

# Ground-Water Tracers — A Short Review

by Stanley N. Davis, Glenn M. Thompson,  
Harold W. Bentley and Gary Stiles<sup>a</sup>

## ABSTRACT

Tracers are used widely to determine the direction and velocity of ground-water movement. Failures of tracer tests are most commonly a result of incorrect choice of tracers, insufficient concentrations of tracers, and a lack of an understanding of the hydrogeologic system being tested. Some of the most useful general tracers are bromide, chloride, rhodamine WT, and various fluorocarbons. For certain purposes, dyed clubmoss and baker's yeast have proved valuable. Many radionuclides including  $^3\text{H}$ ,  $^{82}\text{Br}$ , and  $^{198}\text{Au}$  are almost ideal for numerous purposes, but radiation hazards associated with their use together with local, State, and Federal regulations have discouraged widespread field applications in recent years within the United States.

## INTRODUCTION

As used in hydrology, a tracer is matter or energy carried by water which will give information concerning the direction and/or velocity of the water as well as potential contaminants which could be transported by the water. If sufficient data are collected, the use of tracers can also assist with the determination of hydraulic conductivity,

porosity, dispersivity, and other hydrogeologic parameters. A tracer can be entirely natural such as the heat carried by a plume of geothermal water, it can be accidentally introduced such as chlorides leached from a landfill, or it can be introduced intentionally such as dyes placed in sink holes in order to determine their interconnection with karst resurgences.

The first reported ground-water tracing experiment was almost 2000 years ago when Philip, the tetrarch of Trachonitis, threw chaff into a crater lake and reported that the chaff appeared down-gradient in one of the springs at the headwaters of the Jordan River. Although Josephus reported that the experiment was a success, Mazor (1976) demonstrated by chemical and isotopic measurements that the supposed underground connection would be highly unlikely.

The main emphasis of this review will be on the use of injected tracers to determine certain aquifer characteristics or to determine water velocities and direction, rather than natural or accidentally introduced tracers.

An ideal ground-water tracer is nontoxic, inexpensive, moves with the water, is easy to detect in trace amounts, does not alter the natural direction of the flow of the water, is chemically stable for a desired length of time, is not present in large amounts in the water being studied, and, for most purposes, is neither filtered nor sorbed by the solid medium through which the water moves.

---

<sup>a</sup>Professor, Assistant Professor, Assistant Research Professor, and Research Assistant, respectively, Department of Hydrology and Water Resources, The University of Arizona, Tucson, Arizona 85721.

Discussion open until July 1, 1980.

Almost certainly, the ideal ground-water tracer does not exist. Many tracers, however, are much better than others, particularly some of the recently developed fluorocarbon tracers which will be described in this short review.

Tracer tests using artificially introduced tracers commonly fail. Reasons for failure are numerous, but in our experience the choice of the wrong tracer is the most fundamental problem. Many chemicals are sorbed easily on solid materials in the aquifer and, as a consequence, travel at velocities so low that they do not reach sampling points in a reasonable length of time. Other chemicals are unstable and decompose before they reach sampling points. Still others cannot be detected in small concentrations or are not detectable owing to high natural background concentrations. If these chemicals are introduced in large amounts, density differences between the chemicals and the native ground water will alter flow patterns. Also, ion exchange and secondary chemical precipitation may alter original aquifer permeabilities.

Failures of tracer tests are also caused by a lack of understanding of the hydrologic system. The direction of water flow may not be estimated properly and the tracer may entirely miss a sampling well. Or, the very slow natural velocity of the ground water is not taken into account and sampling points are placed too far from where the tracer is introduced. In normal alluvial aquifers which are some distance from pumped wells, average water velocities are rarely more than 1 to 10 feet (0.3 to 3 metres) per day. Short-term tests which are not associated with pumping wells normally cannot use sampling wells more than a few tens of feet (8 to 15 metres) from tracer injection points. Lastly, dilution through dispersion in the aquifer and through mixing in the injection and sampling wells is commonly not taken into account, so water samples may not contain measurable concentrations of tracers. Dilutions of the tracer of at least tenfold during transit from injection to sampling wells for "slug" injections are almost always experienced and dilutions of tenthousandfold are common.

## TYPES OF TRACERS

### Water Temperature

Because water has a high specific heat capacity compared with most natural materials, water does not change temperature rapidly as it migrates in the subsurface. Temperature anomalies associated with the spreading of warm waste water in the

Hanford Reservation in south central Washington, for example, have been detected more than 5 miles (8 km) from areas where the water entered the subsurface (U.S. Energy Research and Development Adm., 1975). An excellent example of the use of water temperature to trace injected water has been given recently by Keys and Brown (1978).

Changes of water temperature will be accompanied by changes of density and viscosity of the water which in turn will alter the velocity and direction of flow of the water. As an example, injected ground water with a temperature of 40° C will travel more than twice as fast in the same aquifer under the same hydraulic gradient as will water at 5° C. Because the warm water has a slightly lower density than the colder water, buoyant forces will give rise to flow which diverges from the flow direction of the colder ground water. If water temperature is to be used to trace injected water, small temperature contrasts with very accurate temperature measurements should be utilized in order to minimize problems of temperature-induced convection.

### Solid Particles

Solid material in suspension can be a useful tracer where ground water flows in large conduits such as in some basalt, limestone, and dolomite aquifers. Separate numbers printed on small pieces of paper (as punched out from computer cards, for example) can be placed in different sink holes and recovered by sieving water as it emerges from springs. In this way, simultaneous tests can be made of the interconnections among several sink holes and springs. Owing to the relatively large sizes of the pieces of paper, however, the method can only be successful where ground-water flow is within large open passages. Similarly, dyed clubmoss (*Lycopodium*) spores can be used (Gardner and Gray, 1976). The small size, about 30 micrometers in diameter, of the spores and the fact that they are only slightly denser than water means that they are not filtered out of the water as rapidly as are paper fragments. Unfortunately, the use of spores requires special dyes for coloration, plankton nets for collection, and a microscope for spore identification.

