

Simultaneous analyses and applications of multiple fluorobenzoate and halide tracers in hydrologic studies

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Abstract:

An analytical method that employs ion chromatography has been developed to exploit the use of fluorobenzoic acids (FBAs) and halides more fully as hydrologic tracers. In a single run, this reliable, sensitive, and robust method can simultaneously separate and quantify halides (fluoride, chloride, bromide, and iodide) and up to seven FBAs from other common groundwater constituents (e.g. nitrate and sulphate). The usefulness of this analytical method is demonstrated in both field and laboratory tracer experiments. The field study examines the hydrologic response of fractures and the matrix to different flow rates and the contribution of matrix diffusion in chemical transport. Laboratory tracer experiments with eight geologic media from across the USA—mostly from Department of Energy facilities where groundwater contamination is prevalent and where subsurface characterization employing tracers has been ongoing or is in need—reveal several insights about tracer transport behaviour: (1) bromide and FBAs are not always transported conservatively; (2) the delayed transport of these anionic tracers is likely related to geologic media characteristics, such as organic matter, pH, iron oxide content, and clay mineralogy; (3) use of iodine as a hydrologic tracer should take into account the different sorption behaviours of iodide and iodate and the possible conversion of iodine's initial chemical form; (4) the transport behaviour of potential FBA and halide tracers under relevant geochemical conditions should be evaluated before beginning ambitious, large-scale field tracer experiments. Copyright © 2005 John Wiley & Sons, Ltd.

KEY WORDS tracers; fluorobenzoic acids; halides; ion chromatography; transport; groundwater

INTRODUCTION

Many laboratory and field experiments investigating hydrologic processes in the subsurface have obtained crucial data through the use of tracers (Davis *et al.*, 1980). Traditionally, halides (e.g. fluoride, chloride, bromide, and iodide) have been used as water tracers. However, over the past 20 years, the use of fluorobenzoic acids (FBAs) as water tracers has received considerable attention in numerous studies investigating water flow and solute transport in both porous and fractured media (e.g. Hydro Geo Chem, 1986; Bowman and Gibbens, 1992; Boggs and Adams, 1992; Seaman, 1998; Dahan *et al.*, 1999; Hu *et al.*, 2001; Reimus *et al.*, 2003; Mayes *et al.*, 2003; Salve *et al.*, 2004). FBAs are attractive tracers because they do not occur naturally, are detectable at low concentrations, are resistant to degradation, and express low aquatic toxicity (Bowman and Gibbens, 1992; McCarthy *et al.*, 2000). In addition, since the aqueous diffusion coefficient of an FBA is about three times smaller than those of tritium and halides, a diffusivity–tracer approach has been exploited through simultaneous use of FBA and tritium or halide tracers when studying hydrologic processes. Diffusivity–tracer tests have been employed to investigate solute dispersion and diffusive mass transfer between fast- and slow-moving flow regions (e.g. Hu and Brusseau, 1995; Callahan *et al.* 2000; Reimus *et al.*, 2003; Salve *et al.*, 2004).

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Multiple FBA and halide tracers can be applied either simultaneously or sequentially. Depending upon the number and position of the fluorine atom in the benzene ring, there are 16 FBA isomers or derivatives that exhibit similar physicochemical properties and environmental behaviour. (Additional FBA isomers exist when the hydrogen atom in the benzene ring is substituted by a chlorine atom or a fluoromethyl functional group.) The wide variety of FBA isomers is especially useful for studies where other common anionic tracers, such as bromide and chloride, are not suitable and for research objectives that require multiple tracers with similar characteristics.

For example, a field study at the northern Negev Desert, Israel, used seven FBA isomers to examine water flow through discrete natural fractures in unsaturated chalk (Dahan *et al.*, 1999). One isomer was added to each of the seven percolation ponds, which were installed sequentially along an exposed fracture, to delineate flow paths along the fracture plane (Dahan *et al.*, 1999). Another study involving field tracer-transport tests in unsaturated fractured tuff at Yucca Mountain, Nevada, applied four FBA isomers, each at a different fluid release rate (Hu *et al.*, 2001). The tracer results showed significant variability in the hydrologic response of the fractures and the matrix.

With pK_a values that range between 2.7 and 3.8, FBAs exist predominantly as anionic species under the neutral pH condition of normal groundwater, which is two pH units above the pK_a values. The transport behaviour of FBAs in many subsurface environments has been observed to be nonreactive, similar to bromide, which is a commonly used conservative tracer (Davis *et al.*, 1980; Bowman, 1984). When placed in geologic media that contain appreciable amounts of certain minerals (e.g. iron oxides and kaolinite) or of organic matter with net positively charged surfaces that may attract anions, the transport of FBAs (as well as bromide) can be delayed, and FBAs can serve as reactive tracers (Boggs and Adams, 1992; Benson and Bowman, 1994; Jaynes, 1994; Seaman, 1998). In addition, during low-pH conditions, the nonionized form of FBAs exhibits considerable sorption onto soil organic matter (Benson and Bowman, 1994; Seaman, 1998; McCarthy *et al.*, 2000).

A reliable analytical method that can distinguish several FBAs from one another is crucial for multitracer studies. Such a method must be able to detect FBA tracers at low concentrations in the presence of other common anions (e.g. chloride, nitrate, and sulphate) found in soil and groundwaters. A robust analytical method is also needed for field tracer experiments, during which hundreds of samples may be collected over the course of several years.

The most widely used method for FBA analysis, developed by Bowman (1984), uses high-performance liquid chromatography (HPLC) with UV detection after separation via a strong anion exchange (SAX) column. This method has been used effectively in a number of studies and can separate up to six FBAs simultaneously (Bowman and Gibbens, 1992; Benson and Bowman, 1994). However, Bowman's method is subject to interference by several common inorganic anions, including nitrate, iodide, bromide, and chloride. These anions are known to be sensitive to UV detection and show significant absorption in the 195 to 215 nm range (Stetzenbach and Thompson, 1983), a range that includes the 205 and 210 nm wavelengths commonly used for FBA analyses. Analyses conducted with a SAX column are also complicated by the rapid deterioration of the separation column in the presence of a low-pH buffered eluent (TerBerg, 1993); this deterioration significantly limits the throughput of the analysis.

Another analytical method, reversed-phase HPLC, achieves separation by using the different affinities of analytes and the stationary phase of the analytical column. When the solution pH is below the pK_a of the compound, ionizable compounds such as FBAs exist in protonated form, are less soluble, and exhibit larger affinities. Analytical procedures based on reversed-phase HPLC and UV detection have recently been used to separate and quantify as many as seven (Dahan and Ronen, 2001) or ten (Stringfellow *et al.*, 2001) FBA isomers in a single run. Multiple FBAs were simultaneously measured in the presence of interfering compounds such as nitrate and soluble organic matter, and resolution matrix tables were constructed to assist the selection of FBA tracers for use in studies where such interferences may be present (Stringfellow *et al.*, 2001). Stetzenbach *et al.* (1982) reported a trace enrichment method to preconcentrate aqueous samples and

increase sensitivity by three orders of magnitude to allow low-level FBA detection. However, this high sensitivity requires a greater sample volume by the same orders of magnitude.

