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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 more fully exploit the use of fluorobenzoic acids (FBAs) and halides 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 sulfate). The usefulness of this ion chromatographic (IC) analytical method is demonstrated in both field and laboratory tracer experiments. Field experiments in unsaturated tuff featuring fractures or a fault show that this efficient and cost-effective method helps achieve the objectives of tracer studies that use multiple FBAs and/or diffusivity tracers (simultaneous use of one or more FBA and halide).

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 United States—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 behavior: (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) Any use of iodine as a hydrologic tracer should take into account the different sorption behaviors of iodide and iodate and the possible conversion of iodine's initial chemical form. (4) The transport behavior of potential FBA and halide tracers under relevant geochemical conditions should be evaluated before beginning ambitious, large-scale field tracer experiments.

Key Words: tracers, fluorobenzoic acid, groundwater, transport, halides, ion chromatography.

INTRODUCTION

Many laboratory and field experiments investigating hydrologic processes in the subsurface have obtained crucial data through the application of tracer(s) (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; Pearson *et al.*, 1996; Seaman, 1998; Dahan *et al.*, 1999; Hu *et al*., 2001; Hu *et al*., 2002; Nelson *et al*., 2003; Reimus *et al*., 2003; Mayes *et al*., 2003). FBAs are attractive tracers because they do not occur naturally, are detectable at low concentrations, are resistant to degradation, and low aquatic toxicity (Bowman and Gibbens, 1992; McCarthy *et al*., 2000). In addition, since the aqueous diffusion coefficient of an FBA is about 3 times smaller than those of tritium and halides, a diffusivity-tracer approach has been exploited with a simultaneous use of FBA and tritium or halide tracers when studying hydrologic processes. The diffusivity-tracer test has 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; Hu *et al*., 2002; Reimus *et al*., 2003; Salve *et al*., in press).

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 behavior. (Additional FBA isomers exist when the hydrogen atom in the benzene ring is substituted by a chlorine atom or a fluoromethyl functional group.) This 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 a discrete natural fracture in unsaturated chalk (Dahan *et al.*, 1999). One isomer was added to each of the seven percolation ponds, which were installed sequentially along the exposed fracture, to delineate flow path 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. Under high release rates, the fractures acted as the predominant flow pathways, with limited fracture–matrix interaction. Under low release rates, fracture flow was less dominant, with a noticeable contribution from matrix flow.

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 with 2 pH units above the pK_a. The transport behavior of FBAs in many subsurface media 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 minerals (e.g., iron oxides and kaolinite) or of organic matter with net positively charged surfaces that may attract anions, the transport of FBAs (along with bromide) can be delayed, and FBAs can serve as reactive tracers (Boggs *et al*., 1992; Benson and Bowman, 1994; Jaynes, 1994; Seaman, 1998). In addition, during low-pH conditions, the non-inoized form of FBAs exhibits a considerable sorption onto soil organic matter (Benson and Bowman, 1994; McCarthy *et al*., 2000).

A reliable analytical method that can distinguish several FBAs from one another is crucial for multi-tracer 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 sulfate) that preexist in soil and groundwaters. A robust analytical method is also needed for field tracer experiments, which may collect hundreds of samples over a course of several years.

The most widely used method for FBA analysis was developed by Bowman (1984) that 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 7 (Dahan and Ronen, 2001) or 10 FBA isomers (Stringfellow *et al*., 2001) in a single run. The HPLC methods developed by Stringfellow *et al.* (2001) simultaneously measure multiple FBAs in the presence of interfering compounds such as nitrate and soluble organic matter. Resolution matrix tables have been constructed to assist the selection of FBA tracers for use in studies where such interference may be present. In contrast, the reversed-phase HPLC method of Stetzenbach *et al*. (1982) requires a preconcentration of aqueous samples and increases sensitivity by 3 orders of magnitude to allow low-level detection of FBAs. However, this high sensitivity requires a greater sample volume by the same orders of magnitude.

An ion chromatographic (IC) method with conductivity detection was used to separate and analyze three FBAs (Pearson *et al.*, 1992). However, this study found that even a low concentration (1 mg/L) of chloride interfered with the chosen FBAs. Furthermore, the reported detection limit was relatively high at 0.25 mg/L.

Previous analytical methods for FBAs analysis have tested for the interference of common inorganic anions, whether halides as tracers or preexisting groundwater constituents. For example, Seaman (1998) reported a method that simultaneously analyzed 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 analyzes all of the common anions in a single run. In addition, past researchers have traditionally used different instruments and methods to analyze 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, while FBA analyses have been conducted by HPLC with a UV absorbance detector (Turin *et al*., 2002; Reimus *et al*., 2003).

In this work, 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 and generation of wastes [e.g., acids and organic solvents] required in other FBA analytical methods), an analytical column, and a conductivity suppressor. All of these technologies contribute to a robust analytical method that is easy to operate, requires minimal sample pretreatment, and yields a superior 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 multi-tracer experiments and analytical approaches.

MATERIALS AND METHODS

Reagents

We used reagent water with a resistance level of 18 MΩ. 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 1. 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) ion chromatography DX-600 system was used in this study to analyze FBAs and other anions. The system comprises 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 × 50 mm; 4-mm inner diameter and 50-mm length) guard column was used in conjunction with an IonPac AS17 (4 × 50 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 an EGC-KOH cartridge and a CR-ATC (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. Using deionized water only, the EG50 generates high-purity, carbonate-free KOH eluent that minimizes baseline shift, improves retention time stability and resolution, and provides run-to-run reproducibility. An injection loop size of 25 µL was used for sample analyses. Finally, Dionex PeakNet 6.2 software was used for system control, data collection and processing.

