The Use of Sulphur Hexafluoride as a Conservative Tracer in Saturated Sandy Media

by Ryan D. Wilson and Douglas M. Mackay[a]

Abstract

Sulphur hexafluoride (SF_6), a volatile, nontoxic, inorganic compound, behaved identically to bromide in a laboratory column tracer experiment with saturated sandy media. A simple system was used to achieve an SF_6 injection concentration of approximately 7 mg/l, roughly 25% of its solubility. While this system requires more equipment and time than that involved in preparing ionic tracer solutions, certain benefits are realized. The detection limit for SF_6 was approximately 5 μg/l using a simple headspace extraction technique and a gas chromatograph with an electron capture detector. Thus, the tracer could be followed for a three order of magnitude decrease in concentration. For similar resolution, bromide had to be injected at a concentration over 1000 mg/l (typical detection limit approximately 0.5 mg/l). When the required higher concentrations of the ionic tracers may lead to significant geochemical changes or density effects, SF_6 may be the preferable tracer. Furthermore, unlike ionic tracers, the highly volatile SF_6 may be readily removed from water. High volatility does, however, require that some care be taken to limit the potential loss of mass during injection, sampling, and analysis. Since others are developing procedures for analyzing SF_6 in ground water with extremely low detection limits (on the order of 1 ng/l), it appears likely that measurable concentrations could range over six to seven orders of magnitude. This range is considerably wider than typically possible with ionic tracers, and may offer an important advantage in some applications.

Introduction

Ground-water tracers are a common tool used by hydrogeologists to define water velocity and direction in a flow system. Hydrogeologic parameters such as hydraulic conductivity, porosity, flux, hydrodynamic dispersion, dispersivity, and retardation can be inferred from tracer tests. Various types of tracers have been applied to map water movement, including naturally occurring stable and radioactive compounds, heat pulses, and chemicals introduced in a controlled manner. Injected chemicals allow the source control necessary for mass balance analysis, and ultimately, more accurate resolution of the desired aquifer parameters. Effective tracers are nonreactive, conservative, easily detected, nontoxic, occur at very low background concentrations, and do not affect any of the intrinsic properties of the medium.

The most widely used ground-water tracers are ionic salts containing chloride and bromide, which have detection limits of approximately 1.0 and 0.5 mg/l, respectively, with readily available, commonly applied analytical techniques (Davis et al., 1985). To allow accurate resolution of a tracer breakthrough front, or to permit long-term tracking of an injected plume during transport when concentrations are decreased by hydrodynamic dispersion, the tracer must typically be injected at concentrations at least two orders of magnitude above its detection limit. In many cases, the initial input concentration of chloride may have to be even higher because of high background concentrations. The introduction of these ions at high concentrations (100s to 1000s mg/l) may cause significant increases in ionic strength. This can cause decreases in activity coefficients and therefore increases in solubility of some minerals, a reaction called the ionic strength effect (Shternina, 1960). These dissolution reactions can lead to undesirable changes in the aquifer properties (such as porosity variations) and result in misinterpretations of aquifer parameters. Dissolving minerals will also cause variations in ground-water chemistry.

The use of high concentrations of salt tracers may also result in undesirable density effects in the tracer water. Schincariol and Schwartz (1990) found that at typical natural flow rates, a density difference of 0.0008 g/cm^3 between two fluids can give rise to gravitational instabilities, and vertical convective movement of tracer water. A density difference of this magnitude corresponds to an NaCl concentration of 1000 mg/l. Oostrom et al. (1992) demonstrated density effects in bromide and iodide tracer plumes at concentrations as low as 700 mg/l and 2600 mg/l, respectively. Freyberg (1986) describes a field example in which a chloride (892 mg/l) and bromide (324 mg/l) plume sank, at least in part, because of density effects. Unless explicitly accounted for, these convective density effects could confound interpretations of field data.

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[a] University of Waterloo, Department of Earth Science, Waterloo, Ontario, Canada, N2L 3G1.

