EVALUATION OF TRI- AND TETRAFLUOROBENZOATES

AS SOIL AND GROUNDWATER TRACERS

by

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I wish to thank everyone here at Tech who has made the last two years a growing experience.

CHAPTER 1

INTRODUCTION

The following manuscript was prepared for submission to the <u>Soil Science Society of America Journal</u> as the culmination of a thesis project partially fulfilling the requirements for the Degree of Master of Science in Hydrology at the New Mexico Institute of Mining and Technology. The project focused on the evaluation of six previously untested fluorobenzoate (FBAs) isomers, four trifluorobenzoates (TFBAs) and two tetrafluorobenzoates (TEFBAs), for their suitability as soil and groundwater tracers. The manuscript was prepared in keeping with the editorial guidelines set by the Soil Science Society of America and is followed by a set of appendices containing the procedures used and data obtained in the course of the study.

This study was supported by funding from the New Mexico Water Resources Research Institute under project no. AR92-02. This work represents results from the first two years of a three-year study evaluating the suitability of tri- and tetrafluorinated benzoic acids as soil and groundwater tracers. Further work will involve the development of instrumental methods to simultaneously analyze these and all previously tested FBA isomers and reduce their detection limits in natural water samples.

This article, entitled "Tri- and tetrafluorobenzoates as soil and groundwater tracers", presents a series of laboratory investigations evaluating the long-term stability and mobility characteristics of the six FBAs evaluated in the study. The

sorptive properties of the FBA compounds at low pH is also discussed and the results are extended to include previously evaluated FBA isomers.

Appendix A contains the Pk_a determination method used with five TFBA and two TEFBA isomers evaluated in this study, six previously evaluated difluorobenzoate (DFBA) isomers, and pentafluorobenzoate (PFBA). Later, one of the TFBA compounds was eliminated from the study due to chromatographic difficulties. Appendix tables A1 through A15 contain the titration data obtained using the Pk_a determination method in Appendix A with benzoic acid as a reference material.

Appendix B contains the FBA aqueous diffusion coefficient calculation from Tucker and Nelken (1982).

Appendix C contains a discussion of the chromatographic method used to quantify the FBAs in natural water samples.

Appendix D contains the method used to determine the instrumental FBA detection limits in deionized water.

Appendix E contains the method and data used to generate the detector response figure (Fig. 3).

Appendix F1 contains soil batch equilibration data for the 5 mg L^{-1} blank control samples, and 5 mg L^{-1} and 50 mg L^{-1} samples containing Bluepoint, Beardon, and Naff soils.

Appendix F2 contains soil organic matter partition coefficient (K_{oc}^*) calculations and data to support discussion provided in the batch equilibration results section.

Appendix G contains laboratory column breakthrough curve

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(BTC) data. Data tables for saturated and unsaturated BTCs are preceded by column physical data, and calculations, and CXT-FIT parameters used to obtain non-linear fits to the observed BTCs. BTC data are followed by mass recovery calculations and results, and statistical analyses of fitted and observed BTCs.

Appendix H contains a discussion of a field tracer test attempted twice at the Sevilleta National Wildlife Refuge.

Appendix I contains a list of literature citations used in the Appendix sections.

CHAPTER 2

PAPER ENTITLED "TRI- AND TETRAFLUOROBENZOATES AS
NONREACTIVE TRACERS IN SOIL AND GROUNDWATER"

by

C.F. Benson and R.S. Bowman

TRI- AND TETRAFLUOROBENZOATES AS NONREACTIVE TRACERS IN SOIL AND GROUNDWATER

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Abreviations: DFBA, difluorobenzoic acid; TFBA, trifluorobenzoic acid; TEFBA, tetrafluorobenzoic acid; PFBA, pentafluorobenzoic acid; FBA, fluorobenzoate; TFMBA, trifluoromethylbenzoic acid; HPLC, high performance liquid chromatography; CEC, cation exchange capacity; PV, pore volume; BTC, breakthrough curve; OC, mass-based soil organic carbon fraction; C/C_o, relative concentration; Pk_a, negative log acid dissociation constant; K_{oc}^*, organic carbon-based partition coefficient for neutral, protonated, FBA; K_D, overall linear partition coefficient for FBA

ABSTRACT

Several fluorinated derivatives of benzoic acid have proven their usefulness as nonreactive soil and groundwater tracer compounds. In this study four previously untested trifluorobenzoate (TFBA) isomers and two tetrafluorobenzoate (TEFBA) isomers were examined for their suitability as water tracers in saturated and unsaturated environments. Negative log acid dissociation constants (pK_as) determined by base titration ranged from 3.54 to 2.71 at 25°C. A series of laboratory experiments included soil batch equilibration studies with three different soils and soil column tests under saturated and unsaturated conditions. Bromide, a conservative tracer, was used as a reference material in all fluorobenzoate (FBA) stability and mobility studies. Column mobility experiments yielded breakthrough curves for TFBA and TEFBA isomers that were indistinguishable from Br^- under saturated and unsaturated conditions in sandy media. Some sorption of FBAs was seen in low pH, high organic carbon fraction (OC) soils. An algorithm was developed for calculating a linear partition coefficient (K_D) for each FBA isomer based on pK_a, soil OC, pH, and an average organic carbon-based partition coefficient for neutral, protonated FBA (K_{oc}^*). K_{oc}^* was estimated to be 18,200±6,300 L kg^{-1} when total FBA solution concentrations are less than 5 mg L^{-1}.

INTRODUCTION

In hydrologic systems tracers are required to accurately estimate the direction and velocity of water movement. Depending on the amount and quality of information gained via a tracer experiment, parameters dealing with porous medium characteristics and solute behavior may be determined. A tracer may be a particulate, thermal, chemical, or radioactive signal that either occurs naturally or anthropogenically in a hydrologic system (Davis et al., 1980). Added chemical tracers generally afford the most accurate porous medium parameter estimates owing to the unique and discrete nature of their presence in a flow system.

The general requirements a chemical compound must meet for use as a tracer are summarized in Davis et al. (1980). These requirements stress chemical stability over a period of time consistent with the duration of the tracer test and a nonreactive nature that ensures minimal sorption of tracer material to the porous medium. Although no perfect nonreactive chemical tracer exists, the low molecular weight anions, particularly Br⁻, are used since they do not interact with most natural porous media, are non-toxic, and are detectable at μg L^{-1} concentrations in natural waters (Bowman, 1984a).

An existing suite of DFBA isomers and PFBA have exhibited many of the properties required of nonreactive tracers in soil

and groundwater systems (Bowman and Gibbens, 1992). These acids, with pK$_a$s less than 4.0, are anionic at neutral to basic pH, are resistant to chemical and microbial transformations, and are detectable in natural water samples at μg L^{-1} levels via HPLC. Use of FBA tracers is required when inorganic anions such as Br$^-$, Cl$^-$, or NO$_3^-$ are not suitable due to either naturally high background levels, chemical instability, or plant uptake.

The existing suite of FBA isomers exhibiting resistance to chemical breakdown in the environment consists of five DFBA isomers and PFBA. For complex tracer tests involving multiple injection points and/or numerous tracer tests in a single area, an expanded suite of proven FBA compounds is needed. Examples of proposed projects requiring multiple nonreactive tracers are hydrologic characterization at the Waste Isolation Pilot Plant (WIPP) in southeastern New Mexico and the proposed high-level nuclear waste depository at Yucca Mountain, Nevada. At WIPP, o-TFMBA, m-TFMBA, and PFBA were used in a multi-well convergent-flow tracer test to characterize aquifer heterogeneity in fractured dolomite (Stensrud et al., 1990).

The purpose of this work was to evaluate four new TFBA isomers and two new TEFBA isomers as soil and groundwater tracer materials. This study focused on ring-substituted FBAs since previous work with TFMBAs has shown chemical instability in aerobic environments (see Previous Work section, below). It was assumed the higher degree of halogenation, from di- to

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tri- and TEFBA, would increase the stability of the FBA compounds in the natural environment (Atlas and Bartha, 1993, p. 387). This study involved laboratory experiments evaluating the stability of the TFBA and TEFBA compounds in three different soils and their mobility characteristics under saturated and unsaturated conditions. All investigations employed Br⁻ as a reference material against which the mobility, sorptive, and stability characteristics of the TFBA and TEFBA compounds were compared.

PREVIOUS WORK

A comprehensive review of the use of four FBAs as soil and groundwater tracers in a variety of environments up to 1990 may be found in Bowman and Gibbens (1992). In summary, this review concluded that as a class of compounds the FBAs have properties that make them suitable as water tracers in soils and groundwaters. However, the ring-substituted FBAs with more than one fluorine atom (e.g., 2,6-DFBA and PFBA) consistently showed more chemical stability over time than the monofluorobenzoates (o-, m-, and p-isomers) or the TFMBAs (o- and m-isomers) in aerobic, typically unsaturated, environments. This observation led Bowman and Gibbens (1992) to evaluate the remaining DFBA isomers as soil and groundwater tracers. They evaluated four of the DFBA isomers (2,3-, 2,5-, 3,4-, and 3,5-DFBA) in a series of laboratory and field tests

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for their suitability as tracer compounds. All four isomers proved chemically stable for several months and possessed mobility characteristics indistinguishable from Br⁻ under saturated and unsaturated conditions.

More recent, and ongoing, field experiments using FBA compounds as water tracers are dealing with diverse problems in hydrology. For example, Wilson and Mase (1992) used four DFBA isomers, PFBA, o- and m-TFMBA, and Br⁻ in a field experiment at the Borden Canadian Forces Base in Ontario, Canada, to delineate capture zones for pumping wells. In this area groundwater pHs range from 6.8 to 8.0 (Nicholson et al., 1983). Recovery of the tracers was consistent with simulated recoveries modeled at the site. Thus, sorption and degradation processes played insignificant roles in the transport of these tracers (TerBerg, 1993). Boggs et al. (1992), Rehfeldt et al. (1992), and Boggs and Adams (1992), employed PFBA, 2,6-DFBA, o-TFMBA, and Br⁻ to study the macrodispersive characteristics of a heterogeneous aquifer in a natural gradient tracer experiment in Mississippi. Losses in the mass of all tracers over time prompted an investigation into the sorptive properties of the tracer compounds in the aquifer. It was proposed that low groundwater pH and a high amount of iron oxides and kaolinite in the aquifer combined cause anion sorption. Iron oxides and clays exhibit positively charged surfaces that attract anions under low pH conditions. In laboratory column mobility tests using aquifer

material from the site, Br showed a retardation coefficient of 1.2 while the FBA tracers showed a retardation coefficient of 1.1 (Boggs and Adams, 1992). Boggs and Adams (1992) attributed the higher retardation factor for Br to its greater charge density.

At low pH a significant portion of the FBAs are protonated and thus neutral. This leaves them susceptible, as neutral organic molecules, to sorption to organic matter within the porous medium. This mechanism was recognized by Davis et al. (1980) as a reason to avoid using freons and other neutral organic molecules in porous media with high organic carbon fractions.

The present study was designed to expand the suite of proven ring-substituted FBA tracers to include the TFBA and TEFBA isomers that are currently commercially available, and to evaluate potential FBA sorption in relatively low-pH, high-OC soils.

MATERIALS AND METHODS

Fluorobenzoates tested

The six FBA isomers shown in Fig. 1 were obtained from Aldrich Chemical Co, Inc. (Milwaukee, WI). Chemical purities were 97% or greater according to the manufacturer; the compounds were used without further purification. The isomers 2,3,5-TFBA and 2,3,4,6-TEFBA were not commercially available

at the time of this study. Although commercially available, the 2,4,6-TFBA isomer was not evaluated in these studies due to coelution when analyzed with bromide via the HPLC method described below.

Fluorobenzoate properties

The pK_as for these compounds, previously investigated DFBAs, and PFBA were determined for 0.01 M FBA solutions using the half-equivalence point base titration method (Skoog and West, 1980, pp. 570-571). Benzoic acid was used as a reference material to check the accuracy of the method. Temperature was maintained at 25.0±0.2°C using a circulating water bath. Constant ionic strength was ensured throughout the titrations by preparing titrant and titrand solutions from a stock of 0.10 m KCl in degassed, deionized water. Deionized water for all studies reported here was prepared via reverse osmosis with a Milli-RO Plus system, followed by deionization using a Milli-Q water purification system (Millipore Corp., Milford, MA). Resistivity of the purified water was 18 MΩ or greater.