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 m*M* KOH is presented in Table 2.

Field experiments

The experimental setup used in two liquid-release and tracer-transport studies in unsaturated, fractured welded tuff at Yucca Mountain, Nevada, is described in detail in Salve *et al*. (2002). Both 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, a series of tests was conducted by releasing tracer-laced water into two isolated zones within a horizontal injection borehole drilled into the rock formation from the tunnel. The low- and high-permeability zones were located at a distance of 0.75–1.05 m and 2.3–2.6 m, respectively, from the borehole collar. Seepage, if available, was collected in an excavated slot about 1.6 m below the borehole, and the tracer concentration in the seepage collection was analyzed. The tests conducted in the low-permeability zone used bromide and three FBA tracers. Although no seepage occurred in this zone, information about the liquid-intake rates, as well as formation wetting and drying, was obtained and discussed in Salve *et al*. (2002). For the tests (called the fracture study in this paper) conducted in the high-permeability zone, which likely has a well-connected fracture network, the first phase consisted of four liquid-release events with fluoride and four FBA tracers that were different from these FBAs used in the low-permeability zone. One FBA was associated with each event, and each event had a different release rate. The second phase investigated the transport behavior of the applied tracers during flushing through four release events (and rates). No tracers were added in the second phase. The tracer results under different release rates in the high-permeability zone were presented and discussed in Hu *et al*. (2001).

The second study (called the fault study in this paper) investigated flow and transport in a fault embedded in unsaturated tuff (Salve *et al*., in press). The experiment involved the direct release of ~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). Seven months after beginning water release along the fault, when a stable flow regime had been established, a solution containing bromide and pentafluorobenzoic acid (PFBA) were released along the fault for nine days. Afterwards, water without tracers was released along the fault for another seven months. Seepage water was continuously collected in a cavity excavated ~20 m below the test bed and was analyzed for chemical concentration.

Column experiments

Laboratory column experiments were conducted to demonstrate the usefulness of the IC analytical method and to elucidate the transport behavior of the tracers (FBAs and halides) in various geologic media in the United States (Table 3). 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 behavior of inorganic anions. All properties presented in Table 3 were measured according to the standard procedures in *Methods of Soil Analysis* (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). One HPLC pump (Model 301, Alltech Associates, Inc., Deerfield, IL) was connected to the column, and a three-way switching valve was placed in-line to facilitate switching between solutions with and without the tracer of interest. To investigate the simultaneous transport of four halides (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- trifluorobenzoic acid (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 analyzed 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) was carried out to compare the transport behavior of tritium and the anionic tracers used in our column studies. Column effluent fractions were collected with an automated fraction collector (Retriever 500, ISCO Inc., Lincoln, NE) for anion concentration determination by the IC method or for the liquid scintillation counting of tritium.

RESULTS AND DISCUSSION

Separation of inorganic anions

Under a hydroxide gradient condition from a range of 2 to 60 m*M* KOH, the retention times for each FBA solution with a concentration of 10 mg/L are given in Table 1. The wide range in retention times, from 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 m*M* 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 with 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 have a long retention time.

The IC method presented here provides a method detection limit (MDL) ranging from 15.4 to 29.4 µg/L for four FBAs tested with an injection volume of 25 µL, which corresponds to a quantification limit ranging from of 0.38 to 0.74 ng (Table 4). This detection limit was obtained according to the procedure described in Method 300.0 from the U.S. Environmental Protection Agency (1993). The MDL is determined by injecting seven replicates of reagent water spiked with an analyte at a concentration of 3 to 5 times the estimated instrument detection limit (referred to as MDL solution). The MDL is then calculated as (t) × (SD) where *t* is Student's *t* value for a 99% confidence level and a standard deviation (SD) estimate with *n*-1 degrees of freedom (*t* = 3.14 for *n* = 7 replicates). The retention time and peak area precision (expressed as relative standard deviation, or RSD) were also determined from seven replicate injections (Table 4). The peak area RSD of less than 10% is obtained for the MDL solution of low (sub mg/L) concentration, while the peak area RSD for a solution spiked with about 1 mg/L 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 4). 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, while Stringfellow *et al.* (2001) observed a limit of 5 to 7 ng for 14 FBAs. Finally, Dahan and Ronen (2001) reported a detection limit of about 0.5 mg/L 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 boldface in Table 1) can be selected and potentially used in hydrological studies. A representative chromatogram (Figure 1) shows the separation of these seven FBAs and other common anions. Note that although 2,3,4,5-tetrafluorobenzoic acid (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 the existing phosphate concentration.

The use of a reagent-free eluent generator such as the EG-50 produces hydroxide eluent at the desired concentration accurately and reproducibly. 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 m*M* KOH is commonly less than 0.05 μS. In contrast, the observed baseline shift under the same gradient is at least 1 μS if 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 tracer 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 of LiBr. Because the J-13 water contained about 2.5 mg/L of fluoride, a high concentration (307 mg/L) of fluoride was added to the tracer solution. Furthermore, both the released tracer solution and the collected seepage contained about 120 mg/L 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 analyzed, 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. During this study, a long-term tracer test was conducted to investigate the matrix diffusion in unsaturated tuff with an embedded fault (Salve *et al*., in press). 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. Figure 3 demonstrates 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*., in press).