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It may often be desirable to have a wider detection range than the two to three orders of magnitude typically achieved with ionic tracers. For example, in studies of organic solvent dissolution or remediation, the concentrations of interest will generally range from near solubility to below the cleanup standard. In the case of trichloroethylene (TCE) and perchloroethylene (PCE), among the most commonly encountered and studied organic ground-water contaminants, the ground-water concentrations of interest could range over four to six orders of magnitude. Controlled studies with such contaminants, particularly when their sorption and degradation are minimal, require a tracer which is detectable across at least the same concentration range.

Sulphur Hexafluoride Properties

Sulphur hexafluoride (M.W. = 146 g/mol) is a colorless, odorless, tasteless, incombustible gas at room temperature. It was synthesized in the early 20th century, and early laboratory tests have shown it to be resistant to chemical degradation in the presence of NH_3, F_2, Cl_2, Br_2, I_2, HCl, and elemental carbon (Mellor, 1930). Watson et al. (1991) reported that SF_6 is not affected by most chemical or biological processes, such as microbial degradation or sorption. SF_6 is a neutral molecule, and thus will not be affected by electrostatic interactions with either positively or negatively charged subsurface materials.

SF_6 is a dense gas (6.602 g/l) at room temperature, with a melting point of $-50.2°C$ (Lide, 1991). Vapor pressures, solubility values, and dimensionless Henry's Law constants at various temperatures are compiled in Table 1. Calculated Henry's Law constants suggest that at ambient temperature, SF_6 will partition strongly from water to any vapor phase it encounters.

SF_6 has been shown to be nontoxic, even at high concentrations (Lester and Greenberg, 1950). Thus, handling of, and exposure to, SF_6 during tracer tests does not place the user at any health risk, and release to the atmosphere will pose no adverse environmental impact. Atmospheric background concentrations are on the order of 1-2 ppt (parts per trillion) by volume (Watson et al., 1991). For the purposes of subsurface tracer studies, the background concentration in natural ground-water systems is essentially zero. High volatility and the presence of six fluorines makes SF_6 easy to detect in small volume samples using a gas chromatograph (GC) equipped with an electron capture detector. With currently available field GCs, analysis of SF_6 is rapid, so samples may be processed quickly and at low cost on-site. Ongoing research in Britain (Institute of Hydrology, 1990) is reportedly refining analytical procedures to allow detection of SF_6 in ground water at concentrations as low as 1 ng/l (1 part per trillion).

Previous Work

SF_6 has been used most recently as a surface-water tracer in karstic terrain (Ellins et al., 1991), to measure gas exchange rates in streams (Wanninkhof et al., 1990), and to estimate vertical water mixing rates in open ocean basins (Watson et al., 1991). SF_6 has long been in use as an atmospheric tracer, with applications in building (Bassett et al., 1983) and mine shaft (Thimons et al., 1974; Timko and Thimons, 1982) ventilation investigations, and tracking the movement of large air masses in air pollution studies (Cadle et al., 1977). To our knowledge, the potential for use of SF_6 as a ground-water tracer was identified first by Biggin and coworkers (Institute of Hydrology, 1990). Although apparently not yet reported in the scientific literature, their work has reportedly also included development of very sensitive analytical techniques and evaluation via laboratory studies of SF_6 behavior in various porous media.

Goals of This Research

The primary goal of this study was to evaluate the behavior of SF_6 as a tracer in saturated porous media. Sand from the unconfined aquifer at C.F.B. Borden, Ontario, was utilized because its properties have been well studied (Ball et al., 1990; Mackay et al., 1986a, b; Sudicky, 1986). Bromide, which is widely accepted as a conservative tracer, was used to provide a basis of comparison. A related goal was to evaluate a method of introducing SF_6 to water at concentrations approaching its aqueous solubility.

