

T-3254

EMPIRICAL DETERMINATION
OF THE
APPLICABILITY OF FLUOROCARBON TRACERS
IN STUDYING
URANIUM TAILINGS SEEPAGE

by

Maurice Lee Madden

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Engineering Ecology).

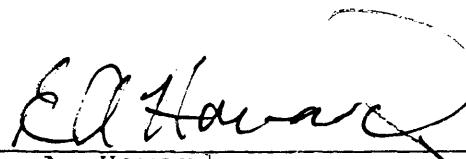
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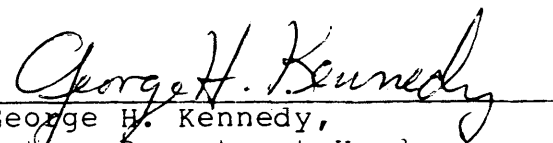

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ABSTRACT

Two halogenated hydrocarbons, difluorotetrachloroethane and trifluorotrchloroethane, were tested to determine if they could be utilized as tracers in a uranium tailings seepage investigation. A seepage investigation is required when the regulatory agencies governing inactive uranium mill tailings assess the potential for groundwater contamination from reclaimed tailings.

There are a variety of processes that affect the transport of the halogenated organic compounds: dispersion, advection, sorption, volatilization and transformation reactions. The combined effect of these processes on the organic tracers within a uranium tailings environment was measured in a series of laboratory column tests. The transport of the organic tracers through the column material was compared to the transport of a non-reactive inorganic tracer, chloride, and a reactive inorganic tracer, sulfate.

Results indicate that the volatilization and acid-catalysis hydrolysis reactions adversely affect the ability of these organic tracers to be used as tracers in uranium tailings seepage studies. The uranium tailings water utilized in this research had a pH of 2 and a sulfate concentration of 3500 mg/l. The uranium tailings environment is

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emphasized because fluorocarbon tracers are successfully utilized in other applications such as surface streams and normal pH aquifers.

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CHAPTER I: INTRODUCTION

In 1980 there were forty-seven uranium mill and tailings sites in the United States. Twenty-two sites were active and twenty-five were inactive. By 1986, only one or two of the sites active in 1980 are still operating. The other twenty-three 1980 active sites are either inactive in 1986 or are in a stand-by mode. The amount of tailings produced by the forty-seven sites is more than 175 million tons (EPA, 1982 and 1983).

There are two major environmental concerns with uranium mill tailings, the emission of radon-222 and the seepage of radionuclides into the groundwater. Radon-222, an intermediate daughter, is a radioactive gas. The emission of radon gas from a tailings pile and its control is beyond the scope of this research, however, one aspect of radon-222 control is of interest. This aspect is the capping of inactive tailings piles required by EPA standards to control the radon-222 emissions into the atmosphere. This capping material will influence the amount of meteoric percolation that reaches the underlying tailings after the site becomes inactive and the tailings are reclaimed.

The effect of the cap upon the quantity and the quality of seepage needs to be evaluated to determine if groundwater beneath the tailings pile is being contaminated. This is one of the major responsibilities of the Department of Energy in

its mission to protect the groundwater at an inactive reclaimed mill site.

The second major environmental concern associated with uranium tailings, is the seepage of the parent radionuclide along with thorium-230 and radium-226, each a daughter radionuclide, into the groundwater. In addition, nonradioactive toxic elements will also seep from the tailings along with the radionuclides. The seepage of these chemical species which will potentially contaminate the groundwater is the major concern of this research investigation. Since the half-lives of uranium-238, thorium-230 and radium-226 are 4.5 billion, 77,000 and 1600 years, respectively, it is obvious that the concern for groundwater contamination will span thousands of years.

In addition to the extremely long time period of contamination there are a variety of site-specific geochemical and hydrologic variables that will determine the severity of groundwater contamination. Not only the severity but the timing of this contamination will depend upon the geochemical properties of the tailings and medium that underlie the tailings. Because of these geochemical and hydrologic variables, EPA maintains a "site-specific" philosophy with regard to standards for inactive uranium mill sites and for control of byproduct materials from uranium ore processing facilities. EPA states that "We recommend site-specific considera-

tion of water protection measures"; further "... the implementing agencies (DOE and NRC) will site-specifically assess the potential for future groundwater contamination and take any appropriate action" (EPA, 1983). "Site-specific" means that the practicality of such remedial actions must be determined site by site.

As part of its environmental assessment reports, the Department of Energy is required (EPA, 1982) to detail the geochemical and hydrologic aspects of the tailings themselves, the soil or medium underlying the tailings, and the aquifer(s) that seepage may contaminate. There are active and standby mill-tailings sites that continue to have a liquid pond on top of the tailings thus producing sufficient hydrologic head to cause significant seepage into the soil and possibly the groundwater beneath the tailings. Even with EPA's standards for soil coverage and other capping material, which could include an impermeable layer between the soil and the tailings, there is potential for seasonal precipitation to cause continued seepage from some tailings sites. It is the DOE's and the EPA's responsibility to determine if the standards promulgated by EPA will in fact protect the groundwater at each existing or standby site and at each inactive (controlled or uncontrolled) site.

The research reported herein was conducted to determine the applicability of fluorocarbon tracers in studying uranium

tailings seepage. The hypothesis of this research is that the use of fluorocarbon tracers will be an effective technique in determining hydrologic flow patterns within the tailings as well as determining the site-specific hydrologic aspects of the soil medium and groundwater underlying the tailings. In addition to the geochemical processes associated with the tailings themselves, the retardation of the fluorocarbons in several soils underlying uranium tailings was also investigated to determine the applicability of fluorocarbon tracers in studying uranium tailings seepage.

CHAPTER II: BACKGROUND

The environmental assessment of uranium tailings seepage can be enhanced by the use of fluorocarbons if these organic compounds can be shown to be appropriate tracers. Tracers are used widely to determine the direction and velocity of groundwater movement. Also, tracers are used to determine if there is seepage from a specific source. Failures of tracer tests are most commonly a result of incorrect choice of tracers, insufficient concentrations of tracers, and a lack of understanding of the hydrogeologic system being tested.

In hydrogeologic studies, a tracer will give information concerning the direction and velocity of the water, as well as potential contaminants that could be transported by the water. A tracer can be entirely natural, such as the heat carried by a plume of geothermal water, or it could be a chemical constituent discharged to the environment by a specific industrial operation, such as the disposition of uranium tailings. A tracer not associated with the process can be introduced intentionally in order to determine if seepage is occurring, and if it is, the direction and velocity that seepage is traveling. In uranium tailings studies done at active sites, the concentration of chloride or sulfate in the aquifer below the tailings pile has been used to determine the contamination plume and the possible extent of

potential radioactive contamination that may migrate from the source. The concentration of chloride and sulfate in the uranium tailings depends upon the process utilized by the mill and the relative amount of pyrite contained in the tailings. The pH of the pore solution in the tailings, as well as actual seepage solution, will depend upon the metallurgical process involved, as well as the pyrite content of the tailings material. Therefore, these chemical species fall under the category of a contaminant tracer that has been introduced into the environment by an industrial process. Chloride is a good tracer, but at most uranium mill sites, it is already present in the seepage from the tailings; therefore, it is difficult to use chloride as a follow-up tracer to determine what is happening at the present time.

A variety of tracers has been used for studying dispersion as well as determining the direction of seepage and the rates of groundwater flow under field conditions. An ideal tracer should:

- 1) be easy to detect in trace amounts,
- 2) be absent or nearly so in the water being studied,
- 3) move with the water being studied,
- 4) not alter the natural direction of the water,
- 5) not be filtered or sorbed by the solid medium in which the water is moving,
- 6) not react chemically with the porous medium,

7) be safe in terms of toxic effects on humans as well as other biota that may come in contact with the tracer, and

8) be inexpensive and readily available.

The ideal groundwater tracer probably does not exist but many tracers are better than others. Fluorocarbons are generally viewed as a stable, nonreactive, and, in low concentrations, non-toxic group of chemicals that can be detected in concentrations of one part per trillion by electron capture gas chromatography.

Chemical Concept

Whenever chemical tracers are employed to study groundwater flow, the question arises: does the tracer migrate at the same rate as the water or is its progress significantly retarded by sorption processes in the aquifer? The chromatographic dispersion (solute transport plus sorption) includes adsorption, absorption, dispersion and advection processes. In the empirical determination of the applicability of fluorocarbon tracers in studying uranium tailings seepage, test columns can be utilized to evaluate the retardation or chromatographic dispersion of the tracers under study. In a stationary column the movement of a tracer can be represented by the equation (Karger et al., 1973, p. 131)

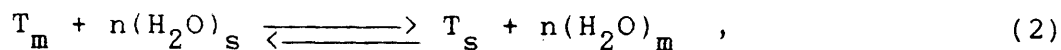
$$V_T = V_w + V_s \cdot K \quad , \quad (1)$$

where:

- V_T = total volume of water necessary to bring the tracer from the column inlet to the column outlet,
 V_w = volume of mobile water in the column,
 V_s = volume of the solid or stationary phase, and
 K = equilibrium constant equal to the ratio of the activity of the tracer in the solid phase to the activity of the tracer in the water phase.

If values of K are much less than 1, the tracer would be found almost entirely in the aqueous phase. The tracer would be carried through the column by an amount of water equal to the total mobile water volume in the column (i.e., for K to equal 0, V_T must equal V_w). If K becomes large, the tracer will be found in the solid phase and is immobile. The extent of the retardation relative to the average water molecule depends upon the volume of the solid phase involved in the equilibrium described by K . It is assumed that the distribution of tracer between the water and solid phases can be treated as an equilibrium process such that the value of K is independent of tracer concentration. This is true for very small concentrations of tracer to which Henry's Law constants are applicable.

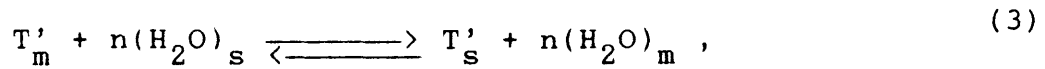
The chemical equilibrium under consideration can be described by



where:

- T = the tracer concentration,
 m = mobile phase, and
 s = sorbed or solid phase.

If a second tracer species T' is now considered, the chemical equilibrium equation would be



Thus if the two tracers were in the same water that was allowed to flow through the column that contained the solid phase, the K of one of the tracers could be compared to the K of the other tracer.

$$\frac{V_T^1}{V_T^2} = \frac{V_W^1 + V_S^1 \cdot K^1}{V_W^2 + V_S^2 \cdot K^2}, \quad (4)$$

$$\text{but } V_W^1 = V_W^2 \text{ and } V_S^1 = V_S^2 .$$

Therefore, the ratio of V_T^1 to V_T^2 is directly proportional to the ratio of the two K's. Thus if one K is known, then a comparison of the concentration of one tracer to the other tracer concentration, as the water exits the column, will approximate the K of the other tracer. If chloride is one of the tracers in the water, then it can be assumed that its K is equal to zero or very close to zero (Ciccioli, et al.,

1980). If the exit concentration of the chloride tracer equals or approaches its inlet concentration as the water phase leaves the column, then the K for the chloride is in fact zero. If the exit concentration of the second tracer equals the inlet concentration of that tracer as the water phase leaves the column, then the K for the second tracer also equals zero and there are no chromatographic dispersive processes occurring. If there is a large negative difference between the outlet and inlet concentrations of the second tracer compared to the difference between the outlet and inlet concentrations of chloride, then it can be concluded that there are significant chromatographic dispersive processes affecting the migration of the second tracer.

A third tracer chemical with a known retardation factor could be added to the solution that flows through the column to provide another comparison for the second tracer with the unknown retardation factor. An example of such a tracer is sulfate. It is generally accepted that the migration of sulfate is retarded by the various chromatographic dispersive processes associated with most soils. Based upon my experience in the copper and uranium beneficiation industry, the sulfate plume will lag in time behind the chloride plume when both chemicals are present in an aquifer.

Chemodynamics

Environmental chemodynamics is the name given to the transport of chemicals in the environment and the relationship to their physical-chemical properties. In the research reported herein, organic fluorocarbon tracers are compared to two inorganic tracers: chloride and sulfate. Fluorocarbons, being organic, may undergo some form of transformation, which may affect their transport in the environment.

The transport of both inorganic and organic tracers or solutes in porous media can be described as the flux of solute into and out of a fixed volume. The conservation of mass equation for this elemental volume is (Freeze and Cherry, 1979, p 389):

$$\begin{aligned}
 & \text{(net rate of change} & & \text{(flux of solute} & & \text{(flux of} \\
 & \text{of mass of solute in} & = & \text{out of the} & - & \text{solute in} \\
 & \text{volume)} & & \text{volume)} & & \text{volume)} & (5) \\
 & & & + & & & \\
 & & & \text{(loss or gain of} & & & \\
 & & & \text{solute mass due to} & & & \\
 & & & \text{reactions).} & & &
 \end{aligned}$$

The physical transport processes that control the flux in and out of the volume are advection and dispersion. The reactions that control the loss or gain of the solute mass within the volume can either be chemical or biochemical for the inorganic and organic tracers under evaluation.

The process by which flowing water transports tracers is termed advection. The advection rate is equal to the specific velocity of the fluid in the aquifer, V , divided by the porosity, n , of the aquifer medium. The transport process that is a result of mechanical mixing of the fluid and molecular diffusion is termed dispersion. Because dispersion is a mixing process the solute or tracer will spread both in the bulk flow direction (longitudinal) and in perpendicular directions to the bulk flow (transverse). In the longitudinal direction some of the water and solute molecules travel more rapidly than the rate of advection and others travel more slowly. The tracer therefore spreads out in the direction of flow and decreases in concentration.

Under laboratory conditions, the only dispersion that can be observed in tracer experiments is on the macroscopic scale. In fact, the dispersion component of the following equation cannot be distinguished from the advection term (Freeze and Cherry, 1979, p. 389):

$$D_x \cdot \frac{\partial^2 C}{\partial x^2} - \frac{v}{n} \cdot \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} ,$$

(6)

where:

x = direction along the flowline,

V = specific velocity,

n = porosity of medium,

D_x = coefficient of dispersion in the x direction,

C = tracer concentration, and

t = time.

The effects of chemical reactions including organic transformation processes are not included in the above transport equation.

Chemical reactions that affect the transport of a solute or tracer within the aquifer or in the laboratory test column can be grouped into many categories. Some of these chemical reactions are : adsorption - desorption, acid - base neutralization, solution - precipitation, oxidation - reduction, ion pairing - complexation, and various organic transformation reactions.