In addition to UV detection, an ion chromatography (IC) method with conductivity detection was used to separate and analyse three FBAs (Pearson *et al.*, 1992). However, this early study found that even a low concentration (1 mg l^{-1}) of chloride interfered with the chosen FBAs. Furthermore, the reported detection limit was relatively high at 0.25 mg l^{-1} .

Previous analytical methods for FBAs analysis have tested for the interference of common inorganic anions, whether halides as tracers or pre-existing groundwater constituents. For example, Seaman (1998) reported a method that simultaneously analysed bromide and four FBAs, with an observed interference between bromide and 3,4-difluorobenzoic acid (DFBA). However, we are not aware of any published research that specifically analyses all of the common anions in a single run. In addition, past researchers have traditionally used different instruments and methods to analyse diffusivity tracers applied in a single experiment. For example, bromide or iodide analyses have conventionally been performed via IC with a conductivity detector or ion-specific electrodes, whereas FBA analyses have been conducted by HPLC with a UV absorbance detector (Turin *et al.*, 2002; Reimus *et al.*, 2003).

In this study, we present an IC method with conductivity detection that can simultaneously separate and quantify multiple FBA isomers, all halides, and other common groundwater anions. Our method applies recent developments in IC technologies, such as a reagent-free eluent generator (to avoid the chemical usage), which contribute to a robust analytical method that is easy to operate, requires minimal sample pretreatment, and yields a very low detection limit. We also describe disparate applications of this method in field and laboratory experiments that were conducted to investigate the flow and transport in subsurface materials. Such investigations are relevant to environmental characterization and remediation, or to a potential geologic repository for high-level nuclear waste. These applications highlight the advantages of multitracer experiments and analytical approaches.

MATERIALS AND METHODS

Reagents

We used reagent water with a resistance level of $18 \text{ M}\Omega$. The water was obtained from a NANOpure Infinity Water Purification System (Barnstead International, Dubuque, IA). Our study also used a total of 14 commercially available FBAs, which were purchased from Aldrich Chemical Co. (Milwaukee, WI). The purity level of each FBA is listed in Table I. All FBA compounds were used without further purification. The other chemicals (LiF , SrBr_2 , CsI , and KIO_3) used in the laboratory column studies were also purchased from Aldrich Chemical Co.

Instrumentation for the analysis of inorganic anions

A Dionex (Dionex Corp., Sunnyvale, CA) IC DX-600 system was used in this study to analyse FBAs and other anions. The system consisted of a GP50 gradient pump, an ED50A electrochemical detector in conductivity mode, and an AS50 autosampler with a thermal compartment for temperature control. For separation purposes, an IonPac AG17 ($4 \times 50 \text{ mm}$; 4 mm inner diameter and 50 mm length) guard column was used in conjunction with an IonPac AS17 ($4 \times 50 \text{ mm}$) analytical column (both columns were maintained at 35°C), along with an ultra anion self-regenerating suppressor that operated at 248 mA in the recycled-water mode. An EG50 eluent generator with a KOH cartridge and a continuously regenerated anion trap column was employed to achieve a gradient separation by producing a varying concentration of KOH over the run at a flow rate of 1.0 ml min^{-1} . Using deionized water only, the EG50 generates high-purity, carbonate-free KOH eluent that minimizes baseline shift, improves retention time stability, resolution, and run-to-run reproducibility. An injection loop size of $25 \mu\text{l}$ was used for sample analyses. Finally, Dionex PeakNet 6.2 software was used for system control, data collection and processing.

Table I. Isomers of FBAs examined in this study

FBA ^a	pK _a ^b	Purity (%)	Retention time ^c (min)
2,3-DFBA	3.29	98	11.7
2,4-DFBA	3.58	98	11.4
2,5-DFBA	3.30	98	11.3
2,6-DFBA	2.85	98	9.85
3,4-DFBA	3.83	98	17.0
3,5-DFBA	3.59	97	15.4
2,3,4-TFBA	3.30	98	13.8
2,3,6-TFBA	2.82	99	11.2
2,4,5-TFBA	3.28	99	13.0
2,4,6-TFBA	2.83	98	10.5
3,4,5 TFBA	3.54	98	18.9
2,3,4,5-TeFBA	3.08	99	15.7
2,3,5,6-TeFBA	2.71	99	12.5
PFBA	2.72	99	14.7

^a TFBA: trifluorobenzoic acid; TeFBA: tetrafluorobenzoic acid; PFBA: pentafluorobenzoic acid.

^b Values of pK_a (negative log acid dissociation constant) are from Benson and Bowman (1994).

^c Retention time obtained from the chromatogram of each FBA solution (10 mg l⁻¹) in the reagent water.

Table II. Hydroxide gradient separation of inorganic anions using EG50

Time (min)	Eluent concentration (mM)	Comments
<i>Equilibration</i>		
-2	2	Preconditioning before sample analysis
<i>Analysis</i>		
4	2	Sample injection at time zero
6	10	Isocratic analysis for fluoride
12	30	Linear gradient
16	45	Separation of bromide from nitrate; linear gradient
20	60	Linear gradient
20.1	2	Linear gradient
		Returns to initial condition for next analysis

We developed a hydroxide gradient method to separate the multiple FBAs, halides, and other common inorganic anions that existed in the groundwater. The timing of each step for a hydroxide gradient run from a range of 2 to 60 mM KOH is presented in Table II.

Field experiments

To study tracer transport in unsaturated, fractured welded tuff at Yucca Mountain, Nevada, two studies were conducted within the Exploratory Studies Facility (ESF), an excavated Yucca Mountain tunnel measuring 8 km long and 8 m in diameter at a depth of about 300 m below the top of the mountain.

In the first study (called the fracture study in this paper), a series of tests was conducted by releasing tracer-laced water into an isolated zone within a horizontal injection borehole drilled into the rock formation from the tunnel (Salve *et al.*, 2002). Seepage was collected in an excavated slot about 1.6 m below the borehole, and the tracer concentration in the seepage collection was analysed. The first phase consisted of four liquid-release events with fluoride and four FBA tracers; one FBA was associated with each event, and each event had a different release rate. The second phase, with no tracers added, investigated the transport

behaviour of the applied tracers during flushing through four release events (and rates). The tracer results under different release rates were presented and discussed in Hu *et al.* (2001).

The second study (called the fault study) investigated flow and transport in a fault embedded in unsaturated tuff (Salve *et al.*, 2004). The experiment involved the release of $\sim 82\,000$ l of water over a period of 17 months into a near-vertical fault under a constant positive head (at ~ 0.04 m). At 7 months after the beginning of the water release along the fault, when a stable flow regime had been established, a solution containing bromide and PFBA was released along the fault for 9 days. Afterwards, water without tracers was released for another 7 months. Seepage water was continuously collected in a cavity excavated ~ 20 m below the test bed and was analysed for tracer concentration.