Materials and Methods

The system used for preparing an aqueous solution of SF_6 is illustrated in Figure 1. The method relies on the diffusion of the gaseous SF_6 through thin-walled polytetrafluorethylene (PTFE) tubing into the water in contact with the tubing. An acrylic tube (51.5 cm long, 7.0 cm diameter) served as a chamber for contact of water with 76.2 m of 1.6 mm diameter PTFE tubing (0.3 mm wall thickness). This gave approximately 0.24 m^2 of surface area available for SF_6 diffusion. Inflow, outflow, and bypass of water was controlled by PVC valves. The charging vessel was sealed on the bottom with a plexiglass plate, and on the top with a removable, rubber O-ring sealed PVC plate. Water was routed to the charger via 1.3 cm threaded PVC pipe. SF_6 was carried from the supply tank by chromatography grade 3.2 mm stainless steel tubing, and plumbed to the inlet end of the PTFE loop through bulkhead fittings fixed to the top plate. Stainless steel tubing was fixed to the outlet end of the

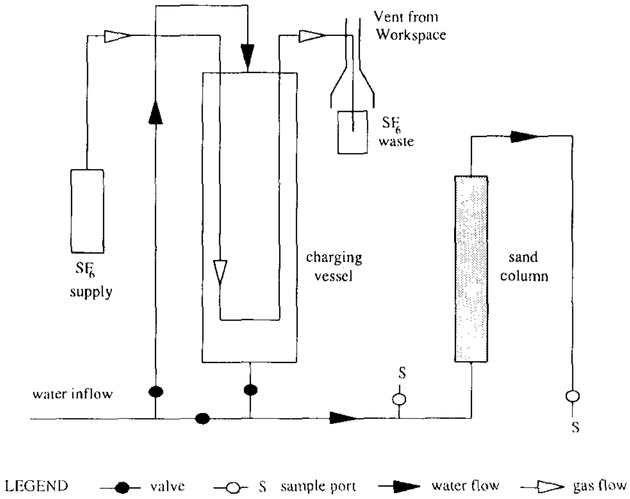

Fig. 1. Schematic of SF_6 gas charging system. Sand column dimensions are 40.0 × 3.25 cm. Charging vessel is 51.5 × 7.0 cm.

PTFE loop to vent excess SF_6. Short lengths of viton tubing were attached to the ends of the vent tubing, pinched with a clamp, and submerged in water. This created about 10-12 p.s.i. (6.9-8.3 KPa) pressure in the PTFE lines to encourage diffusion, and provided a visual check of SF_6 flow. Tracer-tagged water from the charger was carried by 3.2 mm stainless steel tubing to a plexiglass soil column (40.0 cm long, 3.25 cm diameter). Effluent lines from the soil column were also plumbed in 3.2 mm stainless steel to the sampling port. The entire charging vessel and sand column were housed in a fume hood.

The column was wet-packed with sand taken from a 3 kg grab sample obtained from C.F.B. Borden, Ontario. The packed column porosity (ratio of pore water volume to total column volume) was estimated to be 38%. The column was then flushed with CO_2 for two hours to evacuate any trapped oxygen, and then flushed with doubly distilled, deionized water until resaturation. Doubly distilled, deionized water was also used throughout the experiment, supplied via peristaltic pump at 2 ml/min. Water was pumped through the charging vessel and sand column by a Model IP-4 Ismatec low-flow peristaltic pump from Brinkmann Instruments Inc.

KBr salt was added to the charging vessel to an approximate concentration of 1300 mg/l (expressed as KBr). The SF_6 supply was then routed to the charging vessel, and the system allowed to charge overnight. The SF_6 and Br^- spiked water was introduced to the sand column at 2 ml/min for 125 minutes (two pore volumes), after which the charging vessel was taken off the injection line, and tracer-free water was introduced to the column. Samples were introduced through a hypodermic needle tip fixed to the end of the sample port tubing directly into 14.3 ± 0.1 ml crimp-top glass bottles sealed with teflon-faced silicon septa. A needle tip was inserted through the septa to provide a vent during sample collection. The amount of SF_6 mass loss through the vent needle during collection was not determined. This loss, however, was minimized by introducing the water into the sample bottle with minimum agitation of the rising water surface, reducing SF_6 transfer to the headspace. It is possible that the density of SF_6 would also minimize its loss through the vent needle bore. A series of 5 ml samples were taken and then refrigerated at 10° C before GC analysis. Each sample took 2.5 minutes to collect at the 2 ml/min pumping rate. The error in sample volume was estimated to be less than ± 0.25 ml.