The adsorption - desorption reactions involve the transfer of the solute between the aqueous and solid phases. Equation (6) can be modified to include the term for the adsorption - desorption chemical reaction (Freeze and Cherry, 1979, p. 402):

$$D_x \cdot \frac{\partial^2 C}{\partial x^2} - \frac{v}{n} \cdot \frac{\partial C}{\partial x} + \frac{\rho}{n} \frac{\partial S}{\partial t} = \frac{\partial C}{\partial t} \quad , \quad (7)$$

where ρ = bulk mass density,

S = mass of the solute adsorbed on the solid part of the porous medium per unit mass of solids,

n = porosity,

$$\frac{\partial S}{\partial t} = \text{rate at which the solute is adsorbed, and}$$

$$\frac{\rho}{n} \cdot \frac{\partial S}{\partial t} = \text{change in solute concentration in the fluid}$$

$$\text{caused by adsorption.}$$

The adsorption reactions are generally much more rapid than the flow velocity. Also, the amount of solute adsorbed is a function of the solute concentration in solution. Thus, (Freeze and Cherry, 1979, p. 402):

$$- \frac{\partial S}{\partial t} = \frac{\partial S}{\partial C} \cdot \frac{\partial C}{\partial t} , \quad (8)$$

where

$$\frac{\partial S}{\partial C} = \text{partitioning of the solute between the solution and the solid phase.}$$

The partitioning of solutes between liquid and solid phases in a porous medium is determined by laboratory experiments. At low solute concentrations, S , the mass of the solute adsorbed or precipitated on the solids per unit bulk dry mass of the porous medium can be expressed as a function of C , the solute concentration in the fluid (Freeze and Cherry, 1979, p. 403):

$$S = K_d \cdot C^b . \quad (9)$$

where

$$K_d = \text{distribution coefficient that depends upon solute species, nature of porous medium, geochemical reactions, and}$$

b = a coefficient that depends upon the same variables.

The above equation is known as the Freundlich isotherm. The distribution coefficient, K_D , is widely used in groundwater studies. The adsorption and other chemical processes cause the advance rate of the solute or tracer in the longitudinal direction to be retarded. Where the partitioning of the tracer can be adequately described by the distribution coefficient (i.e., fast reversible adsorption, with linear isotherm), the retardation of the front relative to the bulk mass of water is described by the equation (Freeze and Cherry, 1979, p. 404):

$$\frac{v_c}{v_w} = \frac{1}{1 + (\rho/n) \cdot K_D}, \quad (10)$$

where $\frac{v_c}{v_w}$ = relative velocity of solute, and

$1 + (\rho/n) \cdot K_D$ = the retardation factor.

When $K_D = 0$, the solute or tracer is not affected by chemical reactions. Under these conditions the transport of the solute is described by the advection and dispersion components of equation (7). When the distribution coefficient is greater than zero, the chemical reaction or adsorption component of equation (7) becomes increasingly more impor-

tant. Distribution coefficients equal to or greater than 10 generally mean that the solute or tracer will not readily migrate from the source very far and the chemical reactions dominate the advection and dispersion components in the transport equation. The form of equation (10) is very similar to equation (4) and has the same application. If two tracers are tested in a column, the comparison of the tracers can be made by measuring the exit concentration of each tracer, and by knowing the retardation factor of one, the retardation factor of the other can be estimated.

All chloride salts are highly soluble, so chloride is rarely removed from water by precipitation, ion exchange, or adsorption. Chloride in solution is extremely difficult to remove by natural processes. Therefore, the retardation factor for chloride is approximately one. The retardation factor for sulfate is greater than one, and is dependent upon the chemical nature of the porous medium in which the solution is flowing as well as the concentration of the sulfate in the aqueous phase. The retardation factor of the organic fluorocarbon tracers are not known in a uranium tailings environment. In fact, little is known about the chemical behavior of organic tracers in the relatively unusual environment of a uranium tailings pile.

The retardation factor is time dependent, so if organic tracer sorption does occur in uranium tailings, the organic

concentration in a test column effluent will lag behind the chloride concentration. The sulfate will also lag the chloride. Organic compound transformation processes may be occurring in the aqueous phase or on the surface of the porous material. In a column test, the concentration of the organic tracer in the effluent will be an indicator of the magnitude of these transformation and chromatographic dispersion processes. If the organic tracer lags behind the sulfate concentration in the effluent, then significant retardation or transformation processes may be occurring, and this may mean that the organic compound cannot be utilized as a tracer.

Physical-Chemical Properties that Affect Organic Transformation Processes

Compared to the transformation processes that an organic tracer may undergo (all of which will affect the tracer transport characteristics), the retardation processes for chloride and sulfate are fairly simple. Before any significant discussion of the organic solute or tracer transport as defined by equation (7) can take place, it is necessary to consider the physical-chemical properties of the organic compounds of interest. Solubility, partitioning (into other organic compounds), sorption and volatility of an organic compound are of the most concern. These physical-chemical properties have an effect on the solute transport, adsorp-

tion, absorption, and transformation processes. Because of these processes, each organic solute will have its own characteristic migration velocity as shown above in equation (10).

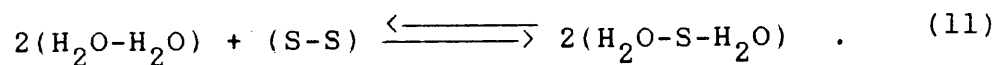
Solubility

Many organic compounds are hydrophobic, that is, they are only slightly soluble in water. Of the various parameters that affect the fate and transport of organic compounds in the environment, water solubility is one of the most important. Highly soluble organic compounds are quickly distributed in the groundwater. These compounds tend to have relatively low adsorption coefficients for solids or the porous medium in which the aqueous phase is flowing. The highly soluble organics are more readily biodegradable by microorganisms. Also, other transformation processes such as photolysis, hydrolysis, and oxidation-reduction and transport routes such as volatilization are also affected by the extent of water solubility.

The solubility of an organic compound as well as an inorganic specie in water may be defined as the maximum amount of the chemical that will dissolve in pure water at a standard temperature and pressure. For practical purposes many organic compound solubilities are so low that they are considered to be insoluble. For dissolution to occur, the

organic solute must distort or disrupt the structure of water created by the strong hydrogen bonds between water molecules. If the organic solute is polar then this is quite feasible, and the solute will be relatively soluble in the aqueous solution.

For nonpolar organic solutes the ability to disrupt the structure of water is more difficult. The process of dissolution for a nonpolar solute, S, in an aqueous phase can be schematically described by (Tanford, 1980):



The reaction driving this equilibrium is strongly to the left because of the energy of the hydrogen bonds between the water molecules. Therefore, nonpolar solutes are very sparingly soluble.

Factors that affect the solubility of organic chemicals in the environment are temperature, salinity, dissolved organic matter, and pH. The two factors that are of most interest in this research are the salinity and pH effects. There are high concentrations of dissolved salts in the aqueous phase of most uranium tailings. Also, the pH of the aqueous phase generally is low. Seepage liquid can have a pH as low as 2. Salinity increases will generally cause a decrease in the solubility of most organic compounds. Hydrogen ion concentration affects solubility also but most

of the investigative work to date has been in normal ground-water pH ranges of 6.0 to 8.5. The organic acids would be expected to increase in solubility as pH increases. The organic bases should increase in solubility as the pH decreases. The neutral organic compounds such as chlorinated alkanes, which are under investigation in this research, may be affected by pH. There are little, if any, data available to correlate the solubility change of a chlorinated alkane to low pH's.

Partitioning

During the past 50 years, many empirical correlations have been developed between the structure and reactivity of various organic compounds. In recent years this correlation analysis approach has been applied to environmental concerns, including the partitioning of an organic compound in an aquifer. Since partition coefficients may be considered to be conditional equilibrium constants, it is possible to relate them to the physical-chemical properties of the organics being partitioned (Chiou et al., 1982). Of interest is the relationship between the octanol-water partition coefficient, K_{OW} , and the water solubility of a chemical, S , (Chiou, et al., 1982):

$$\log K_{OW} = -0.0862 \log S + 0.710 \quad , \quad (12)$$

where:

$K_{ow} = (C_o/C_w)$, in which C_o is the equilibrium concentration of the compound in octanol and C_w is its equilibrium concentration in the aqueous phase, and

S = molar solute solubility.

The above is only one of eighteen different correlation equations in which the solubility can be defined as a function of the octanol/water partition coefficient (Lyman, et al., 1982). The octanol/water partition coefficient is not the same as the ratio of an organic compound's solubility in octanol to its water solubility, because the organic and aqueous phases of the binary octanol/water system are not pure octanol and pure water (Lyman, et al., 1982).

The octanol/water partition coefficient has become a key parameter in studies of the environmental fate of organic compounds. Not only is the partition coefficient related to water solubility, but it has been found to be related to sediment adsorption coefficients as well. Values of the octanol/water partition coefficient can be considered to have some meaning in themselves because they relate the tendency of the organic compound to partition itself between an organic phase, such as soil organics, and the aqueous phase flowing through the porous medium (Lyman, et al., 1982). The medium does not have to be saturated. Organic compounds with low partition coefficients (less than 10) are considered to be hydrophilic--having high water solubilities and low solid

adsorption coefficients. Organic compounds with high partition coefficients are considered to be hydrophobic. There may not be a relationship between high octanol/water partition coefficients and solid adsorption coefficients (Lyman, et al., 1982).

Octanol/water partition coefficient values are often reported as log K_{OW} numbers. The fluoroethane tracers used in this research have log values on the order of 3.0. The log K_{OW} for 1,2-difluorotetrachloroethane is 2.82.

Sorption

Not only water solubility but also sediment "sorption" and bioconcentration can be estimated from the K_{OW} of an organic compound. The uptake of neutral organic chemicals by soil material is dependent upon the amount of organic matter in the soil. This uptake is the result of solute partitioning (dissolution in two or more phases) rather than physical or chemical adsorption (Chiou, 1981 and Chiou, et al., 1982, and Karickhoff, et al., 1979). Therefore, sorption is the term used to account for both adsorption and absorption (dissolution). Adsorption reactions may be significant for polar compounds.

The major controlling factor in the partitioning of organic chemicals between the soil organic matter and the aqueous phase is the solubility or insolubility of the solute

within the aqueous phase (Chiou, 1981 Chiou, et al., and 1982). But Chiou (1981) has noted that the poor retention of organic compounds by soil organic matter is likely the result of soil being composed of abundant highly polar polymers of large molar volume. These polymers can be classified as: (1) sedimentary humic substances, (2) algal kerogens, (3) lip-tinitic kerogens, or (4) humic kerogen. In most soils this organic matter is concentrated in the fine-grained fraction, consequently, organic contaminant sorption is dependent on grain-size variations (Karickhoff, et al., 1979).

Correlation expressions have been developed to relate organic compound sorption to readily measured or available parameters. Karickhoff et al. (1979) showed that the sorption of an organic compound by soil organic matter could be expressed by:

$$\log K_{OC} = 1.00 \log K_{OW} - 0.21 \quad , \quad (13)$$

where:

K_{OC} = the partition coefficient between soil organic carbon and water (g solute sorbed/g soil organic carbon/g solute/m³ solution).

As noted above, sorption is normally viewed as readily reversible in most soils because of humic and kerogen substances. Recent tests have found that for highly sorbed organic compounds the description equilibrium may require weeks to months to achieve (Karickhoff, 1983). The sorption-desorption rate of organic compounds in an aquifer system is

an important parameter in studying the migration and/or transformation of those compounds. It is obvious from the Chiou and Karickhoff publications that all of the evidence has not yet been gathered to determine the exact sorption behavior of specific organic solutes.

Volatility

Volatilization is the process by which an organic compound sublimates or evaporates into the vapor phase from either the solid or liquid phase. Volatilization could be an important transport process in which an organic tracer is removed from the groundwater under study or from a stationary column test in the laboratory. The rate of volatilization from a soil is affected by many factors including the physical and chemical properties of the soil, and environmental conditions. Physical-chemical properties such as vapor pressure and solubility of the organic compound are also very important in volatilization processes. The concentration of the organic solute in the porous medium either in the aqueous phase or the solid phase affects the volatilization rate from the soil. Bulk properties of the soil such as organic matter content, porosity, density, and clay content also affect the volatilization rate (Lyman et al., 1982). All the independent variables that can affect volatilization are generally

grouped into three categories (Lyman et al., 1982; Tinsley, 1979):

- 1) the rate at which the solute migrates to a surface,
- 2) the rate of transfer across the surface to the atmosphere, and
- 3) the rate of migration away from the surface.

In groundwater, the rate of migration of an organic compound to the top of the capillary fringe, or to some part of the unsaturated zone from where it can vaporize, is controlled by the many adsorption and absorption processes, vertical groundwater flow, and solute diffusion. The tendency to escape across an interface is a function of the vapor pressure of the organic compound. Values of the vapor pressure for the two organic tracers utilized in this research are reported in Table 1.

Table 1

Vapor Pressure of the Two Fluorocarbon Tracers Used in This Research

1,2,2-trifluoro-1,1,2-trichloroethane	139.6 mm Hg at 4°C
	336.1 mm Hg at 25°C
1,2-difluoro-1,1,2,2,-tetrachloroethane	99.0 mm Hg at 37°C

Organic Transformation Processes

The physical-chemical properties of an organic compound or an inorganic chemical determines the transport manner of that chemical. There are transformation processes that change the physical-chemical properties of a specific chemical. If a specific organic compound is to be utilized as a tracer, then it must be resistant to these transformation reactions. If it is not, then the tracer would not be suitable for the investigative environment in which it is meant to be used. As was shown in the overall transport equation (7), if the tracer is transformed to some other compound, then the chemical reaction term of the equation will be dominant and the retardation factor could be very large. In the above discussion the comparison of the chloride exit concentration from the test column is to be compared to the organic exit concentration relative to the inlet concentration. This comparison will allow the retardation factor for the organic tracer to be evaluated with respect to the chloride retardation factor which is known and fairly constant. If the organic tracer undergoes some physical-chemical property changes due to the transformation processes then its exit concentration will reflect a retardation effect.