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 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. This concentration 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 waters (mine water and tracer solution) have similar concentrations of chloride, nitrate, and sulfate (Table 5). The seepage solution collected after releasing mine water, however, exhibits concentrations that are about 3 times higher for these anions, presumably from solution–rock interactions as the solution passed through the rock 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 as well as the anion exchange process occurring from the high concentration of bromide applied. This type of data could be used in transport modeling 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 a column packed with a geologic medium. 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 tested FBAs exhibited identical breakthrough curves (with symmetrical behavior and negligible tailing) and conservative (not retarded) transport—the same transport behavior as that of tritium and bromide**.** A representative breakthrough curve for the Hanford sediment is shown in Figure 4b. Such conservative behavior 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 United States (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 subsurface sample in Figure 5a. These samples contained appreciable amounts of minerals, such as kaolinite and iron (Fe) oxides, which possess positively charged surfaces and contribute to anion sorption. Several reports have documented the reactive behavior of FBA tracers in similar media (Boggs and Adams, 1992; Seaman, 1998).

Selective extraction was used to target the different fractions of Fe in the sample. For example, citrate-bicarbonate-dithionite (CBD) extractable Fe contains crystalline iron oxide minerals such as hematite, goethite, lepidocrocite, and ferrihydrite, while ammonium oxalate extraction targets noncrystalline Fe oxides, including ferrihydrite and ferrihydrite-like minerals (Loeppert and Inskeep, 1996). Both the SRS subsurface and Oak Ridge media had a relatively high crystalline Fe oxide content, along with Wisconsin soil and Livermore alluvium (Table 3). As determined by x-ray diffraction, the clay mineralogy of the SRS subsurface 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 anion exchange capacity (AEC). The AEC values for the media are listed in Table 3, which shows an AEC value as high as 4.04 meq/100 g sample for the SRS subsurface medium. The measured AEC value for Oak Ridge sediment was not as large as the AEC values for other media, such as the Livermore alluvium that did not exhibit noticeable sorption of FBAs. The sorption of FBAs in the Oak Ridge medium was probably related to the medium's 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 the measured pH of the effluent samples for the Livermore column was 6.69 ± 0.23 (n = 30). At Oak Ridge sediment with low pH values, an appreciable proportion of FBA exists in non-polar non-ionized, which can then be sorbed onto organic matter and clay fraction of the mineral phase. At pH value of 4.12 for Oak Ridge column, the proportion of non-ionized form is 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 Livermore column, the proportion for all these four FBAs is less than 0.1%.

We also examined the transport behavior of FBAs in two samples with a high organic matter content, 2.3% for Owngate soil and 8.7% for Wisconsin soil, respectively. 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 (1993) 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 6. The *R* values of FBAs in the SRS subsurface, Oak Ridge sediment, and Wisconsin soil exhibited a sequence that follows the pK_a values of the four tested FBAs (3,4-DFBA > 3,4,5-TFBA > 2,6-DFBA > PFBA): the smaller the pK_a value, the smaller the *R* value. At a certain pH, a compound with a smaller 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 a combination of the electrostatic attraction for proportion of anionic FBA 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 medium and Wisconsin soil).

To a lesser extent, the sorption of bromide also occurred in these media. Nevertheless, the observed mass recovery for these tracers in these three media was about 100% (Table 6), indicating the absence of solute–media interactions that lead to mass loss (i.e., irreversible sorption or degradation). In the SRS subsurface and Wisconsin soil samples, PFBA exhibited a similar retardation to that of bromide. PFBA also showed the smallest retardation among the tested FBAs. Thus, if only one FBA isomer is needed as a hydrologic tracer, 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 reactive 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 1) was observed in the columns packed with Wisconsin soil and Oak Ridge sediment. Tritium sorptions of similar magnitude have been reported in numerous publications (e.g., Wierenga *et al*., 1975; van Genuchten and Wierenga, 1977; Gaber *et al*., 1995; Hu and Brusseau, 1996). For example, the retardation factor for tritium was measured to be 1.17 in an aggregated tropical soil (Seyfried and Rao, 1987) and 1.2 in a column packed with glass beads and porous kaolinite spheres (Hu and Brusseau, 1996). The interaction of tritium with solid surfaces has been postulated to occur via hydroxyl exchange with clay lattice hydroxyls (Stewart and Baker, 1973). This process is more pronounced in kaolinite minerals that have available hydroxyl groups at platelet surfaces.

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; Sheppard and Thibault, 1992; Yoshida *et al*., 1992). The disparate sorption behavior 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 to FBA and other halide anions, a significant sorption of fluoride has been commonly reported with minerals such as hydrous iron oxide, montmorillonite, and calcite (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.

CONCLUSION

To further exploit the applications of FBAs and halides 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 with a high sensitivity. The usefulness of the developed analytical method was shown in both field and laboratory tracer experiments. In field tests examining transport and matrix-diffusion behavior in unsaturated tuff that feature 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 modeling. Laboratory tracer experiments with eight geologic media across the United States, which were mostly related to DOE facilities with prevalent groundwater contamination, further demonstrated potential applications of the IC analytical method.

Our studies showed that the transport behavior 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. Iodine is one of commonly used hydrologic tracers. 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 behavior of potential FBA and halide tracers under relevant geochemical conditions before embarking on ambitious, large-scale field tracer experiments.

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Figure Legends

Figure 1 IC chromatogram of inorganic anions. All FBA isomers have a concentration of 5 mg/L. Other anions have the following concentrations: fluoride, 3.6 mg/L; chloride, 7.2 mg/L; bromide, nitrate, and sulfate, 14.3 mg/L; phosphate, 21.4 mg/L.

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

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.

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 m*M* 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 hours and 1.47 hours, respectively).