A recently reported novel tracer is a small time bomb which is carried by cave waters to inaccessible points. When the bomb explodes, the location of the explosion is determined by seismic methods at the surface (Arandjelovic, 1977).

Numerous investigators have introduced viruses and bacteria into aquifers in order to study

the movement of microorganisms in ground water. Because laboratory tests to detect fecal coliform are well developed, they are the most commonly used bacteria for ground-water tracers. Viruses are considerably more difficult to detect and are not as commonly used; however, when used, the relatively large plant viruses have been popular. Even though viruses are very small, they will not travel long distances in ground water unless the aquifers are exceedingly permeable. The individual viruses have unbalanced electrical charges which are attracted by surface charges on solid particles. The degree of resulting adsorption is a function of both the pH and ionic concentration of the ground water (Drewry and Eliassen, 1967). In general, viruses will travel longer distances in the subsurface if ionic concentrations are low and the pH of the ground water is high.

Recent experiments using baker's yeast (*Saccharomyces cerevisiae*) have been encouraging (Wood and Ehrlich, 1978). Tests were made in the laboratory as well as in the field near Stanton, Texas, and were a part of an extensive program by the U.S. Geological Survey to evaluate various ground-water tracers. Penetration of more than 7 meters into a sand-and-gravel aquifer was measured after less than 48 hours of injection. Yeast has advantages of low cost, negligible health hazard, and moderately easy detection. The greatest use of yeast may be to provide information concerning the potential travel of pathogenic bacteria, inasmuch as the movement of yeast cells in ground water more closely resembles these pathogens than most other easy-to-use tracers.

### **Ionized Substances**

Several substances, such as common salt, will almost entirely ionize when dissolved in water. The ionization in turn will increase the electrical conductivity of the water containing the tracer. This fact was used in tracer tests almost 100 years ago when electrodes were placed in wells to detect the arrival time of salt tracers. Unfortunately, rather high concentrations of salt solutions must be introduced as tracers in order to produce significant changes in the electrical conductivity of the water at sampling points some distance away. These concentrated solutions will be denser than the native ground water and will tend to sink to the bottom of the aquifer and not follow the natural flow paths of the water. As a consequence of this problem, tracers are usually diluted so much in order to reduce their density effects that specific analytical detection of selected ions must be

utilized rather than electrical conductivity.

The number of ion types which might be used is very large. However, because of low cost, ease of detection, and low sorption, chloride ( $\text{Cl}^-$ ) and bromide ( $\text{Br}^-$ ) are most popular. Other ions used from time to time for special purposes are  $\text{Li}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$ ,  $\text{I}^-$  and  $\text{SO}_4^{--}$ . Owing to sorption by cation exchange and to the relatively high natural abundances of most of the foregoing ions,  $\text{Br}^-$  offers one of the best possibilities as a general tracer for ground-water studies. Also, most bromide compounds have relatively low toxicities.

The concentration of  $\text{Br}^-$  in natural waters is roughly 1/300 that of  $\text{Cl}^-$ . Inasmuch as  $\text{Cl}^-$  concentrations in potable water commonly range between 1 and 100 mg/liter, expected background concentrations of  $\text{Br}^-$  will be less than 1 mg/liter in most aquifers of interest. Detection of  $\text{Br}^-$  is rather easy with a specific ion electrode which will have a lower limit of detection of about 0.05 mg/liter. If natural water has 30 mg/liter of  $\text{Cl}^-$  (suggesting the natural presence of 0.1 mg/l of  $\text{Br}^-$ ) and if the  $\text{Br}^-$  tracer is introduced with a concentration of 1,000 mg/liter, then a dilution of  $10^4$  of the tracer is possible before it is masked by the natural background.

Owing to the somewhat higher costs of bromide salts, sodium chloride (common salt) is favored by many hydrogeologists. Concentrations of  $\text{Cl}^-$  in the introduced tracer should not exceed about 3,000 mg/liter because of increased density of the solution. If, as above, the native ground water has 30 mg/liter, then a dilution of only  $10^2$  of the tracer is possible. This is commonly not satisfactory.

Iodide,  $\text{I}^-$ , has been used successfully as a tracer for surface water (Rodda, 1977) and somewhat less successfully as a subsurface tracer (Wagner, 1977). Iodide tends to be sorbed to a greater extent than either  $\text{Br}^-$  or  $\text{Cl}^-$ . Natural concentrations of  $\text{I}^-$ , however, are very low, generally less than 0.01 mg/liter, and methods for sensitive analysis of  $\text{I}^-$  are relatively simple, so  $\text{I}^-$  will probably remain as a moderately popular tracer.

Chelating agents with heavy metals can be used to produce complexes which commonly have a zero charge. These complexes in turn will have low sorption on natural materials. One of the most widely used chelating compounds is ethylene diamino tetraacetic acid (EDTA). Some of the heavy metals which have been used as tracers are copper, zinc, cobalt, and lead. Higher costs of chemicals and detection methods together with problems of toxicity of many compounds have discouraged the widespread use of heavy metals as tracers. However, neutron activation analysis,

while relatively expensive, can provide a very sensitive method of detection of many metals thus allowing the use of tracers at extremely low dilutions. Keys and Boulogne (1969) have proposed the use of californium-252 as a down-the-well neutron source for activation of traceable anions that are already present in the water.

More recently, ground-water tracing experiments using organic anions such as benzoate (Malcolm *et al.*, 1979) have shown that compounds of this type will be particularly useful. The sensitivity of detection and the precision of measurement are very good using liquid chromatography, and, like other anions, they are highly mobile in natural aquifer materials.