Aqueous diffusion coefficients at 25°C for the four TFBAs and the two TEFBAs were estimated from their molecular structures using the Hayduk and Laudie method (Tucker and Nelken, 1982). The Hayduk and Laudie method uses a variation of the Stokes-Einstein equation for estimating the aqueous diffusion of a spherical solute molecule in water.

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Fluorobenzoate analysis

An anion exchange HPLC method was developed to simultaneously quantify 2,3,4-; 2,3,6-; 2,4,5-; and 3,4,5-TFBA; and 2,3,4,5- and 2,3,5,6-TEFBA. The method was designed to quantify these FBAs in the presence of the reference material/tracer Br^- and the common soil and groundwater interferant anions NO_2^-, NO_3^-, and Cl^-. The method developed was a modification of a procedure described by Bowman (1984b). The instrumentation consisted of a Model 501 pump, Model U6-K manual injector, Model 994 programmable photodiode array detector, and a Model 5200 printer/plotter, all from Waters Chromatography Division, Millipore Corp. The analytical column used for this work was a 4.6-mm x 250-mm stainless steel column packed with 5-μm Spherisorb SAX by Regis Chemical Co. (Morton Grove, IL). The injection syringes used were series 800 glass 25-μL syringes from Hamilton Co. (Reno, NV). An injection volume of 25-μL was used for all chromatographic analyses in this study. The mobile phase was a 20 mM KH_2PO_4 buffer with a pH of 2.75, adjusted with 20 mM H_3PO_4, with acetonitrile, 18% (v/v), as an organic modifier. Acetonitrile for mobile phase preparation was OmniSolv HPLC grade (EM Science, Gibbstown, NJ). The aqueous portion of the mobile phase was filtered through a 0.45-μm nylon filter membrane prior to the addition of the acetonitrile. The flow rate was 2.0 mL min^{-1}. The detection wavelength was 205 nm.

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Batch soil equilibration tests

Batch soil equilibrations were conducted to evaluate the stability and sorption characteristics of the TFBA and TEFBA isomers. Three soils, chosen on the basis of their differing physical and chemical properties, were used in these studies. Bluepoint fine sand (Typic Torripsamments) is from a flood plain deposit in central New Mexico and has a CEC of 0.036 mol_c (Na^+) kg^{-1}, an organic carbon fraction of 0.001, 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 0.156 mol_c (Na^+) kg^{-1}, an organic carbon fraction of 0.020, and a pH (1:1 aqueous extract) of 7.1. Naff silt loam (Ultic Argixerolls) is an agricultural soil from the Palouse region of eastern Washington. It has a CEC of 0.111 mol_c (Na^+) kg^{-1}, an organic carbon fraction of 0.021, and a pH (1:1 aqueous extract) of 6.6. Twenty-gram samples of <2.0-mm soil were placed in 50-mL Oak Ridge-type polypropylene centrifuge tubes. Twenty mL of an aqueous solution of Br^-, TFBAs, and TEFBAs was added to each tube. Two aqueous solutions were used. One solution contained 75 mg L^{-1} Br^- and 50 mg L^{-1} of each FBA. The other was a ten-fold dilution of the above, containing 7.5 mg L^{-1} Br^- and 5.0 mg L^{-1} of each FBA. Triplicate samples were prepared with each soil type at both solution concentrations. Soil blanks containing 20.0 grams soil and 20.0 mL deionized water were prepared in triplicate for each soil type to monitor

analytical background effects caused by the soil extracts. Tube blanks, containing 20 mL of tracer solution only, were prepared in triplicate for each solution concentration to monitor any potential FBA sorption onto the walls of the centrifuge tubes. The tubes were capped, shaken, and stored in the dark at room temperature ($24 \pm 2°C$). Periodically, the tubes were centrifuged at 12,000xg for 30 min and 0.20-mL subsamples of the supernatant collected for HPLC analysis. Centrifugation was performed using a refrigerated centrifuge maintained at 22-27°C. The soil was resuspended after subsamples were taken and replaced in storage after each sampling episode. The subsamples were stored in the dark in 2.0-mL glass vials. The equilibrium tests were continued for 70 d.

Laboratory column mobility tests

The mobility characteristics of the four TFBA and two TEFBA isomers were compared to those of Br^- in laboratory experiments under saturated and unsaturated flow conditions. Duplicate clear PVC tubes (45-cm long by 9.14-cm I.D.), fitted on one end with a mesh screen, plexiglass endcap with outflow hose-barb, and 100 mm of 6.5-mm polyvinyl tubing, were used as experimental columns. Columns were covered with aluminum foil to inhibit the growth of algae. Both columns were packed with the Bluepoint fine sand to a bulk density of 1.6 Mg m^{-3}. The columns were slowly saturated from the bottom with Socorro tap

water. The tap water had a pH of 7.81, total dissolved solids of 772 mg L^{-1}, conductivity of 750 mS m^{-1}, and hardness of 201 mg L^{-1} $CaCO_3$. After saturation, a constant ponded depth of 5 cm was established above the soil surface using a Mariotte siphon. Flow through the columns was set at 0.8 mL min^{-1}, using a pinchclamp on the outflow tubing, and was continued for several days to stabilize flow rates and water contents. Under a steady flow rate of 0.8 mL min^{-1}, the resulting PVs were 776 mL and 767 mL for columns 1 and 2, respectively. These PV values corresponded to a porosity and volumetric water content of 0.32 for both columns. After the PV measurements were taken the flow was allowed to re-equilibrate to 0.8 mL min^{-1}, whereupon tap water input ceased and a 2.0-PV tracer slug containing 75 mg L^{-1} Br^- and 50 mg L^{-1} of each of the FBA isomers in tap water was added. Mixing between the tracer slug and the tap water was minimized by removing non-labeled ponded water prior to the addition of the tracer slug. The tracer slug was also applied at a constant ponded depth of 5 cm. After all of the tracer slug had infiltrated tap water flow was resumed at the same constant ponded depth of 5 cm, again without mixing at the inlet. Effluent samples were collected approximately every 0.03 PV after the commencement of the tracer slug addition, using Retriever II automatic fraction collectors from ISCO Inc. (Lincoln, NE). Samples were then analyzed in approximately 0.1-PV intervals for the FBAs and Br^- via HPLC.

Following the saturated flow study, each column was emptied of the Bluepoint soil and carefully filled with <2-mm fine sand (unclassified) collected from a large dune in the vicinity of the Bluepoint soil. The fine sand used has a CEC of 0.0031 mol_c (Na^+) kg^{-1}, an organic carbon fraction of 0.0001, a pH (1:1 aqueous extract) of 7.5, and a silica sand content of 96.9%. This material provided a greater degree of desaturation under reduced flow rates than the Bluepoint soil. Both columns were packed to a bulk density of 1.6 Mg m^3 and slowly filled from the bottom with tap water to initially saturate them. The columns were leached with tap water for several days to remove trapped gases. Once flow had equilibrated, saturated pore volumes were measured in order to determine porosities within the columns. Saturated pore volumes were 901 mL and 895 mL for columns 1 and 2, respectively. The porosity of both columns was 0.37. Column outlets were opened, pinchclamps removed, and the Mariotte siphon apparatus was replaced with a gearmotor-driven syringe pump from Soil Measurement Systems (Tucson, AZ). A 9-cm filter paper was placed on top of the sand surface to aid water distribution. The syringe pump was then set to deliver 0.4 mL min^{-1} and the columns were allowed to desaturate. When the outflow rate equalled the inflow rate the PVs had stabilized at 763 mL and 775 mL, or 85% and 87% saturation, for columns 1 and 2, respectively. The lower portions of both columns were saturated. A 2.0-PV slug of Br^- (75 mg L^{-1}) and

FBAs (50 mg L^{-1} each), prepared in tap water, was added at the 0.4-mL min^{-1} flow rate. Effluent samples were again collected approximately every 0.03-PV after the commencement of tracer addition using automatic fraction collectors. Samples were analyzed in approximately 0.1-PV intervals for Br$^-$ and the FBAs via HPLC.

RESULTS AND DISCUSSION

Fluorobenzoate properties

The pK$_a$s for the six FBAs evaluated in this study along with six previously evaluated DFBAs, PFBA, and the reference material benzoic acid are reported in Table 1. Previously reported pK$_a$s for the DFBA isomers and PFBA are also presented in Table 1. The pK$_a$s for the TFBA and TEFBA isomers range 3.54 to 2.71 indicating they are all more than 99% anionic at pHs greater than 5.54.

Estimated aqueous diffusion coefficients for the TFBA and TEFBA isomers and the previously studied DFBA isomers and PFBA are presented in Table 2. The diffusion coefficients were nearly identical at 7.5 x 10^{-10} m^2 sec^{-1} and 7.4 x 10^{-10} m^2 sec^{-1} for the TFBA and TEFBA isomers, respectively. These values fall within the range for DFBA isomers and PFBA (Bowman and Gibbens, 1992) and are near the diffusion coefficients of 18 to 20 x 10^{-10} m^2 sec^{-1} reported for the common inorganic tracer anions Br$^-$, Cl$^-$, and I$^-$ (Wheast, 1983). Only in flow regimes

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where aqueous diffusion represents a significant component of the total hydrodynamic dispersion (i.e., very low pore water velocities and/or heavily aggregated soils) would these differences in diffusion coefficients cause differences in the macroscopic transport behavior between the TFBA and TEFBA isomers and the common inorganic tracer anions (Brusseau, 1993).

Fluorobenzoate analysis

A chromatogram of a Beardon soil extract containing the TFBA and TEFBA isomers (5 mg L^{-1}) and bromide (7.5 mg ^{-1}L) is presented in Fig. 2. The elution of the FBAs is in the order of decreasing pK_a. The apparent inversion of elution order between 2,4,5-TFBA and 2,3,4-TFBA was consistent throughout all analyses and is attributed to the overlapping pK_a values (Table 1).

Table 2 lists detection limits for the TFBA and TEFBA isomers evaluated in this study and compares them to detection limits measured for the previously evaluated DFBA isomers and PFBA. Detection limits were measured as the injected mass that gave a signal equal to twice the normal baseline noise signal. Band broadening due to longer elution time explains the higher detection limits for 2,3,6-TFBA and 2,3,5,6-TEFBA. Figure 3 illustrates the linearity of the detector response, in absorbance units, to the TFBA and TEFBA isomers between 150 and 1500 ng (6 to 60 mg L^{-1} with a 25-μL injection volume).

For this work FBA concentrations were kept between 1.0 and 50.0 mg L^{-1}, and Br^- concentrations were kept between 1.0 and 75.0 mg L^{-1}. Calibration for all analytes used single concentration external standards within the linear range, usually between 10.0 and 20.0 mg L^{-1}. Calibration was repeated after every 10 samples to check for potential instrument drift.

Batch soil equilibration tests

Results of the batch soil equilibration tests using Bluepoint, Beardon, and Naff soils are presented in Fig. 4. Data are plotted in terms of relative concentration (concentration of the compound divided by the initial concentration in solution) versus time. Figures shown are for the low concentration (5 mg L^{-1} for FBAs and 7.5 mg L^{-1} for Br^-) spike solutions. The same trends existed in the samples with high initial concentration solutions, but the sorption was not proportionally as great. Blank control samples showed no FBAs occurring naturally in any of the soils nor any FBA sorption to the centrifuge tube material. Figure 4 shows that for the Bluepoint soil there was no decrease in solution concentration during the 70 d of the experiment and the FBA concentrations were not statistically different (at the 95% level) from Br^- concentrations. Relative concentrations above 1.0 indicate potential anion exclusion of the FBAs and Br^-. Figure 4 also shows that the FBAs in contact with the Beardon and Naff soils

decreased in concentration over time. The solution concentration decreases were greater for FBAs with higher pK_as (weaker acids) and for the more acidic, higher organic carbon content Naff soil.

For both Beardon and the Naff soils quantitative recovery of all the FBA isomers was achieved after the system pH in each sample tube was raised to 10 with 0.20 mL of 50% (m/m) aqueous NaOH (Table 3). This indicated that although some of the weaker FBAs may have been protonated and sorbed as neutral organic molecules to soil organic matter, they were not chemically or microbially degraded.

