Age Dating Groundwater Plumes Based on the Ratio of 1,1-Dichloroethylene to 1,1,1-Trichloroethane: An Uncertainty Analysis

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In principle, when 1,1-dichloroethylene (DCE) is formed from the hydrolysis of 1,1,1-trichloroethane (TCA), the ratio of DCE to TCA can be used to determine how long hydrolysis has been occurring and, consequently, the age of a TCA release to groundwater. The rate of hydrolysis appears to depend only on groundwater temperature, and sorption does not appear to have a significant effect on the hydrolysis rate. This article focuses on the uncertainties and biases in estimating the age of a TCA release from DCE/TCA ratios.

Two methods are examined: (1) the use of one-time ratio measurements together with a laboratory-derived hydrolysis rate constant and (2) the use of time series data collected over a number of years. When the uncertainty in concentration measurements is small, the principal uncertainty for one-time measurements is due to the uncertainty in estimating the rate of hydrolysis at groundwater temperatures from laboratory data. For one-time measurements, we estimate 95% confidence levels for time estimates under favorable conditions of about ±25%. When time series data are available, using these data may be more or less accurate. The principal source of uncertainty then is due to uncertainty in concentration measurements. In interpreting field data, the age obtained should be recognized as an average based on when contact between water and TCA began. This may be different than a spill date for pure phase spills of TCA. Under some circumstances time estimates can be made when biodegradation of TCA as well as hydrolysis occurs.

Keywords: solvent, degreasing, uncertainty, hydrolysis, TCA

Introduction

Because of its historical use as a vapor degreasing and cold cleaning solvent, 1,1,1-trichloroethane (TCA) is now frequently detected at chemical contamination sites, including about half of all National Priority List sites (ATSDR, 2002). TCA was first produced in commercial quantities in the United States by Dow Chemical Company in 1954 under the trade name Chlorothen (C&E News, 1962). It was initially used as a cold cleaning solvent for machinery, particularly electrical machinery because of its excellent solvency for waxes, oils, and greases but limited solvent action on electrical insulating varnishes (Standen, 1964). Widespread use of TCA began in the 1960s when it replaced carbon tetrachloride as the cold cleaning solvent of choice. In the 1970s, TCA supplanted trichloroethylene (TCE) as a vapor degreasing solvent after issues were raised regarding TCE’s effect on ozone formation as well as its potential carcinogenicity (Doherty, 2000; Morrison and Murphy, 2002).

At chemical contamination sites where TCA has been detected and multiple owner/operators have been identified, searches for the party responsible for the cleanup often involve a determination of when a release occurred. Smith et al. (1994) have suggested that the ratio of 1,1-dichloroethylene (DCE) to TCA can be used to date a release based on the rate of chemical hydrolysis of TCA. Inherent in this approach are a number of assumptions, including that:

- the hydrolysis rate constant can be determined with acceptable accuracy, either based on laboratory data or field measurements;
- the rate of hydrolysis is constant over time, i.e., the groundwater temperature is constant over time;
- biodegradation of TCA and DCE is either unimportant or can be adequately modeled;
- the effects of chromatographic separation or differing volatilization rates on the DCE/TCA ratio are either negligible or can be modeled; and
- the length of time that hydrolysis has occurred can be related to the date of release.

In this article, we address these issues with respect to the uncertainty in age-dating TCA releases based on DCE/TCA ratios.

Background

A number of studies have shown that the chemical hydrolysis of TCA leads to the formation of DCE and acetic acid (Vogel and McCarty, 1987a; Cline and Delfino, 1989). The reaction proceeds via loss of chlorine and formation of a chemical intermediate that subsequently undergoes either elimination of
hydrogen (dehydrochlorination) to yield DCE or a series of substitution reactions to yield acetic acid. The first step in either pathway is the same—loss of chlorine and formation of the carbocation intermediate (CH₃C⁺Cl₂):

\[ \text{CH}_3\text{C}l_2 \rightarrow \text{CH}_3\text{C}^+\text{C}l_2 + \text{Cl}^- \]  

(1)