The samples were taken individually from refrigeration and shaken on an orbital shaker at 400 r.p.m. for one minute. A 10 μl aliquot was drawn from the headspace and immediately injected onto the GC for SF_6 analysis. A simple mass balance calculation using the Henry's constants compiled in Table 1 and the Henry's Law relationship [equation (1)] reveals that at 7° C, 99.1% of the available SF_6 mass will be in the sample headspace at equilibrium (which is assumed after one minute of vigorous shaking).

$$H_{cc} = \frac{\text{concentration in headspace}}{\text{concentration in water}} \qquad (1)$$

A 10 μl gas-tight syringe was used for headspace delivery, so accuracy of volume delivery was expected to be ± 0.05 μl. The sample was returned to refrigeration for later bromide analysis.

SF_6 analysis was performed on a model 8610 Gas Chromatograph from SRI Industries, Torrence, CA. The GC was equipped with a 7 m long 0.53 mm wide-bore capillary column, and a model 140BN electron capture detector with a radioactive nickel-63 source and external controller-amplifier (Valco Instrument Co. Inc.). The ECD signal was acquired and integrated by a personal computer, using Peaksimple II Data System software from SRI Industries. SF_6 eluted from the gas chromatograph in 38 seconds, allowing quick processing of samples. A series of SF_6 standards were made for calibration of the GC. With the column temperature set at 28° C, air blanks eluted in the same time as SF_6. The concentration that resulted in a peak area three times the air blank peak response was defined as the detection limit. This was determined to be 5 μg/l. A Corning model 476128 bromide-specific electrode, and Corning model 476067 double junction reference electrode were used for bromide analysis.

Observations and Discussion

Charging Vessel Performance

After allowing SF_6 to diffuse through the PTFE tubing into water within the charging vessel for approximately 18 hours, an SF_6 concentration of at least 7 mg/l was attained. This concentration is approximately 25% of the experimental solubility limits for SF_6 tabulated in Table 1, and approximately three orders of magnitude higher than our detection limit. A wider detection range would be easily achieved by using a more sensitive analytical method with a lower detection limit.

There are two possible reasons for not achieving maximum theoretical concentrations: salting out effects due to the presence of the bromide salt, and kinetic controls on mass transfer. Morrison and Johnston (1955) measured a

Table 1. Solubility, Vapor Pressure, and Henry's Law Constants for SF_6

Temperature (° C)	*Solubility (mg/l)*	*Vapor pressure (atm)*	*Henry's Law constants (dimensionless) (Conc./Conc.)*
2	74.0	13.4*	87.5
7	57.5	15.3*	110.6
10.9	51.5**	17.3	121.7
12	48.5	17.5*	128.8
12.5	48.2**	18.0	129.4
14.2	45.6**	18.7	135.9
17	42.6	19.8*	144.1
19.6	40.4**	21.2	150.6
22	37.5	22.3*	160.9
25	35.2	23.9*	169.7
27	34.2	25.0*	173.5
27.8	33.9**	25.4	174.6
29.6	33.2**	26.3	177.2

*Data from CRC, 1991.

**Data from Morrison and Johnston, 1955. Remaining solubility and vapor pressures extrapolated from presented data. Henry's Law constants calculated by: (1 atm/solubility)/RT; where R = ideal gas constant, and T = temperature Kelvin.