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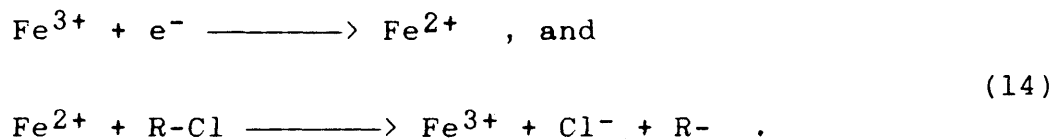
Redox

Many inorganic and organic compounds can either accept electrons and be reduced or donate electrons and be oxidized. These reactions are termed redox reactions. Redox reactions are important because the oxidized form could have completely different transport properties than the reduced form. Also, there are substantial variations in the oxidizing and reducing environments in a groundwater or in a tailings pore water that would affect redox transitions.

Investigation of inorganic systems have provided a sufficient amount of data to show the effect of redox reactions on the different inorganic complexes that can occur in the natural environment. These investigations relate the complex stability to the Eh or pE measurement and the pH measurement for the system. The Eh and the pH of the system are the factors controlling for the form of the inorganic chemical, and to what complex compound it will be bound.

It is not possible to represent organic systems in terms of the redox characteristics of the environment (Tinsley, 1979), but redox reactions are a factor in determining the behavior of organic compounds. Generally, the rate of breakdown increases with lower Eh values (Tinsley, 1979).

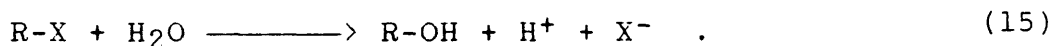
It is known that the reduced form of iron, ferrous iron, enhances breakdown rates in accordance with the following mechanism:



The iron is recycled and acts catalytically and the free hydrocarbon radical, R-, combines with a proton from some donor molecule in the system. If the system has a low pH, then there are ample protons available to combine with the free radical. If the system contains a large amount of ferrous iron and a very low pH, as is the case with a uranium tailings, then the above redox reaction could be very important in the transformation of halogenated alkanes.

Hydrolysis

Hydrolysis is a chemical transformation process in which an organic chemical reacts with water. When the organic is a halogenated hydrocarbon, the products are generally a new carbon-oxygen bond and a free inorganic ionized species:

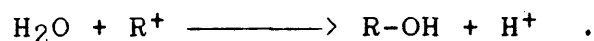
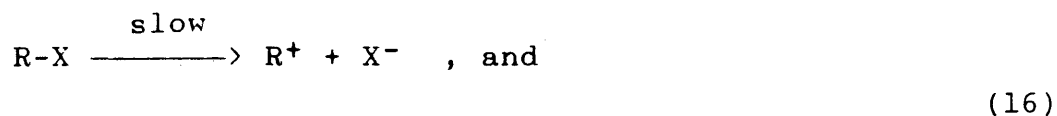


In hydrolysis reactions, the effect of pH must be considered for the potential of water to dissociate to form hydrogen ions, and hydroxide ions will control the hydrolysis

reaction rates. Hydrogen ions and other groups that are deficient in electrons are classified as electrophiles (electron lovers). An electrophile is attracted to an atom that has a slight negative charge or a lone pair of electrons or to the electrons of a double bond. Hydroxide ions are nucleophile substances. Nucleophile substances have an excess of nonbonding electrons and thus are nucleus lovers. In an acid environment the hydrolysis reaction is acid-catalyzed and the water molecule acts as a nucleophile as it is attracted to the positive charge of the carbon in a halogenated hydrocarbon. The tendency for a compound to react with water, or the hydrogen or hydroxide ion, is determined by the charge distribution on that molecule.

Hydrolysis, as represented by equation (15), is probably the most important transformation reaction of organic compounds in the environment. In normal pH groundwaters the hydrolysis reaction is primarily a nucleophile (water or hydroxide ion) attack on an electrophile (carbon atom) and the nucleophile displaces a leaving group such as a chloride. In acid-catalysis hydrolysis the water molecule will be more nucleophilic than the hydroxide ion. In extremely acidic environments such as uranium tailings pore water, the actual reaction mechanisms are unknown. In normal pH groundwater the rate-determining reaction step is the ionization of R-X in equation (15) to give a planar carbonium

ion and an ionized halide. The carbonium ion then undergoes a rapid nucleophilic attack. This is demonstrated in the following set of reaction equations:



Generally, the hydrolysis of organic compounds is a first-order reaction (Tinsley, 1979). Therefore, the rate of disappearance of RX is directly proportional to the concentration of the compound:

$$- \frac{d(RX)}{dt} = k_T \cdot (RX) \quad , \quad (17)$$

where:

k_T = hydrolysis rate constant, and

(RX) = concentration of RX at any point in time, t.

The rate constant, k_T , is a function of the acid-catalyzed, base-catalyzed, and neutral hydrolysis rate constants associated with the overall reaction.

The equation that relates the k_T to all of the other rate constants is:

$$K_T = k_O + k_H(H^+) + k_{OH}(OH^-) + K_{HA_i}(HA_i) + K_{B_j}(B_j) \quad . \quad (18)$$

where:

- k_T = total hydrolysis rate constant,
- k_O = rate constant for neutral hydrolysis,
- k_H = rate constant for acid-catalyzed hydrolysis,
- k_{OH} = rate constant for base-catalyzed hydrolysis,
- k_{HA} = rate constant for general acid-catalysis,
- k_B = rate constant for general base-catalysis,
- (H^+) = hydrogen ion concentration,
- (OH^-) = hydroxyl ion concentration,
- (HA) = general acid concentration,
- (B) = general base concentration, and
- i, j = indices to identify different acids and bases.

When the general acid and base concentrations are small or unknown then the last two terms are dropped. At low pH the second term is dominant and

$$k_T = k_H(H^+) \quad \text{or} \quad \log k_T = \log k_H - \text{pH} . \quad (19)$$

At high pH the third term is dominant and

$$k_T = k_{OH}(OH^-) \quad \text{or} \quad \log k_T = \log k_{OH} + \log k_w + \text{pH} . \quad (20)$$

At neutral conditions the first term is dominant and

$$k_T = k_O \quad \text{or} \quad \log k_T = \log k_O . \quad (21)$$

Figure 1 illustrates the variation of the overall hydrolysis rate constant with pH (Tinsley, 1979).

The intercept I_{AN} indicates the pH at which the rates of the acid- and neutral- catalyzed processes are equal. At pH values below this point the acid-catalyzed reaction is dominant while above this point the neutral-catalyzed process is dominant. In the case of uranium tailings pore water the pH, which is approximately 2, is below this point for most organic compounds. Therefore, the hydrolysis reaction in acid uranium tailings is controlled by the acid-catalyzed reactions. Also, there are other acid constituents that will cause the k_{HA} and (HA) values in equation (18) to become important. In these very low pH environments the acid-catalyzed reactions may be very important. When combined with the fact that the aqueous phase has a high salinity concentration, the hydrolysis reactions (acid-catalyzed) that do not occur in the "normal" environment will occur in the harsh environment of the uranium tailings.

Hydrolysis reactions normally depend upon the attack of nucleophilic agents such as the water molecule or the hydroxide ion on the organic compound. Acid catalysis enhances nucleophilic attack by influencing the charge distribution in the carbon molecule. Molecules that are susceptible to hydrolysis are molecules in which the electron

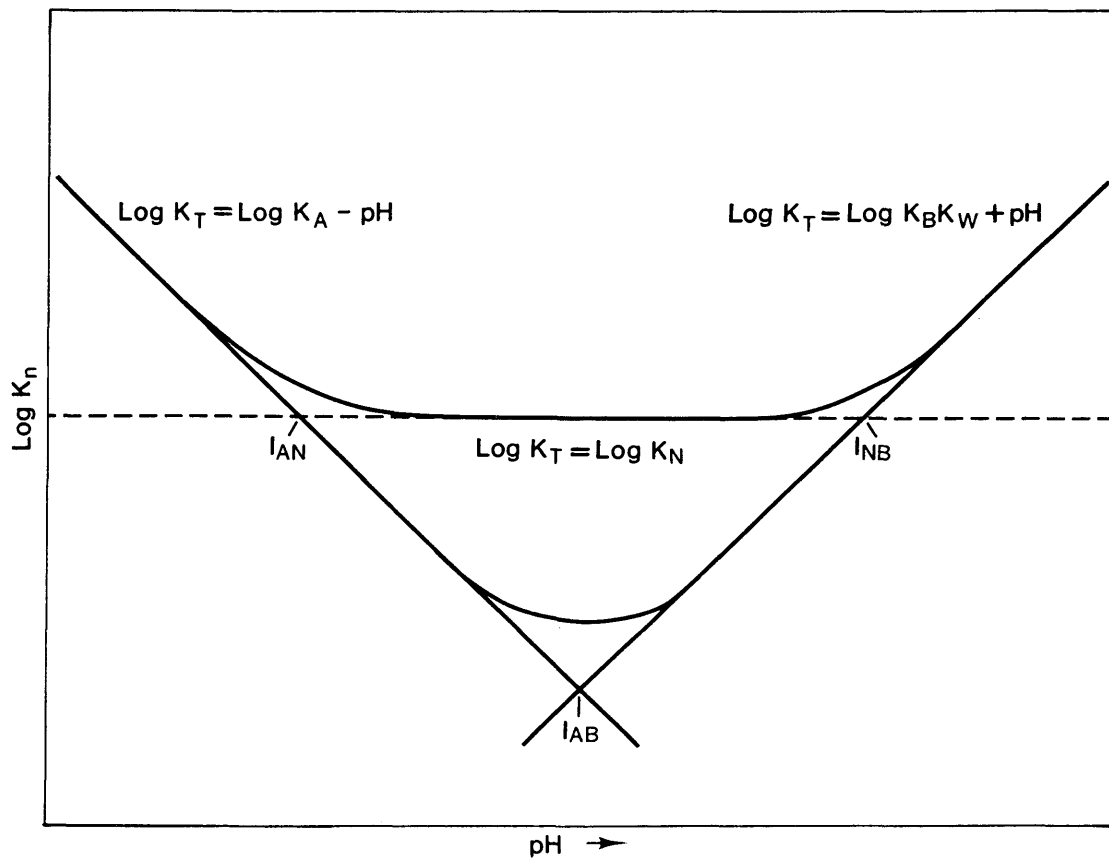


Figure 1. Variation in the Overall Hydrolysis Rate Constant with pH

distribution gives some charge separation, facilitating nucleophilic attack. Some halogenated compounds are susceptible to hydrolysis. The electronegativity difference of the halogen atoms and the carbon produces the necessary charge separation for nucleophilic attack. Some chlorinated hydrocarbon compounds are not readily susceptible to hydrolysis. Those halogenated compounds that do not show a susceptibility to hydrolysis are compounds that have increasing chlorination and/or fluorination.

Table 2 illustrates the variability of hydrolysis rate constants and the half-life of the hydrolysis reaction for various halogenated hydrocarbon compounds (Tinsley, 1979).

The above hydrolysis reactions occur under neutral conditions with the water molecule acting as the nucleophile, or under basic conditions with the hydroxide ion being the nucleophile. No acid-catalyzed processes have been tabulated (Tinsley, 1979). The rate constants have been calculated for pH 7 to simulate conditions that would be encountered in the actual environment. Unfortunately, there is not a lot of reaction rate data for acid environments.

Dehalogenation

Hydrolysis is just one of three major reaction routes that describe halogen transformation processes. The other

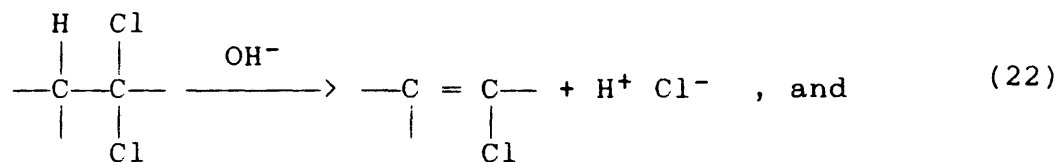
Table 2
Hydrolysis Rates at 25°C and pH 7
of Some Halogenated Compounds

Rate Constants (sec⁻¹)

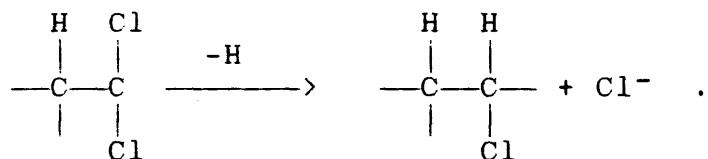
Compound	k_n	$k_b[\text{OH}^-]$	k_n	$t_{1/2}$
CH ₃ F	7.44×10^{-10}	5.82×10^{-14}	7.44×10^{-10}	30 yr
CH ₃ Cl	2.37×10^{-8}	6.18×10^{-13}	2.37×10^{-8}	339 days
CH ₃ Br	4.09×10^{-7}	1.41×10^{-11}	4.09×10^{-7}	20 days
CH ₃ I	7.28×10^{-8}	6.47×10^{-12}	7.28×10^{-8}	110 days
CH ₃ CHClCH ₃	2.12×10^{-7}	---	2.12×10^{-7}	38 days
CH ₃ CH ₂ CH ₂ Br	3.86×10^{-6}	---	3.86×10^{-6}	26 days
ClC(CH ₃) ₃	3.02×10^{-11}	---	3.02×10^{-2}	23 s
CH ₂ Cl ₂	3.2×10^{-11}	2.3×10^{-15}	3.2×10^{-11}	704 yr
CHCl ₃	---	6.9×10^{-12}	6.9×10^{-12}	3500 yr
CHBr ₃	---	3.2×10^{-11}	3.2×10^{-11}	686 yr
CCl ₄	---	4.8×10^{-7}	4.8×10^{-7}	7000 yr (1 ppm)
C ₆ H ₅ CH ₂ Cl	1.28×10^{-5}	---	1.28×10^{-5}	15 hr

two are dehydrohalogenation and reductive dehalogenation. The latter two are illustrated in the following examples (Hill, 1978; Tinsley, 1979):

Dehydrohalogenation -



Reductive Dehalogenation -



The above reactions may be either abiotic or microbially mediated.

It is known that many uranium and copper tailings, as well as heap leaching piles, contain reductive microorganisms that mediate sulfate to sulfite and ferric to ferrous reactions. It can be assumed that these microorganisms will also mediate the dehydrohalogenation and reductive dehalogenation reactions of halogenated organics.

Fluorocarbon Tracer Studies

Ciccioli, et al. (1980) have demonstrated in laboratory studies using columns with limestones and silicate sands that surface interactions between a variety of halogenated organic

compounds (which include fluorocarbons) and mineral grain surfaces are nonspecific and the strength of the interaction or sorption is a function of the polarity of the organic molecule. By knowing the relative sorptive strengths or dipole moments of a series of similar halogenated organic tracers, Ciccioli, et al. (1980) has proposed a method to calculate the velocity of the water as well as being able to determine the flow direction of a contaminant plume within an aquifer.