### Stable Isotopes

Several naturally occurring stable isotopes of the common elements have been used as ground-water tracers. Of these, the following pairs have been most useful:  $^1\text{H}$ - $^2\text{H}$ ,  $^{12}\text{C}$ - $^{13}\text{C}$ ,  $^{14}\text{N}$ - $^{15}\text{N}$ ,  $^{16}\text{O}$ - $^{18}\text{O}$ ,  $^{32}\text{S}$ - $^{34}\text{S}$ , and  $^{86}\text{Sr}$ - $^{88}\text{Sr}$ . The need for special analytical equipment, the tedious nature of the analyses, and the high total costs have discouraged the use of most stable isotopes for artificially injected tracers. Stable isotopes, however, have been very useful for many special hydrologic studies.

"Heavy water" containing relatively large concentrations of  $^2\text{H}$  (deuterium) has been used successfully as an injected tracer. Although detection of  $^2\text{H}$  is most sensitive with a mass-spectrometer, Thorp and Gamble (1972) found that the inexpensive falling-drop method of determination of water density was a satisfactory method to estimate  $^2\text{H}$  content of their artificially injected "heavy water" tracer. Cory and Horton (1968) also obtained good results using infrared spectrophotometry to measure  $^2\text{H}$  concentrations down to 0.1 mol %.

### Radioactive Tracers

The literature on tracers during the late 1950's and early 1960's was filled with optimistic predictions concerning the usefulness of artificially injected radioactive tracers. Since that time, the increased awareness of radiation hazards which spawned a maze of local, State, and Federal regulations has halted most field tests using radioactive tracers in the United States, Canada, and many European countries. Nevertheless, certain injected radionuclides will continue to be used, particularly for tracing nonpotable water which is isolated from surface aquifers (Wagner, 1977), for short-term

**Table 1. Commonly Used Radioactive Tracers for Ground-Water Studies**

Radio-nuclide	Radiation	Half-Life (y=year, d=day, h=hour)	Chemical Compound
$^3\text{H}$	$\beta^-$	12.3y	$\text{H}_2\text{O}$
$^{32}\text{P}$	$\beta^-$	14.3d	$\text{Na}_2\text{HPO}_4$
$^{51}\text{Cr}$	$\gamma$	27.8d	EDTA-Cr & $\text{CrCl}_3$
$^{60}\text{Co}$	$\beta^-, \gamma$	5.25y	EDTA-Co & $\text{K}_3\text{Co}(\text{CN})_6$
$^{82}\text{Br}$	$\beta^-, \gamma$	35.4h	$\text{NH}_4\text{Br}$ & $\text{NaBr}$
$^{85}\text{Kr}$	$\beta^-, \gamma$	10.7y	Kr (gas)
$^{131}\text{I}$	$\beta^-, \gamma$	8.1d	I & KI
$^{198}\text{Au}$	$\beta^-, \gamma$	2.7d	$\text{AuCl}_3$

tests of water movement within the wells themselves, and for carefully controlled laboratory experiments. Low-level concentrations of certain radionuclides have been used to trace injected waste (Sanitary Engineering Research Laboratory, 1954) and the movement of fluids used for the secondary recovery of petroleum (Wagner, 1977).

Radioactive tracers which have been used most commonly in hydrogeology are given in Table 1. Of those listed,  $^3\text{H}$  has been most widely used because it forms part of the water molecule and travels with the ground water. If it were not hazardous and if it were easier to detect in very small trace amounts, it would be an ideal tracer (Kaufman, 1961). Another widely used tracer has been  $^{60}\text{Co}$  complexed with EDTA. The radioactive cobalt is a high-energy gamma source that is easily detected in water. A general review of radioactive tracers has been given by Gaspar and Oncesco (1972).

The use of radioactive tracers to study the movement of ground water as it enters and exists from nonpumping wells has been outlined by Drost and others (1968). If  $^{198}\text{Au}$  is mixed with water in the well, the  $^{198}\text{Au}$  tends to be sorbed by the well screen on the downstream side where the water is leaving the well. Measurement of the distribution of radioactivity on the well screen at an appropriate time after tracer injection will, therefore, show the direction of ground-water flow in the vicinity of the well. In addition, by using a mixing equation, ground-water velocity or, quantity (volume per unit time) of water flowing through the well can be determined. The following basic equations can be used:

$$\frac{C_t}{C_o} = e^{-Bt} \quad \text{in which,}$$

- $C_t$  = concentration of tracer in the well at time  $t$ ,  
 $C_o$  = original concentration of tracer in the well at time = 0, and  
 $B$  = a factor which is constant for simple, steady state conditions.

If  $B$  is constant, then

$$B = \frac{Q}{V} \quad \text{in which}$$

- $Q$  is volume of water per unit time flowing through the well and  $V$ , the volume of water in the well.

For fully penetrating wells in isotropic and homogeneous aquifers,

$$Q = 2dmn_e\bar{v} \quad \text{in which}$$

- $d$  is the effective diameter of the well,  
 $m$  is the saturated thickness of the aquifer,  
 $n_e$  is the effective porosity of the aquifer, and  
 $\bar{v}$  is the average velocity of the ground water outside of the well (in the aquifer).

Inasmuch as  $V$ ,  $d$ ,  $m$ , and  $n_e$  can either be estimated closely or measured during well construction and  $t$ ,  $C_t$ , and  $C_o$  are measured during the tracer test, the value of  $\bar{v}$  can be determined. The foregoing assumes that the native ground water does not contain the tracer, that the tracer is stable and does not decay (or that the half-life of the tracer is very long compared to the length of the test), that the tracer is mixed uniformly in the well at the start of the test and continuously thereafter, and that the well screen intercepts flow from the entire thickness of the aquifer. Drost and others (1968) have given a more complete treatment of the above relationships with equations which account for the radioactive decay of the tracer.