Column experiments

Laboratory column experiments were conducted to demonstrate the usefulness of the IC analytical method and to elucidate the transport behaviour of the tracers (FBAs and halides) in various geologic media in the USA (Table III). These media were obtained within or near several Department of Energy (DOE) complex sites, including: the Savannah River Site (SRS) in South Carolina; the Oak Ridge Reservation in Tennessee; the Hanford Site in Washington; the Idaho National Engineering and Environmental Laboratory (INEEL) site in Idaho Falls, Idaho; the Nevada Test Site (NTS) in Mercury, Nevada; a location in Santa Fe near Los Alamos National Laboratory, New Mexico; and a site of Lawrence Livermore National Laboratory in Livermore, California. A sample of Wisconsin surface soil with a high amount of organic matter was also included in the experiment. The wide variety of sample types provided an opportunity to examine the influence of organic matter, clay mineralogy, soil pH, and texture on the transport behaviour of inorganic and organic anions. All properties presented in Table III were measured according to the standard procedures (Klute, 1986; Sparks, 1996).

A glass column (2.5 cm inner diameter, 15.0 cm length; Kontes, Vineland, NJ) was incrementally packed with the air-dried soil/sediment sample (<2 mm) to obtain uniform bulk densities. The packed column was slowly wetted from the bottom to establish saturation, and approximately 100 pore volumes of electrolyte solution (5 mM CaCl_2) were pumped through the column prior to the transport study. There were no visible air pockets after the column had been saturated.

The apparatus and methods employed for the miscible displacement column studies were similar to those used in previous experiments (Hu and Brusseau, 1995). An HPLC pump (Model 301, Alltech Associates, Inc., Deerfield, IL) was connected to the column, and a three-way valve was placed in-line to facilitate switching between solutions with and without the tracer of interest. To investigate the simultaneous transport of four halide species (F^- , Br^- , I^- , and IO_3^-) and four FBAs, we dissolved the following chemicals in the 5 mM CaCl_2 electrolyte solution: LiF, SrBr_2 , CsI, KIO_3 , 2,6-DFBA, 3,4-DFBA, 3,4,5-TFBA, and PFBA (each with an initial concentration of 1×10^{-4} M). The four FBAs were chosen because they cover the pK_a range of FBAs and can be analysed in a single run. Two iodine species were also used, as iodide and iodate have been reported to coexist in the environment (e.g. Yuita, 1994). In addition, a separate transport run of tritium (activity 33 kBq l^{-1}) was carried out to compare its transport behaviour with the anionic tracers. Column effluent fractions were collected with an automated fraction collector (Retriever 500, ISCO Inc., Lincoln, NE) for anion analysis by the IC method or for the liquid scintillation counting of tritium.

RESULTS AND DISCUSSION

IC analytical method

Under a hydroxide gradient condition from a range of 2 to 60 mM KOH, the retention times for *each* FBA solution with a concentration of 10 mg l^{-1} are given in Table I. The wide range in retention times, from

Table III. Information and properties of samples used in the column experiments^a

Sample	Hanford sediment	LLNL alluvium	NTS tuff	INEEL basalt	Owngate soil	Oak Ridge sediment	SRS subsoil	Wisconsin soil
Description	Composite of core samples 9–12 m below surface	0.7 m below surface	Crushed tuff ~300 m below surface	Crushed basalt core 0.3 m below surface	Surface soil	Composite of core samples 2–3 m below surface	Composite of sediment 12 m below surface	Surface soil
Location	Richland, WA	Livermore, CA	Mercury, NV	Idaho Falls, ID	Sante Fe, NM	Oak Ridge, TN	Aiken, SC	Plover, WI
pH	7.34	6.24	6.13	6.83	7.70	4.50	5.36	5.90
Organic matter	0.06	0.03	0.14	0.04	2.3	0.12	0.07	8.7
Particle size	89.0	42.0	89.1	77.4	35.0	7.68	76.7	67.0
	7.9	25.6	8.8	21.1	39.2	70.9	3.50	21.0
	3.1	32.4	2.1	1.5	25.7	21.4	19.8	12.0
CEC	7.37	26.3	4.54	1.67	15.1	9.41	1.78	14.1
AEC	0.01	0.35	0.18	0.13	0.01	0.12	4.0	0.01
Iron-CBD	3.26	9.78	1.48	3.12	3.82	1.08	15.9	10.1
Iron-oxalate	0.94	0.94	0.12	12.9	0.21	0.18	0.20	5.86

^a CEC: cation exchange capacity; AEC: anion exchange capacity; CBD: citrate-bicarbonate-dithionite; oxalate: ammonium oxalate. Sample pH value was measured in a 1:1 soil/deionized water suspension.

9.85 to 18.9 min, for these 14 FBA isomers demonstrates the feasibility of good separation and accurate quantification of multiple FBAs. We also tested the retention times of these FBAs under a gradient condition from a range of 2 to 40 mM KOH, and the resulting retention times exhibited an even wider range, from 9.94 to 21.3 min, with the same peak sequence. Depending upon a particular scenario and potential interferences, the gradient range and steepness of change can be fine-tuned to achieve optimal separation.

We did not observe a correlation between the pK_a values and the retention times of the FBAs. In an alkaline eluent solution with a pH of ~ 12 , each FBA is expected to exist in anionic form. The different affinities (and hence retention times) between each FBA and the alkanol quaternary ammonium functional group of low hydrophobicity that is packed in the analytical IC column depend on the different polarities among the FBAs. A highly polarizable FBA anion, which possesses an easily deformable electron cloud and exhibits a hydrophobic character, will likely have a long retention time from its strong interactions with the hydrophobic packing materials.

The IC method presented here provides a method detection limit (MDL) ranging from 15.4 to 29.4 $\mu\text{g l}^{-1}$ for four FBAs tested with an injection volume of 25 μl , which corresponds to a quantification limit ranging from 0.38 to 0.74 ng (Table IV). This detection limit was obtained according to the procedure described in Method 300.0 from the US Environmental Protection Agency (1993). The retention time and peak area precision, expressed as relative standard deviation (RSD), were also determined from seven replicate injections (Table IV). The peak area RSD of less than 10% is obtained for the MDL solution of low (sub-milligram per litre) concentration, and the peak area RSD for a solution spiked with about 1 mg l^{-1} analyte is less than 2% (data not shown).

The MDL for FBAs is comparable to those of other anions obtained by the same procedure (Table IV). In addition, the quantification limit for FBAs by this method is better than those observed for FBAs by other methods. For example, Bowman (1984) tested four FBAs and reported a limit in the range of 1.2 to 2.5 ng, and Stringfellow *et al.* (2001) observed a limit of 5 to 7 ng for 14 FBAs. Dahan and Ronen (2001) reported a detection limit of about 0.5 mg l^{-1} for each of 13 FBAs studied but did not specify the injection volume that was used.