An important limitation to the use of fluorocarbons stems from the fact that they are organic compounds and as such, they are strongly sorbed by many other organic materials. Therefore, they will generally be unsuitable for tracing water in aquifers that are highly enriched in organic matter, either natural or man-induced.

The halogenated hydrocarbon testing results of Ciccioli, et al. (1980) are shown in Table 3. All tracers gave the same retention time on the sand column. This indicates that increasing levels of chlorination have not produced additional retention of the tracer. It is conceivable that mechanisms would exist where fluorination would increase retention (Ciccioli, et al., 1980). The observation that all the organic tracers are unretarded by sorption processes on the sand column is borne out by the

Table 3
Retention Times of Halocarbon Tracers
in Laboratory Columns

Tracer	Retention Time, sec	
	Sand	Limestone
<u>C₂Cl_nF_{6-n} series</u>		
n = 2	160	67.8
n = 3	159	83.6
n = 4	158	116.9
n = 6	158	335.0
<u>CH_{4-n}Cl_n series</u>		
n = 2		62.2
n = 3		61.1
n = 4		82.4
<u>CCl_nF_{4-n} series</u>		
n = 2	157	53.6
n = 3	157	60.0
n = 4	160	82.4
<u>CBr_nF_{4-n} series</u>		
n = 2	157	61.5
n = 3		83.8
Cl ⁻	158	54.0
Ar		56.0
CHCl ₂ F	158	53.0
SF ₆	156	52.6

observation that Cl^- , which would be expected to be unre-
tained, had retention times equal to those of the halo-
genated hydrocarbon.

Significant variations in retention times on the lime-
stone column were observed. It should be noted that increas-
ing levels of chlorination did give rise to increasing reten-
tion. The halogenated ethanes showed a linear relationship
between the number of chloride atoms added to the organic and
the retention time observed in the column test for limestone.
The halogenated methane retention time was a nonlinear rela-
tionship as chlorination increases.

No retention was observed on the sand because the popu-
lation of nonspecific sites in the relatively pure material
was negligible. The adsorption of the halogenated organic
tracers onto the sand would require that the sites occupied
by strongly bound water molecules would have to be made ac-
cessible to the tracer. The dipolar strength of the tracers
was not sufficient to displace the water molecule. By intro-
ducing ionic species in the aqueous phase there may have been
some retention of the halogenated organic tracers. The lime-
stone provided a greater number of sites as well as a greater
variety of sites that could react with the tracers. This
diversity and greater population size caused the linear rela-
tionship between the retention time and the number of halogen
atoms on the organic compound. The retardation process known

as chromatographic fractionation took place on the surface sites of the limestone.

The Ciccioli, et al. (1980) experiment showed that the nonspecific nature of the interaction mechanisms responsible for halogenated organic tracer retardation has significant and positive consequences for utilizing these tracers in groundwater systems. Also, the fluorochloroethanes conform well to the expectations for good tracers. The range of adsorbent properties in different natural porous media is due to many factors. Two of these factors are: (1) differences in specific surface area, and therefore the numbers of adsorbent sites available, and (2) differences in the types and relative abundances of adsorbent sites at their surfaces (Ciccioli, et al., 1980). Differences of the first kind will retard or accelerate all solutes equally, thus having no effect on relative rates of solute migration. Differences of the second kind do, however, have the potential to change relative solute migration rates, possibly even rearranging the sequence of solute travel times through an adsorbent material.

Thompson, et al. (1974), Thompson and Hayes (1979), and Thompson, et al., (1980) investigated the use of fluorocarbons as tracers in groundwater and stream studies. Fluorocarbon tracers are extremely stable, and among all organic compounds, they are not likely to be appreciably

adsorbed by most materials. Simple fluorochloro organic compounds can have very low toxicity. Fluorocarbons with no double bonds are not easily biodegradable. They are generally odorless and tasteless and thus can be used in surface and groundwaters that may be diverted for public use (Thompson, et al., 1980). The fluorochlorocarbon compounds have a high affinity for electron absorption, which makes them detectable in water in concentrations as low as one part per trillion using electron capture gas chromatography (Thompson, et al., 1980).

Fluorocarbons may be useful in several types of hydrologic studies. Their physical properties make them suitable for qualitative or quantitative use in surface and aquifer water. Fluorocarbons should be excellent chemical tracers for investigating the migration of seepage fluids or wastes that are discharged into aquifers. A small amount of fluorocarbon tracer added to uranium tailings pore water should provide a simple means of monitoring movement of the seepage from the tailings.

Studies done by Thompson, et al. (1974) Thompson and Hayes (1979), Thompson et al. (1980) and Ciccioli, et al. (1980) have been in neutral groundwaters and surface waters. Tests carried out in laboratory columns to date have been with porous materials and aqueous solutions that represent a "normal" aquifer environment. The aqueous environment in

uranium tailings is far from normal. Studies to date have reported retention of the fluorocarbons to some extent, but none have reported any transformation of the fluorocarbon tracers.

If the transport or retention transformation of a specific fluorocarbon is relatively small, then that organic compound can be successfully utilized as a tracer. If there is significant retention but no major transformation of the fluorocarbon compound, its use may still be beneficial in determining if seepage from a reclaimed uranium tailings pile is continuing after control measures are implemented. If the fluorocarbon compound undergoes a major transformation process by any one of the reaction mechanisms summarized above, or is significantly volatilized, then the applicability of the organic tracer to study uranium tailings seepage would be minimal. The purpose of this research was to determine if two specific fluorocarbon tracers, difluorotetrachloroethane and trifluorotrighloroethane, can be utilized to study seepage from uranium tailings.

CHAPTER III: RESEARCH METHODOLOGY

Methodology

The research methodology used to determine the applicability of fluorocarbon tracers in uranium tailings is fairly simple. The fluorochlorocarbon compound was added to uranium tailings water and allowed to flow through a column of uranium tailings. The inlet and outlet concentrations of the organic tracer was determined by electron capture gas chromatography. Chloride and sulfate in the test column's influent and effluent concentrations were determined by standard analytical procedures. The chloride, sulfate and organic compound concentrations in the column's influent were kept at a constant level for an individual test. By comparing the difference between the inlet and outlet concentrations for all three tracers (organic and inorganics) the effect of transport retardation and/or transformation of the fluorocarbon tracer was determined.

Column effluent samples were taken on an equal volume basis without a time determination. Since all three tracers are in the aqueous phase, only equal effluent sample volumes were needed over the span of the column test because the difference between the inlet and the outlet concentration for each species is the important factor.

In many field investigations it is not feasible to continuously add a constant concentration of tracer to a flow

regime, either a surface flow or an aquifer. It was important to evaluate the feasibility of introducing the fluorocarbon compound as a spike into the flow regime. This evaluation was conducted by continuously adding a known concentration of the organic tracer to one test column and a spike of the organic tracer to another test column. The constant organic tracer concentration influent was continued until an effluent flow began. The organic tracer spike was introduced into the second column and allowed to seep into the porous material. Next, uranium tailings water that did not contain any organic tracer was added to the second column until effluent flow began. The two columns were of equal length with the same cross-sectional area. The volume of porous material was the same in each column. Therefore, the volume of water that percolated through the material in column one equaled (approximately) the volume of water that percolated through the same type of material in column two. The feasibility of using a spike of the organic tracer was determined by comparing the effluent concentrations of the two columns. Figure 2 shows the arrangement of the two columns.

A series of batch tests were conducted as a control or check on the column tests. A sample portion (300 ml) of the column material, tailings or soil, was placed in a 1000 ml beaker. Then 300 ml of the uranium tracer solution was mixed with the porous material. After four days of intermittent

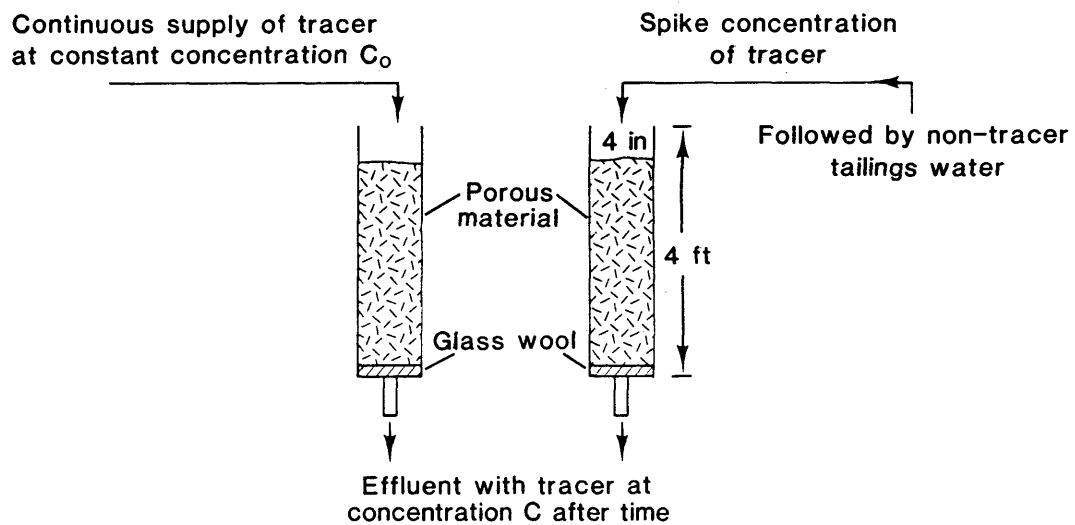


Figure 2. Column Design Used for the Evaluation of Fluorocarbon Tracers in This Study.

mixing the aqueous phase was sampled and analyzed for the organic compound. The analytical results were compared with the organic compound concentration in the test column effluents. Details of the batch tests conducted are given in Appendix A (Batch Tests).

To determine the possible loss of the organic tracers due to volatilization during the batch tests, a 300 ml aliquot of the uranium/tracer solution was placed in a beaker that did not contain any solid material. A sample of the tracer solution was taken before and after the four day "batch" test period. The concentration of the organic tracer in solution after the "batch" test period was compared to the starting concentration to determine the amount volatilized (see Appendix A, Batch Test, volatilization check).

Columns

The columns that were used in this research were made from glass tubes that were four feet in length and four inches in diameter. A total of four columns could be utilized at any one time. This allowed a set of four tests to be conducted at the same time. This arrangement not only saved time, but also equated the pass through volumes for the constant and the spike organic tracer tests.

Each glass tube had a plexiglass plug fitted into the bottom. The plug had been drilled and tapped to allow a 1/4 inch plastic pipe nipple to be placed into it. Approximately

1/2 inch of glass-wool was placed in the bottom of the columns and on top of the plexiglas plug. The glass-wool would keep the column drain (1/4 inch plastic nipple) from becoming plugged with the solid material when placed in the column. The porous material was placed into the four columns to the same height, thus, equal volumes. The length of the solid volume was established at 38 inches for all the tests. This left a space at the top of the column of 10 inches to allow the tracer solution to be placed on top of the solid volume.

Tracer Solution

The tracer solution was made by taking a uranium tailings water and mixing into it a set amount of tracer. An artificial solution to represent uranium tailings water did not have to be made up because the uranium tailings water used was collected from a "stand-by" operation in New Mexico. The aqueous solution was collected from horizontal drains installed into the tailings pile to drain the phreatic water in order to maintain stability in the dam. Therefore, the collected solution represented water that had actually percolated through uranium tailings material. The measured pH of the tailings solution was 2. The chloride concentration was 450 mg/l. The sulfate concentration was 35,000 mg/l. The chloride concentration seemed low based upon the author's experience in the uranium processing industry. The sulfate

concentration was in the expected range. The specific tailings pile from which the solution was collected always had a pond on top, due to the discharge of water from the underground mine that provided the uranium ore for the mill. The mine water could not be discharged as an effluent from the mine site, therefore, it was discharged onto the tailings pile so that it could evaporate. It did evaporate but it also provided hydraulic head to cause a continuing seepage flow.

Three 19-liter containers of uranium tailings water were collected. One container was used to mix one tracer, difluorotetrachloroethane. Another container was used for the trifluorotrichloroethane tracer. The liquid in the third container was not mixed with any tracer. The unmixed solution was used in the spike tests.

The two fluorochloroethane tracers are both insoluble in water. In order to place the organic tracers into solution with the water, they were first mixed with isopropyl alcohol. Isopropyl alcohol is miscible in water and because of their partitioning coefficients the fluorocarbons will accompany the isopropyl alcohol into the aqueous phase. To prepare the alcohol/tracer mixture, approximately 1/2 of a 100 microliter pipet volume of the organic tracer was placed in 500 milliliters of isopropyl alcohol. The alcohol/tracer solution is then mixed with 19 liters of the uranium tailings

water. At exactly 50 microliters, the tracer concentration in the uranium tailings solution would be 4100 micrograms/liter (density of tracer - 1.56 gm/cm^3). Even with a constant temperature bath, it was difficult to achieve the one-half pipet volume for difluorotetrachloroethane because it is a solid at room temperature.

Porous Material

The porous materials placed in the test columns were collected samples of uranium tailings and two different soil types. The grain size, determined by screen analysis, of the tailings material is 65 percent below 200 mesh (74 microns). One bulk soil sample was obtained from the side of a trench installed in the alluvial fill, down-gradient of the uranium tailings pile. The purpose of the alluvial trench is to intercept any seepage migrating from the tailings in the alluvial material. The other bulk soil sample was obtained from the side of an arroyo several miles down gradient from the tailings pile.

The adsorptive properties of the tailings and the soils is a function of the amount and type of clay in the respective materials and the mineral composition of the bulk material. The different porous materials were analyzed by x-ray diffraction (XRD) to determine their mineral compositions, the percentage of clay-size material and the mineral composition of the clay fraction.

A representative portion of each sample was initially ground to approximately -60 mesh (250 microns). A split of each -60 mesh sample was ground to -325 mesh (44 microns), mounted in a standard aluminum holder and scanned with the x-ray diffractometer to determine the mineral compositions of the bulk samples. The results of the x-ray scans are summarized in Table 4. A second split of each -60 mesh sample was subjected to a settling procedure based on Stokes' Law. A weighed amount of each sample (20 gms) was mixed with deionized water and antiflocculants, then brought up to volume in a 1000 ml cylinder with deionized water and stirred. The mixture was allowed to settle for 19.5 hours and then a 20 ml aliquot of the -2 micrometer material was siphoned off (settling distance determined by Stokes' Law) into preweighed containers. The -2 micrometer fraction was air dried and weighed to determine the weight percent of -2 micrometer material (clay-size). The results of the settling procedure are summarized in Table 5.