Figure 5 Breakthrough curves of tritium and anionic tracers in a column homogeneously packed with (a) Savannah River Site subsurface sediment (column residence times for tritium and anionic tracers were 1.36 hours and 1.70 hours, respectively) and (b) Wisconsin soil (column residence times for tritium and anionic tracers were 4.08 hours and 1.87 hours, respectively).

Table 1. 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] DFBA: difluorobenzoic acid; 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] Obtained from a 10 mg/L of FBA solution in the reagent water.

Table 2. Hydroxide gradient separation of inorganic anions using EG50

Time (min)	Eluent conc. (m*M*)	Comments
Equilibration		
–2	2	Preconditioning before sample analysis
Analysis		Sample injection at time zero
4	2	Isocratic analysis for fluoride
6	10	Linear gradient
12	30	Separation of bromide from nitrate; linear gradient
16	45	Linear gradient
20	60	Linear gradient
20.1	2	Returns to initial condition for next analysis

Table 3. 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 subsurface	Wisconsin soil
Description		Composite of core samples 9–12 m depth 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 depth below surface	Composite of sediment 12 m below surface	Surface soil
Location		Richland, WA	Livermore, CA	Mercury, NV	Idaho Falls, ID	Santa Fe, NM	Oak Ridge, TN	Aiken, SC	Plover, WI
pH	(standard unit)	8.5	8.0	8.9	8.5	7.7	4.5	5.4	5.9
Organic matter	(%)	0.06	0.03	0.14	0.04	2.30	0.12	0.07	8.70
Particle size	sand (%)	n.a.	n.a.	n.a.	n.a.	n.a.	7.7	76.7	67.0
	silt (%)	n.a.	n.a.	n.a.	n.a.	n.a.	70.9	3.5	21.0
	clay (%)	n.a.	n.a.	n.a.	n.a.	n.a.	21.4	19.8	12.0
CEC	(meq/100 g)	7.37	26.32	4.54	1.67	15.08	9.41	1.78	14.08
AEC	(meq/100 g)	0.007	0.35	0.18	0.13	0.008	0.12	4.04	0.009
Iron-CBD	(g Fe/kg)	3.26	9.78	1.48	3.12	3.82	10.83	15.92	10.08
Iron-oxalate	(g Fe/kg)	0.94	0.94	0.12	12.90	0.21	1.84	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. n.a.: not available (waiting for the analysis results).

Table 4. Parameters obtained by the IC method for halide tracers and other anions[a]

Anion	Method detection limit (ug/L)	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%
Sulfate	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.

Table 5. Change of anion concentration during a tracer test

	Mine water		**Tracer solution**		**Mine water seepage**		**Tracer seepage**	
	(35 measurements) Concentration (mg/L)		(6 measurements) Concentration (mg/L)		(36 measurements) Concentration (mg/L)		(262 measurements) Concentration (mg/L)	
Anion	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	15.32	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	0.000[b]	0.000	0.000	0.000	0.011	0.060
Sulfate	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 nine days after the release of tracer solution. The concentration then gradually decreased in response to the seven months of mine water flushing.

[b] Below the detection limit presented in Table 4.

Table 6. Summary of retardation factor and mass recovery in the column experiments

Sample	Hanford sediment		Oak Ridge sediment		SRS subsurface		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	13.74	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.

Figure 1

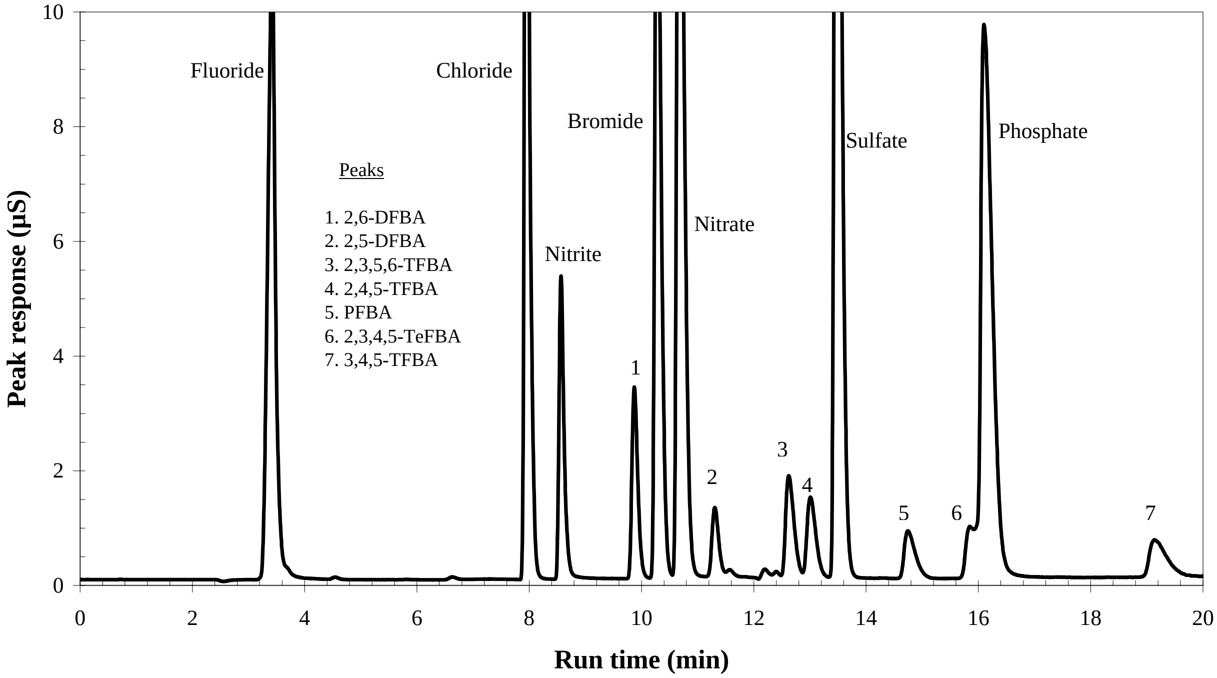

Peak response (μS)
Run time (min)
0
2
4
6
8
10
12
14
16
18
20
Fluoride
Chloride
Bromide
Nitrite
Nitrate
Sulfate
Phosphate
Peaks
1. 2,6-DFBA
2. 2,5-DFBA
3. 2,3,5,6-TFBA
4. 2,4,5-TFBA
5. PFBA
6. 2,3,4,5-TeFBA
7. 3,4,5-TFBA
1
2
3
4
5
6
7