The most important present-day application of radioactive tracers is in the use of natural atmospheric or artificially produced environmental radionuclides to estimate the amount of time that ground water has been isolated from the atmosphere. Radionuclides which have been used to "date" ground water are  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{32}\text{Si}$ , and  $^{39}\text{Ar}$ . Of these  $^3\text{H}$  and  $^{14}\text{C}$  have been applied most widely. The detailed treatment of dating water by radionuclides is beyond the scope of this paper. A useful summary of the extensive literature of the topic has been given by Payne (1972).

Radionuclides originating in the subsurface may also some day prove to be practical tracers

for the hydrogeologist. The radioactive decay of  $^{238}\text{U}$  produces  $^{234}\text{U}$  as the first daughter product to have a half-life of more than a few hours. The half-life of  $^{234}\text{U}$  is  $2.47 \times 10^5$  years. Under equilibrium conditions, which are closely approached within  $2 \times 10^6$  years, the activities of  $^{238}\text{U}$  and  $^{234}\text{U}$  will be equal. For a variety of reasons, however,  $^{234}\text{U}$  can be selectively leached from the solid part of an aquifer. Variations of the  $^{234}\text{U}/^{238}\text{U}$  disequilibrium in ground water are a function of the past leaching history of the solid materials as well as the present geochemical conditions in the aquifer. Disequilibrium of  $^{234}\text{U}/^{238}\text{U}$  has been used by Kaufman, Rydell, and Osmond (1969) as well as other researchers to trace regional ground-water movement.

### Organic Dyes

Various organic dyes of low to negligible toxicity have long been used as ground-water tracers. Because most of them are sorbed rather easily on solid materials, these tracers are best adapted to tests having travel distances of water in aquifer of only a few feet or else within very permeable aquifers such as recent basalt, gravel, and cavernous carbonate rocks. Besides their general low toxicity, many of the dyes have advantages of ease of detection, high sensitivity, and relatively low cost of the chemicals. The most useful of the dyes can be detected visually in concentrations of a few parts per million, by fluorometers in parts per billion, and theoretically by sorption on activated charcoal and subsequent desorption, even less than 0.1 part per billion. Practically, however, trace amounts of natural organic compounds may interfere with detection at such low concentrations.

Most tracer tests with dyes can be affected by decomposition by strong light, changes of pH, and temperature fluctuations, in addition to sorption on solid surfaces. Chemical characteristics of dyes and analytical methods for their detection have been summarized by numerous authors (André and Molinari, 1976; Smart and Laidlaw, 1977). Field techniques used in sampling and analyzing tracers in surface streams, which would also apply to many karst situations, are summarized very well by Church (1975). Excellent examples of tracing karst waters abound in the literature. Bauer and Zötl (1972) have reported results from the Austrian Alps where tracer paths (in map view) actually cross due to flow at different levels in a karst system. Examples of extensive dye tests in West Virginia have been reported by Medville

(1977) and in Indiana by Murdock and Powell (1968).

The most commonly used dye in karst studies has been sodium fluorescein because it is nontoxic in low concentrations and is relatively inexpensive. It is a characteristic bright yellowish-green in dilute concentrations. Fluorescein, however, decomposes rapidly in the sunlight and is sorbed by most solids. Smart and Laidlaw (1977) made an extensive comparison of 8 tracer dyes including fluorescein and concluded that rhodamine WT (orange), lissamine FF (green), and amino G acid (blue) are the most useful for water tracing. Aulenbach, Bull, and Middlesworth (1978) have recently reported successful tracer tests in permeable sands and gravels using rhodamine WT which compared favorably with tritium tests made at the same time.

Recently, certain types of blue fluorescent dyes have been used in increasing amounts in textiles, paper and other materials to enhance the white appearance of these products. These optical brightener dyes can be used as artificially injected tracers. Also, water contaminated from domestic waste will contain some detectable optical brighteners. Examples of tracing with optical brighteners in karst systems have been given by Glover (1972) and Quinlan, McCann, Andrews, and Branstetter (1977).

## Gases

Numerous gases have been used as subsurface tracers, but the tracing has most commonly been of the movement of air in the nonsaturated zone. Chemically inert but radioactive  $^{133}\text{Xe}$  and  $^{85}\text{Kr}$  appear to be quite suitable for many purposes (Robertson, 1969; Wagner, 1977); nevertheless as already noted, legal restrictions prevent the widespread use of radioactive tracers.

Radon is a special case. It is present in the subsurface, but owing to the short half-life (3.82 days) of the principal isotope,  $^{222}\text{Rn}$ , and the absence of parent uranium nuclides in the atmosphere, radon is virtually absent in surface water which has reached equilibrium with the atmosphere. Surveys of radon in surface streams and lakes have, therefore, been useful in detecting places where diffuse ground water enters surface waters (Rogers, 1958).

Ethylmercaptan, a gas with a strong odor, has been used in karst areas to establish the degree of interconnection among various cavernous openings. Late summer or late winter conditions are usually ideal when thermal convection of cave air is most

active and when passages are not flooded with ground water. Other types of gases traced by odor are possible. One of the least expensive and most effective sources of olfactory tracer gases reported has been recently expired skunks, which are most readily obtained from nearby highways.

Gases dissolved in water can also be used as tracers for the movement of water. If naturally occurring gases are used for injected tracers, a large contrast must exist between natural concentrations and concentrations at saturation. Common gases found in nature are shown in Table 2. Gases such as  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and  $\text{CO}_2$  tend to ionize upon solution and are too active chemically to make good tracers. In addition,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ , and  $\text{CO}$  are quite toxic in moderate-to-large concentrations. Because of their nonreactive and nontoxic nature, noble gases are attractive tracers. Helium is used quite widely as a tracer in various industrial processes. It has also been used to a limited extent as a ground-water tracer (Carter and others, 1959). Nonradioactive krypton is another possible candidate as a tracer. It is somewhat more soluble than helium (Table 2) but its background concentration in shallow ground water will be higher. Neon and xenon are other possible candidates. Generally, sorption of the heavier gases (krypton and xenon) on natural materials should be larger than the lighter gases (helium and neon). Present methods of separation and analysis are quite expensive, so tracing ground water with noble gases is beyond the scope of most routine hydrogeologic work.