Table 4

Mineralogy of Porous Media Used in This Study,
Based on X-ray Diffraction (XRD) Analyses

(given as approximate weight percent)

<u>Mineral</u>	<u>Sample</u>		
	<u>Tailings</u>	<u>Alluvial Soil</u>	<u>Arroyo Soil</u>
Quartz	> 80	65	37
Calcite	----	17	< 3
Dolomite	----	--	< 3
K-feldspar	10	3	6
Plagioclase	< 3	3	5
Mica-illite	< 3	< 3	< 3
Clays	< 5	5	5
Gypsum	---	3	3

Table 5

Clay Percentages of the Porous Media Used in This Study

<u>Sample</u>	<u>Weight %</u> <u>Clay Size (< 2 micrometer)</u>
tailings	4.1
alluvial soil	22.1
arroyo soil	16.2

A portion of each clay-size fraction was prepared as an oriented mount by drawing clay + water onto a millipore filter and glueing it to the glass slide. The oriented mounts were then analyzed by XRD scanning. The results of the XRD analysis of the clay fractions are summarized in Table 6.

Table 6

Mineralogy of the Clay Sized Fraction of the Porous Media Used in This Study, Based on X-ray Diffraction Analyses.

(Numbers represent approximate percentages.)

<u>Mineral</u>	<u>Sample</u>		
	<u>Tailings</u>	<u>Alluvial Soil</u>	<u>Arroyo Soil</u>
Montmorillonite	10	10	15
Kaolinite	65	9	33
Chlorite	3	12	--
Quartz	12	20	26
Calcite	--	40	6
Dolomite	--	--	3
K-feldspar	3	--	5
Plagioclase	--	--	4
Mica-illite	< 3	< 3	< 3

Test Procedures

With the porous material in the test columns the tracer solution was placed on top of the material and allowed to percolate through to the bottom. First an inlet sample of the tracer solution was taken. All column test samples were collected in 20 ml pull-seal glass ampules. Sample ampules were sealed by simply heating the top with a propane torch. No sample preservation procedures are required for the tracer.

Two columns were placed side by side. The first column was for a constant tracer concentration influent. The second column was for a spike tracer concentration. An aliquot (in this experiment an aliquot is defined as a volume of 100 ml) of the tracer solution was poured into both columns, and the aliquot solution was allowed to seep below the surface top. Another aliquot of the tracer solution was poured into the first column and allowed to seep below the surface. An aliquot of the non-tracer uranium tailings liquid was poured into the second column and allowed to seep below the surface. These last two steps were repeated until effluent began to flow from the bottom of the test columns. No further aliquots were added to the columns. Equal 50 ml effluent samples were collected from each column until effluent flow diminished. After the inlet aliquots were stopped, the effluent flow was totally due to gravity force.

The volume of pore water removed under gravity is the specific yield of a porous material. The volume of water retained within the pores of the material is the specific retention of the material. This retention is due to the water molecules clinging to the material particles because of surface tension. The tracer, being either the inorganic ions or the organic compound, should have a preference for the retained water only under conditions of adsorption.

Details of the test series conducted, and effluent volumes collected are given in Appendix A (Tests 1 through 8).

Since one of the major goals of this research was to determine if a spike solution of the organic tracer could be utilized to detect seepage from a reclaimed uranium tailings pile, a column test was conducted for each organic tracer to evaluate this application (see Appendix A, Tests 9 and 10). Two columns were set up with tailings and soil in both columns. Thirty inches of the tailings material were placed into two columns. An aliquot of an organic tracer solution was poured on top of the tailings and allowed to seep below the surface. Then 12 inches of soil material was placed on top of the tailings. This left approximately 6 inches of space to pour aliquots of the non-tracer solution into the column. A point to note is that due to capillary action part of the tracer aliquot diffused into the dry soil material

when it was placed on top of the tailings. Aliquots of the non-tracer solution were poured into the columns after the surface of the soil had sufficient time to dry. The intention of this procedure was to represent time intervals between precipitation events on an actual tailings disposal pile.

In addition to the effluent samples for each column test, an influent sample was also collected for each column test. The influent sample served two purposes: (1) it was required in order to compare inlet and outlet concentrations of both the inorganic and the organic tracers, and (2) it also provided a means to determine if the organic tracer concentration changes in the uranium tailings solution over time.

The column influent and effluent samples were analyzed for chloride, sulfate, and the respective organic tracer compound. Eighty percent of the samples were analyzed by one lab. Due to time constraints at this lab, approximately twenty percent of the samples were analyzed at a second lab. A set of split samples was sent to each lab for comparison.

CHAPTER IV: RESULTS

Using unsaturated tailings and soil material in the glass columns provided a means to observe the migration rate of the aqueous phase down through the porous column. It took approximately 12 hours for a tailings/tracer test to be completed. A soil/tracer test took approximately 24 hours. The time span for the tailings/soil cover test was 72 hours.

Calculation of the retardation coefficient for the two different organic tracers relative to the retardation coefficients for chloride and sulfate was not necessary to determine if the two organic tracers can be used to study uranium tailings seepage. The concentration of the organic tracer in the column effluent samples was so low for each test that the calculation would be meaningless.

The analytical results from the column tests are tabulated in Tables 7 through 16 in Appendix B. The analytical results from the batch test are presented in Table 17 in Appendix B.

A plot of the ratio of the effluent concentration, C , to the influent concentration, C_0 , vs. time for each column test will facilitate the evaluation of the results. The log of C/C_0 is a more convenient form to plot when three tracer species are being compared.

When a tracer at concentration C_0 is continuously introduced into a test column at a constant concentration,

the tracer input can be represented as a step function. If the tracer moves through the column without any dispersion, advection or reaction changes, the tracer front will exit from the column as a step function. A $\log C/C_0$ vs. time plot for an ideal non-reactive tracer is shown in Figure 3(a). A non-reactive but retained tracer would have a $\log C/C_0$ vs. time plot similar to Figure 3(b). In the figures, t_0 represents the time the tracer exits the column. If the tracer undergoes transformation or if its concentration is reduced by volatilization, the $\log C/C_0$ will not approach zero as time increases.

Figures 4 through 11 are the $\log C/C_0$ vs. time plots for each tracer species (chloride, sulfate and organic compound) for the individual constant influent column tests. The results from the spike tests are not plotted, except for tests 4 and 6 because the spike results are essentially the same as the constant influent results.

The volatilization batch test results show that there is a significant difference between the concentration of the organic tracer in the uranium tailings water at the start of the test and the concentration at the end of the test. For the trifluorotrachloroethane tracer, the difference is 5000 micrograms per liter. For the difluorotetrachloroethane tracer, the difference is 2140 micrograms per liter. Results of the batch test series are given in Appendix B, Table 17.

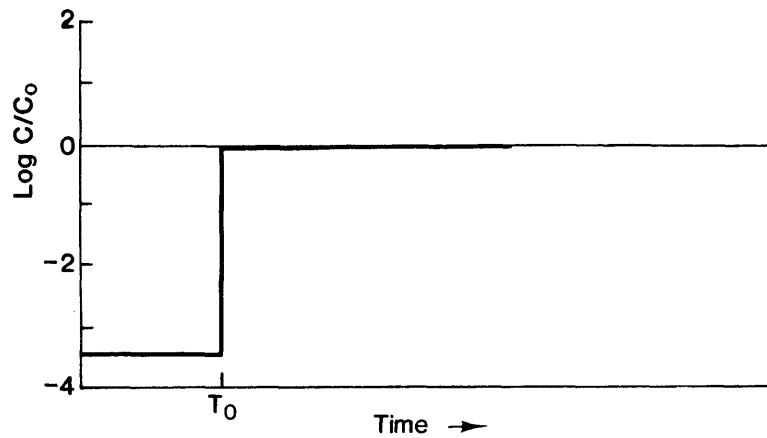


Figure 3a. $\text{Log } C/C_0$ vs. Time: An Ideal Non-reactive Tracer Step Function When the Tracer Front Exits a Test Column at Time, T_0 .

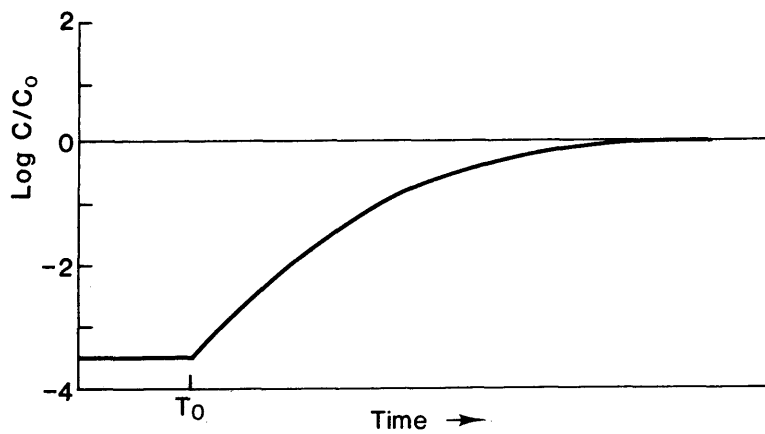


Figure 3b. $\text{Log } C/C_0$ vs. Time: A Non-Reactive But Retained Tracer Function When the Tracer Front Exits a Test Column at Time, T_0 .

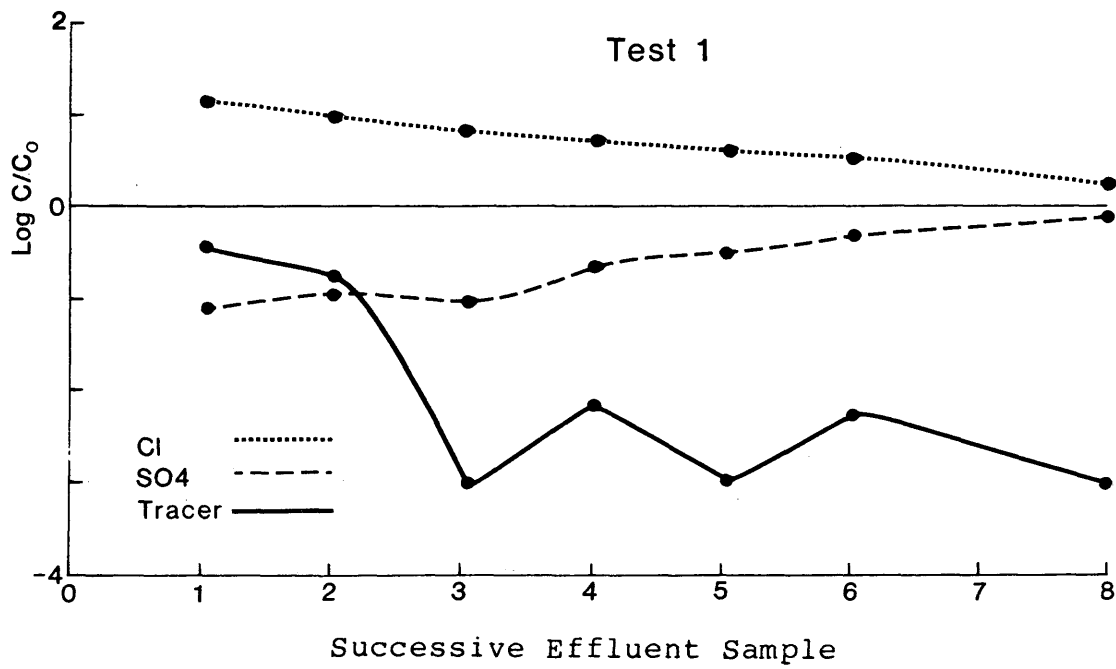


Figure 4. Results of Column Test 1 Using Difluorotetrachloroethane as the Organic Tracer and Uranium Mill Tailings as the Porous Material.

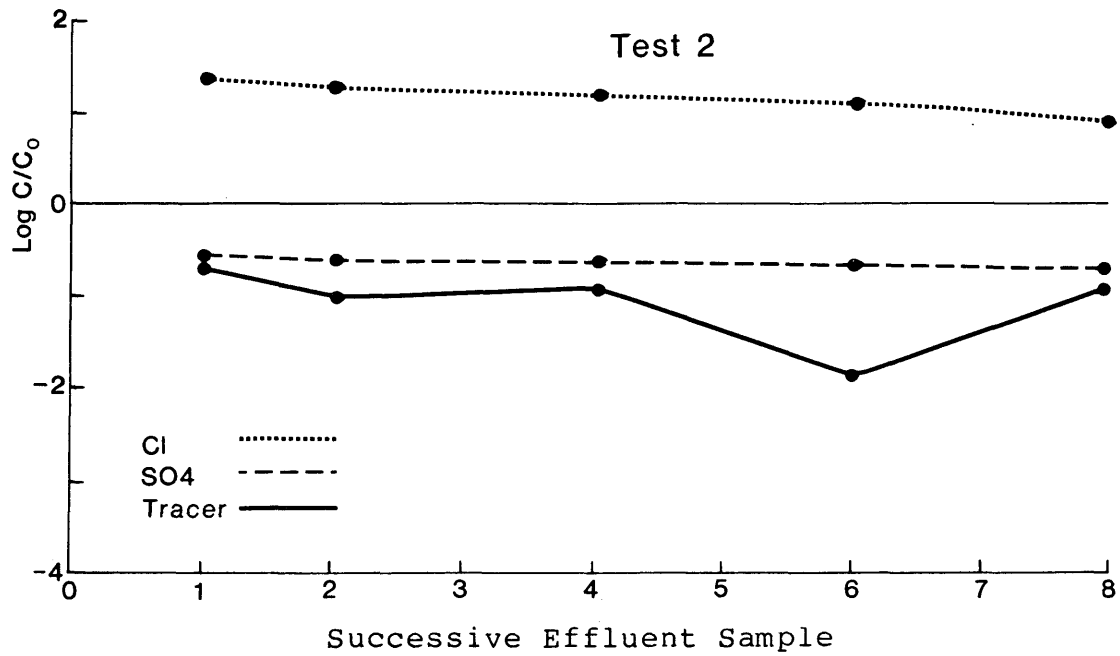


Figure 5. Results of Column Test 2 Using Difluorotetrachloroethane as the Organic Tracer and Alluvial Soil as the Porous Material.