Figure 2

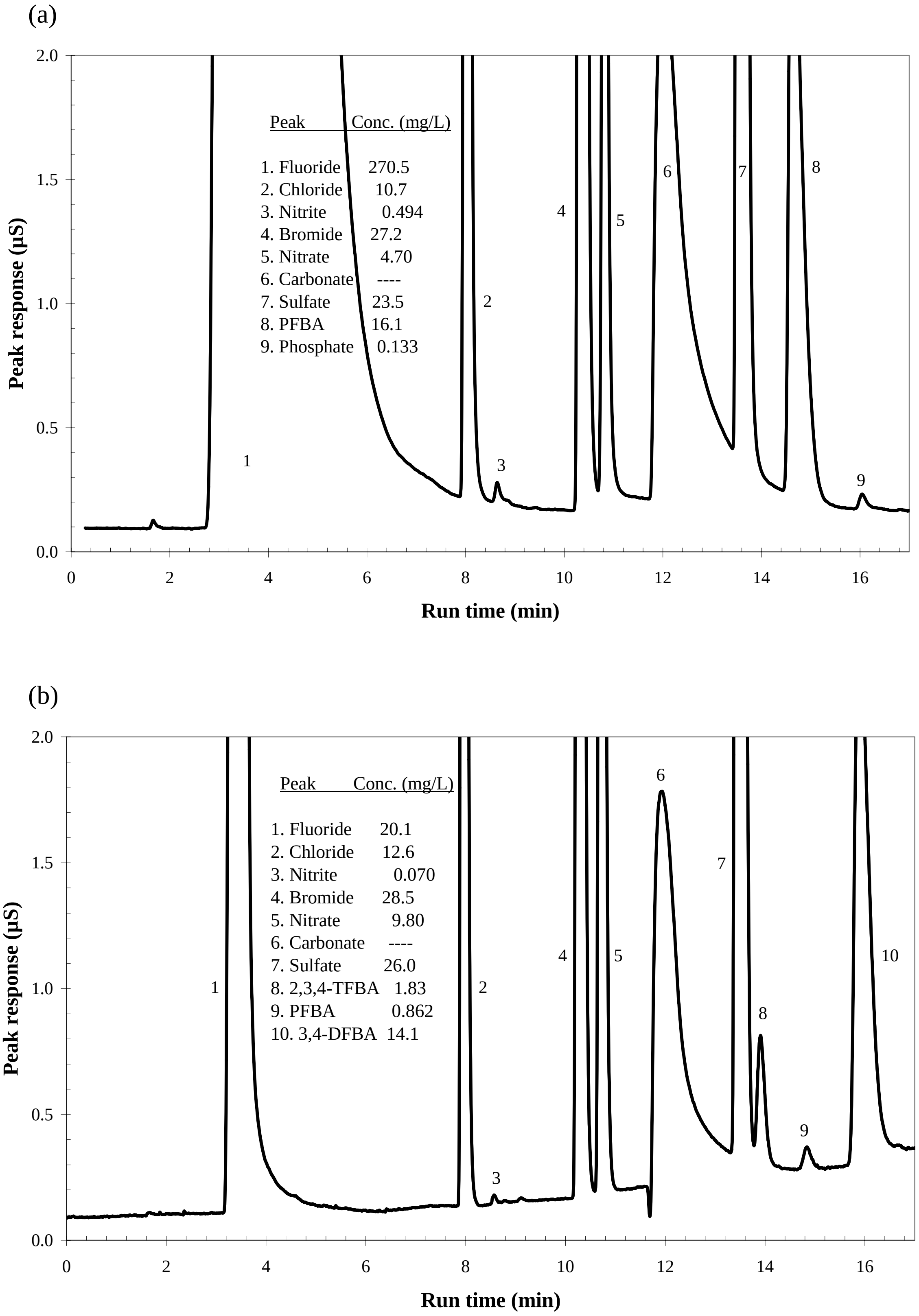