Gases dissolved in ground water through natural processes are rarely determined by routine chemical analyses. Nevertheless, gases, particularly the noble gases, hold considerable promise as indicators of the past history of the water (Sugisaki, 1969; Mazor, 1972; Skukolyukov, Sharif-Zade, and Ashkinadzee, 1973). The solubilities of the heavier noble gases (Ar, Kr, and Xe) are quite sensitive to temperature whereas the lighter noble gases (He and Ne) are not. Thus variations of the concentration ratios of heavy to light gases should be primarily a function of surface temperatures at the time of recharge.

## Fluorocarbons

Numerous artificial gases and liquids have been produced during the past 50 years. Many of these are potentially useful as tracers but a full treatment of all possibilities cannot be given here. One group of chemicals which appears well suited in some circumstances for tracing are the fluorocarbons

**Table 2. Atmospheric Gases Dissolved in Water (Noble gas, nitrogen, and oxygen calculated from Benson and Krause, 1976. Atmospheric abundances from Butcher and Charlson, 1972)**

Gas	A	Abundance in Atmosphere (ppm, vol/vol)	Molecular Weight	Boiling Point (C°)	In Equilibrium with Atmosphere Dissolved in Distilled Water (Mg gas/liter)		In Equilibrium with Gas at 760 mm (Mg gas/liter)	
					At 5°C	At 20°C	At 5°C	At 20°C
Nitrogen, N <sub>2</sub>		780,840	28.016	-196	20.47	15.24	26.21	19.52
Oxygen, O <sub>2</sub>		209,460	32.000	-183	12.87	9.27	61.5	44.26
Argon, Ar		9,340	39.944	-186	0.781	0.566	83.65	60.64
Carbon Dioxide, CO <sub>2</sub>		330	44.010	-79	0.9	0.6	2770	1690
Neon, Ne		18.18	20.183	-246	$1.95 \times 10^{-4}$	$1.72 \times 10^{-4}$	10.74	9.46
Helium, He		5.24	4.003	-269	$8.68 \times 10^{-6}$	$8.24 \times 10^{-6}$	1.6	1.5
Methane, CH <sub>4</sub>		2.0	16.042	-162	$6.8 \times 10^{-5}$	$4.6 \times 10^{-5}$	34	23
Krypton, Kr		1.14	83.70	-152	$4.02 \times 10^{-4}$	$2.66 \times 10^{-4}$	352	234
Hydrogen, H <sub>2</sub>		0.5	2.016	-269	$9 \times 10^{-7}$	$8 \times 10^{-7}$	1.9	1.6
Nitrous Oxide, N <sub>2</sub> O	0.5 (Variable)		48.01	-89	$8.1 \times 10^{-4}$	$3.3 \times 10^{-4}$	2700	1100
Carbon Monoxide, CO		0.2	28.01	-192	$8 \times 10^{-6}$	$6 \times 10^{-6}$	39	28
Xenon, Xe		0.087	131.30	-107	$9.43 \times 10^{-5}$	$5.73 \times 10^{-5}$	1084	658
Ammonia, NH <sub>3</sub>	Trace (Variable)		17.03	-33	—	—		
Hydrogen Sulfide, H <sub>2</sub> S	Trace (Variable)		34.08	-61	—	—	6000	3850
Sulfur Dioxide, SO <sub>2</sub>	Trace (Variable)		64.06	-10	—	—		
Nitric Oxide, NO	Trace (Variable)		30.01	-152	—	—	86	62
Radon, Rn	Trace (Variable)		222	-62	—	—	4500	2300

(Thompson, Hayes and Davis, 1974). These are used generally as industrial solvents, foaming agents, propellants, refrigerants, and fire-extinguisher chemicals. Chemical compositions and physical characteristics of some important fluorocarbons are given in Table 3.

Two of the compounds, CCl<sub>3</sub>F and CCl<sub>2</sub>F<sub>2</sub>, are particularly important industrial chemicals that have been manufactured extensively around the world and have been released to the atmosphere during the past 30 to 40 years. The buildup of these compounds in the global atmosphere is responsible for their equally extensive distribution in the upper part of the hydrosphere. Consequently, their presence in subsurface water is evidence that the ground water contains some recharge since about the mid 1940's. Preliminary measurements of CCl<sub>3</sub>F in several aquifer systems (Thompson and Hayes, 1978) have demonstrated that the CCl<sub>3</sub>F content can be used, in much the same manner as tritium, for studies of recent recharge.

Fluorocarbon compounds appear to offer a number of advantages over most conventional tracers for many ground-water applications. They are extremely nonreactive and do not break down chemically under normal ground-water conditions. They are easily detectable in water in very low concentrations with an optimum working range of between 1 and 100 parts per trillion (1 ppt =  $1 \times 10^{-12}$  g/ml), although much lower concentrations are measurable for some tracers under optimum conditions. Tracer measurement capability in this range enables an enormous volume of water to be labeled easily with a small amount of tracer. For example, 1 g of tracer (about 0.5 ml) labels 2.6 million gallons of water at the maximum working concentration, 100 ppt. Another important consideration is that many of the tracers have very low toxicities. Most of the compounds investigated thus far have acute toxicities rated about equivalent to carbon dioxide which is, of course, a major component of carbonated drinks. As a result,