Assuming that only the protonated form of the organic molecules were sorbed onto soil organic matter (Chiou et al., 1989; Grathwohl, 1990), estimating potential FBA sorption involves calculating an environment's ability to protonate the FBA ions. The fraction of FBA isomer found as a protonated species in a given environment is a function of the FBA isomer's pK_a and the natural water's pH. Assuming activity coefficients for all species are similar,

$$HA = (HA + A^-) * (10^{pH-pK_a} + 1)^{-1} \qquad (1)$$

where HA and A^- are the solution concentrations of the protonated and deprotonated forms of the FBA, respectively. Assuming that sorption of the protonated form of the FBA is a linear function of its solution concentration, a soil organic

matter partition coefficient, K_{oc}^*, *for the protonated FBA species alone*, may be calculated based on Eq.[1], total FBA concentration in solution, the soil OC, and the concentration of FBA compound sorbed onto the soil in mg/kg.

$$K_{oc}^* = (Conc.\ of\ Soil\text{-}Bound\ HA\ /\ HA\ in\ Solution) * (OC)^{-1} \quad (2)$$

The total mass sorbed was calculated by measuring concentration decreases during the course of the batch studies. The concentration of neutral FBA in solution was calculated from the total FBA solution concentration (HA + A⁻) using Eq.[1]. K_{oc}^* calculations were based on day 70 sample concentrations. Bluepoint soil batch results were not included in K_{oc}^* determinations due to the absence of any observed decrease in solution concentrations in this low-OC soil. Similarly, no FBA solution concentration decreases were seen for the low-pK_a 2,3,6-TFBA and 2,3,5,6-TEFBA in the Beardon soil. Concentration decreases for these samples, if any, were less than the resolution of the analytical method.

An overall distribution coefficient, K_D, for the neutral and anionic FBA species in solution can thus be estimated by multiplying the K_{oc}^* by the soil OC and the neutral FBA fraction in solution.

$$K_D = S/(HA + A^-) = K_{oc}^* * OC * (10^{pH-pK_a} + 1)^{-1} \quad (3)$$

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Here S is the concentration of FBA isomer sorbed to the soil. Unlike the K_{oc}^* the overall K_D is based on the total FBA concentration in solution, not just the concentration of the protonated species.

Table 4 shows the K_{oc}^*'s determined for each FBA isomer experiencing concentration loss in the batch equilibration studies with initial solution concentration of 5 mg L^{-1}. The average K_{oc}^* for the TFBAs and TEFBAs evaluated in this study was 18,200 L kg^{-1}, with a standard deviation of 6,300 L kg^{-1}. The calculated average neglects the 2,4,5- and 2,3,6-TFBA and the 2,3,5,6-TEFBA data from the Beardon soil because of negligible observed concentration decreases. As noted earlier, the fractions of FBA sorbed in the 50 mg L^{-1} samples were less than those observed in the 5 mg L^{-1} samples. These results indicate non-linear sorption and therefore a non-constant K_{oc}^* between 5 and 50 mg L^{-1}. Thus, the estimated K_{oc}^* may only apply to FBA solutions with concentrations of approximately 5 mg L^{-1} or less.

Although it is based on only a small number of samples, use of Eq.[3] and the K_{oc}^* value cited above can give an indication of sorption potential, K_D, of FBAs in a given environment. The range of K_Ds for the FBAs evaluated in this study was 0.01 L kg^{-1} to 0.10 L kg^{-1} in the Beardon soil and 0.05 L kg^{-1} to 0.34 L kg^{-1} in the Naff soil. Estimating a K_D specific to a tracer in a given subsurface environment may aid in selecting the appropriate FBA tracer compounds where high

soil organic carbon fractions and/or low soil pHs prevail.

Laboratory column mobility tests

The results for the saturated and unsaturated soil column leaching experiments are presented in Figs. 5 and 6. For both of the flow conditions the duplicate columns gave similar results. The differences between the observed FBA and Br^- C/C_0 values were summed over the entire BTC and over the upslope region only. In both cases, at the 95% level of significance, there was no difference between the means of the FBA and Br^- concentrations. Therefore, the BTCs for the TFBA and TEFBA isomers were indistinguishable from Br^-. Tracer retardation factors calculated with the non-linear least squares regression program CXTFIT (Parker and Van Genuchten, 1984) ranged from 0.95 to 0.98 for the duplicate columns under the saturated and unsaturated flow conditions. These retardation factors indicate a small amount of anion exclusion.

Mass recoveries for the FBAs and Br^- in all of the column tests ranged from 101% to 104%, indicating that no degradation or sorption occurred over the six-day duration of the experiments.

SUMMARY AND RECOMMENDATIONS

The experiments described above evaluated the physical, chemical stability, and mobility characteristics of four TFBA

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and two TEFBA isomers not previously evaluated for use as soil and groundwater tracers.

The results indicate that although sorption to organic matter in soils may occur under some soil pH and organic matter content conditions, all of the FBAs are chemically stable over a period of at least 70 d. In order to estimate the potential sorption to a given field soil the K_D may be calculated from Eq.[3], the soil pH, the soil OC, the pK_a of the desired FBA isomer, the total concentration of FBA in solution, and a K_{oc}^* of 18,200 L/Kg. Since the DFBA and PFBA isomers are chemically very similar to the TFBA and TEFBA isomers examined here, a K_{oc}^* of 18,200 L/Kg is likely reasonable for them as well.

Sorption was nonlinear between 5 and 50 mg L^{-1} solution concentrations. Thus, the K_{oc}^* and the resulting K_Ds calculated for the FBAs are non-constant in this range. The results provided herein are for solution concentrations of approximately 5 mg L^{-1}. The results also suggest that no sorption of the FBAs will occur to mineral surfaces, making these compounds appropriate for use in fractured, or sand or gravel aquifers.

The experimental conditions here did not include any strictly anaerobic environments. Such environments have been shown to allow biologically mediated reductive dehalogenation processes (Atlas and Bartha, 1993, p. 386). Since chlorobenzoates have been shown to be degraded by this

mechanism (Suflita et al., 1982), the defluorination of the FBAs under similar conditions may be possible. The stability of FBA isomers under strictly anaerobic conditions remains to be investigated. In the case of chlorinated hydrocarbons such as some pesticides, higher degrees of chlorine substitution lead to greater recalcitrance of the pesticide (Atlas and Bartha, 1993, p. 387). The same trend can be expected to hold for organo-fluorine compounds since the carbon-fluorine bond is stronger than the carbon-chlorine bond. Therefore, since the DFBA isomers were shown to be stable for periods of over 3 months in field soils and aquifers (Bowman and Gibbens, 1992), it is likely that the TFBA and TEFBA isomers are stable for at least this long.

All of the FBAs evaluated in this study showed transport properties indistinguishable from Br⁻. This was also the case with previously tested DFBA isomers (Bowman and Gibbens, 1992). The TFBA and TEFBA isomers evaluated in this study have detection limits similar to PFBA and the DFBA isomers (results herein), indicating that any of these 14 acids and Br⁻ could be used together in studies requiring several tracers and quantified simultaneously via HPLC. Studies that require fewer tracers may selectively employ those isomers least subject to sorption if the organic fraction in the porous medium is significant or those least subject to analytical interference from inorganic anions or dissolved organics in the sample matrix.

Absent any other factors, cost is key in choosing which TFBA or TEFBA isomers to use in a study. In this suite of potential soil/groundwater tracers 3,4,5-TFBA at $28 per gram was the most expensive. All other FBAs evaluated in this study ranged in price from $13 to $15 per gram in 5-g quantities. It should be noted here that in addition to being the most expensive, 3,4,5-TFBA is also the weakest acid in this suite making it the one most susceptible to sorption in soil/water systems. Where only one tracer is required for a field test bromide is still the most desirable compound due to its very low price of only a few cents per gram.

The toxicity of the FBA compounds has not been fully investigated. Early studies with white rats indicate that the benzoic acid moiety substituted with fluorine is less toxic than any other type of halogen-substituted benzoate and only slightly more toxic than unsubstituted benzoic acid (Hager and Starkey, 1943). Very little information exists on the fate of these compounds in man. Until more definite human toxicity information becomes available these compounds should not be used where the possibility of contaminating drinking water resources exists.

ACKNOWLEDGEMENTS

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FIGURE CAPTIONS

Fig. 1.   Acronyms, structures, and chemical names of the
           fluorobenzoates used in this study.

Fig. 2.   Chromatogram of a 25-μL injection of the four TFBA
           and two TEFBA isomers (5 mg L^{-1}) and Br⁻ (7.5 mg L^{-1})
           in a Beardon soil extract. HPLC conditions are as
           described in the Materials and Methods section.

Fig. 3.   Detector response as a function of analyte
           concentration for Br⁻ and the six FBAs evaluated
           in this study.

Fig. 4.   Results of batch equilibration tests using the six
           FBA isomers and Br⁻ with three soils at 24±2°C.
           Symbols, connected by solid lines, are same as used
           in Fig. 3.

Fig. 5.   Breakthrough curves for the six FBA isomers and Br⁻
           in a column of Bluepoint soil under saturated
           conditions. Symbols, connected by solid lines, are
           same as used in Fig. 3.

Fig. 6.   Breakthrough curves for the six FBA isomers and Br⁻
           in a column of sand under unsaturated
           conditions. Symbols, connected by solid lines, are
           same as used in Fig. 3.

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FLUOROBENZOATES
TESTED IN THIS STUDY

2,3,4-TFBA	2,4,5-TFBA	2,3,6-TFBA
2,3,4-trifluoro-benzoate	2,4,5-trifluoro-benzoate	2,3,6-trifluoro-benzoate

3,4,5-TFBA	2,3,4,5-TEFBA	2,3,5,6-TEFBA
3,4,5-trifluoro-benzoate	2,3,4,5-tetrafluoro-benzoate	2,3,5,6-tetrafluoro-benzoate

Fig. 1.   Acronyms, structures, and chemical names of the fluorobenzoates used in this study.

Fig. 2.   Chromatogram of a 25-μL injection of the four TFBA
           and two TEFBA isomers (5 mg L^{-1}) and Br$^-$ (7.5 mg L^{-1})
           in a Beardon soil extract. HPLC conditions are as
           described in the Materials and Methods section.

Fig. 3. Detector response as a function of analyte concentration for Br⁻ and the six FBAs evaluated in this study.

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FBA isomers and Br⁻ with three soils at 24±2°C.
Symbols, connected by solid lines, are same as used
in Fig. 3.

Fig. 5. Breakthrough curves for the six FBA isomers and Br⁻
in a column of Bluepoint soil under saturated
conditions. Symbols, connected by solid lines, are
same as used in Fig. 3.

Fig. 6.   Breakthrough curves for the six FBA isomers and Br⁻ in a column of sand under unsaturated conditions. Symbols, connected by solid lines, are same as used in Fig. 3.

Table 1. pK$_a$s For fluorinated benzoic acids at 25°C. Values in parentheses are standard deviations for triplicate analyses

Compound	pK$_a$ This Study	pK$_a$ Reported
Benzoic Acid	4.21(±.01)	4.21†
3,4-DFBA	3.83(±.01)	3.7‡
3,5-DFBA	3.59(±.01)	3.4‡
2,4-DFBA	3.58(±.01)	N/A
3,4,5-TFBA	3.54(±.01)	N/A
2,5-DFBA	3.30(±.01)	3.2‡
2,3,4-TFBA	3.30(±.02)	N/A
2,3-DFBA	3.29(±.01)	3.2‡
2,4,5-TFBA	3.28(±.01)	N/A
2,3,4,5-TEFBA	3.08(±.01)	N/A
2,6-DFBA	2.85(±.01)	3.0‡
2,4,6-TFBA	2.83(±.01)	N/A
2,3,6-TFBA	2.82(±.01)	N/A
PFBA	2.72(±.02)	2.7‡
2,3,5,6-TEFBA	2.71(±.01)	N/A

†   Serjeant (1984)

‡   Bowman and Gibbens (1992)

Table 2. Aqueous diffusion coefficients and detection limits for DFBA, TFBA, and TEFBA isomers, and PFBA.