Based on the retention time of individual FBAs, halides, and other common anions, seven FBAs (shown in bold in Table I) can be selected and potentially used in hydrological studies. A representative chromatogram

Table IV. Parameters obtained by the IC method for halide tracers and other anions^a

Anion	Method detection limit ($\mu\text{g l}^{-1}$)	Retention time (min)	Retention time precision (RSD, %)	Area precision (RSD, %)
Fluoride	3.84	3.40	0.13	5.2
Iodate	21.7	3.76	0.11	8.8
Chloride	11.1	7.95	0.17	4.6
Nitrite	26.1	8.54	0.10	6.7
2,6-DFBA	23.0	9.51	0.09	7.9
Bromide	17.7	9.82	0.06	6.3
Nitrate	6.60	10.68	0.15	2.7
Sulphate	41.6	13.46	0.15	1.7
PFBA	29.4	14.16	0.24	8.8
3,4-DFBA	17.6	15.37	0.37	6.3
Phosphate	39.4	16.07	0.03	6.1
Iodide	19.9	16.76	0.12	9.4
3,4,5-TFBA	15.4	18.57	0.09	4.7

^a All with an injection volume of 25 μl .

(Figure 1) shows the separation of these seven FBAs and other common anions. Note that although 2,3,4,5-TeFBA has a retention time (15.7 min) close to that of phosphate (16.1 min), a typical groundwater sample has only a trace concentration of phosphate. Therefore, 2,3,4,5-TeFBA could potentially be used as a tracer in situations where the researchers have prior knowledge of existing phosphate concentration.

Use of a mature IC technology developed for separation and quantification, coupled with conductivity detection, yields a robust method for simultaneous measurement of FBA tracers. After more than 3000 runs over a 1 year period, there was no observable deterioration of column performance. The use of a reagent-free eluent generator produces hydroxide eluent at the desired concentration accurately and reproducibly, which contributes to retention time stability. Furthermore, the carbonate-free hydroxide that is generated greatly reduces baseline shifts during a gradient run, improving signal-to-noise ratios. The observed shift from 2 to 60 mM KOH is commonly less than 0.05 μS . In contrast, the observed baseline shift under the same gradient is at least 1 μS when using a bottle eluent delivery system with an eluent prepared from hydroxide chemicals.

Demonstration of the IC method in field experiments

In this section, we demonstrate the utility of multiple FBA tracers in field applications and the usefulness of our IC analytical method to determine the presence and concentration of several FBAs, halide tracers, and other common anions in a single run. Figure 2 shows the chromatograms of liquid samples collected in the fracture study discussed above. Figure 2a is an IC chromatogram for a seepage sample collected after releasing dual tracers (PFBA and fluoride) in the first tracer release event, and Figure 2b is from a seepage sample collected after releasing two additional FBA tracers (2,3,4-TFBA and 3,4-DFBA) from two ensuing events. Figure 2b demonstrates the lingering presence of fluoride due to its sorption on the rock formation in the flow pathways (Hu *et al.*, 2001), as well as the gradual flushing of FBA tracers from the low-permeability region. Note that all water (referred to as mine water), introduced into the ESF for mining-related activities and scientific investigations (including these tracer tests), was groundwater that was pumped from well J-13 (located near Yucca Mountain) and then spiked with 20–30 mg l^{-1} of LiBr. Because the J-13 water contained

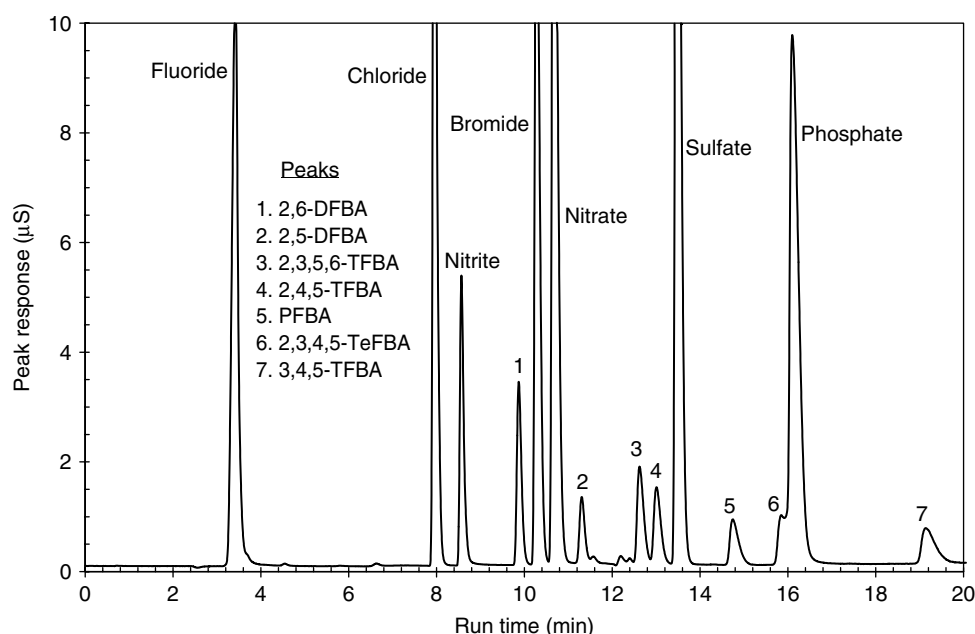


Figure 1. IC chromatogram of inorganic anions. All FBA isomers have a concentration of 5 mg l^{-1} . Other anions have the following concentrations: fluoride, 3.6 mg l^{-1} ; chloride, 7.2 mg l^{-1} ; bromide, nitrate, and sulphate, 14.3 mg l^{-1} ; phosphate, 21.4 mg l^{-1}