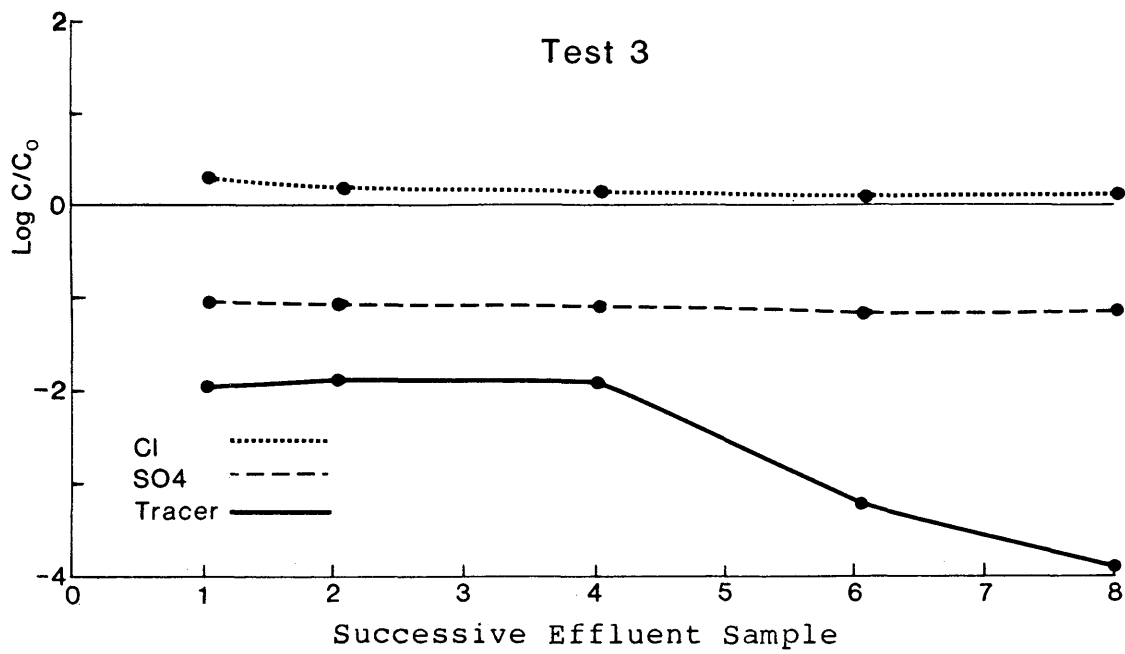


Figure 6. Results of Column Test 3 Using Difluorotetrachloroethane as the Organic Tracer and Arroyo Soil as the Porous Material.

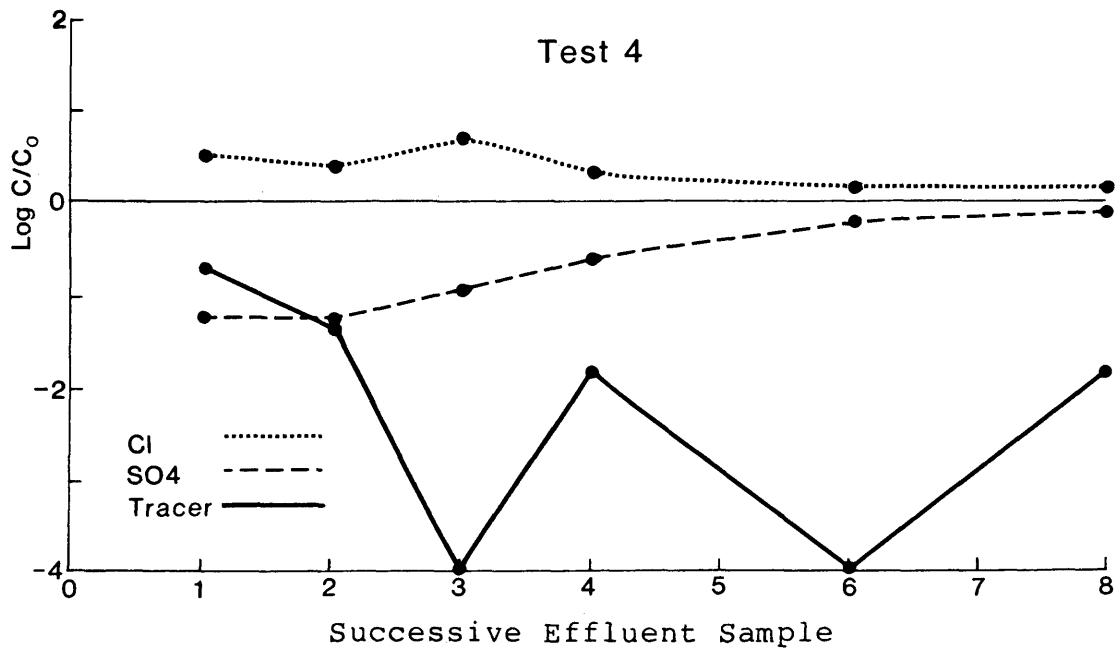


Figure 7. Results of Column Test 4 Using Difluorotetrachloroethane as the Organic Tracer and Uranium Mill Tailings as the Porous Material.

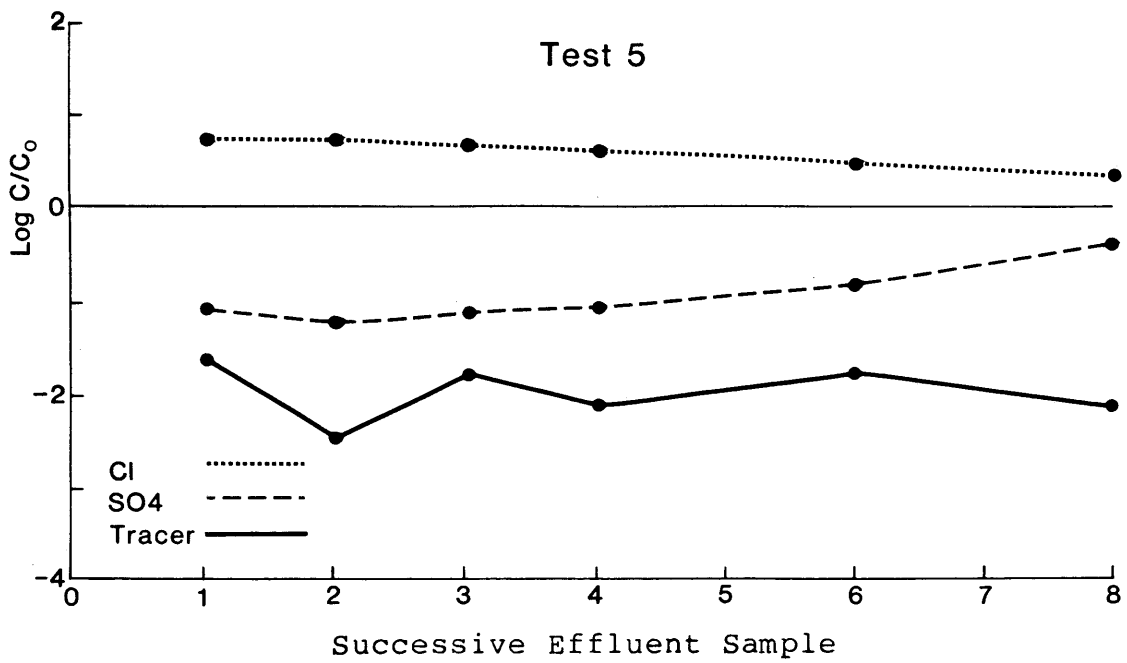


Figure 8. Results of Column Test 5 Using Trifluorotrchloroethane as the Organic Tracer and Uranium Mill Tailings as the Porous Material.

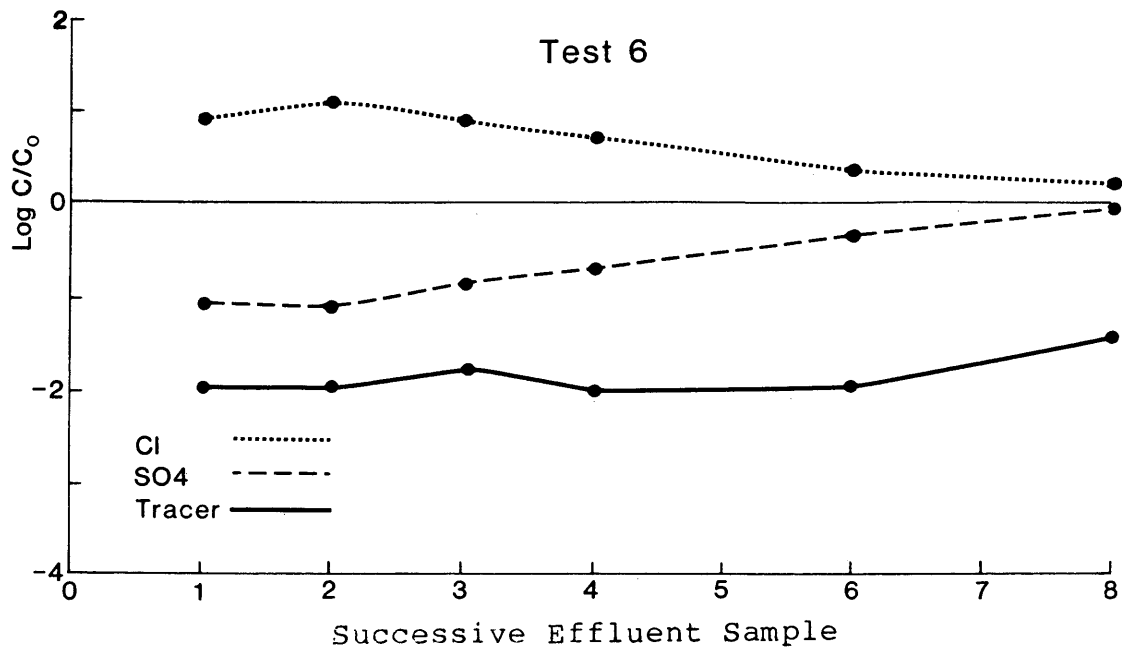


Figure 9. Results of Column Test 6 Using Trifluorotrchloroethane as the Organic Tracer and Uranium Mill Tailings as the Porous Material.

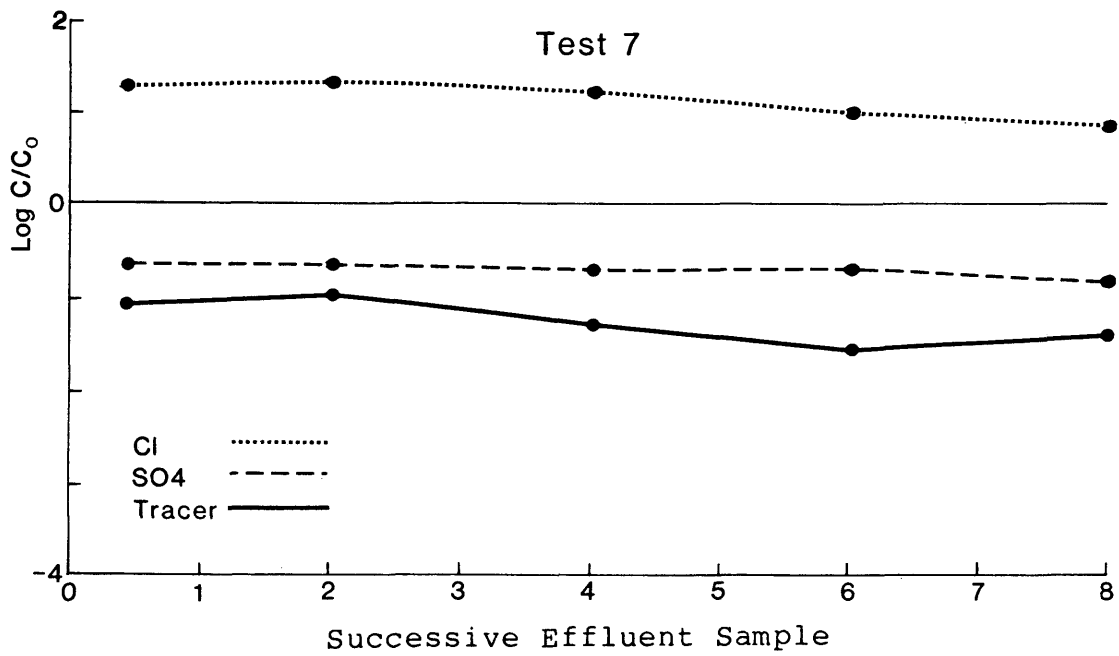


Figure 10. Results of Column Test 7 Using Trifluorotrchloroethane as the Organic Tracer and Alluvium Soil as the Porous Material.

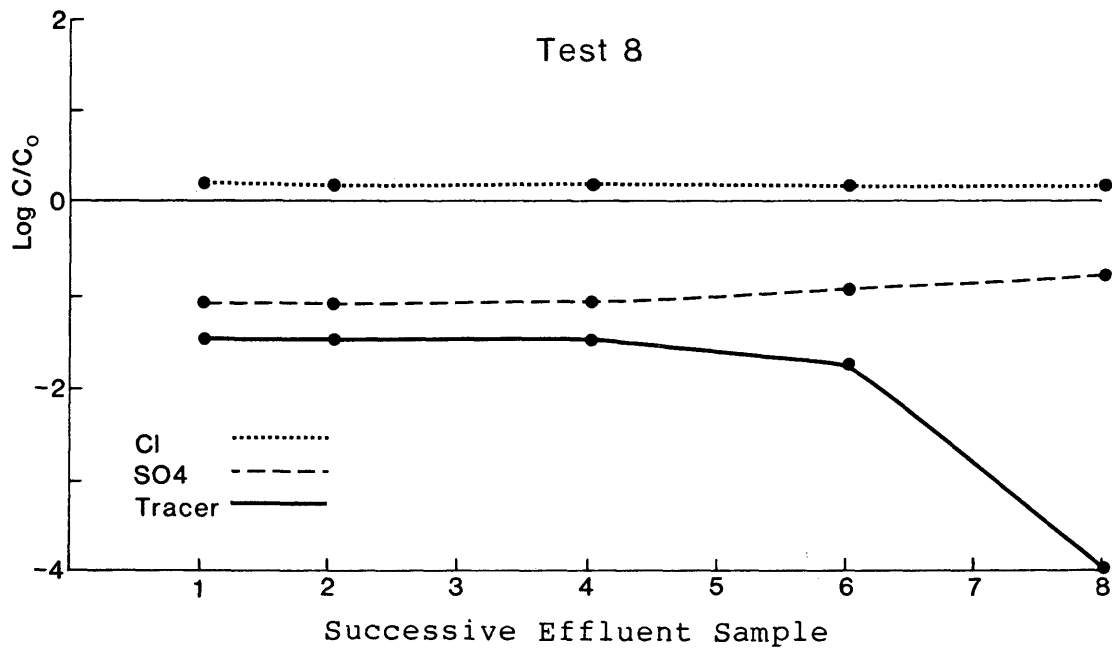


Figure 11. Results of Column Test 8 Using Trifluorotrchloroethane as the Organic Tracer and Arroyo Soil as the Porous Material.