Fluorobenzoate	Aqueous Diffusion Coefficient ($m^2sec^{-1}*10^{-10}$)	Detection Limit (ng)
2,3-DFBA	7.6†	2.9§
2,5-DFBA	7.6†	2.8§
3,4-DFBA	7.6†	2.1§
3,5-DFBA	7.6†	2.6§
2,6-DFBA	7.6†	2.1¶
PFBA	7.2‡, 7.2†	2.5¶
2,3,4-TFBA	7.5†	1.8
2,3,6-TFBA	7.5†	3.6
2,4,5-TFBA	7.5†	2.0
3,4,5-TFBA	7.5†	2.1
2,3,4,5-TEFBA	7.4†	2.5
2,3,5,6-TEFBA	7.4†	4.2

†   Estimated by Hayduk and Laudie method (Tucker and Nelken, 1982)

‡   Measured by Walter (1982)

§   Bowman and Gibbens (1992)

¶   Bowman (1984b)

Table 3. Relative FBA concentrations in Naff and Beardon
soils before and after treatment with sodium hydroxide.

Compound	C/C_o Before Naff	C/C_o After Naff	C/C_o Before Beardon	C/C_o After Beardon
3,4,5-TFBA	0.73	1.09	0.86	1.06
2,4,5-TFBA	0.83	1.00	0.99	1.06
2,3,4-TFBA	0.84	0.99	0.93	0.99
2,3,4,5-TEFBA	0.88	1.15	0.97	1.15
2,3,6-TFBA	0.90	0.96	1.01	1.00
2,3,5,6-TEFBA	0.97	0.98	1.02	1.08

Table 4. K_{oc}^* values for the six fluorobenzoates in the batch equilibration studies.

Fluorobenzoate	Naff Soil K_{oc}^* (L/Kg)	Beardon Soil K_{oc}^* (L/Kg)
3,4,5-TFBA	17,600	26,500
2,3,4-TFBA	10,200	21,100
2,4,5-TFBA	17,800	†
2,3,4,5-TEFBA	18,700	14,000
2,3,6-TFBA	27,700	†
2,3,5,6-TEFBA	10,000	†

† No measurable sorption

INTRODUCTION TO APPENDICES

This set of appendices provides the reduced data used to create all tables and figures presented in the text of "Tri- and Tetrafluorobenzoates as Soil and Groundwater Tracers." Data are also presented for duplicate column mobility tests, under saturated and unsaturated conditions, and 50-mg/L batch study tests not illustrated in the text. Methods not fully discussed in the text are described in the appropriate appendix section preceding the presentation of data obtained using that method.

The topics in the appendices appear in the same order as they appear in the main text. Reference to field tests of tracer stability in a sandy aquifer appear in the appendices, but not in the text due to the inconclusive results of the field experiments.

APPENDIX A. pK_a DETERMINATION METHOD

For this method <u>all solutions</u>, titrant and titrand, were prepared from deionized water which was previously boiled, allowed to cool, and adjusted to an ionic strength of 0.10 with KCl. This maintained a constant ionic strength in the fluoro-organic solution during titration with NaOH. The sodium hydroxide solution was prepared from a 50% NaOH solution to minimize carbonate error. In this procedure 25 mL of a 0.01 N fluoro-organic solution was placed in a 250-mL beaker which, in turn, was suspended in a temperature-controlled circulating water bath held at 25.0±0.2°C. The fluoro-organic solution was titrated with 0.01 N sodium hydroxide (NaOH) in 1.00-mL aliquots from a 25-mL burette. The titrant pH was recorded after each addition of base. All Ph measurements were taken using a Beckman PHI-45 Ph meter with a Beckman 39845 combination electrode, both from Beckman Instruments, Fullerton CA. Each titration was continued until the titrant Ph reached 11.0. The Ph meter was calibrated at pH 7.00 and 4.00 with standard buffers. The uncertainty inherent in the pH measurements was ±0.01 pH unit. Benzoic acid with a known pK_a of 4.21 (Serjeant, 1984, p. 308) was used as a reference material to ensure the accuracy of the method. Each acid was analyzed in triplicate.

The pH value obtained with each addition of base was plotted against the amount of NaOH added to generate titration curves for each acid. The pH of the one-half equivalence point was used to evaluate the pK_a of the titrated acid. The one-half equivalence point was determined on each titration curve as one-half the volume of base required to reach the titration endpoint (point of maximum slope on the titration curve). A single-point method was used in this study because of the large range of acid strengths between all the FBAs tested. Gran plots meant to linearize the titration curves, and thereby estimate the acid's equilibrium constant accurately, became curved as pK_a values went below about 3.9. As acid strengths increased there became no linear region on the Gran plots from which to determine a slope. Thus, the range of acid strengths over which the linear Gran function can be applied is quite narrow (Schwartz, 1987, Pehrsson, et al., 1976, Gran, 1988) and therefore was not used in this study.

During the titration of a weak to moderately weak acid the pK_a for the acid may be written as $pK_a = pH - \log[(A^-)/(HA)]$, where (A^-) and (HA) are the activities of the deprotonated and protonated acid species, respectively. At the one-half

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APPENDIX A. (Continued)

equivalence point, the concentrations of A^- and HA are equal and the pK_a expression may be written as $pK_a = pH - log[f_{a^-}/f_{HA}]$ where f_{a^-} and f_{HA} are the activity coefficients of the deprotonated and protonated acid species, respectively. Assuming that activity coefficient for uncharged species in aqueous solution is unity, the pK_a expression becomes $pK_a = pH - log f_{a^-}$. At an ionic strength of 0.10 with KCl the activity coefficient for a monovalent ion is 0.77 (Ride, 1991, p. 5-99). The pK_a values were therefore evaluated at the one-half equivalence point as $pK_a = pH - 0.77$ (Skoog and West, 1980, pp. 570-571).

Appendix Table A1. Titration Curve Data for Benzoic Acid

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	3.07	3.07	3.08
1	3.18	3.18	3.17
2	3.27	----	3.27
3	3.37	3.36	3.37
4	3.46	3.45	3.45
5	3.54	3.53	3.54
6	3.67	3.61	3.62
7	3.70	3.69	3.69
8	3.77	3.76	3.76
9	3.83	3.82	3.83
10	3.90	3.89	3.90
11	3.96	3.95	3.96
12	4.03	4.02	4.03
13	4.10	4.09	4.09
14	4.16	4.16	4.16
15	4.23	4.22	4.22
16	4.30	4.29	4.29
17	4.37	4.36	4.37
18	4.45	4.44	4.44
19	4.53	4.52	4.53
20	4.63	4.62	4.62
21	4.73	4.47	4.72
22	4.86	4.84	4.84
23	5.02	4.99	4.99
24	5.23	5.19	5.20
25	5.64	5.54	5.54
26	8.45	7.30	6.80
27	9.98	9.95	9.88
28	10.35	10.33	10.31
29	10.55	10.54	10.52
30	10.68	10.66	10.66
31	10.78	10.76	10.76
32	10.85	10.83	10.84
33	10.92	10.90	10.91
34	10.97	10.95	10.96

Appendix Table A2. Titration Curve Data for 3,4-DFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.90	2.90	2.90
1	2.97	2.97	2.97
2	3.04	3.03	3.04
3	3.11	3.10	3.11
4	3.18	3.17	3.18
5	3.25	3.24	3.24
6	3.31	3.30	3.34
7	3.37	3.37	3.37
8	3.43	3.43	3.43
9	3.49	3.49	3.50
10	3.55	3.55	3.56
11	3.62	3.61	3.62
12	3.67	3.67	3.68
13	3.73	3.73	3.74
14	3.80	3.80	3.81
15	3.87	3.87	3.87
16	3.93	3.94	3.94
17	4.00	4.06	4.01
18	4.08	4.09	4.09
19	4.16	4.17	4.17
20	4.26	4.27	4.27
21	4.36	4.37	4.37
22	4.50	4.50	4.50
23	4.66	4.67	4.67
24	4.90	4.91	4.90
25	5.36	5.38	5.36
26	8.90	9.09	8.93
27	9.95	10.04	9.98
28	10.01	10.35	10.32
29	10.50	10.53	10.56
30	10.64	10.65	10.64
31	10.73	10.74	10.74
32	10.82	10.80	10.86
33	10.87	10.68	10.88
34	10.93	10.93	10.93

Appendix Table A3. Titration Curve Data for 3,5-DFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.77	2.76	2.76
1	2.82	2.81	2.82
2	2.88	2.87	2.87
3	2.93	2.92	2.93
4	2.99	2.98	2.99
5	3.04	3.04	3.04
6	3.10	3.09	3.10
7	3.15	3.15	3.15
8	3.21	3.21	3.21
9	3.26	3.26	3.26
10	3.32	3.31	3.32
11	3.37	3.37	3.37
12	3.43	3.43	3.43
13	3.49	3.49	3.49
14	3.55	3.55	3.55
15	3.61	3.61	3.61
16	3.67	3.67	3.68
17	3.74	3.74	3.75
18	3.81	3.82	3.82
19	3.89	3.90	3.91
20	3.98	3.99	4.00
21	4.08	4.10	4.11
22	4.20	4.22	4.24
23	4.36	4.38	4.41
24	4.57	4.61	4.65
25	4.95	5.04	5.14
26	7.40	8.60	9.13
27	9.82	9.91	10.04
28	10.25	10.28	10.37
29	10.46	10.49	10.55
30	10.61	10.63	10.69
31	10.71	10.72	10.78
32	10.79	10.80	10.85
33	10.86	10.86	10.91
34	10.91	10.91	10.97

Appendix Table A4. Titration Curve Data for 2,4-DFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.90	2.90	2.92
1	2.99	2.99	3.00
2	3.08	3.08	3.09
3	3.17	3.16	3.17
4	3.25	3.25	3.26
5	3.35	3.35	3.35
6	3.45	3.45	3.46
7	3.55	3.56	3.56
8	3.67	3.68	3.68
9	3.82	3.82	3.82
10	3.99	3.99	3.99
11	4.22	4.23	4.23
12	4.64	4.65	4.65
13	9.08	8.90	8.50
14	10.18	10.16	10.09
15	10.48	10.48	10.14
16	10.65	10.66	10.63
17	10.76	10.79	10.77
18		10.88	10.85
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Appendix Table A5. Titration Curve Data for 3,4,5-TFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.75	2.76	2.76
1	2.79	2.80	2.80
2	2.85	2.85	2.85
3	2.90	2.91	2.90
4	2.95	2.96	2.96
5	3.00	3.01	3.01
6	3.06	3.06	3.07
7	3.11	3.12	3.11
8	3.17	3.17	3.17
9	3.22	3.22	3.22
10	3.27	3.27	3.27
11	3.32	3.33	3.33
12	3.38	3.38	3.39
13	3.44	3.44	3.44
14	3.50	3.50	3.51
15	3.56	3.57	3.57
16	3.62	3.63	----
17	3.69	3.70	----
18	3.76	3.77	----
19	3.85	3.85	----
20	3.94	3.95	3.95
21	4.04	4.06	4.05
22	4.17	4.18	4.18
23	4.33	4.35	4.35
24	4.55	4.59	4.56
25	4.98	5.07	5.02
26	8.50	8.77	8.90
27	9.84	9.90	9.92
28	10.25	10.27	10.30
29	10.48	10.49	10.51
30	10.63	10.64	10.65
31	10.74	10.74	10.75
32	10.82	10.82	10.82
33	10.89	10.89	10.89
34	10.95	10.95	10.95

Appendix Table A6.   Titration Curve Data for 2,5-DFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.59	2.58	2.59
1	2.63	2.63	2.63
2	2.67	2.67	2.67
3	2.71	2.71	2.72
4	2.76	2.75	2.76
5	2.80	2.80	2.81
6	2.85	2.84	2.85
7	2.89	2.89	2.90
8	2.93	2.94	2.94
9	2.97	2.98	2.99
10	3.03	3.03	3.03
11	3.07	3.08	3.08
12	3.12	3.13	3.13
13	3.17	3.18	3.18
14	3.23	3.23	3.23
15	3.28	3.28	3.28
16	3.34	3.34	3.34
17	3.41	3.40	3.41
18	3.47	3.48	3.48
19	3.55	3.55	3.55
20	3.63	3.64	3.64
21	3.72	3.73	3.74
22	3.84	3.84	3.85
23	3.99	3.99	3.99
24	4.19	4.19	4.19
25	4.53	4.53	4.53
26	6.12	6.06	6.28
27	9.79	9.79	9.83
28	10.26	10.25	10.27
29	10.49	10.49	10.51
30	10.64	10.63	10.65
31	10.74	10.73	10.75
32	10.82	10.82	10.82
33	10.88	10.88	10.88
34	10.94	10.94	10.94