Table 2. Free-Solution Diffusion Coefficients (D*) for SF_6 in Water, at 20° C

D^* (cm^2/s)	*Reference*
1.24 E-05	Calculated as per Othmar and Thakar, 1953
1.92 E-05	Calculated as per Scheibel, 1954
1.22 E-05	Calculated as per Wilke and Chang, 1955
1.23 E-05	Calculated as per Hayduk and Laudie, 1974
0.78-1.25 E-05	Wanninkhof et al., 1987

25% decrease in the solubility of SF_6 in a 35,000 mg/l NaCl solution, and Wanninkhof et al. (1991) measured similar effects in sea water. The salt concentration used in this experiment (1300 mg/l) is an order of magnitude less than that in sea water. If the salting out effect of SF_6 by KBr was similar to that by NaCl, the 75% depression in SF_6 solubility was not likely caused solely by that mechanism.

Mass transfer kinetics are likely the dominant factor controlling the maximum SF_6 concentration possible with the designed apparatus over the allowed time period. The SF_6 charging unit had a volume of 8.08×10^{-3} m^3, of which 3.77×10^{-5} m^3 (0.5%) was occupied by PTFE tubing. This left 8.04×10^{-3} m^3 of water into which SF_6 must diffuse, because no mechanical mixing was possible with the present charging vessel configuration. The manner in which the PTFE tubing was installed did not allow the average spacing of tubing to be quantified; however, an average separation of 2 cm was estimated by visual inspection. By taking a typical value for SF_6 free-solution diffusion coefficient (Table 2) of 1.2×10^{-9} m^2/s, it can then be estimated that after SF_6 has diffused out of the PTFE tubing, 23 hours would be required to allow SF_6 diffusion to saturate the area between the PTFE tubes. Since the charging unit was allowed to charge for only 18 hours, the mass transfer limitation may be related to a lack of mechanical mixing, diffusion of SF_6 through the PTFE tubing itself, or a combination of both.

SF_6 Tracer Performance

A constant flow rate column test was conducted with Borden sand. For the first 125 minutes (two pore volumes), the influent water contained SF_6 and bromide. The mean concentration and standard deviation of each solute (triplicate analysis) were 7.0 ± 1.2 mg/l and 1300 ± 40 mg/l, respectively. For the remainder of the experiment, the influent water contained no tracer.

The concentration histories (breakthrough curves, or BTCs) of both tracers in the column effluent are shown in Figure 2. The concentrations of both tracers have been normalized to their respective injection concentrations to facilitate comparison. Although there was a difference of three orders of magnitude in the initial concentrations of SF_6 and bromide, the ratio of detection limit to initial concentration was similar for each solute: 6.6×10^{-4} for SF_6, and 7.7×10^{-4} for bromide. Thus the experimental conditions provided similar ranges of detection. The average and standard deviation of SF_6 and bromide concentrations on the plateau segment of the breakthrough curves were 7.1 ± 1.1 mg/l and 1200 ± 70 mg/l, respectively. These are comparable to the injection values, as was expected. In spite of the analytical variability in the SF_6 data, sulphur hexafluoride and bromide clearly demonstrate very similar transport behavior. Both solutes break through at the same time with the same sharp front, both elute at the same time, and both define the same degree of tailing effect. This similarity of behavior suggests that SF_6 is at least as conservative and chemically nonreactive as bromide. It should be noted that the potential problems related to the use of ionic tracers discussed elsewhere in this study were not obvserved. In an upflowing laboratory column, density effects would not be evident unless the injection concentration of bromide was much higher than that used. Changes in major ion composition in the effluent water were not monitored.