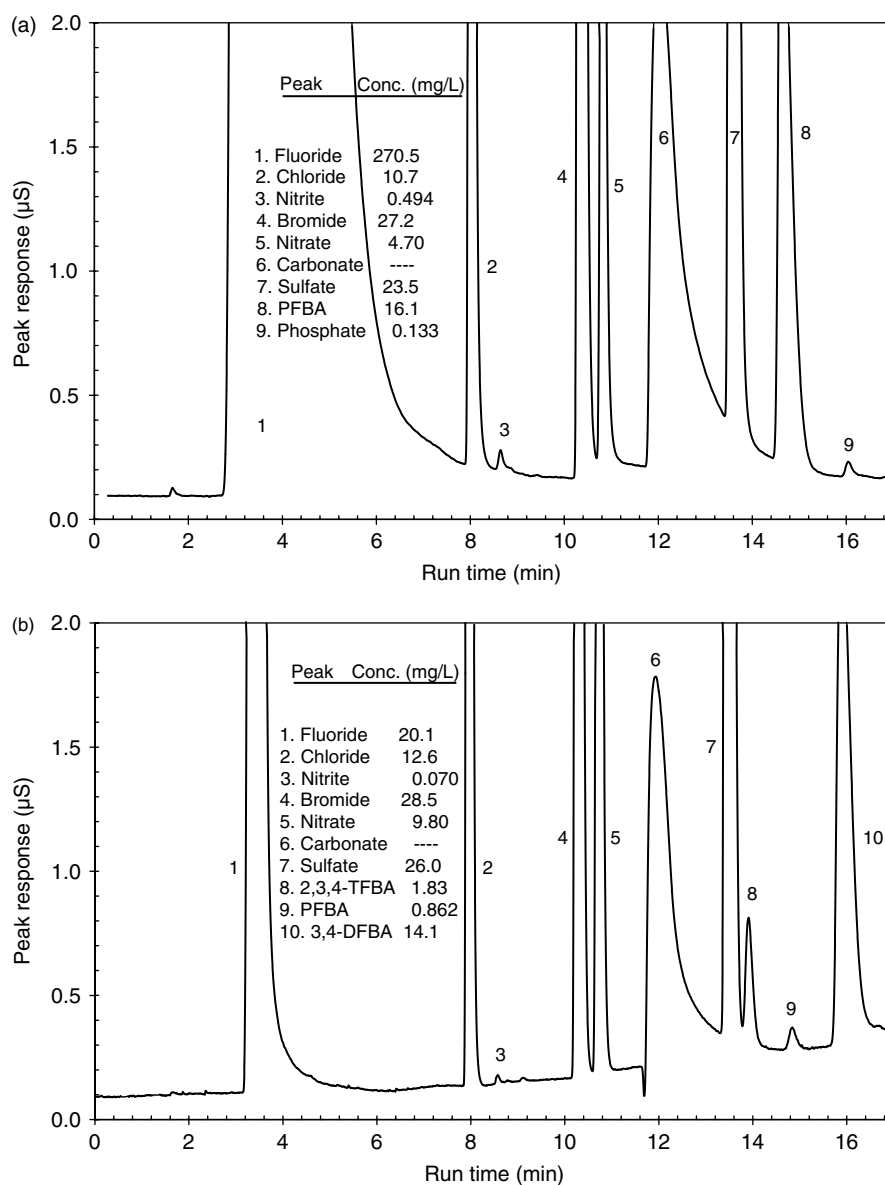


Figure 2. IC chromatograms of inorganic anions for seepage samples collected during two phases of fracture tracer studies at Yucca Mountain, Nevada

about 2.5 mg l^{-1} of fluoride, a high concentration (307 mg l^{-1}) of fluoride was added to the tracer solution. Furthermore, both the released tracer solution and the collected seepage contained about 120 mg l^{-1} of bicarbonate, which was converted into carbonate in the alkaline pH condition of the eluent during the IC run; the resulting carbonate peak (not quantifiable) is shown in Figure 2. The peak retention time of 3,4-DFBA is close to that of phosphate, but phosphate is only occasionally present at a concentration above the detection limit (as shown in Figure 2a). Out of more than 400 samples analysed, only about 20 exhibited a small, yet detectable, peak that is presumably phosphate. Furthermore, there was no pattern in the observed phosphate concentration for these 20 samples. Therefore, the detection and quantification of 3,4-DFBA were not compromised.

Figure 3 shows the chromatograms for the liquid samples collected in the fault study. A dual tracer of PFBA and bromide was applied, and the anionic constituents in the released tracer solution are shown in a chromatogram (Figure 3a). Figure 3b shows the chromatogram for a representative seepage sample collected about 20 m below the release point, demonstrating the ability of the IC analytical method to separate and quantify diffusivity tracers (e.g. bromide and PFBA), as well as other common anions, in a single run. Results from these diffusivity tracers indicate significant effects of matrix diffusion on transport through a fault within unsaturated tuff (Salve *et al.*, 2004).

The simultaneous measurement of tracers and other anions has several advantages. First, it is economical because it requires just one instrument. The procedure also provides a quick turnaround time, allowing timely

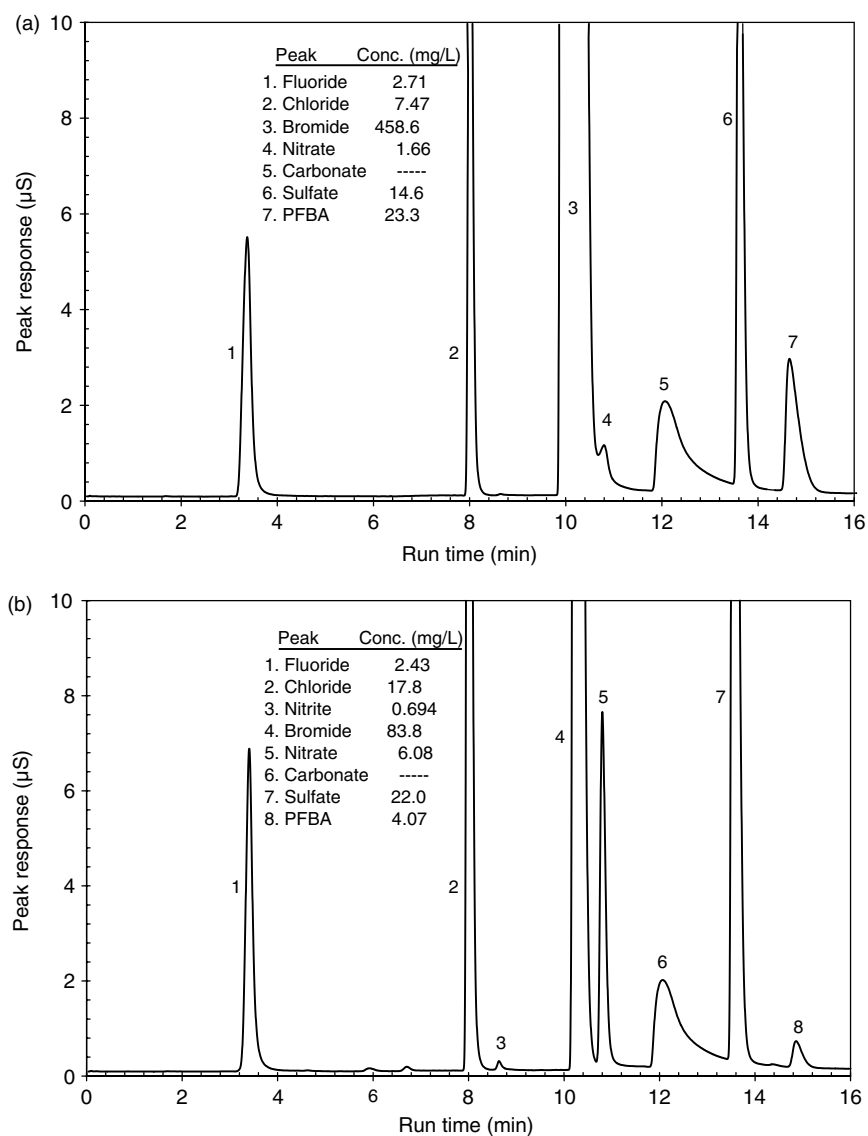


Figure 3. IC chromatograms of inorganic anions for samples collected from a fault tracer study at Yucca Mountain, Nevada: (a) released tracer solution; (b) collected seepage solution

modification of test plans and experimental implementation. In addition, simultaneous measurement provides the researchers with the concentration of all major anions (except bicarbonate) present in a water sample. These data can then be used to conduct the charge balance calculation that is helpful in data processing and interpretation. Last, but not least, the simultaneous measurement of major anions (tracers and others) enhances the interpretation of experimental results.