Appendix Table A7. Titration Curve Data for 2,3,4-TFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.60	2.61	2.62
1	----	----	2.66
2	2.68	2.69	2.71
3	2.72	2.73	2.75
4	2.76	2.78	2.79
5	2.81	2.82	2.83
6	2.85	2.87	2.88
7	2.90	2.91	2.92
8	2.95	2.95	2.97
9	3.00	3.00	3.02
10	3.04	3.05	3.07
11	3.09	3.10	3.12
12	3.14	3.15	3.17
13	3.19	3.20	3.22
14	3.25	3.26	3.28
15	3.31	3.32	3.33
16	3.38	3.39	3.40
17	3.44	3.46	3.46
18	3.52	3.53	3.55
19	3.61	3.62	3.63
20	3.71	3.71	3.72
21	3.82	3.83	3.84
22	3.96	3.97	3.98
23	4.17	4.17	4.18
24	4.51	4.51	4.51
25	6.18	6.08	5.80
26	9.82	9.89	9.78
27	10.28	10.32	10.25
28	10.50	10.55	10.49
29	10.65	10.68	10.65
30	10.76	10.79	10.77
31	10.84	10.88	10.86
32	10.91	10.93	10.93
33	10.96	10.99	10.99
34	11.01	11.04	11.03

Appendix Table A8. Titration Curve Data for 2,3-DFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.57	2.58	2.59
1	2.62	2.63	2.63
2	2.66	2.67	----
3	2.70	2.71	----
4	2.75	2.75	2.76
5	2.79	2.80	2.80
6	2.83	2.84	2.85
7	2.88	2.88	2.89
8	2.92	2.93	2.93
9	2.97	2.97	2.98
10	3.02	3.02	----
11	3.06	3.07	3.07
12	3.11	3.12	3.12
13	3.16	3.17	3.17
14	3.21	3.22	3.22
15	3.27	3.27	3.28
16	3.33	3.33	3.33
17	3.40	3.39	3.39
18	3.46	3.46	3.46
19	3.53	3.54	3.53
20	3.61	3.62	3.61
21	3.71	3.71	3.71
22	3.83	3.82	3.82
23	3.96	3.96	3.95
24	4.15	4.14	4.13
25	4.45	4.46	4.43
26	5.52	5.50	5.30
27	9.73	9.70	9.63
28	10.24	10.23	10.20
29	10.48	10.48	10.46
30	10.63	10.63	10.61
31	10.73	10.73	10.72
32	10.81	10.81	10.82
33	10.88	10.88	10.88
34	10.93	10.93	10.93

Appendix Table A9. Titration Curve Data for 2,4,5-TFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.59	2.59	2.58
1	2.63	2.62	2.62
2	2.68	2.67	2.66
3	2.72	2.72	2.71
4	2.76	2.76	2.80
5	2.81	2.80	2.84
6	2.85	2.85	2.89
7	2.90	2.89	----
8	2.94	2.94	----
9	2.99	2.98	2.98
10	3.03	3.03	3.03
11	3.09	3.08	3.08
12	3.13	3.13	3.13
13	3.18	3.18	3.18
14	3.24	3.24	3.23
15	3.30	3.29	3.29
16	3.36	3.35	3.35
17	3.42	3.42	3.41
18	3.49	----	----
19	3.58	3.57	3.56
20	3.67	3.66	3.65
21	3.77	3.76	3.76
22	3.90	3.89	3.88
23	4.07	4.05	4.04
24	4.31	4.28	4.27
25	4.87	4.77	4.73
26	9.38	9.16	9.16
27	10.12	10.03	10.05
28	10.41	10.37	10.37
29	10.59	10.55	10.56
30	10.70	10.68	10.68
31	10.79	10.77	10.77
32	10.86	10.84	10.84
33	10.92	10.91	10.90
34	10.94	10.94	----

Appendix Table A10.   Titration Curve Data for 2,3,4,5-TEFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.45	2.45	2.46
1	2.48	----	2.51
2	2.52	2.53	2.54
3	2.56	2.57	2.58
4	----	2.61	2.61
5	2.63	2.64	2.65
6	2.67	2.68	2.69
7	2.72	2.72	2.73
8	2.75	2.76	2.77
9	2.80	2.80	2.81
10	2.84	2.85	2.85
11	2.89	2.89	2.90
12	2.93	2.94	2.95
13	2.98	2.99	3.00
14	3.04	3.04	3.05
15	3.09	3.10	3.11
16	3.15	3.16	3.17
17	3.22	3.22	3.23
18	3.29	3.30	3.30
19	3.37	3.38	3.39
20	3.47	3.47	3.49
21	3.58	3.59	3.60
22	3.73	3.73	3.74
23	3.94	3.94	3.95
24	4.30	4.30	4.33
25	6.28	6.25	6.30
26	9.73	9.71	9.72
27	10.20	10.21	10.21
28	10.46	10.47	10.47
29	10.63	10.63	10.64
30	10.75	10.75	10.75
31	10.83	10.83	10.84
32	10.90	10.90	10.91
33	10.96	10.96	10.96
34	11.00	11.00	11.00

Appendix Table A11. Titration Curve Data for 2,6-DFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.29	2.28	2.28
1	2.32	2.31	2.31
2	2.34	2.34	2.34
3	2.37	2.37	2.37
4	2.41	2.40	2.40
5	2.44	2.44	2.44
6	2.47	2.47	2.47
7	2.51	2.50	2.51
8	2.54	2.54	2.54
9	2.58	2.57	2.58
10	2.62	2.61	2.62
11	2.66	2.65	2.65
12	2.70	2.69	2.70
13	2.74	2.73	2.74
14	2.78	2.78	2.79
15	2.83	2.83	2.84
16	2.89	2.88	2.88
17	2.94	2.94	2.95
18	3.00	3.00	----
19	3.07	3.07	----
20	3.15	3.15	3.16
21	3.24	3.24	3.25
22	3.36	3.35	3.34
23	3.50	3.49	3.50
24	3.70	3.69	3.71
25	4.08	4.06	4.09
26	8.01	8.30	7.96
27	9.97	10.00	9.96
28	10.36	10.38	10.34
29	10.57	10.58	10.55
30	10.70	10.71	10.69
31	10.80	10.81	10.79
32	10.87	10.88	10.87
33	10.94	10.94	10.93
34	10.99	10.99	----

Appendix Table A12. Titration Curve Data for 2,4,6-TFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.27	2.27	2.27
1	2.30	2.29	2.78
2	2.33	2.33	2.32
3	----	2.36	2.35
4	----	2.39	2.39
5	2.45	2.42	2.42
6	2.46	2.45	2.45
7	2.50	2.49	2.49
8	2.53	2.53	2.53
9	2.57	2.57	2.57
10	2.61	2.60	2.61
11	2.65	2.64	2.65
12	2.69	2.68	2.69
13	2.73	2.73	2.73
14	2.78	2.78	2.78
15	2.83	2.83	2.83
16	2.88	2.88	2.88
17	----	2.93	----
18	----	3.01	3.01
19	3.07	3.08	3.08
20	3.16	3.16	3.16
21	3.27	3.26	3.26
22	3.38	3.38	----
23	3.53	3.53	3.54
24	3.78	3.77	3.77
25	4.30	4.30	4.28
26	8.99	9.10	8.88
27	9.99	10.03	9.97
28	10.34	10.35	10.32
29	10.54	10.54	10.53
30	10.66	10.66	10.65
31	10.76	10.76	10.73
32	10.83	10.83	10.81
33	10.90	10.89	10.86
34	10.94	10.93	10.92

Appendix Table A13. Titration Curve Data for 2,3,6-TFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.24	2.25	2.26
1	2.27	2.29	2.28
2	2.31	2.31	2.32
3	2.34	2.34	2.35
4	2.37	2.37	2.38
5	2.40	2.41	2.42
6	2.43	2.44	2.45
7	2.47	2.48	2.49
8	2.51	2.51	2.52
9	2.54	2.55	2.56
10	2.58	2.59	2.60
11	2.62	2.63	2.63
12	2.66	2.67	2.68
13	2.71	2.71	2.72
14	2.76	2.76	2.77
15	2.81	2.81	2.82
16	2.86	2.87	2.87
17	2.92	2.93	2.93
18	2.99	2.99	3.00
19	3.06	3.06	3.07
20	3.15	3.15	3.15
21	3.24	3.25	3.26
22	3.36	3.37	3.38
23	3.53	3.53	3.54
24	3.78	3.78	3.79
25	4.39	4.35	4.43
26	9.42	9.41	9.58
27	10.18	10.17	10.26
28	10.48	10.48	10.53
29	10.66	10.66	10.69
30	10.77	10.78	10.81
31	10.86	10.87	10.89
32	10.93	10.94	10.96
33	10.99	11.01	11.01
34	11.04	11.05	----

Appendix Table A14. Titration curve data for PFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	----	2.14	2.15
1	----	2.17	2.18
2	----	2.20	2.22
3	----	2.23	2.25
4	----	2.27	2.28
5	----	2.30	2.32
6	----	2.34	2.35
7	----	2.38	2.38
8	----	2.41	2.42
9	----	2.45	2.46
10	----	2.49	2.50
11	----	2.53	2.54
12	----	2.57	2.58
13	----	2.62	2.63
14	----	2.67	2.67
15	----	2.72	2.73
16	----	2.77	2.78
17	----	2.83	2.84
18	----	2.89	2.91
19	----	2.97	2.98
20	----	3.05	3.07
21	----	3.16	3.17
22	----	3.28	3.31
23	----	3.45	3.50
24	----	3.70	3.80
25	----	4.36	4.99
26	----	9.48	9.60
27	----	10.16	10.20
28	----	10.46	10.46
29	----	10.62	10.62
30	----	10.73	10.73
31	----	10.82	10.81
32	----	10.89	10.88
33	----	10.94	10.94
34	----	11.00	10.98

Appendix Table A15. Titration Curve Data for 2,3,5,6-TEFBA

NaOH (ml)	pH (Trial #1)	pH (Trial #2)	pH (Trial #3)
0	2.15	2.14	2.14
1	2.17	2.16	2.17
2	2.20	2.20	2.20
3	2.23	2.23	2.24
4	2.26	2.26	2.27
5	2.29	2.29	2.30
6	2.33	2.33	2.34
7	2.36	2.37	2.37
8	2.40	2.40	2.41
9	2.44	2.44	2.45
10	2.48	2.48	2.48
11	2.51	2.52	2.53
12	2.56	2.56	2.57
13	2.63	2.61	2.61
14	2.65	2.66	2.67
15	2.70	2.71	2.71
16	2.76	2.76	2.77
17	2.82	2.82	2.83
18	2.89	2.89	2.90
19	2.96	2.97	2.98
20	3.05	3.05	3.07
21	3.15	3.16	3.17
22	3.28	3.29	3.30
23	3.46	3.47	3.48
24	3.74	3.77	3.77
25	4.58	4.82	4.77
26	9.35	9.47	9.40
27	10.04	10.12	10.06
28	10.35	10.38	10.35
29	10.53	10.57	10.55
30	10.66	10.69	10.67
31	10.76	10.78	10.76
32	10.83	10.84	10.83
33	10.89	10.91	10.89
34	10.94	10.96	10.94

APPENDIX B. CALCULATION OF AQUEOUS DIFFUSION COEFFICIENTS.

This calculation used the relation found on page 17-20 of the Handbook of Chemical Property Estimation Methods (Tucker and Nelken, 1982) for calculating aqueous diffusion coefficients.

$$D_{BW} = \frac{13.26 \times 10^{-5}}{n_W^{1.14} * V'_B{}^{0.589}}$$

The term n_W refers to the viscosity of water in centipoise (cp) in g cm^{-1} sec^{-1}. The Handbook provides a table of viscosities for a range of water temperatures. Estimations in this study used 25.0°C.
The term V'_B refers to molar volume in cm^3 mol^{-1}. This estimation method assumes spherical molecules. The Handbook provides values for the volume of component molecules and elements. The values for each component of a molecule is summed to yield the molar V'_B. Thus, molar volumes may be determined for any molecule and used in the relation provided by Hayduk and Laudie. Not surprisingly, since this estimation method doesn't account for substitution positions, the TFBA compounds have one value and the TEFBA compounds have another.

APPENDIX C.   CHROMATOGRAPHIC METHOD.