Thirty of the 130 samples were analyzed three times to test the precision of the SF_6 analytical procedure. The results are shown in Figure 3. Samples were chosen from each region of the breakthrough curve to avoid bias. All aspects of sample collection, preanalysis storage, and preparation were standardized to remove as many sources

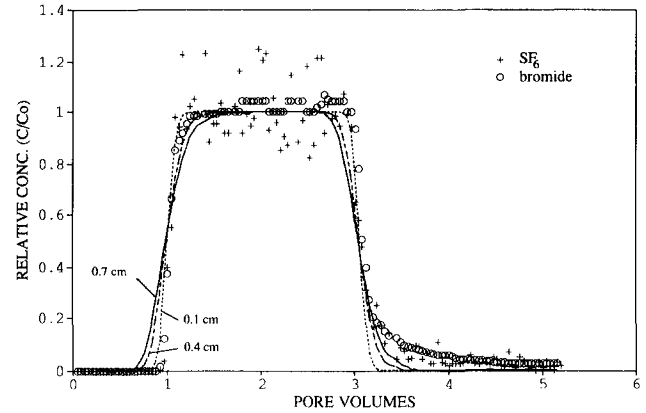

Fig. 2. Concentration histories of sulphur hexafluoride and bromide in Borden sand column, compared to simulations using Ogata-Banks analytical solution. Model curves are labelled with dispersivities used.

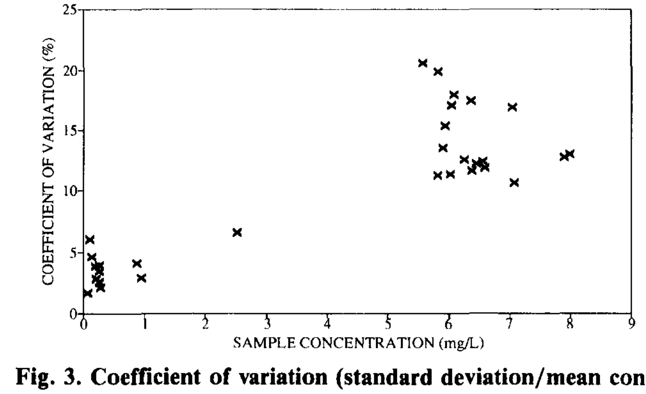

Fig. 3. Coefficient of variation (standard deviation/mean concentration) of 30 triplicate analyses as a function of mean concentration. Bimodal distribution illustrates the analytical bias described in the text.

of error as possible. For the 20 samples on the breakthrough plateau that were reanalyzed, the coefficients of variation of the SF_6 results were typically 12-20% of the mean value. For the 10 samples with lower concentrations, the coefficients of variation were approximately 2-5% of the mean. This difference may be due in part to the higher driving force for diffusive mass loss in the higher concentration samples. This mass loss could have occurred either out the vent needle during sample collection, or out the injection syringe during sample transfer to the GC. Possible bias from either procedure could not be quantified or differentiated from one another. The variability in SF_6 concentrations on the breakthrough plateau, and the variability in individual reanalyzed samples is, however, consistent with the ± 10-20% variability often encountered in GC analysis. We suspect that analytical precision can be improved by using alternative procedures such as automated purge and trap techniques. The analytical method under development in Britain (Institute of Hydrology, 1990) may also prove to be useful in work of this type.

Breakthrough data are often matched to curves generated by computer models to allow estimation of physical parameters such as dispersivity. A model employing the Ogata-Banks exact analytical solution of the one-dimensional solute transport equation was used to generate a series of theoretical breakthrough curves. Comparison of the BTCs generated by the model (Figure 2) shows that the breakthrough curves for SF_6 and bromide are visibly asymmetric. The breakthrough front is sharper than that calculated by the model. The elution front is more spread out, showing evidence of solute tailing. The asymmetry of the SF_6 and bromide BTCs was a result of physical nonequilibrium (Brusseau and Rao, 1989). Regions of the pore space in the column were occupied by an immobile water phase. This immobile phase may represent intragranular porosity, dead-end pores, or hydration shells around the sand grains. A comprehensive study of the Borden sand by Ball et al. (1990) suggests that although intragranular porosity is present in Borden sand, it is not significant enough to cause physical nonequilibrium to the extent observed in this work. The likely cause in this case is probably regions of dead-end pores or immobile zones created by the packing of nonspherical sand grains. Changes in solute velocity along the column arising from mobile to immobile zone mass transfer create a compressive breakthrough front (Brusseau and Rao, 1989). When the solute source is removed, spreading out or tailing during elution occurs as immobile to mobile zone mass transfer, which is slower than advection, takes place.