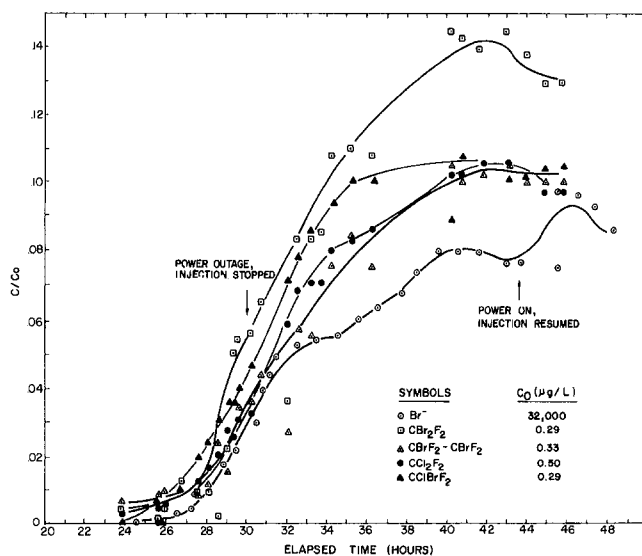
**Table 3. Physical Properties of Fluorocarbon Compounds**

Chemical Formula	CCl <sub>2</sub> F <sub>2</sub> (Freon-12)	CCl <sub>3</sub> F (Freon-11)	CBrClF <sub>2</sub>	CBr <sub>2</sub> F <sub>2</sub>	CCl <sub>2</sub> F-CClF <sub>2</sub> (Freon-113)	CBrF <sub>3</sub> -CBrF <sub>2</sub>
Molecular Weight	120.92	137.37	165.37	209.93	187.38	259.85
Boiling Point, 1 atm, °C	-29.79	23.82	-4.00	24.50	47.57	47.26
Density, Liquid, 25°C, g/cc	1.311	1.476	1.81	2.306	1.565	2.163
Solubility in H <sub>2</sub> O, 1 atm and 25°C, wt %	0.028	0.11	unknown	unknown	0.017	unknown

many of the fluorocarbon tracers are suitable for direct use in municipal-water supplies. The sorptive properties of these tracers on natural media have not been completely characterized, but in preliminary field tests using fluorocarbons along with  $\text{Br}^-$ , relatively little difference in sorption was observed in a sand-and-gravel aquifer in Aurora, Nebraska. Figure 1 shows tracer breakthrough curves for four fluorocarbons and a bromide tracer in an observation well 90 ft from the injection point. The bromide appears to break through slightly behind the bulk of the fluorocarbons, but considering that it lags behind by only a small amount (30-60 minutes) after a period of 30 hours, the tracer separation is of minor significance.

Other points of interest relate to the comparison of the operational characteristics of the bromide versus the fluorocarbon tracers. The bromide tracer was significantly easier to handle because the fluorocarbons are dissolved gases and are subject to loss by volatilization from open-water samples. Thus sampling for bromide could be done using inexpensive air-lift pumps. This technique was not suitable for fluorocarbon sampling because major amounts of fluorocarbons are lost from the water when it is purged with bubbles. The bromide samples, being nonvolatile, can be stored indefinitely without concern for tracer loss to the atmosphere. In addition, continuous measurement of bromide is easily possible using a selective ion electrode in a flow-through sample cell. The fluorocarbons are measured by gas chromatography and therefore each sample must be measured individually.

The advantages of the fluorocarbon technique apparent in the Nebraska test (Figure 1) were: (1) The capability for multiple tracer analyses. Each water sample was analysed simultaneously for four fluorocarbons,  $\text{CCl}_2\text{F}_2$ ,  $\text{CClBrF}_2$ ,  $\text{CBr}_2\text{F}_2$  and  $\text{CBrF}_2\text{-CBrF}_2$ . This capability will be particularly useful wherever multiple tracer tests are needed. (2) The extreme sensitivity of the detection technique. As with most halocarbons, the tracers used have a high electron-capturing cross section. Consequently they are easily detectable in picogram quantities using an electron capture gas chromatograph detector. The sensitivity is particularly evident when comparing input concentrations ( $C_0$ ) of the fluorocarbons used in the Nebraska test with the  $C_0$  of the bromide shown in the legend of Figure 1. Most of the fluorocarbons are injected at concentrations of a few tenths of a part per billion, whereas the



**Fig. 1. Breakthrough curves for various tracers from a test in Aurora, Nebraska. Tracers were fed simultaneously into a 700-gpm flow of water which was being injected into a well. The samples were collected from an observation well 90 feet away. The quantity " $C_0$ " is the concentration of the tracer in the injected water and " $C$ " is the concentration measured in the samples from the observation well.**

bromide was injected at 32 parts per million, nearly 5 orders of magnitude greater. The ability to use and detect tracers at very low concentrations has important practical and economic implications, enabling large volumes of water or effluent to be labeled very inexpensively, using only a small amount of tracer.

Ciccioli, *et al.* (1978) have demonstrated in laboratory studies using columns with limestones and silicate sands that surface interactions between a variety of halocarbon species (which include fluorocarbons) and mineral grain surfaces are nonspecific and the strength of the interaction or sorption is a function of the degree of polarization of the organic molecule. Thus, by knowing the relative sorptive strengths (dipole moments) of a series of similar tracers, a method has been proposed to calculate the true velocity of the water when all of the tracers used in a test are sorbed to varying degrees. This technique, if successful when applied in the field, will enhance usefulness of fluorocarbons as tracers.

An important limitation to the use of fluorocarbons stems from the fact that they are organic compounds and as such, they become dissolved in or strongly sorbed by many other organic materials. Therefore, they will generally be unsuitable for tracing water in subsurface coal, peat, oil shale, and other natural organic-rich rocks.