All chromatographic analyses performed during this investigation were performed using the method outlined in the Materials and Methods section. No deviations were necessary from this method except for the gradual decrease in ionic strength (adjusted by decreasing the PO_4^{-2} concentration) as the column aged. One problem that caused a delay in analyzing some samples was caused by variability of the strength of the packing material in some new columns. These columns showed <u>very</u> long retention times initially, but eventually gave good separations using the mobile phase and conditions outlined above. During the "Equilibration" time, retention times fell rapidly and no accurate or efficient work could be done with any mobile phase.

Remedy...use columns from Regis that are from a lot of columns known to have good, reliable separatory quality at the beginning of use. Request a column from that lot if possible when reordering. If not possible, flush the new column with a 100 mg L^{-1} solution of tracers overnight at 0.5 mL min^{-1}. This should have the effect of speeding the rate at which the column gives effective separations in a reasonable amount of time.

If any questions arise during use that cannot be related to the Water's machinery or a mobile phase problem, Fax a chromatogram and a description of your problem to Susan Lye @ Regis: Fax no. 708/967-5876.

APPENDIX D.   DETECTION LIMIT CALCULATIONS.

   The detection limits for the FBAs and Br⁻ were calculated
using 25 μL injections of a standard tracer mix   containing
0.2 mg L^{-1} of each FBA and Br⁻. The real-time responses of the
individual compounds were recorded using a strip chart
recorder. The baseline noise was averaged over the period of
the total elution time for all of the compounds and compared
to the peak heights obtained from the analyte peaks. This
process was repeated three times and the concentration that
gave a peak height of twice the averaged baseline noise (the
Detection Limit (D.L.) signal) was linearly interpolated from
the analyte peak heights.

Compound	Concentration	Avg Signal Height(cm)	Avg 2xbase Height(cm)	Average D.L. (mg/L)
Br	0.2008	9.67	2.87	0.05986
3,4,5-TFBA	0.2016	6.89	2.87	0.08462
2,4,5-TFBA	0.2010	7.15	2.87	0.08114
2,3,4-TFBA	0.2048	8.18	2.87	0.07195
2,3,4,5-TEFBA	0.2052	6.08	2.87	0.09873
2,3,6-TFBA	0.2110	4.20	2.87	0.14412
2,3,5,6-TFBA	0.2022	3.42	2.87	0.16883

The following calculation, based on the 25 μL injection volume
used, was used to convert the average D.L. concentration to a
D.L. mass:

D.L. (conc.)*(25*10^{-6} L)*10^6 ng/mg=D.L. (mass in ng)

The following mass-based D.L.s were determined:

Compound	D.L. (ng)
Br	1.5
3,4,5-TFBA	2.1
2,4,5-TFBA	2.0
2,3,4-TFBA	1.8
2,3,4,5-TEFBA	2.5
2,3,6-TFBA	3.6
2,3,5,6-TEFBA	4.2

APPENDIX E. DETECTOR RESPONSE WITH INCREASING ANALYTE CONCENTRATIONS.

All injection volumes were 25 μL. Curves were forced through (0,0) because the non-linear region of the curve was at very low concentration. Linearity was seen at concentrations less than 1 mg L^{-1} for all analytes, during detection limit studies, and up to 75 mg L^{-1} for bromide during routine analysis.
Solutions used: 60 mg L^{-1}, 1:2 of 60 mg L^{-1}, 1:5 of 60 mg L^{-1}, 1:10 of 60 mg L^{-1}, and a forced (0,0) intercept.

3,4,5-TFBA

Conc. (mg/L)	Height (AU)
0	0
6.14	0.02203
12.28	0.04536
30.70	0.1130
61.40	0.22215

2,4,5-TFBA

Conc. (mg/L)	Height (AU)
0	0
6.16	0.02003
12.32	0.04083
30.8	0.10176
61.6	0.19917

2,3,4-TFBA

Conc. (mg/L)	Height (AU)
0	0
6.06	0.0240
12.12	0.04886
30.3	0.12279
60.6	0.24505

2,3,4,5-TFBA

Conc. (mg/L)	Height (AU)
0	0
6.20	0.01674
12.4	0.03417
31.0	0.08543
62.0	0.17048

Bromide

Conc. (mg/L)	Height (AU)
0	0
6.21	0.02285
12.42	0.046
31.05	0.11423
62.10	0.22426

2,3,6-TFBA

Conc. (mg/L)	Height (AU)
0	0
6.16	0.00995
12.32	0.02032
30.80	0.05109
61.60	0.10154

2,3,5,6-TEFBA

Conc. (mg/L)	Height (AU)
0	0
6.04	0.01017
12.08	0.02049
30.20	0.05127
60.40	0.10062

APPENDIX F1. SOIL BATCH EQUILIBRATION STUDY DATA. The 5-mg L^{-1} data from this set were used to create figures 4,5, and 6. The 50-mg L^{-1} data were not used to generate any figures in the text because better, more apparent, trends were seen in the low-concentration results. Results for the tube blanks at 5 mg L^{-1} are also presented. All data for the six FBA compounds and bromide are expressed as relative concentrations.

Appendix Table F1.1. Results for the 5 mg L^{-1} Blank Batch Equilibration Experiment

5 mg/L Blank results						
Days	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Bromide
1	1.000	0.992	0.988	0.959	1.057	1.048	0.997
3	0.984	0.992	0.988	0.973	1.012	1.010	0.997
5	1.016	1.057	1.000	0.988	1.025	1.035	1.015
7	1.014	1.040	1.008	0.973	0.990	0.992	0.993
14	1.010	1.052	1.024	0.979	1.012	1.017	0.997
21	1.006	1.046	1.004	0.982	1.016	1.016	1.007
28	1.012	1.060	1.016	0.988	1.012	1.010	1.016
35	1.047	1.079	1.012	1.008	1.057	1.035	1.044
42	1.022	1.058	1.020	0.975	1.033	1.029	1.025
49	1.035	1.065	1.026	1.004	1.059	1.045	1.020
56	1.043	1.052	1.032	0.998	1.031	1.052	1.032
63	1.004	1.038	1.008	0.982	1.012	1.029	1.000
70	1.035	1.036	1.032	1.008	0.980	1.047	0.993

Appendix Table F1.2. Results for the 5 mg L⁻¹ and 50 mg L⁻¹ Batch equilibration Experiments Using Bluepoint Sand

		Results for batch equilibration using Bluepoint soil and 5 mg/L initial solution conc.					
Days	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Bromide
1	1.058	1.047	1.023	1.007	1.003	1.041	1.020
3	1.020	1.019	1.018	1.006	1.014	1.021	1.027
5	1.046	1.078	1.052	1.018	1.052	1.031	1.020
7	1.041	1.077	1.035	1.006	1.031	1.035	1.008
14	1.023	1.071	1.028	0.999	1.042	1.034	1.024
21	1.012	1.071	1.022	0.985	1.014	1.003	1.081
28	1.029	1.090	1.030	1.008	1.020	1.030	1.024
35	1.043	1.060	1.023	0.975	1.007	1.011	1.018
42	1.048	1.091	1.056	1.008	1.056	1.035	1.044
49	1.074	1.113	1.061	1.032	1.077	1.071	1.041
56	1.065	1.093	1.039	1.020	1.033	1.039	1.041
63	1.036	1.105	1.052	1.031	1.021	1.036	1.026
70	1.018	1.056	1.025	1.010	0.983	1.049	1.049
		Results for batch equilibration using Bluepoint soil and 50 mg/L initial solution conc.					
Days	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Bromide
1	1.057	1.031	1.049	1.033	1.003	1.008	0.998
3	1.059	1.040	1.044	1.040	1.018	1.006	0.991
5	1.050	1.066	1.060	1.003	1.022	0.997	0.967
7	1.068	1.079	1.079	1.033	1.049	1.041	0.990
14	1.057	1.071	1.079	1.036	1.056	1.040	1.010
21	1.028	1.062	1.049	1.023	1.039	1.010	0.996
28	1.076	1.078	1.068	1.035	1.039	1.008	0.967
35	1.056	1.067	1.054	1.029	1.038	1.009	0.973
42	1.058	1.084	1.079	1.030	1.024	1.012	0.984
49	1.095	1.096	1.092	1.041	1.042	1.035	1.021
56	1.051	1.058	1.037	1.007	1.009	0.985	0.964
63	1.025	1.080	1.068	1.039	1.029	1.024	1.019
70	1.061	1.068	1.016	1.002	1.019	1.008	1.015

Appendix Table F1.3. Results for the 5 mg L⁻¹ and 50 mg L⁻¹ Batch Equilibration Experiments Using Beardon Soil

Results for batch equilibration using Beardon soil and 5 mg/L initial solution conc.						
Days	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Bromide
1	0.965	1.039	1.013	0.984	1.036	1.068	1.070
3	0.909	1.001	0.995	0.980	1.046	1.063	1.054
5	0.915	1.071	1.025	0.990	1.050	1.038	1.047
7	0.914	1.065	1.022	0.989	1.023	1.087	1.055
14	0.876	1.020	1.001	0.994	1.050	1.049	1.030
21	0.879	1.022	0.992	0.962	1.027	1.052	1.011
28	0.860	1.029	0.972	0.956	1.026	1.052	1.011
35	0.888	1.034	0.975	0.966	1.024	1.044	1.029
42	0.893	1.021	0.979	0.978	1.027	1.063	1.014
49	0.926	1.055	0.994	0.993	1.060	1.084	1.037
56	0.916	1.023	0.992	0.968	0.992	1.025	1.034
63	0.878	0.996	0.934	0.961	1.013	1.016	1.059
70	0.863	0.995	0.928	0.973	1.015	1.033	1.063

Results for batch equilibration using Beardon soil and 50 mg/L initial solution conc.						
Days	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Bromide
1	1.031	1.068	1.075	1.069	1.085	1.070	0.967
3	0.985	1.025	1.029	1.028	1.050	1.039	1.006
5	0.957	1.070	1.069	1.016	1.068	1.043	1.003
7	0.981	1.070	1.070	1.036	1.064	1.043	1.029
14	0.973	1.044	1.037	1.011	1.059	1.042	1.009
21	0.925	1.043	1.028	1.017	1.059	1.038	0.988
28	0.983	1.072	1.063	1.039	1.067	1.045	1.001
35	0.960	1.059	1.043	1.025	1.067	1.036	1.006
42	0.962	1.050	1.046	1.017	1.063	1.044	1.003
49	0.994	1.074	1.067	1.026	1.046	1.055	1.003
56	0.992	1.069	1.055	1.015	1.055	1.026	0.999
63	1.028	1.047	0.990	1.003	1.025	1.023	1.034
70	1.011	1.049	1.007	0.980	1.032	1.031	1.045

Appendix Table F1.4. Results for the 5 mg L^{-1} and 50 mg L^{-1} Batch Equilibration Experiments Using Naff Soil

Results for batch equilibration using Naff soil and 5 mg/L initial solution conc.						
Days	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Bromide
1	0.966	1.023	1.018	1.025	1.065	1.078	1.100
3	0.918	1.025	1.018	1.023	1.073	1.088	1.113
6	1.036	0.975	0.976	0.998	1.045	1.055	1.081
10	1.010	0.971	0.974	0.998	1.043	1.078	1.095
14	1.018	0.979	0.976	0.996	1.049	1.049	1.047
21	0.871	0.922	0.921	0.947	0.992	1.027	1.029
28	0.793	0.893	0.901	0.926	0.971	1.067	1.095
35	0.779	0.888	0.893	0.920	0.986	1.022	1.095
42	0.775	0.882	0.887	0.916	0.978	1.022	1.036
49	0.745	0.859	0.862	0.901	1.022	1.016	1.017
56	0.711	0.812	0.816	0.866	0.953	1.049	1.048
70	0.727	0.831	0.844	0.879	0.904	0.973	1.068

Results for batch equilibration using Naff soil and 50 mg/L initial solution conc.						
Days	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Bromide
1	0.958	1.025	1.055	1.026	1.036	1.035	1.000
3	0.881	0.956	0.986	0.980	0.985	1.004	1.010
6	0.915	0.983	1.017	1.012	1.017	1.025	1.042
10	0.928	1.000	1.036	1.034	1.033	1.029	1.061
14	0.901	0.967	1.007	1.007	1.019	1.002	0.975
21	0.967	1.014	1.015	1.020	1.013	1.028	1.046
28	0.943	0.996	0.997	1.009	1.002	1.052	1.018
35	0.946	0.994	0.995	1.001	0.995	1.036	1.036
42	0.956	0.994	0.996	1.017	0.984	1.036	1.006
49	0.917	0.963	0.960	0.986	1.013	0.985	0.988
56	0.912	0.946	0.974	0.997	0.985	1.016	1.009
70	0.919	0.949	0.961	0.989	0.997	1.000	1.013

APPENDIX F2. K_{oc}^* Calculations.