In the fault tracer study, for example, the two types of released water (mine water and tracer solution) have similar concentrations of chloride, nitrate, and sulphate (Table V). The seepage solution collected after releasing mine water, however, exhibits concentrations that are about three times higher for these anions, presumably from water–rock interactions as the solution passed through the formation. The seepage solution obtained after applying the tracer solution still shows high, although a bit decreased, concentrations of these anions. The reduced concentrations reflect the continuing dilution of the antecedent salts in the formation fluid and the anion-exchange process occurring from the high concentration of bromide applied. This type of data could be used in transport modelling studies that incorporate water–rock interaction and mechanistic anion-exchange processes.

Laboratory column experiments

Laboratory tests further illustrate the usefulness of the IC analytical method in investigating the simultaneous transport of multiple tracers in columns packed with various geologic media. A representative chromatogram from the Hanford column experiment is shown in Figure 4a to demonstrate the separation and quantification of multiple anionic tracers. For the samples obtained from Hanford, INEEL, NTS, and Livermore, all four FBAs tested exhibited identical breakthrough curves (with symmetrical behaviour and negligible tailing) and conservative (not retarded) transport—essentially the same transport behaviour that was observed for tritium and bromide. A representative breakthrough curve for the Hanford sediment is shown in Figure 4b. Such conservative behaviour is expected in geologic media with predominantly negatively charged surfaces and nonacidic pH conditions, which is consistent with other reports (e.g. Bowman and Gibbens, 1992; Turin *et al.*, 2002).

In highly weathered sediments from the southeastern USA (such as the Oak Ridge and SRS samples used in this study), however, some or all of the FBAs that were studied exhibited retarded transport, as shown for the SRS subsoil sample in Figure 5a. These samples contained appreciable amounts of minerals such as kaolinite and iron oxides, which possess positively charged surfaces and contribute to anion sorption. Several

Table V. Change of anion concentration during a tracer test

Anion	Concentration (mg l ⁻¹)							
	Mine water (35 measurements)		Tracer solution (6 measurements)		Mine water seepage (36 measurements)		Tracer seepage (262 measurements)	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Bromide	23.8	3.59	470	5.87	19.0	9.00	48.6 ^a	25.0 ^a
Chloride	7.32	0.59	7.73	0.61	22.3	7.01	15.3	3.98
Fluoride	2.60	0.47	2.70	0.057	2.17	0.42	2.31	0.541
Nitrate	2.16	2.70	1.74	0.51	8.40	2.70	4.85	1.57
Phosphate	0.024	0.078	0 ^b	0	0	0	0.011	0.060
Sulphate	14.0	2.49	13.7	2.32	34.5	9.16	23.7	5.93

^a The bromide concentration in the tracer seepage solutions increased over time during the 9 days after the release of tracer solution. The concentration then gradually decreased in response to the 7 months of mine water flushing.

^b Below the detection limit presented in Table IV.

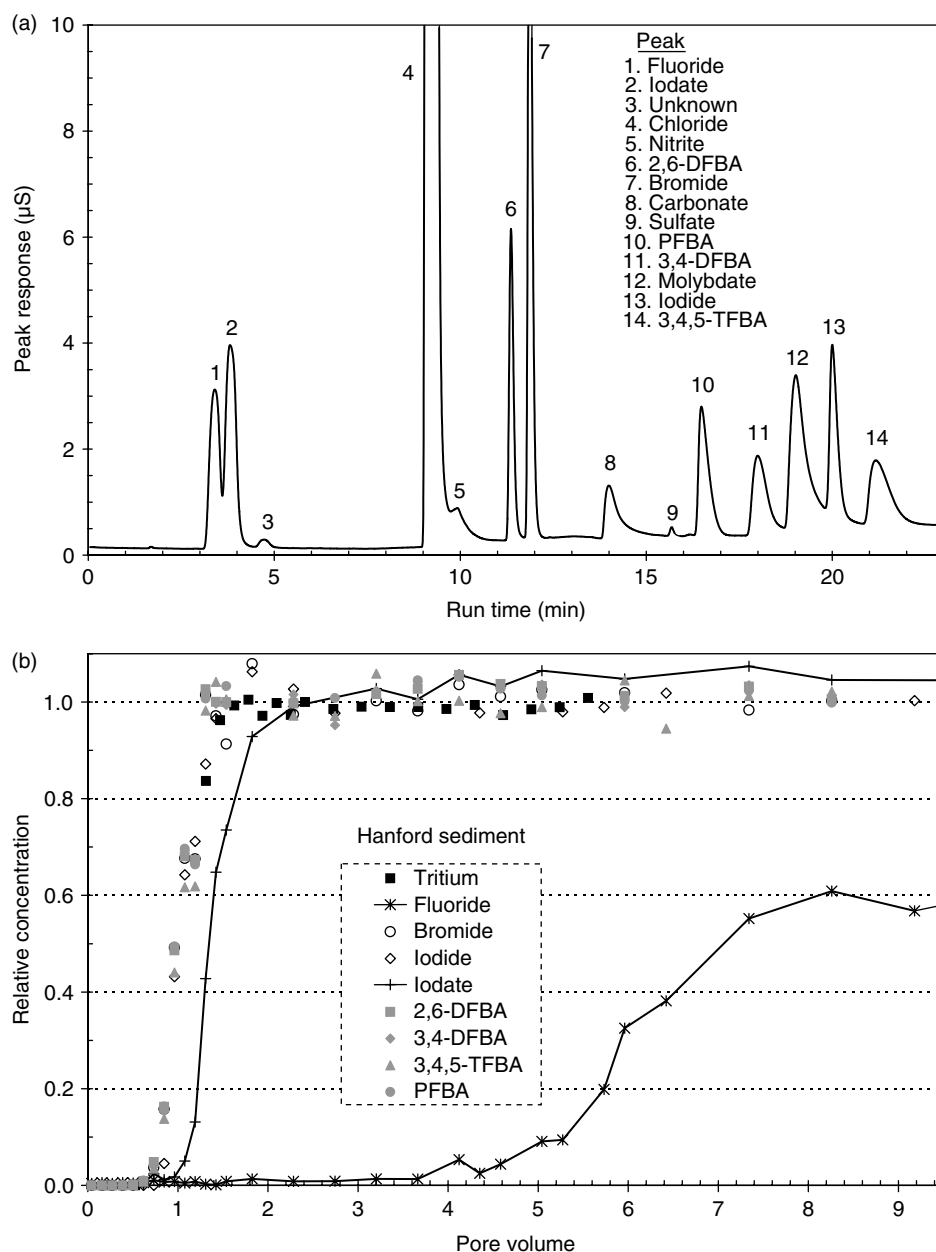


Figure 4. Transport of tracers in a column homogeneously packed with Hanford sediment. (a) IC chromatograms of inorganic anions for a representative column effluent sample. Note that a gradient condition over a range of 2 to 40 mM KOH was employed and that molybdate was applied as a tracer. (b) Breakthrough curves of tracers (column residence times for tritium and anionic tracers were 1.94 h and 1.47 h respectively)

reports have documented the reactive behaviour of FBA tracers in similar media (Boggs and Adams, 1992; Seaman, 1998; McCarthy *et al.*, 2000).