The average linear velocity used in the model was calculated based on the flux applied to the sand column. The porosity used in the velocity estimate was calculated as the ratio between (1) the pore volumn calculated from the difference between the wet and dry weight of the packed sand column, and (2) the total volume of the column. Longitudinal dispersivities employed were estimated from data compiled by Gelhar (1986), and Neuman (1990), relating dispersivity to experiment scale. The values used ranged between 0.1 and 0.7 cm. While the model curves fit the experimental breakthrough fronts, they do not capture the tailing elution fronts. This is because the model assumes a uniform distribution of solute velocities, which may have not been true in this experiment because of the effects of physical nonequilibrium described above.

Considerations for Laboratory and Field Use of SF_6

Two drawbacks to the use of SF_6 as a conservative tracer are (1) the time and equipment needed to prepare a solution for injection, and (2) the volatility of the gas. Although it is easier and quicker to mix a bromide solution for a tracer study, some situations may require a long-duration source. Field tests over a long period of time would require either a very large reservoir or repeated preparation and introduction of tracer solutions. Breakthrough data from such pulse type injection functions can be difficult to interpret. The SF_6 charging system relies on diffusion of a gas through PTFE tubing. Therefore, once installed and running, a constant supply of tracer-tagged water with a relatively uniform concentration can be introduced with very little maintenance required.

The volatility of SF_6 can create problems if care is not taken during during sampling and analysis. In most field applications, trapped air should not normally be present in the saturated zone, and volatilization of SF_6 should not occur as long as the tracer is not used near the capillary fringe. A properly designed and implemented handling protocol, similar to that commonly used for volatile organic chemicals, should prevent significant SF_6 loss during sample collection and analysis.

In this work, the detection limit for SF_6 using a simple headspace technique was approximately 5 μg/l. Since others are developing procedures for analyzing SF_6 in ground water with extremely low detection limits (on the order of 1 ng/l), the range of measurable concentrations could be six or seven orders of magnitude. This range is considerably wider than typically possible with bromide and other ionic tracers. Such a wide detection range may often be desirable. For example, in studies of organic solvent dissolution or remediation, the concentrations of interest may range from near solubility to below cleanup standards, which may span six to seven orders of magnitude. In such cases, SF_6 may serve as a tracer with a similar detection range. An added advantage may be that SF_6 can be detected using the analytical method appropriate for halogenated organics.

Summary

An effective ground-water tracer should allow delineation of subsurface flow systems without altering geochemical or physical conditions. This study shows that sulphur hexafluoride (SF_6) may meet these goals and offers promise for use as a tracer in some cases. SF_6 was found to behave identically to bromide in a laboratory column experiment with saturated silica sand from the Borden aquifer, including breakthrough asymmetry and tailing indicative of physical nonequilibrium transport. For equivalent resolution of the tracer behavior, however, the injection concentrations of the two were quite different: approximately 1300 mg/l and 7 mg/l for bromide and SF_6, respectively. High concentrations of bromide and other ionic tracers may have undesirable effects on the geochemistry of the system or cause convective density effects. SF_6, which is nonionic, is unlikely to significantly affect geochemistry. Additionally, the low required injection concentrations eliminate solution density problems.

The preparation of a spike solution is more complicated for SF_6 than for ionic tracers, but the SF_6 method developed in this work is amenable to long-term, uniform concentration spiking. The high volatility of SF_6 requires that the tracer be used in field applications below the water table; otherwise, mass loss to the unsaturated zone will occur. Lastly, the detection range for SF_6 is potentially much broader than typically possible for ionic tracers. In some applications, the specific advantages of SF_6 may warrant its use as a tracer of ground-water flow.

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