## SUMMARY

A large number of tracer types and techniques have been reviewed; of these, most have relatively limited or specialized use. Anionic tracers (such as  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) and dyes appear to have been in general use for a long period of time and are still used for a broad range of ground-water tracing applications. The anions are particularly useful because of their low susceptibility to adsorption or ion exchange processes on natural aquifer materials. Dyes have been extensively applied largely because they are visually detectable even after moderate dilution and are measurable by means of fluorometry in very low concentration. However, the strong sorptive tendencies of most dyes limit their general purpose application largely to karst areas where ground water moves by conduit flow. Many excellent radioisotope tracers are available but are generally not acceptable for use in near-surface ground water because of the potential radiation hazard they pose. Many stable isotopes and inert gases are also useful as tracers but have received relatively little attention because of problems of low solubility, difficulty of handling and expense of analysis. The fluorocarbons, which are non-charged molecules, will be potentially very useful as tracers due to their extreme sensitivity of detection, their stability and low toxicity. Also, the presence of two compounds,  $\text{CCl}_3\text{F}$  and  $\text{CCl}_2\text{F}_2$ , in modern recharge makes the fluorocarbon measurement technique important in studies where these compounds are used to define zones of high or low recharge.

## ACKNOWLEDGMENTS

The authors are indebted to Professor John M. Hayes of Indiana University who first suggested using fluorocarbons as tracers and contributed greatly to the solution of numerous technical problems related to their analyses. Ideas concerning tracing in karst areas were provided initially by Richard L. Powell.

The tracing test in Nebraska made use of facilities provided by the Old West Regional Commission, operated jointly by the Water Resources Center at the University of Nebraska and U.S. Geological Survey District Office in Lincoln. The data presented here represent a portion of the results obtained in a cooperative research project involving the Nebraska Water Resources Center at Lincoln, the U.S. Geological Survey, and the University of Arizona. For the physical operation of the test, and the bromide data, the authors are completely indebted to the

following persons: William Lichtler and Eric Lappala from the U.S. Geological Survey, District Office in Lincoln; Edwin Weeks, David Redinger, and Donald Signor from the Lubbock, Texas, District Office; Randy Bassett from the Denver Regional Center; and Edward Kouma and David Stannard of the Water Resources Center at Lincoln.

Funding for the fluorocarbon tracer research was provided by a subcontract with Oak Ridge National Laboratory, Oak Ridge, Tennessee operated by the Union Carbide Corporation for the U.S. Department of Energy.

## REFERENCES

- André, J. C. and J. Molinari. 1976. Mises au point sur les différents facteurs physiochimique influant sur la mesure de concentration de traceurs fluorescents et leurs conséquences pratiques en hydrologie. *Jour. Hydrology*. v. 30, pp. 257-286.
- Arandjelovic, D. 1977. Determining groundwater flow in karst using "Geobomb." In *Karst Hydrology*, edited by J. S. Tolson, and F. L. Doyle. *Memoirs of the 12th Congress of the Int. Assoc. Hydrogeologists*, University Alabama Press in Huntsville, pp. 399-400.
- Aulenbach, D. B., J. H. Bull, and B. C. Middlesworth. 1978. Use of tracers to confirm ground-water flow. *Ground Water*. v. 16, no. 3, pp. 149-157.
- Bauer, F. and J. Zötl. 1972. Karst of Austria. In *Karst, Important Karst Regions of the Northern Hemisphere*. Edited by M. Herak and V. T. Stringfield, Amsterdam, Elsevier Publ. Co., pp. 225-265.
- Benson, B. B. and D. Krause, Jr. 1976. Empirical laws for dilute aqueous solutions of nonpolar gases. *Jour. Chemical Physics*. v. 64, no. 2, pp. 689-709.
- Butcher, S. S. and R. J. Charlson. 1972. *An introduction to air chemistry*. New York, Academic Press, 241 pp.
- Carter, R. C., and others. 1959. Helium as a ground-water tracer. *Journal Geophysical Research*. v. 64, pp. 2433-2439.
- Church, M. 1975. Electrochemical and fluorometric tracer techniques for streamflow measurements. *British Geomorphological Research Group, Technical Bull.* No. 12, 73 pp.
- Ciccioli, P., W. T. Cooper, P. M. Hammer, and J. M. Hayes. 1978. Organic solute-mineral surface interactions: A new method for the determination of ground-water velocities. *Water Resources Research*. In press.
- Cory, C. C. and J. H. Horton. 1968. Movement of water tagged with  $^2\text{H}$ ,  $^3\text{H}$ , and  $^{18}\text{O}$  through acidic kaolinitic soil. *Soil Sci. Soc. America Proc.* v. 32, pp. 471-475.
- Drewry, W. A. and R. Eliassen. 1967. Virus movement in ground water. *Jour. Water Pollution Control Federation*. v. 40, no. 4, pp. 257-271.
- Drost, W., D. Klotz, A. Koch, H. Moser, F. Neumaier, and W. Ravert. 1968. Point dilution methods of investigating ground-water flow by means of radioisotopes. *Water Resources Research*. v. 4, pp. 125-146.
- Gardner, G. D. and R. E. Gray. 1976. Tracing subsurface flow in karst regions using artificially colored spores. *Assoc. Engr. Geologists Bull.* v. 13, pp. 177-197.