Selective extraction was used to target the different fractions of iron in the sample. For example, citrate–bicarbonate–dithionite-extractable iron contains crystalline iron oxide minerals such as hematite,

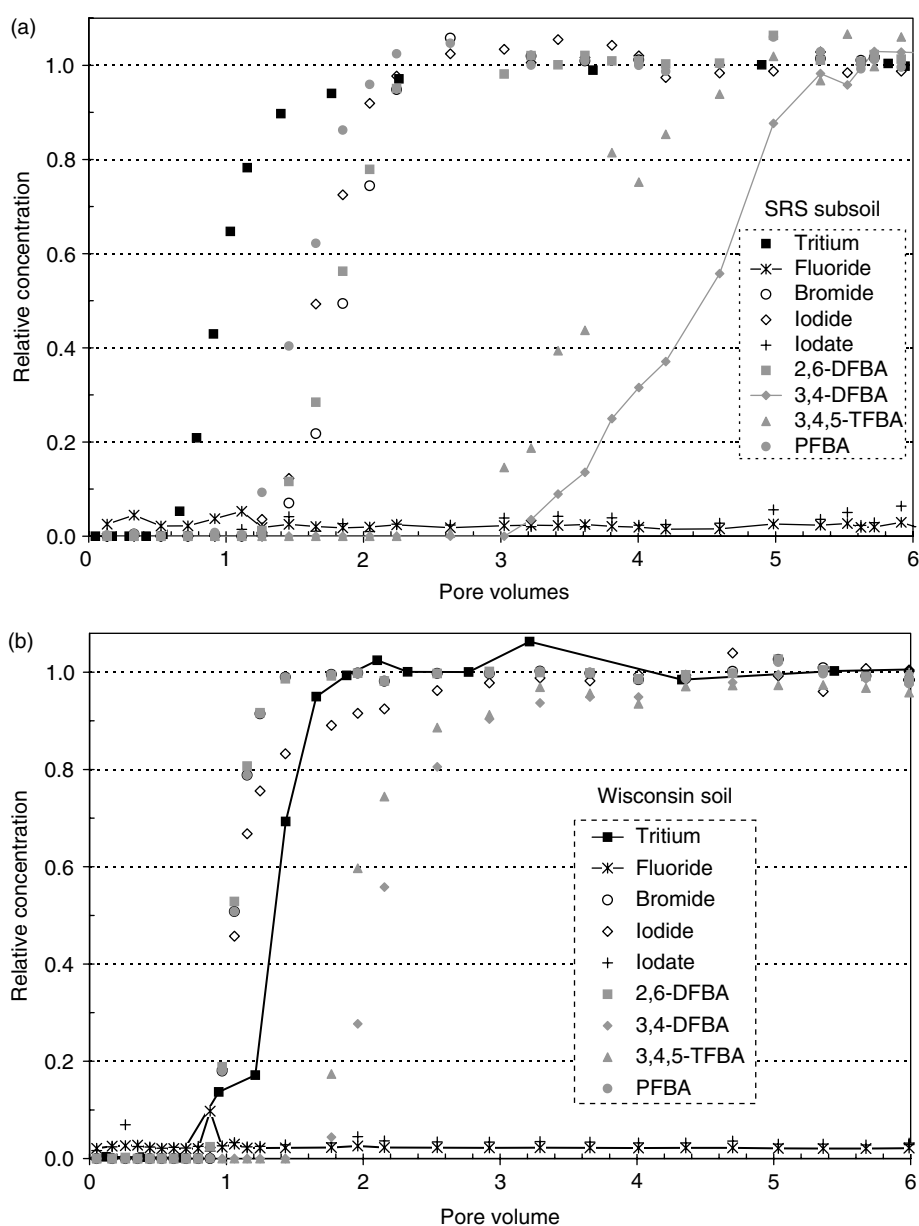


Figure 5. Breakthrough curves of tritium and anionic tracers in a column homogeneously packed with (a) SRS subsoil sediment (column residence times for tritium and anionic tracers were 1.36 h and 1.70 h respectively) and (b) Wisconsin soil (column residence times for tritium and anionic tracers were 4.08 h and 1.87 h respectively)

goethite, lepidocrocite, and ferrihydrite, whereas ammonium oxalate extraction targets noncrystalline iron oxides, including ferrihydrite and ferrihydrite-like minerals (Loeppert and Inskeep, 1996). Both the SRS subsoil and Oak Ridge sediment had a relatively high crystalline iron oxide content, along with Wisconsin soil and Livermore alluvium (Table III). As determined by X-ray diffraction, the clay mineralogy of the SRS subsoil sample consisted mainly of kaolinite, goethite, and hydroxy-interlayered vermiculite (Seaman, 1998). The anion sorption capacity of the geologic media was also reflected in the measured AEC. The AEC values

for the media are listed in Table III, which shows an AEC value as high as 4.04 meq/100 g sample for the SRS subsoil. The measured AEC value for Oak Ridge sediment was not as large as other media, such as the Livermore alluvium, which did not exhibit noticeable sorption of FBAs. Observed sorption of FBAs in the Oak Ridge sediment was probably related to its low pH value. The measured pH in the effluent samples for the Oak Ridge column was 4.12 ± 0.02 ($n = 41$), which is very close to the pK_a values of FBAs, compared with a pH value of 6.69 ± 0.23 ($n = 30$) from the Livermore column. For Oak Ridge sediment with low pH values, an appreciable proportion of FBA exists in a nonionized form, which can then be sorbed onto organic matter and the clay fraction of the mineral phase. At a pH value of 4.12 measured from the Oak Ridge column, the proportions occurring in a nonionized form are 33.9%, 20.8%, 5.1%, and 3.8% for 3,4-DFBA, 3,4,5-TFBA, 2,6-DFBA, and PFBA respectively, as calculated by the Henderson–Hasselbach equation (McCarthy *et al.*, 2000). At the pH value of 6.69 for the Livermore column, the proportion for all four FBAs is less than 0.1%.