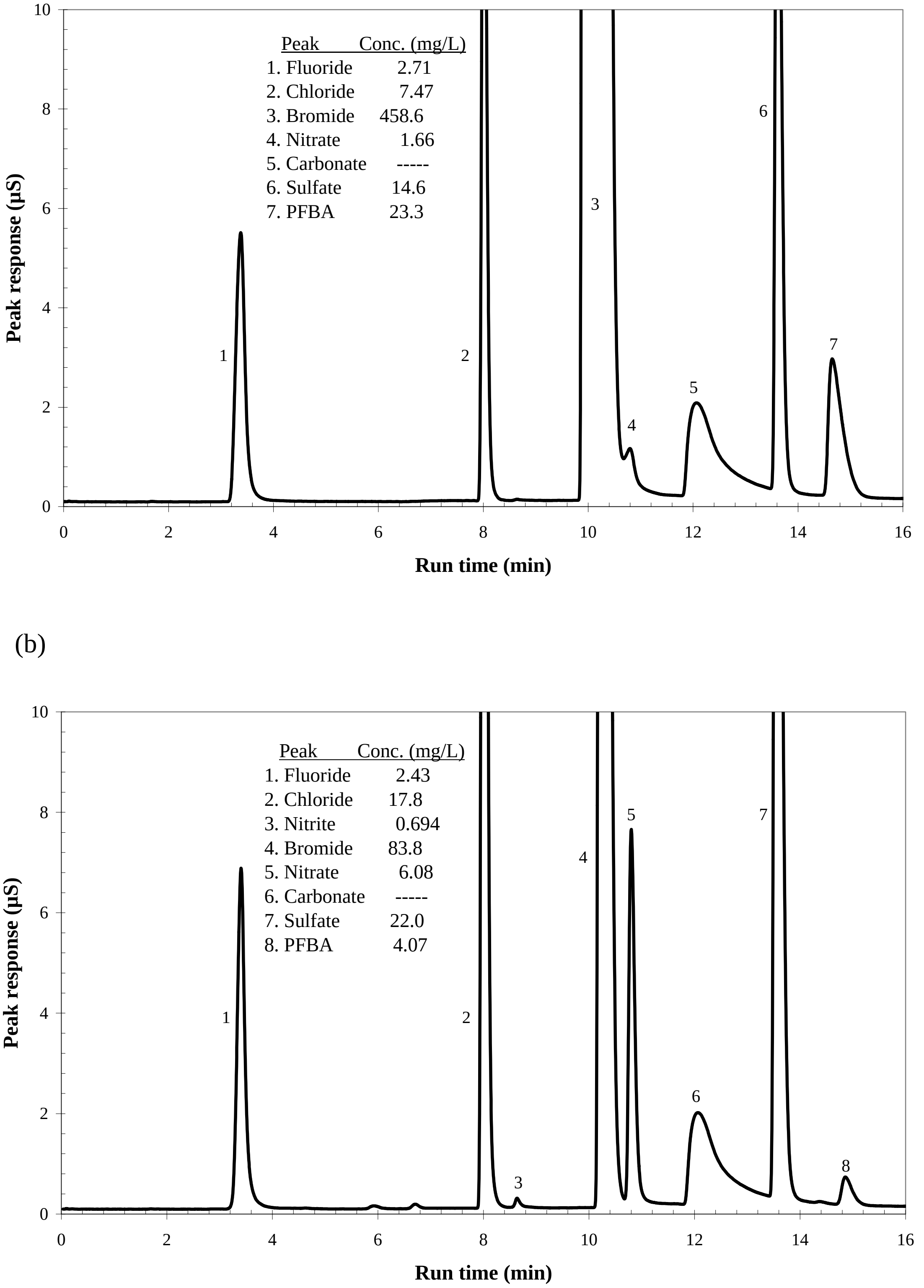