Figures 12 and 13 graphically represent the decrease with time of the organic tracer concentration in the uranium tailings water in the 19-liter storage containers. Both the difluorotetrachloroethane and the trifluorotrachloroethane tracer show a decrease in concentration with time. The difluorotetrachloroethane tracer concentration decreased approximately 2000 micrograms per liter in twelve days. The trifluorotrachloroethane tracer concentration decreased approximately 3500 micrograms per liter in six days.

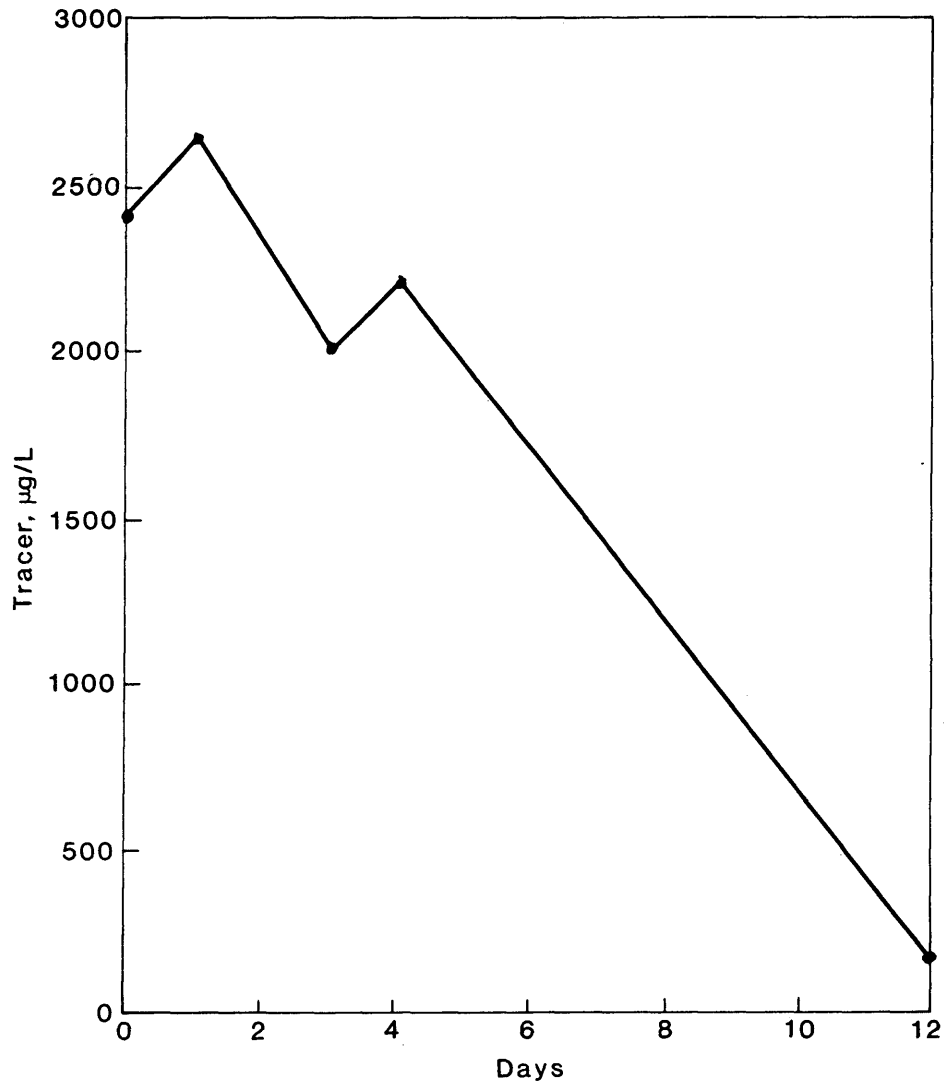


Figure 12. Concentration of Difluorotetrachloroethane Tracer in the Uranium Tailings Water Influent Mixture vs. Time in Units of Days.

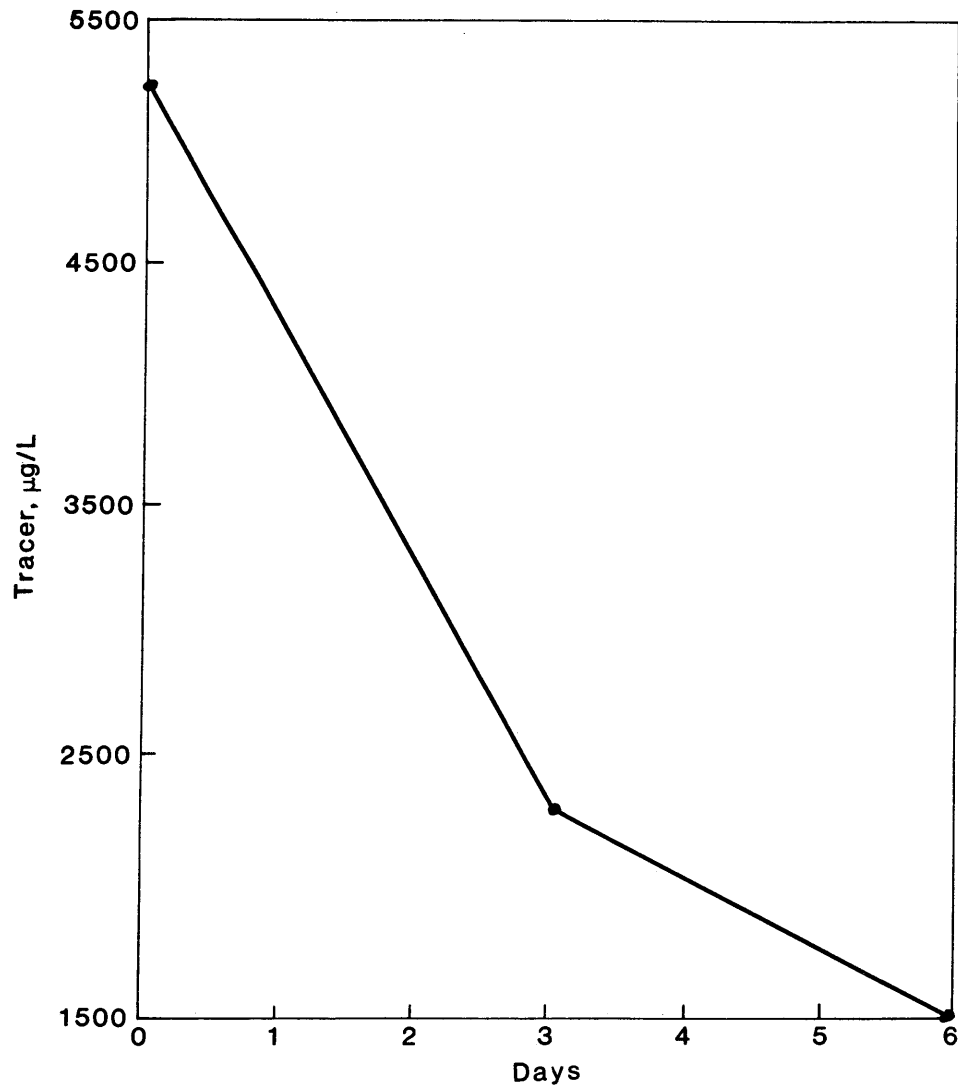


Figure 13. Concentration of Trifluorotrchloroethane Tracer in the Uranium Tailings Water Influent Mixture vs. Time in Units of Days.

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CHAPTER V: DISCUSSION

The combination of volatilization and reactive transformation has an adverse effect on the ability of the organic compounds tested to be successfully used as tracers in uranium tailings seepage studies. Both processes reduced the organic tracer concentration in the uranium tailings water.

Chromatographic dispersion is a very complex phenomenon, as demonstrated by equation (7) (p. 13). Normally advection, dispersion, and sorption are the only processes included in chromatographic dispersion, and other processes such as volatilization and reactive transformation are treated separately. Volatilization effects are not important in the study of the inorganic species transport, but they are important in the study of the organic species transport. Reactive transformation effects are very important in studying the transport of the organics. When volatilization and reactive transformation processes are combined with chromatographic dispersion, the overall transport of the tracer describes the chemodynamics of that tracer. The plots of the $\log C/C_0$ vs. time for the different tracer species presented in Chapter IV represent the chemodynamics of the different tracer species.

Organic Tracer Compounds

It is difficult to distinguish the volatilization effects from the reactive transformation effects on the organic tracer transport in the test columns. The plot of the log C/C_0 vs. time for the volatilization batch test, as shown in Figure 12, indicates that there may be significant organic concentration losses due to volatilization. Figures 13 and 14 also support the argument that the concentration of the organic tracer in the uranium tailings water is being reduced by volatilization, but it may also be due to transformation reactions.

Compared to the column tests the volatilization batch test occurred over a long time period: 4 days for the batch test versus 1 day for the column tests. The decrease in the organic tracer concentration in the uranium tailings water was observed over a long time period also, 6 and 12 days. Figures 4 through 12 in Chapter V show that the log C/C_0 value for the organic compound does not approach zero for any of the column tests. This means that the concentration of the organic compound is reduced by some process as the solution migrates through the column material. Based upon the large negative values for the log C/C_0 , the reduction is significant. The detection limit in terms of log C/C_0 would be represented by a -12 value. Since the time variable is less in the column tests than in the batch test, the volatil-

ization effects are less. The volatilization rate would also be reduced by the fact that the top of the porous material was always kept wet and there was always a downward movement of the tracer solution.

The decreased organic concentration observed in the effluent of the column tests cannot be due totally to volatilization; therefore, some other processes must be occurring to reduce the influent concentration to the effluent levels. The reduction is due to either the transformation of the organic compound by a chemical reaction or the adsorption of the compound by the organic matter in the tailings and soil material. In order to definitively evaluate the adsorption of the organic tracer, an analysis of the porous material for total organic carbon (TOC) matter is required. The TOC analyses were not incorporated into this research investigation. The determination of the amount of the organic tracer adsorbed by the TOC was not attempted for this investigation because the purpose was not to determine the exact mechanism(s) of the tracer chemodynamics.

The various transformation reactions that may have taken place within the uranium tailings water, or within the column as the tracer solution migrated down through the porous material, are summarized in Chapter II. The decrease in the concentration of the organic tracer in the uranium tailings water with time (see Figures 13 and 14) may not have

been totally due to volatilization effects. Because the pH of the tracer solution was so low, pH = 2, and because there are acidic components in the solution other than the hydrogen ion, acid-catalysis hydrolysis may be a major reaction mechanism.

The plots of $\log C/C_0$ vs. time for the column tests suggest that the rate of acid-catalyzed hydrolysis increases when there is a sediment surface area available for interaction between the aqueous and solid phases. The redox and pH of the environment system would indicate that the above reaction is the predominant one.

The hydrolysis reaction described in Chapter II is a first order reaction. The hydrolysis mechanism of a halogenated organic compound in a very acidic solution may be a second-order reaction. The rate can be expressed as:

$$\text{rate} = k [\text{H}_3\text{O}^+] [\text{R-C-X}],$$

where:

k = the acid-catalysis rate constant,

H_3O^+ = the hydronium concentration, and

R-C-X = the halogenated organic concentration.

The above acid-catalyzed hydrolysis reaction is not observed in a normal groundwater environment with a pH range of 6 to 8. In order to determine the exact reaction mechanism(s) the transformation products and their respective concentrations are needed. These concentrations were not measured for this

investigation, because a determination of the exact reaction mechanism(s) was not an objective of this study.

Chloride

The chloride concentration in the effluent samples varied with the tailings material used. There were two tailings bulk samples collected. The different observed effluent concentrations can be explained by the fact that at this specific standby uranium mill site a chemical binder had been utilized to reduce wind-blown particulate matter from the tailings pile. The chemical binder was a Mg-Cl base solution which was sprayed on the top of the tailings. The first bulk sample was obtained from an area in which the binder was used. The low pH of the uranium solution dissolved the Mg-Cl as the solution percolated through the porous material, and the effluent chloride concentrations were elevated above the influent levels (by a factor of 10 in some cases). As the chloride was leached out, the chloride concentration decreased in the column effluent. The second bulk tailings sample was from an area where the binder was not used. The elevated chloride concentrations in the second bulk sample were due to the chloride salt residue as a result of evaporation during disposition. The chloride concentration in the effluent from the second bulk sample also showed a decrease with time, but the initial concentrations were not

as elevated as those with the first tailings bulk sample. The alluvial soil column tests also showed elevated chloride effluent concentrations when compared with the arroyo soil. The mineral compositions of the two bulk soil samples do not indicate why this phenomenon should occur.

Sulfate

The concentration of sulfate in the column effluent samples behaved as expected. At first, the sulfate concentration would be low due to the adsorptive reactions, and then increase as the total pass-through volume increases. The breakthrough point is where, with respect to location or when with respect to time, the effluent concentration approaches the influent concentration, i.e., $\log C/C_0 =$ zero. The tailings column tests show that it takes approximately 8 effluent sample volumes (400 to 500 ml) for this breakthrough to occur for sulfates. Due to the adsorptive properties of the soils, the sulfate migration front concentration did not approach the zero value for the $\log C/C_0$. The ability of the $\log C/C_0$ vs. time plots to describe the overall chemodynamics of a specific constituent in a column test is confirmed by the sulfate concentrations measured in the column effluent samples.

CHAPTER VI: CONCLUSIONS AND RECOMMENDATIONS

The primary objective of this investigation was to determine if two halogenated hydrocarbons, difluorotetrachloroethane and trifluorotrchloroethane, can be used as tracers in the study of uranium tailings seepage. In order to accomplish this objective, the distribution or transport of the two proposed tracers in a uranium tailings environment were investigated.