We also examined the transport behaviour of FBAs in two samples with a high organic matter content, 2.3% for the Owngate soil and 8.7% for the Wisconsin soil. The breakthrough curve results indicate some sorption of FBAs with these soils (a higher retardation for Wisconsin soil than Owngate soil), indicating the interaction of the FBAs with the organic matter in the soil; retardation for the Wisconsin soil is presented in Figure 5b. In laboratory experiments using two soil samples that had a similar organic matter content to the Wisconsin soil sample used here, Jaynes (1994) reported a slight sorption of 3,4-DFBA and 3,5-DFBA and conservative transport of PFBA and 2,6-DFBA.

The retardation factor R and mass recovery, calculated by moment analyses of the breakthrough curves, are listed in Table VI. The R values of FBAs in the SRS subsoil, Oak Ridge sediment, and Wisconsin soil exhibited a sequence that follows the pK_a values of the four FBAs tested (3,4-DFBA > 3,4,5-TFBA > 2,6-DFBA > PFBA): the lower the pK_a value, the smaller the R value. The sorption maximum for organic acids on hydrous oxide surfaces often occurs near their pK_a value due to the combined effects of pH on oxide surface charge and on acid dissociation. The nondissociated form of the organic acid can either protonate uncharged surface sites to initiate an electrostatic interaction or neutralize the hydroxyl groups resulting from a ligand exchange at the oxide surface, thus enhancing the sorption process (Seaman, 1998). At a given pH, a compound with a lower pK_a value will have a smaller proportion in the protonated form that can be electrostatically sorbed onto anion sorption sites. The observed sorption of FBAs was likely caused by a combination of the electrostatic attraction for a portion of the FBA in anionic form onto positively charged sites (e.g. for the SRS and Wisconsin media) and partitioning of organic FBAs in organic matter (e.g. Oak Ridge sediment and Wisconsin soil).

Table VI. Summary of retardation factor and mass recovery in the column experiments

Sample	Hanford sediment		Oak Ridge sediment		SRS subsoil		Wisconsin soil	
	Retardation factor	Mass recovery	Retardation factor	Mass recovery	Retardation factor	Mass recovery	Retardation factor	Mass recovery
Tritium	1.02	0.95	1.17	1.01	0.99	0.99	1.36	1.06
Fluoride	13.7	0.98	>100 ^a	0.42	603	0.14	>44 ^a	0.09
Bromide	1.01	1.02	2.48	1.00	1.87	0.98	1.05	0.95
Iodide	1.05	1.01	n.a.	0.20	1.70	0.96	1.19	1.00
Iodate	1.41	1.06	>100 ^a	0.16	49	0.83	>52 ^a	0.02
2,6-DFBA	1.01	1.01	1.55	1.01	1.82	0.98	1.11	0.96
3,4-DFBA	1.01	1.01	7.09	1.01	4.39	1.03	2.26	0.99
3,4,5-TFBA	1.04	1.00	6.25	0.96	3.62	1.04	2.16	0.96
PFBA	1.01	1.01	1.11	1.04	1.57	0.97	1.14	0.96

^a To obtain the extent of sorption for tracers with large sorption, an alternate approach, such as a batch sorption study, is more appropriate than the column approach.

To a lesser extent, sorption of bromide also occurred in these media. Nevertheless, the observed mass recovery for these tracers in these three media was about 100% (Table VI), indicating the absence of solute–media interactions that lead to mass loss (i.e., irreversible sorption or degradation). In the SRS subsoil and Wisconsin soil samples, PFBA exhibited a similar retardation to that of bromide. PFBA also showed the smallest retardation among the FBAs tested. Thus, if only one FBA isomer is needed as a hydrologic tracer, then PFBA is the best choice, next to bromide, because of PFBA's limited potential for sorption and its resistance to degradation. (PFBA's resistance to degradation can be attributed to its possessing the highest number of fluorine atoms in the benzene ring.) Our results show that the potential delayed transport of anionic tracers, such as bromide and FBAs, must be taken into account when designing and interpreting tracer tests in hydrologic studies.

Tritium has been considered an ideal water tracer (Davis *et al.*, 1980). However, a slight retardation of tritium (with a retardation factor larger than unity) was observed in the columns packed with Wisconsin soil and Oak Ridge sediment. Tritium sorption of similar magnitude, postulated to occur from the interaction of tritium with clay lattice hydroxyl groups via hydroxyl exchange (Stewart and Baker, 1973), has been reported in numerous publications (e.g. van Genuchten and Wierenga, 1976; Seyfried and Rao, 1987; Gaber *et al.*, 1995).

In reducing environments, aqueous iodine usually occurs as the mobile iodide anion (I^-). Under more oxidizing conditions, iodine may be present as the more reactive iodate anion (IO_3^-), which exhibits retarded transport because iodate interacts with clays and organic matter (Couture and Seitz, 1983; Yoshida *et al.*, 1992). The disparate sorption behaviour of iodide and iodate was confirmed in our study, which consistently showed the sorption of iodate to be much higher and mass recovery to be much lower than for iodide. Even in the Hanford sediment, a noticeable sorption of iodate took place, with an observed retardation factor of 1.4. Care should be exercised with regard to the potential conversion of iodine species under different geochemical conditions—even when the iodide form is applied during a tracer study—because the conversion of iodide to iodate or elemental iodine will confound the interpretation of a tracer study's results.

Compared with FBA and other halide anions, a significant sorption of fluoride has been commonly reported with minerals such as hydrous iron oxide, kaolin, and montmorillonite (Bower and Hatcher, 1967; Farrah and Pickering, 1986; Bar-Yosef *et al.*, 1988). We observed a significantly high sorption and a low mass recovery of fluoride in all eight media that were examined. Thus, fluoride is the least appropriate halide for use as a hydrologic tracer because of its strong specific chemical binding to mineral surfaces.

CONCLUSIONS

To exploit the applications of FBAs and halides further as hydrologic tracers, an IC analytical method was developed. The method, which can simultaneously separate and quantify up to seven FBAs and halides from other common groundwater constituents in a single run, was shown to be robust and sensitive. The usefulness of the analytical method developed was shown in both field and laboratory tracer experiments. In field tests examining transport and matrix-diffusion behaviour in unsaturated tuff that features fractures and a fault, the IC analytical method offered multiple advantages. Its single-run capability made the method efficient and cost effective. The method also increased confidence in sample analyses from charge balance calculations and provided anion results for a database that could be used in water–rock interaction modelling. Laboratory tracer experiments with eight geologic media from the USA, mostly sampled at DOE facilities with prevalent groundwater contamination, further demonstrated potential applications of the IC analytical method.

Our studies showed that the transport behaviour of FBAs, as well as bromide, was not ubiquitously conservative. The delayed transport of these tracers is related to media characteristics, such as the presence of organic matter, pH, iron oxide content, and clay mineralogy. As a redox-sensitive element, iodine can exist in various forms, including iodide and iodate. Of the two forms, iodate was found to have a greater tendency for retention in geologic media. Our results also demonstrate the value of evaluating the transport behaviour

of potential FBA and halide tracers under relevant geochemical conditions before embarking on ambitious, large-scale field tracer experiments.

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