This appendix provides data and calculations used to determine the K_{oc}^* values seen in Table 4. of the manuscript. Calculations are numbered 1 thru 8.

#1 Fraction of FBA in solution as neutral species. Eq.[1] in the text was used with soil pH and FBA pK_a data provided in the manuscript to determine the fraction of FBA in neutral form.

#2 Total mass withdrawn. This value was obtained by multiplying 0.0002 L by the C/C_0 value on each sampling day prior to day 70 and summing the results for each soil. The values are listed in Appendix Table F2.2.

#3 Total mass remaining in each system. This value was calculated by subtracting the withdrawn masses (#2) from the product of the C_0 given in Appendix Table F2.1 and 0.02 L.

#4 Total mass sorbed in each system. This value was calculated with the following equation:

$(1-C/C_0) * (\#3) =$ Mass Sorbed

#5 The total mass remaining in each <u>solution</u> was calculated by taking the difference of #3 and #4 above.

#6 The amount of neutral acid in solution in each system is calculated as the product of #1 and #5 above.

#7 The K_D of each neutral FBA species in solution. This parameter was calculated using the results for sorbed mass in #4 and solution neutral mass in #6 and the dry soil mass used, and the day 70 solution volume of 0.0174 L. The Bluepoint, Beardon, and Naff soils had moisture contents of 0.97%, 3.02%, and 2.02%, respectively. These moisture contents lead to average dry soil masses used in the equilibration tests of 19.82, 19.40, and 19.61 grams for the Bluepoint, Beardon, and Naff systems, respectively. The calculation was as follows:

$(\#4/\text{Dry Mass of Soil})/(\#6/0.0174 \text{ L}) = K_D$

#8 The K_{oc}^* of the neutral FBA species in solution was calculated by dividing the result of #7 by each soil's organic carbon fraction.

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Appendix Table F2.1. Initial C_0 Data for Soil Batch Equilibration Tests.

Compound	Bluepoint High mg/L	Bluepoint Low mg/L	Beardon High mg/L	Beardon Low mg/L	Naff High mg/L	Naff Low mg/L
Bromide	75.2	7.52	75.2	7.52	74.9	7.49
2,3,4-TFBA	50.6	5.06	50.6	5.06	50.6	5.06
2,3,6-TFBA	51.0	5.10	51.0	5.10	51.0	5.10
2,4,5-TFBA	50.4	5.04	50.4	5.04	51.6	5.16
3,4,5-TFBA	50.8	5.08	50.8	5.08	49.8	4.98
2,3,4,5-TEFBA	51.4	5.14	51.4	5.14	51.4	5.14
2,3,5,6-TEFBA	51.6	5.16	51.6	5.16	51.0	5.10

Appendix Table F2.2. Total FBA Masses Removed Over Course of Equilibration Study.

Fluorobenzoate	Beardon Soil (mg FBA removed)	Naff Soil (mg FBA removed)
3,4,5-TFBA	0.011869	0.011022
2,4,5-TFBA	0.013478	0.012276
2,3,4-TFBA	0.01198	0.012026
2,3,4,5-TEFBA	0.013049	0.012622
2,3,6-TFBA	-NA-	0.013272
2,3,5,6-TEFBA	-NA-	0.013764

APPENDIX G. LABORATORY COLUMN BREAKTHROUGH CURVE DATA. This appendix section provides data used in Figures 7 and 8. Data from duplicate columns also appear. The presentation of the Relative Concentration vs. P.V. data are preceded by column data and flow information used to generate best fit curves to the real bromide BTCs via CXT FIT.

Appendix Table G1. Saturated Column Physical Data

Calculations were performed to determine the density of packing material, the porewater velocity, and the volumetric water content in each column under saturated and unsaturated flow conditions. Saturated columns were packed Bluepoint fine sand from the Sevilleta National Wildlife Refuge.

Saturated Column #	Empty Mass (g)	Full Dry Mass (g)	Column Volume (cm^3)	Bulk Density (g/cm^3)
1	926	4880	2427.6	1.63
2	915	4924	2427.6	1.65

Saturated Column #	Saturated Mass (g)	Volumetric H$_2$O Content(-)	Pore Volume (ml)
1	5656	0.32	776
2	5691	0.32	767

Porewater velocity calculations involved the column internal area, total fluid flow over the period of time used to run the column test, the time used to run the test, and the column's volumetric water content. Unsaturated columns were packed with fine sand from dunes in the SNWR.

Saturated Column #1 Porewater Velocity:
$V = (4276.84 \text{ cm}^3)/((5250 \text{ min})*(65.6 \text{ cm}^2)*0.32) = \underline{0.039 \text{ cm/min}}$

Saturated Column #2 Porewater Velocity:
$V = (4071.64 \text{ cm}^3)/((5250 \text{ min})*(65.6 \text{ cm}^2)*0.32) = \underline{0.037 \text{ cm/min}}$

The pathlength for the saturated column test was 39.0 cm because of swelling in the column material over the course of experiment.

Appendix Table G2. Unsaturated Column Physical Data

Unsaturated Column #	Empty Mass (g)	Full Dry Mass (g)	Column Volume (cm^3)	Bulk Density (g/cm^3)
1	882	4837	2427.6	1.63
2	873	4851	2427.6	1.64

Unsaturated Column #	Saturated Mass (g)	Unsaturated Mass (g)	Volumetric H$_2$O Content
1	5738	5600	0.37
2	5746	5626	0.37

Unsaturated Column #	Saturated P.V. (cm³)	Unsaturated P.V. (cm³)	Percent Saturation
1	901	763	85
2	895	775	87

Unsaturated Column #1 Porewater Velocity:
$$V = (3358.7 \text{ cm}^3)/((8100 \text{ min})*(65.6 \text{ cm}^2)*0.37) = \underline{0.017 \text{ cm/min}}$$

Unsaturated Column #2 Porewater Velocity:
$$V = (3171.3 \text{ cm}^3)/((8150 \text{ min})*(65.6 \text{ cm}^3)*0.37) = \underline{0.016 \text{ cm/min}}$$

The pathlength used for the unsaturated flow experiment was 37.0 cm, since there was no swelling of the fine sand used in the experiment.

CXTFIT parameters used for all curve fitting:

Version 2 of the program was used for flux concentrations.

First order decay was allowed in the event microbial activity decreased the concentration of the tracers over the course of the experiment.

Dimensionless units were used for concentration and time. Normalized concentration was used for concentration and Pore Volumes were used for time values.

In the saturated flow experiment tracer slugs were 2.042 and 2.057 pore volumes for columns #1, and #2, respectively.

In the unsaturated flow experiment tracer slugs were 2.157, and 1.962 pore volumes for columns #1, and #2, respectively.

CXTFIT Results

Saturated Column #1
$R^2 = 0.997$
$D = 8.35 \text{ cm}^2/\text{Day}$
$R = 0.96$

Saturated Column #2
$R^2 = 0.997$
$D = 7.92 \text{ cm}^2/\text{Day}$
$R = 0.98$

Unsaturated Column #1
$R^2 = 0.998$
$D = 3.38 \text{ cm}^2/\text{Day}$
$R = 0.95$

Unsaturated Column #2
$R^2 = 0.997$
$D = 3.95 \text{ cm}^2/\text{Day}$
$R = 0.95$

Appendix Table G3. Breakthrough Curve Data for Column #1 Under Saturated Conditions (Data are expressed as relative concentrations for the six fba compounds and bromide.)

Saturated Flow Data For Column #1									
Pore Volumes	3,4,5- TFBA	2,4,5- TFBA	2,3,4,5- TEFBA	2,3,4,- TFBA	2,3,6- TFBA	2,3,5,6- TEFBA	Br Obs.	Br	Fitted
0.206	0.000	0.000	0.000	0.000	0.000	0.000	0		0
0.417	0.000	0.000	0.000	0.000	0.000	0.000	0		0
0.607	0.000	0.000	0.000	0.000	0.000	0.000	0		0
0.719	0.015	0.019	0.019	0.017	0.024	0.027	0.014		0.0008
0.801	0.054	0.071	0.069	0.066	0.076	0.079	0.067		0.0233
0.915	0.240	0.280	0.279	0.274	0.303	0.305	0.317		0.2909
0.993	0.564	0.631	0.627	0.623	0.672	0.668	0.671		0.6301
1.099	0.933	0.959	0.960	0.956	0.964	0.953	0.966		0.9233
1.206	1.014	1.021	1.019	1.014	1.016	1.035	1.006		0.9925
1.393	1.031	1.031	1.033	1.012	1.025	1.042	1.02		1
1.601	1.028	1.030	1.031	1.028	1.032	1.042	1.021		1
1.810	1.023	1.025	1.022	1.026	1.021	1.006	1.021		1
2.197	1.022	1.027	1.025	1.023	1.024	1.020	1.027		1
2.618	1.027	1.029	1.029	1.027	1.019	1.006	1.023		1
2.806	0.993	0.994	0.994	0.994	0.984	0.987	1.002		0.9938
2.914	0.871	0.866	0.863	0.866	0.856	0.865	0.862		0.8578
3.019	0.571	0.542	0.544	0.547	0.515	0.539	0.516		0.4377
3.100	0.198	0.171	0.173	0.173	0.156	0.170	0.161		0.1547
3.211	0.019	0.013	0.013	0.015	0.012	0.011	0.015		0.0181
3.317	0.000	0.000	0.000	0.000	0.000	0.000	0.006		0.0012
3.523	0.000	0.000	0.000	0.000	0.000	0.000	0		0
3.711	0.000	0.000	0.000	0.000	0.000	0.000	0		0
3.913	0.000	0.000	0.000	0.000	0.000	0.000	0		0
4.225	0.000	0.000	0.000	0.000	0.000	0.000	0		0
4.403	0.000	0.000	0.000	0.000	0.000	0.000	0		0

Appendix Table G4. Breakthrough Curve Data for Column #2 Under Saturated Conditions (Data are expressed as relative concentrations for the six FBA compounds and bromide.)

			Saturated Flow Data For Column #2					
Pore Volumes	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Br⁻ Obs	Br⁻ Fitted
0.104	0.000	0.000	0.000	0.000	0.000	0.000	0	0
0.408	0.000	0.000	0.000	0.000	0.000	0.000	0	0
0.614	0.000	0.000	0.000	0.000	0.000	0.000	0	0
0.808	0.035	0.045	0.044	0.043	0.051	0.051	0.052	0.0155
0.914	0.196	0.235	0.230	0.229	0.259	0.259	0.264	0.2257
1.021	0.653	0.704	0.759	0.689	0.737	0.736	0.726	0.6988
1.099	0.902	0.923	0.917	0.907	0.946	0.939	0.924	0.9133
1.202	0.988	0.992	0.986	0.976	1.002	1.003	1.002	0.9916
1.302	1.029	1.027	1.027	1.027	1.026	1.022	1.018	0.9995
1.796	1.042	1.041	1.039	1.035	1.039	1.038	1.035	1
2.106	1.045	1.042	1.042	1.040	1.037	1.030	1.036	1
2.416	1.047	1.042	1.040	1.037	1.037	1.036	1.037	1
2.714	1.026	1.022	1.021	1.027	1.023	1.022	1.023	1
2.901	0.959	0.952	0.951	0.952	0.949	0.953	0.948	0.9511
3.001	0.744	0.716	0.721	0.726	0.699	0.710	0.702	0.6462
3.107	0.250	0.218	0.222	0.223	0.195	0.207	0.214	0.2001
3.206	0.039	0.029	0.031	0.031	0.025	0.027	0.031	0.0306
3.315	0.008	0.006	0.006	0.007	0.006	0.005	0.006	0.0018
3.397	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.0001
3.501	0.000	0.000	0.000	0.000	0.000	0.000	0	0
4.315	0.000	0.000	0.000	0.000	0.000	0.000	0	0
4.612	0.000	0.000	0.000	0.000	0.000	0.000	0	0

Appendix Table G5. Breakthrough Curve Data for Column #1 Under Unsaturated Conditions (Data are expressed as relative concentrations for the six FBA compounds and bromide.)