Halogenated hydrocarbons generally do not degrade or undergo transformation reactions very fast in natural environments, even though their migration may be retarded by chromatographic dispersion. The migration of the two halogenated organic compounds tested in this research is adversely affected by an acid-catalyzed hydrolysis reaction in a relatively short time period. The hydrolysis reaction time period is less than one day when the organic tracer solution is in contact with the tailings or the soil material. The tailings and soil porous material seem to catalyze the transformation reaction.

The decrease of the organic tracer concentration in the uranium tailings water that was made up as a stock solution may also be due to an acid-catalyzed hydrolysis reaction. Based upon the results of the batch test, volatilization definitely has a significant effect on the transport of the organic tracers. The transport path is from the solution to

the atmosphere which means that the organic tracer cannot be utilized with any reliability in uranium tailings water environment.

The combined chemodynamic processes, especially chemical transformation and volatilization, adversely affect the ability of the organic compounds tested to be used as tracers in uranium tailings environments. The system environment is emphasized because fluorocarbon tracers are successfully utilized in other applications, such as surface streams and "normal pH" aquifers. Additional research should be conducted to ascertain the exact transformation products of the halogenated hydrocarbon tracers for two reasons:

- 1) to confirm the results of this research, and
- 2) to determine if an acidic aqueous phase could be utilized to transform other halogenated hydrocarbons that have been discharged into the groundwater and present a potential environmental problem.

The additional research should be conducted at a location where there is immediate access to a gas chromatograph, so that the organic tracer concentration in the influent and effluent can be determined as quickly as possible. Also, additional volatilization tests need to be conducted. A recommendation would be to determine the volatilization rate of the organic compounds in water at different pH's, such as

6, 4, 3, and 2, and compare the results with additional uranium tailings solution tests.

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Appendix A

Test Series

Test 1

tracer: Difluorotetrachloroethane
 column material: tailings
 column 1 influent: constant tracer/uranium solution
 column 2 influent: spike (first aliquot-tracer/uranium
 solution; all aliquots thereafter nontracer uranium
 water)

effluent volumes collected	column 1 sample #	column 2 sample #
first 50 ml	1-c	1-s
second 50 ml	2-c	2-s
third 50 ml	3-c	3-s
fourth 50 ml	4-c	4-s
fifth 50 ml	5-c	5-s
sixth 50 ml	6-c	6-s
seventh 50 ml	---not analyzed---	---
eighth 50 ml	8-c	8-s

total effluent volume collected = 400 ml

Test 2

tracer: Difluorotetrachloroethane
 column material: alluvial soil
 column 1 influent: constant tracer/uranium solution
 column 2 influent: spike (first aliquot-tracer/uranium
 solution; all aliquots thereafter nontracer uranium
 water)

effluent volumes collected	column 1 sample #	column 2 sample #
first 50 ml	1-c	1-s
second 50 ml	2-c	2-s
third 50 ml	---not analyzed---	---
fourth 50 ml	4-c	4-s
fifth 50 ml	---not analyzed---	---
sixth 50 ml	6-c	6-s
seventh 50 ml	---not analyzed---	---
eighth 50 ml	8-c	8-s

total effluent volume collected = 400 ml

Test 3

tracer: Difluorotetrachloroethane
 column material: arroyo soil
 column 1 influent: constant tracer/uranium solution
 column 2 influent: spike (first aliquot-tracer/uranium solution; all aliquots thereafter nontracer uranium water)

effluent volumes collected	column 1 sample #	column 2 sample #
first 50 ml	1-c	1-s
second 50 ml	2-c	2-s
third 50 ml	---not analyzed---	
fourth 50 ml	4-c	4-s
fifth 50 ml	---not analyzed---	
sixth 50 ml	6-c	6-s
seventh 50 ml	---not analyzed---	
eighth 50 ml	8-c	8-s

total effluent volume collected = 400 ml

Test 4 - repeat spike test

tracer: Difluorotetrachloroethane
 column material: tailings (second bulk sample)
 column 1 influent: no constant test
 column 2 influent: spike (first aliquot-tracer/uranium solution; all aliquots thereafter nontracer uranium water)

effluent volumes collected	column 1 sample #	column 2 sample #
first 50 ml		1-s
second 50 ml		2-s
third 50 ml		3-s
fourth 50 ml		4-s
fifth 50 ml		not analyzed
sixth 50 ml		6-s
seventh 50 ml		not analyzed
eighth 50 ml		8-s

total effluent volume collected = 400 ml

Test 5

tracer: Trifluorotrchloroethane
 column material: tailings (second bulk sample)
 column 1 influent: constant tracer/uranium solution
 column 2 influent: spike (first aliquot-tracer/uranium solution; all aliquots thereafter nontracer uranium water)

effluent volumes collected	column 1 sample #	column 2 sample #
first 50 ml	1-c	1-s
second 50 ml	2-c	2-s
third 50 ml	3-c	3-s
fourth 50 ml	4-c	4-s
fifth 50 ml	---not analyzed---	
sixth 50 ml	6-c	6-s
seventh 50 ml	---not analyzed---	
eighth 50 ml	8-c	8-s

total effluent volume collected = 400 ml

Test 6 - repeat spike test

tracer: Trifluorotrchloroethane
 column material: tailings (first bulk sample)
 column 1 influent: no constant test
 column 2 influent: spike (first aliquot-tracer/uranium solution; all aliquots thereafter nontracer uranium water)

effluent volumes collected	column 1 sample #	column 2 sample #
first 50 ml		1-s
second 50 ml		2-s
third 50 ml		3-s
fourth 50 ml		4-s
fifth 50 ml		not analyzed
sixth 50 ml		6-s
seventh 50 ml		not analyzed
eighth 50 ml		8-s

total effluent volume collected = 400 ml

Test 7

tracer: Trifluorotrchloroethane
 column material: alluvial soil
 column 1 influent: constant tracer/uranium solution
 column 2 influent: spike (first aliquot-tracer/uranium
 solution; all aliquots thereafter nontracer uranium
 water)

effluent volumes collected	column 1 sample #	column 2 sample #
first 50 ml	1-c	1-s
second 50 ml	2-c	2-s
third 50 ml	---not analyzed---	
fourth 50 ml	4-c	4-s
fifth 50 ml	---not analyzed---	
sixth 50 ml	6-c	6-s
seventh 50 ml	---not analyzed---	
eighth 50 ml	8-c	8-s

total effluent volume collected = 400 ml

Test 8

tracer: Trifluorotrchloroethane
 column material: arroyo soil
 column 1 influent: constant tracer/uranium solution
 column 2 influent: spike (first aliquot-tracer/uranium
 solution; all aliquots thereafter nontracer uranium
 water)

effluent volumes collected	column 1 sample #	column 2 sample #
first 50 ml	1-c	1-s
second 50 ml	2-c	2-s
third 50 ml	---not analyzed---	
fourth 50 ml	4-c	4-s
fifth 50 ml	---not analyzed---	
sixth 50 ml	6-c	6-s
seventh 50 ml	---not analyzed---	
eighth 50 ml	8-c	8-s

total effluent volume collected = 400 ml

Test 9

tracer: Trifluorotrachloroethane
 column material: tailings/alluvial soil
 column 1 influent: constant tracer/uranium solution
 column 2 influent: spike (first aliquot-tracer/uranium
 solution; all aliquots thereafter nontracer uranium
 water)

effluent volumes collected	column 1 sample #
first 50 ml	1-s
second 50 ml	2-s
third 50 ml	3-s

total effluent volume collected = 150 ml

Test 10

tracer: Difluorotetrachloroethane
 column material: tailings/alluvial soil
 column 1 influent: constant tracer/uranium solution
 column 2 influent: spike (first aliquot-tracer/uranium
 solution; all aliquots thereafter nontracer uranium
 water)

effluent volumes collected	column 2 sample #
first 50 ml	1-s
second 50 ml	2-s
third 50 ml	3-s

total effluent volume collected = 150 ml

Batch Test (Control)

Beaker No.	porous material	organic tracer
1	tailings	trifluorotrichloroethane
2	alluvial soil	trifluorotrichloroethane
3	arroyo soil	trifluorotrichloroethane
4	tailings	difluorotetrachloroethane
5	alluvial soil	difluorotetrachloroethane
6	arroyo soil	difluorotetrachloroethane
volatilization check		
7	liquid only	trifluorotrichloroethane
8	liquid only	difluorotetrachloroethane

Appendix B

Table 7

Results of Column Test #1 Using
Difluorotetrachloroethane as the Organic Tracer
and Uranium Mill Tailings as the Porous Material

sample	Cl mg/l	SO4 mg/l	tracer ug/l
influent	435	35400	2400
duplicate (lab 1)	460	36000	2200
duplicate (lab 2)	520	31000	1800
effluent samples 50 ml each			
1-constant	5000	2600	800
1-spike	4500	3100	610
2-c	4300	4300	260
2-s	4300	3100	125
3-c	3300	4200	0
3-s	3200	5000	40
4-c	2300	8600	14
4-s	2900	11000	32
5-c	2100	14000	0
5-s	1700	16000	45
6-c	1400	18000	12
6-s	1300	21000	32
8-c	700	24000	0
8-s	700	28000	28

Table 8

Results of Column Test #2 Using
Difluorotetrachloroethane as the Organic Tracer
and Alluvial Soil as the Porous Material

sample	Cl mg/l	SO4 mg/l	tracer ug/l
influent	420	37000	2600
duplicate (lab 2)	480	30000	2200
effluent samples 50 ml each			
1-constant	7900	9700	610
1-spike	8100	7400	100
2-c	7200	8400	200
2-s	8000	7100	40
4-c	5900	8300	290
4-s	6300	7000	33
6-c	5200	7600	28
6-s	4500	6700	0
8-c	4400	7300	290
8-s	4100	7400	45

Table 9

Results of Column Test #3 Using
Difluorotetrachloroethane as the Organic Tracer
and Arroyo Soil as the Porous Material

sample	Cl mg/l	SO4 mg/l	tracer ug/l
influent	420	37000	2600
effluent samples 50 ml each			
1-constant	700	3600	33
1-spike	500	3700	0
2-c	570	3500	38
2-s	540	4000	40
4-c	560	3500	38
4-s	520	3700	40
6-c	540	3300	46
6-s	560	4000	2
8-c	550	3400	5
8-s	540	4400	3

Table 10

Results of Column Test #4 Using
Difluorotetrachloroethane as the Organic Tracer
and Uranium Mill Tailings as the Porous Material*

sample	Cl mg/l	SO4 mg/l	tracer ug/l
influent	500	36000	2000
effluent samples 50 ml each			
1-spike	1500	2000	400
2-s	1100	2000	90
3-s	2000	3900	0
4-s	1000	7700	30
6-s	700	20000	0
8-s	700	28000	28

* different collection area for tailings bulk sample

Table 11

Results of Column Test #5 Using
Trifluorotrchloroethane as the Organic Tracer
and Uranium Mill Tailings as the Porous Material*

sample	Cl mg/l	SO4 mg/l	tracer ug/l
influent	470	35000	5100
duplicate (lab 1)	420	32000	4600
effluent samples 50 ml each			
1-constant	2000	2400	120
1-spike	1800	2300	44
2-c	2000	2200	17
2-s	1750	2300	0
3-c	1800	2300	58
3-s	1500	2500	51
4-c	1700	2400	28
4-s	1300	2800	37
6-c	1400	4800	75
6-s	1100	9000	69
8-c	1000	15000	31
8-s	800	20000	109

* second tailings area

Table 12

Results of Column Test #6 Using
Trifluorotrchloroethane as the Organic Tracer
and Uranium Mill Tailings as the Porous Material

sample	Cl mg/l	SO4 mg/l	tracer ug/l
influent	470	35000	5100
duplicate (lab 1)	420	32000	4600
effluent samples 50 ml each			
1-spike	3700	2800	60
2-s	4800	2800	62
3-s	3600	3900	77
4-s	2700	6200	49
6-s	1000	15000	56
8-s	700	27000	210

Table 13

Results of Column Test #7 Using
Trifluorotrchloroethane as the Organic Tracer
and Alluvial Soil as the Porous Material

sample	Cl mg/l	S04 mg/l	tracer ug/l
influent	450	34000	2300
effluent samples 50 ml each			
1-constant	7100	7900	180
1-spike	8000	6400	60
2-c	7500	8100	230
2-s	8000	6900	20
4-c	6600	7600	160
4-s	6100	7000	45
6-c	5000	7500	80
6-s	5100	6900	40
8-c	3600	5200	90
8-s	3600	5400	0

Analytical results from lab 2

Table 14

Results of Column Test #8 Using
Trifluorotrchloroethane as the Organic Tracer
and Arroyo Soil as the Porous Material

sample	Cl mg/l	SO4 mg/l	tracer ug/l
influent	450	34000	2300
effluent samples 50 ml each			
1-constant	600	3200	92
1-spike	500	3100	45
2-c	560	3200	97
2-s	500	3200	0
4-c	570	3300	90
4-s	600	3100	40
6-c	550	4000	36
6-s	560	3700	55
8-c	550	4600	0
8-s	520	4200	0

Analytical results from lab 2

Table 15

Results of Column Test #9 Using
Trifluorotrchloroethane as the Organic Tracer
and Tailings/Alluvial Soil as the Porous Material

sample	Cl mg/l	SO4 mg/l	tracer ug/l
influent	470	34000	1500
effluent samples 50 ml each			
1-spike	1200	3500	0
2-s	1400	3700	0
3-s	2000	7000	0

Table 16

Results of Column Test #10 Using
Difluorotetrachloroethane as the Organic Tracer
and Tailings/Alluvial Soil as the Porous Material

sample	Cl mg/l	S04 mg/l	tracer ug/l
influent	500	36000	150
effluent samples 50 ml each			
1-spike	1500	4300	0
2-s	1300	3500	0
3-s	2400	7400	0

Table 17
Results of the Batch Tests

sample	Cl mg/l	SO4 mg/l	tracer ug/l
<u>Trifluorotrachloroethane tracer</u>			
starting solution	470	35000	5100
after 4 days of intermittent mixing			
tailings	1500	39000	34
alluvial	1000	11000	5
arroyo	600	7500	81
volatilization (liquid only)	500	36000	103
<u>Difluorotetrachloroethane tracer</u>			
starting solution	450	35000	2200
after 4 days of intermittent mixing			
tailings	1700	33000	520
alluvial	1000	16000	0
arroyo	500	8000	0
volatilization (liquid only)	530	33000	60