(a)
Peak Conc. (mg/L)
1. Fluoride 270.5
2. Chloride 10.7
3. Nitrite 0.494
4. Bromide 27.2
5. Nitrate 4.70
6. Carbonate ----
7. Sulfate 23.5
8. PFBA 16.1
9. Phosphate 0.133
1
2
3
4
5
6
7
8
9
Peak response (µS)
0.0
0.5
1.0
1.5
2.0
0
2
4
6
8
10
12
14
16
Run time (min)
(b)
Peak Conc. (mg/L)
1. Fluoride 20.1
2. Chloride 12.6
3. Nitrite 0.070
4. Bromide 28.5
5. Nitrate 9.80
6. Carbonate ----
7. Sulfate 26.0
8. 2,3,4-TFBA 1.83
9. PFBA 0.862
10. 3,4-DFBA 14.1
1
2
3
4
5
6
7
8
9
10
Peak response (µS)
0.0
0.5
1.0
1.5
2.0
0
2
4
6
8
10
12
14
16
Run time (min)

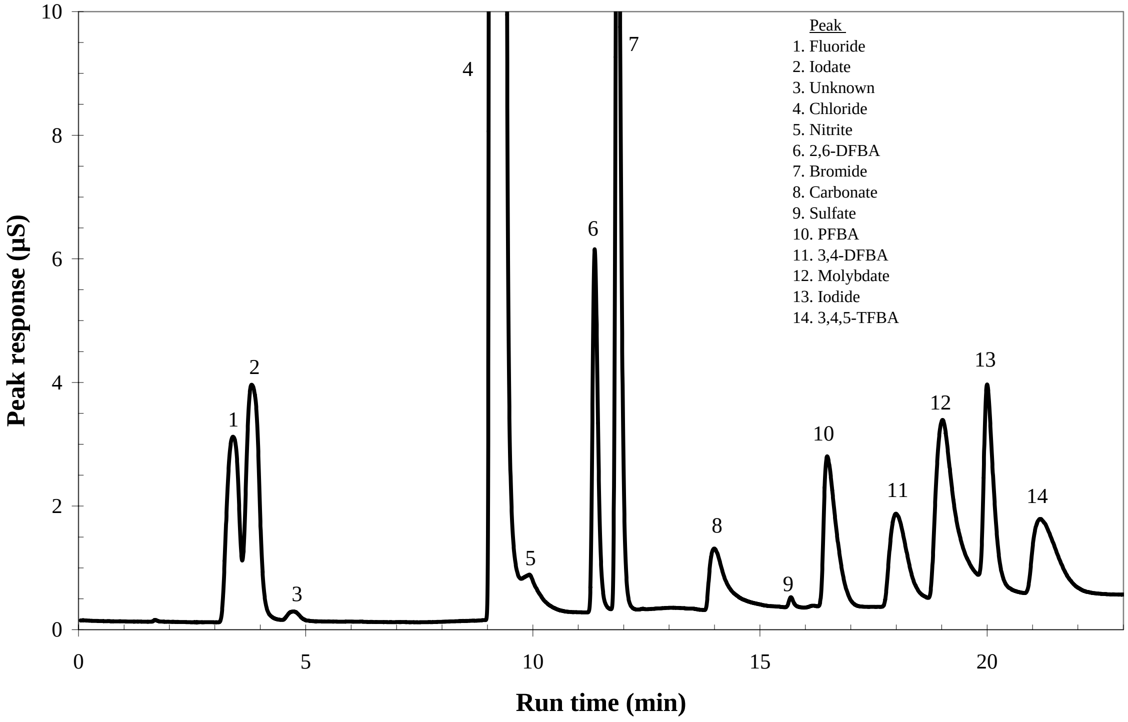
Figure 3


(a)

(b)
Peak Conc. (mg/L)
1. Fluoride 2.71
2. Chloride 7.47
3. Bromide 458.6
4. Nitrate 1.66
5. Carbonate -----
6. Sulfate 14.6
7. PFBA 23.3
Peak response (µS)
Run time (min)
0
2
4
6
8
10
12
14
16
1
2
3
4
5
6
7
Peak Conc. (mg/L)
1. Fluoride 2.43
2. Chloride 17.8
3. Nitrite 0.694
4. Bromide 83.8
5. Nitrate 6.08
6. Carbonate -----
7. Sulfate 22.0
8. PFBA 4.07
Peak response (µS)
Run time (min)
1
2
3
4
5
6
7
8

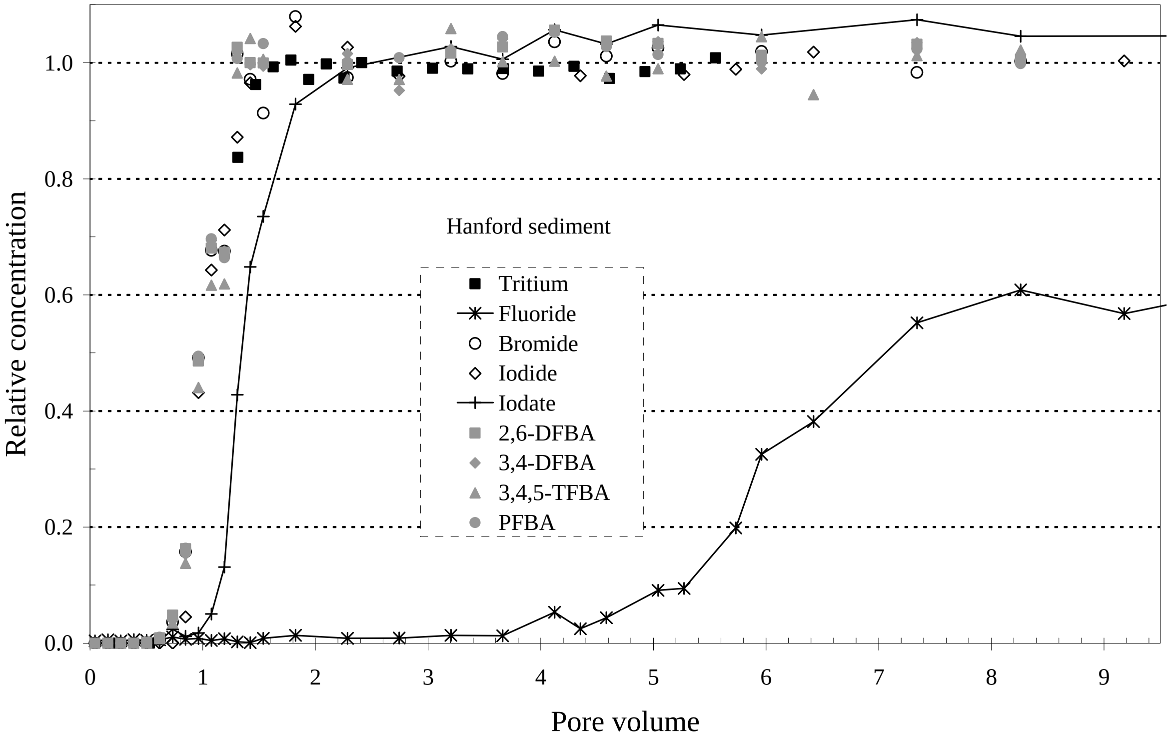
Figure 4

(a)



Peak response (µS)
Run time (min)
0
2
4
6
8
10
0
5
10
15
20
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Peak
1. Fluoride
2. Iodate
3. Unknown
4. Chloride
5. Nitrite
6. 2,6-DFBA
7. Bromide
8. Carbonate
9. Sulfate
10. PFBA
11. 3,4-DFBA
12. Molybdate
13. Iodide
14. 3,4,5-TFBA