- Gaspar, E. and M. Oncescu. 1972. Radioactive tracers in hydrology. Amsterdam, Elsevier Pub. Co., 342 pp.
- Glover, R. R. 1972. Optical brighteners—a new water tracing reagent. Transactions Cave Research Group, Great Britain. v. 14, no. 2, pp. 84-88.
- Kaufman, M. I., H. S. Rydell, and J. K. Osmond. 1969.  $^{234}\text{U}/^{238}\text{U}$  disequilibrium as an aid to hydrologic study of the Floridan aquifer. Jour. Hydrology. v. 9, pp. 374-386.
- Kaufman, W. J. 1961. Tritium as a ground-water tracer. American Soc. Civil Eng. Trans. Paper 3202, pp. 436-446.
- Keys, W. S. and R. F. Brown. 1978. The use of temperature logs to trace the movement of injected water. Ground Water. v. 16, no. 1, pp. 32-48.
- Keys, W. S. and A. R. Boulogne. 1969. Well logging with Californium-252. Soc. Prof. Well Logg. Analysts, 10th Annual Logging Symposium, Houston, Texas, Trans. pp. 1-25.
- Malcolm, R. L., G. R. Aiken, E. M. Thurman, and P. A. Avery. 1979. Hydrophilic organic solutes as tracers in ground-water recharge studies. A.C.S. Symp. on Processes Involving Contaminants and Sediments. April 1-6, 1979, Honolulu, Hawaii.
- Mazor, E. 1972. Paleotemperatures and other hydrological parameters deduced from noble gases dissolved in ground waters, Jordan Rift Valley, Israel. Geochimica et Cosmochimica Acta. v. 36, pp. 1321-1336.
- Mazor, E. 1976. The Ram Crater Lake, a note on the revival of a 2000-year-old ground-water tracing experiment. In Interpretation of Environmental Isotope and Hydrochemical Data. In Groundwater Hydrology. Int. Atomic Energy Agency, Vienna, pp. 179-181.
- Medville, D. M. 1977. Karst hydrology in the upper Elk River basin, West Virginia. National Speleological Soc. Bull. v. 39, no. 1, pp. 18-26.
- Murdock, S. H. and R. L. Powell. 1968. Subterranean drainage routes of Lost River, Orange County, Indiana. Indiana Acad. of Sci. v. 77, pp. 250-255.
- Payne, B. R. 1972. Isotope hydrology. In Advances in Hydrosience. V. T. Chow, editor. v. 8, pp. 95-138.
- Quinlan, J. F., M. R. McCann, W. M. Andrews, and J. A. Branstetter. 1977. Heavy metals and optical brighteners as ground-water tracers in central Kentucky karst: Implications concerning regional hydrology. In Karst Hydrology, edited by J. S. Tolson and F. L. Doyle. Memoirs of the 12th Congress of the Int. Assoc. Hydrogeologists, Univ. Alabama Press in Huntsville, pp. 535-536.
- Robertson, J. B. 1969. Behavior of xenon-133 gas after injection underground. U.S. Geol. Survey Open File Report ID022051, 37 pp.
- Rodda, J. C. 1977. Institute of Hydrology Research Report 1974-6. Institute of Hydrology (Wallingford, England), pp. 54-57.
- Rogers, A. S. 1958. Physical behavior and geologic control of radon in mountain streams. U.S. Geol. Survey Bull. 1052E, pp. 187-211.
- Sanitary Engineering Research Laboratory, University of California, Berkeley. 1954. Report on the investigation of travel of pollution. California State Water Pollution Control Board Pub. 11, 218 pp.
- Shukolyukov, Yu. A., V. B. Sharif-Zade, and G. Sh. Ashkinadze. 1973. Neon isotopes in natural gases. Geochemistry International 1973, pp. 346-354.
- Smart, P. L. and I.M.S. Laidlaw. 1977. An evaluation of some fluorescent dyes for water tracing. Water Resources Research. v. 13, no. 1, pp. 15-33.
- Sugisaki, R. 1969. Measurement of effective flow velocity of groundwater by means of dissolved gases. American Jour. Science. v. 259, pp. 144-153.
- Thompson, G. M., J. M. Hayes, and S. N. Davis. 1974. Fluorocarbon tracers in hydrology. Geophysical Research Letters. v. 1, pp. 177-180.
- Thompson, G. M. and J. M. Hayes. 1978. Trichloro-fluoromethane in ground water. A possible tracer and indicator of ground-water age. Water Resources Research. In press.
- Thorp, J. and E. E. Gamble. 1972. Annual fluctuation of water levels in the soils of the Miami catena, Wayne County, Indiana. Earlham College, Science Bull. no. 5, 26 pp.
- United States Energy Research and Development Administration. 1975. Water management operations, Hanford Reservation, final environmental statement, v. 1. ERDA, Washington, D.C. 435 pp.
- Wagner, O. R. 1977. The use of tracers in diagnosing interwell reservoir heterogeneities. Jour. Petroleum Technology. November 1977, pp. 1410-1416.
- Wood, W. W. and G. G. Ehrlich. 1978. Use of baker's yeast to trace microbial movement in ground water. Ground Water. v. 16, no. 6, pp. 398-403.

\* \* \* \*

*Stanley N. Davis received his academic training at the University of Nevada, University of Kansas, and Yale University where he received his Ph.D. in Geology in 1955. He has taught at a number of universities including Stanford University, University of Missouri, and Indiana University. He is presently Professor in the Department of Hydrology and Water Resources at the University of Arizona. Dr. Davis has authored and coauthored numerous articles and three books on general topics of hydrogeology and environmental geology.*

*Glenn M. Thompson received his Ph.D. in Geology at Indiana University in 1976. He is currently an Assistant Professor in the Department of Hydrology and Water Resources at the University of Arizona. His academic interests and journal publications are primarily in the areas of hydrochemistry and analytical chemistry. The development and evaluation of fluorocarbon tracer technology is one of his principal research activities.*

*Harold W. Bentley received his A.B. in Chemistry from Clark University in 1966 and a Ph.D. in Physical Chemistry at Northeastern University in 1973. Prior to his graduate studies he worked in radiochemistry and chemical oceanography at Woods Hole Oceanographic Institution. His interests until recently have been the characterization of gas and solid state molecular electronic structure by ultraviolet spectroscopy. He joined the Department of Hydrology and Water Resources at the University of Arizona in 1977, where his interests now include noble gases in ground water, the dating of old ground water by chlorine-36, and ground-water solute transport.*

*Gary Stiles received his B.A. in Psychology from the University of Arizona in 1972. He spent three years with Cooksley Geophysics, Inc. as a field representative and is currently a research assistant in the Department of Hydrology and Water Resources at the University of Arizona.*