Unsaturated Flow Data For Column #1								
Pore Volumes	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Br Obs.	Br Fitted
0.497	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0
0.611	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0
0.696	0.000	0.000	0.000	0.000	0.000	0.00	0.01	0.0003
0.809	0.011	0.012	0.012	0.012	0.014	0.01	0.03	0.0368
0.892	0.235	0.246	0.243	0.242	0.257	0.26	0.29	0.2385
1.003	0.775	0.781	0.779	0.780	0.789	0.79	0.77	0.7192
1.113	0.965	0.965	0.966	0.967	0.969	0.97	0.96	0.958
1.195	1.002	0.997	0.996	0.992	0.994	1.00	0.99	0.994
1.305	1.004	1.003	1.003	1.004	1.003	1.00	1.00	0.9998
1.711	1.019	1.016	1.013	1.018	1.017	1.02	1.01	1
2.110	1.010	1.010	1.010	1.016	1.022	1.02	1.01	1
2.496	1.028	1.025	1.022	1.020	1.001	1.02	1.01	1
2.895	1.011	1.009	1.009	1.016	1.021	1.02	1.01	0.9975
3.007	0.949	0.950	0.950	0.954	0.943	0.96	0.92	0.893
3.091	0.629	0.628	0.622	0.629	0.626	0.62	0.63	0.581
3.203	0.151	0.153	0.151	0.149	0.149	0.15	0.18	0.1484
3.314	0.032	0.032	0.032	0.031	0.032	0.03	0.04	0.0155
3.394	0.016	0.016	0.016	0.016	0.016	0.02	0.02	0.0019
3.503	0.006	0.006	0.006	0.006	0.006	0.01	0.01	0.0001
3.609	0.005	0.005	0.005	0.005	0.005	0.00	0.01	0
3.793	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0
4.001	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0
4.402	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0

Appendix Table G6. Breakthrough Curve Data for Column #2 Under Unsaturated Conditions (Data are expressed as relative concentrations for the six FBA compounds and bromide.)

Unsaturated Flow Data For Column #2								
Pore Volumes	3,4,5-TFBA	2,3,4-TFBA	3,4,5-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA	Br⁻ Obs.	Br⁻ Fitted
0.590	0.000	0.000	0.000	0.000	0.000	0.000	0	0
0.692	0.000	0.000	0.000	0.000	0.000	0.000	0	0.001
0.795	0.031	0.034	0.033	0.032	0.034	0.036	0.04	0.0435
0.895	0.317	0.327	0.322	0.320	0.327	0.335	0.35	0.2935
0.993	0.707	0.714	0.707	0.706	0.710	0.716	0.72	0.6842
1.090	0.946	0.944	0.940	0.940	0.935	0.938	0.94	0.9189
1.212	0.978	0.981	0.981	0.981	0.980	0.979	0.99	0.9928
1.308	0.991	0.991	0.992	0.995	0.997	0.996	0.99	0.9993
1.599	0.995	0.998	1.000	1.001	1.005	1.006	1.01	1
2.013	1.016	1.019	1.017	1.017	1.000	1.018	1.02	1
2.402	1.017	1.023	1.021	1.026	1.000	1.027	1.02	1
2.701	1.008	1.009	1.007	1.009	1.016	1.017	1.01	0.9925
2.808	0.924	0.924	0.921	0.922	0.898	0.925	0.92	0.8639
2.914	0.489	0.490	0.485	0.486	0.474	0.489	0.5	0.4743
2.992	0.208	0.210	0.207	0.207	0.204	0.211	0.23	0.2005
3.096	0.068	0.069	0.068	0.068	0.068	0.070	0.08	0.0368
3.199	0.022	0.023	0.023	0.022	0.025	0.025	0.03	0.004
3.300	0.010	0.011	0.011	0.010	0.012	0.012	0.01	0.0003
3.498	0.007	0.008	0.008	0.008	0.007	0.008	0.01	0
3.790	0.004	0.004	0.004	0.004	0.004	0.004	0	0
4.092	0.000	0.000	0.000	0.000	0.000	0.000	0	0
4.978	0.000	0.000	0.000	0.000	0.000	0.000	0	0

Appendix Table G7. Mean and Standard Deviation Values of the Difference Between the FBA Concentrations and the Observed Curves for Bromide

All comparisons were between relative concentrations given in the preceding appendix tables G.3. through G.6. In no case does the sum of the differences in relative concentration, between an FBA isomer and observed Br$^-$ data, become greater than ± 1.96 times the standard deviation of those differences. Therefore, no significant difference exists, at the 95% confidence level, between the FBA and the observed Br$^-$ curves. This analysis considered upslope values for C/C_o only. Analysis of the differences between the observed FBA and Br$^-$ curves over the entire curve gave similar results.

Experiment	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA
Column-1 Sat.	-0.025(0.038)	-0.007(0.018)	-0.008(0.010)	-0.002(0.020)	0.002(0.007)	0.003(0.013)
Column-2 Sat.	-0.020(0.029)	-0.007(0.011)	-0.002(0.017)	-0.013(0.016)	0.004(0.008)	0.003(0.006)
Column-1 Unsat.	-0.006(0.021)	-0.005(0.016)	-0.006(0.017)	-0.006(0.017)	-0.003(0.014)	-0.001(0.015)
Column-2 Unsat.	0.008(0.011)	0.006(0.008)	0.007(0.009)	0.007(0.010)	0.006(0.008)	0.004(0.006)

Appendix Table G8. Mean and Standard Deviation Values of the Difference Between the FBA Concentrations and the Fitted Curves for Bromide

All comparisons were between relative concentrations given in the preceding appendix tables G.3. through G.6. In no case does the sum of the differences in relative concentration, between an FBA isomer and fitted Br^- data, become greater than ± 1.96 times the standard deviation of those differences. Therefore, no significant difference exists, at the 95% confidence level, between the FBA and fitted Br^- curves. This analysis considered upslope values for C/C_0 only. Analysis of the differences between the FBA and fitted Br^- curves over the entire curve gave similar results.

Experiment	3,4,5-TFBA	2,4,5-TFBA	2,3,4-TFBA	2,3,4,5-TEFBA	2,3,6-TFBA	2,3,5,6-TEFBA
Column-1 Sat.	-0.005(0.031)	0.013(0.019)	0.012(0.019)	0.010(0.019)	0.022(0.019)	0.023(0.019)
Column-2 Sat.	-0.005(0.022)	0.009(0.011)	0.013(0.020)	0.013(0.020)	0.019(0.016)	0.018(0.016)
Column-1 Unsat.	-0.005(0.020)	0.007(0.022)	0.006(0.021)	0.006(0.022)	0.009(0.024)	0.010(0.025)
Column-2 Unsat.	0.003(0.015)	0.006(0.017)	0.005(0.015)	0.002(0.014)	0.006(0.015)	0.008(0.018)

Appendix Table G9. Mass Recovery of the Six FBA Compounds and Br⁻ in the Column Experiments

The trapezoid rule was used to integrate area under the breakthrough curves:

$$Area = \sum_{i=0}^{N-1} (PV_{i+1} - PV_i) \; .5 \; (C/C_{o_i} + C/C_{o_{i+1}}) \tag{4}$$

Where N = # of measurements.

The total area was then divided by the number of pore volumes that comprised the tracer slug in each experiment to yield a normalized total mass recovered. The following is a list of pore volumes used in the mobility studies.

Column	Saturated (P.V.s)	Unsaturated (P.V.s)
Column #1	2.042	2.157
Column #2	2.057	1.962

The following table provides the mass recoveries in percent for all compounds in each experiment.

Compound	Saturated Column #1	Saturated Column #2	Unsaturated Column #1	Unsaturated Column #2
3,4,5-TFBA	102.5	103.5	102.1	101.7
2,4,5-TFBA	103.1	103.5	102.1	102.0
2,3,4-TFBA	103.0	103.6	101.9	101.9
2,3,4,5-TEFBA	102.7	103.1	102.2	102.0
2,3,6-TFBA	102.8	103.5	102.0	101.1
2,3,5,6-TEFBA	102.9	103.4	102.4	102.4
Bromide	102.8	103.3	102.0	102.6

APPENDIX H. FIELD STUDY INFORMATION. Natural gradient flowback experiment. This set of experiments was not conclusive therefore no data or discussion of the procedure is given in the manuscript text.

Introduction:
        This natural gradient flowback test was conducted twice. The first test was started on 9/19/92 and the second on 2/19/93. In both cases the well field used by Dr. Bowman at the TECH Hydrology study area in the Sevilleta National Wildlife Refuge was used (see Bowman and Gibbens, 1992 for a description of the well field and the geology of the study site). The tracer slug was introduced into an injection well (Central well in a 3-well line running North-South) while an up-gradient pumping well, 3-meters distant (West), was pumped to draw the tracer slug up gradient. A waiting period followed, after which the injection well was pumped to recover the tracer. Samples of the pumpback water were taken at 5 or 10 minute intervals and analyzed for the FBA isomers and bromide. In these Tests, no tracer was recovered. The following is a detailed description of each test.

Field Test #1
        On 9/19/92, a 20-liter slug of tracer solution (400 mg L^{-1} FBAs, and 1000 mg L^{-1} Br$^-$), prepared in MSEC tap water, was injected while the up-gradient well was pumped at a rate of 50 liters per minute (LPM). The pumping was continued for 8 hours to draw the tracer slug away from the injection well. Bailer samples showed a concentration of 0.5 mg L^{-1} for the FBAs at this time. The well field was left alone for three months after which the injection well was pumped for 4 hours. Weather didn't permit more pump time. Samples were taken in 5 minute intervals and screened via HPLC in 25 minute intervals. No sign of FBA tracer compounds was seen in any of the screened samples. The injection well was pumped again on 1/12/93 for 12 hours. Samples were taken in 10-minute intervals and screened via HPLC in 20-minute intervals. No sign of the FBA tracers was seen in any of the screened samples. A third pumpback episode was conducted to see if the tracers could be recovered. On 1/25/93 the injection well was pumped for another 12 hours and sampled in 10-minute intervals. The samples were screened in 30-minute intervals, and again no sign of tracer compounds was found via.

        Three potential problems were found with the first aquifer test and were remedied in the second test to the best of our abilities. First, it was hypothesized that a density difference between the injected slug, around 5000 mg L^{-1}, and the native water at the Sevilleta, 2000 mg/L, may have caused density-driven gradients to "sink" the tracer slug before it was recovered. This potential problem was addressed in the

second aquifer tracer test by reducing the tracer concentration in, and increasing the volume of, the injected slug. Second, the pump time of 8 hours during the injection of the tracer slug may have allowed some or all of the injected slug to migrate toward and out of the pumping well. This problem was remedied in the second aquifer test by reducing the pumping from the pumping well during tracer injection from 8 hours to 2 hours. Thirdly, it was also hypothesized that uncertainties in regional groundwater flow may have taken the tracer slug away from the test area more rapidly than during the successful tracer pumpback test conducted by Joe Gibbens in 1989 (Bowman and Gibbens, 1992). This problem was addressed in the second aquifer test by reducing the residence time of tracer in the aquifer to 6 weeks instead of 3 months.

The second aquifer test was begun on 2/19/93 when a 30-liter slug of tracer solution (200 mg L^{-1} FBAs and 800 mg L^{-1} Br$^-$) with a TDS of 2240 mg L^{-1} was injected in the same injection well used in aquifer test #1. The pumping well was pumped for 2 hours at 70 LPM, beginning with the initiation of tracer injection. Water samples were taken every 10 minutes during this pumping to ensure that the tracer slug did not travel up-gradient all the way to the pumping well. The slug was allowed to reside in the aquifer for 6 weeks, after which the injection well was pumped for 12 hours at a rate of 68 LPM. Samples of the pumped water were taken in five-minute intervals during the first six hours of pumping, and in ten-minute intervals during the second six hours of pumping. The samples were screened via HPLC in 25-minute intervals and 30-minute intervals for the first, and second six-hour sampling period, respectively. No FBA tracer compounds were found in any of the screened samples. No FBA tracer compounds were found in the samples taken from the water pumped from the aquifer during the second tracer injection.

APPENDIX I. REFERENCES USED IN APPENDICES.

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