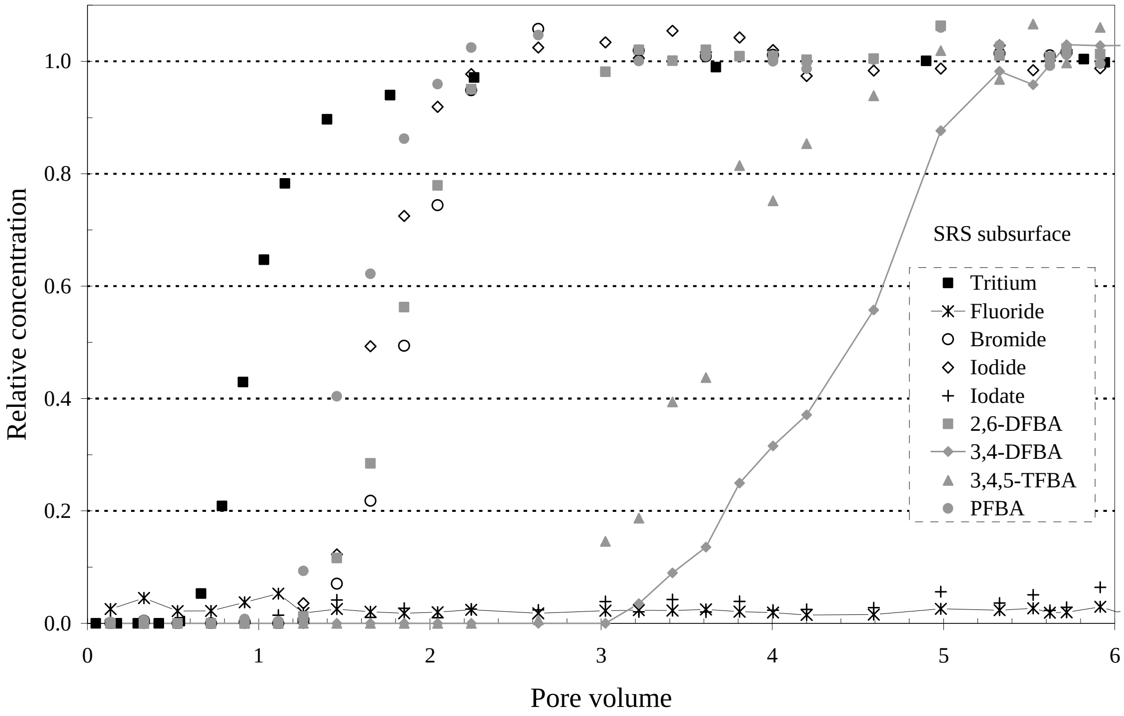
(b)



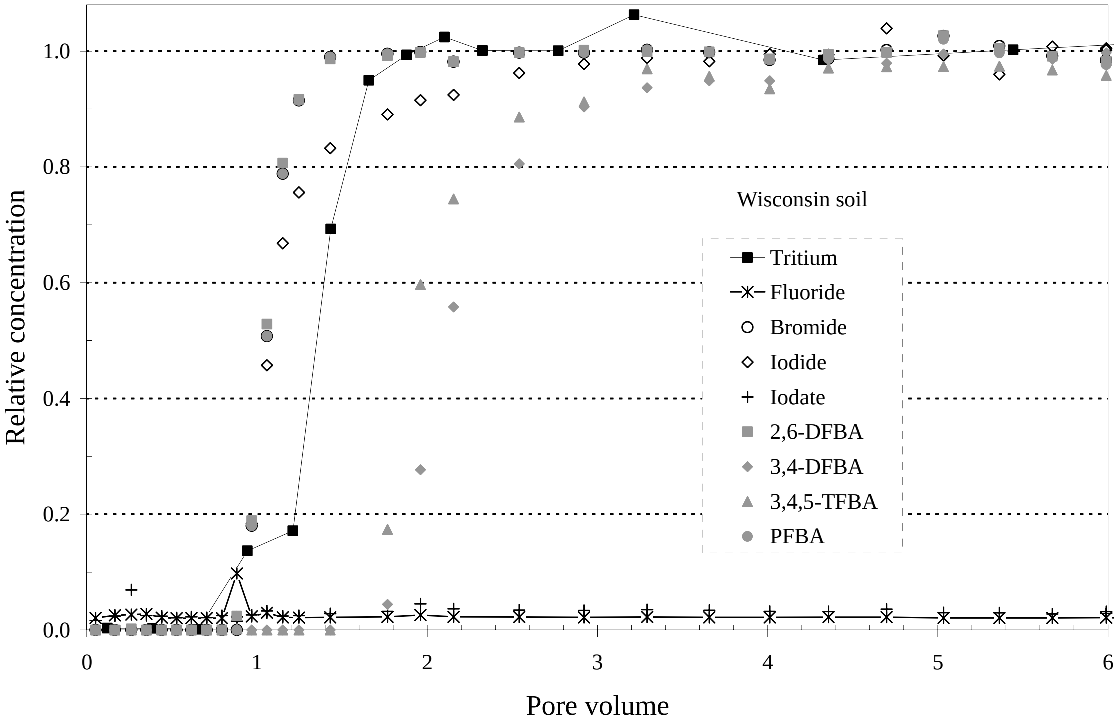
Relative concentration
Pore volume
0.0
0.2
0.4
0.6
0.8
1.0
0
1
2
3
4
5
6
7
8
9
Hanford sediment
Tritium
Fluoride
Bromide
Iodide
Iodate
2,6-DFBA
3,4-DFBA
3,4,5-TFBA
PFBA

Figure 5

(a)


SRS subsurface
Tritium
Fluoride
Bromide
Iodide
Iodate
2,6-DFBA
3,4-DFBA
3,4,5-TFBA
PFBA
Relative concentration
0.0
0.2
0.4
0.6
0.8
1.0
Pore volume
0
1
2
3
4
5
6

(b)


Wisconsin soil
Tritium
Fluoride
Bromide
Iodide
Iodate
2,6-DFBA
3,4-DFBA
3,4,5-TFBA
PFBA
Relative concentration
0.0
0.2
0.4
0.6
0.8
1.0
Pore volume
0
1
2
3
4
5
6