interferences from inorganic anions or soluble organics present in the sample matrix. In field studies requiring only a single tracer, Br⁻ remains the most attractive due to its much lower cost (one-tenth to one-hundredth that of the fluorobenzoates, depending upon the particular isomer, at current prices).

Based upon the demonstrated stability and lack of reactivity of pentafluorobenzoate and the four difluorobenzoates tested here, it is highly likely that 2,4-DFBA, the six possible trifluorobenzoate isomers, and the three possible tetrafluorobenzoate isomers will likewise prove to be useful anionic water tracers. Most of these compounds are available commercially, and all should be amenable to µg L⁻¹-level quantitation in water samples via HPLC. Thus, up to 16 ring-substituted, multifluorobenzoates could potentially be used in investigations requiring a large number of exotic tracers.

The possible toxicity of the fluorobenzoates remains largely uninvestigated. Until more information becomes available regarding the health effects of these compounds, they should not be used where contamination of drinking-water sources is possible.

References


Robert S. Bowman earned his B.A. in Chemistry at the University of California at Berkeley, and his Ph.D. in Soil Chemistry at New Mexico State University. Following five years with the USDA's Water Conservation Laboratory in Phoenix, Arizona, he joined New Mexico Institute of Mining and Technology as Assistant Professor of Hydrology in 1987. His research emphasizes transport of reactive and nonreactive solutes in soils and aquifers.

Joseph F. Gibbens earned his B.S. in Geology at the University of North Dakota in 1987, and his M.S. in Hydrology at New Mexico Institute of Mining and Technology in 1989. He is currently a Hydrologist with Consolidation Coal Company in Pittsburgh, Pennsylvania, where he works on hydrological responses to surface and underground coal mining.