Formation of the carbocation is the rate-limiting step. The carbocation is then capable of undergoing nucleophilic substitution, via several steps, to yield HCl and the hydrolysis product, acetic acid, as shown in Eq. (2a):

\[ \text{CH}_3\text{C}^+\text{C}l_2 + \text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} \text{ (acetic acid)} + 3\text{HCl} \]  

(2a)

Or, the carbocation can undergo elimination of hydrogen (resulting in net dehydrochlorination of the TCA) to yield DCE and HCl as shown in Eq. (2b):

\[ \text{CH}_3\text{C}^+\text{C}l_2 + \text{Cl}^- \rightarrow \text{CH}_2 = \text{C}l_2 + 1,1-\text{DCE} + \text{HCl} \]  

(2b)

This mechanism, initial formation of a carbocation followed by formation of competing substitution/elimination products, is referred to as the SN1/E1 mechanism and is well known in organic chemistry (March, 1985). Because the rates of the substitution and elimination reactions depend on the initial formation of the carbocation, and because formation of the carbocation is the rate-limiting step for both reactions, both reactions are first order and the temperature dependence of the rate of TCA loss can be described by a single Arrhenius equation. This temperature dependence has been demonstrated by a number of researchers at temperatures generally ranging from about 25 to 120 °C (Clénet and Delahay, 1989; Haag and Mill, 1988, Gerkens and Franklin, 1989; Jeffers et al., 1989). The general form of the Arrhenius equation is shown in Eq. (3):

\[ k = A e^{-\frac{E_a}{R T}} \]  

(3)

where \( k \) is the first order rate constant for TCA loss, \( A \) is the Arrhenius constant, \( E_a \) is the activation energy (kJ/mol), \( R \) is the gas constant (8.3145 × 10⁻³ kJ/mol-K), and \( T \) is the absolute temperature in Kelvin. The total abiotic degradation rate constant for TCA is equal to the sum of the individual rate constants for the substitution and elimination pathways as indicated in Eq. (4) where the subscripts \( s \) and \( e \) refer to reactions expressed in Eq. (2a) (substitution) and Eq. (2b) (elimination), respectively:

\[ k = k_s + k_e \]  

(4)

From the kinetic equations:

\[ [\text{TCA}] = [\text{TCA} \text{ at } t=0] e^{-k t} \]  

(5)

and

\[ [\text{DCE}] = \frac{k_e}{k_s} [\text{TCA} \text{ at } t=0] (1 - e^{-k t}) \]  

(6)

where \( t \) is the time and where bracketed quantities are molar. It follows that the elapsed time may be estimated by

\[ t = \frac{1}{k_s} \ln \left(1 + \frac{k_e [\text{DCE}]}{k_s [\text{TCA}]} \right) \]  

(7)

The elapsed time can be obtained by substituting values in the right side of Eq. (7) (Method 1). Alternatively, if one has time series data, the logarithm term in Eq. (7) can be plotted on the \( y \) axis versus time on the \( x \) axis. A best-fit straight line then has a slope equal to the estimated \( k \) and an \( x \) intercept equal to the estimated date at which hydrolysis began (Method 2). To our knowledge, no one has performed a detailed assessment of the uncertainty associated with time estimates obtained using either of these techniques. This is a task that we now undertake.

**Uncertainty Using Method 1**

Using Method 1, the time elapsed from the onset of hydrolysis can be estimated from a single measurement of the molar ratio of \( [\text{DCE}]/[\text{TCA}] \) and a measurement of the groundwater temperature. The rate of hydrolysis at temperature \( T \) and the fraction of DCE formed \( (k_e/k) \) can be derived from laboratory data.

In Eq. (7), \( t \) is a function of the variable \( k, a = [\text{DCE}]/[\text{TCA}] \), and \( b = k_e/k \). Denote any one of these variables as \( x_i \). Then since the \( x_i \) are uncorrelated, and, as described below, can be assumed to have relative uncertainties \( \delta x_i/x_i < 1 \), the uncertainty in \( t \) is given by the theory of error propagation (Mandel, 1964) as

\[ \delta t = \left( \sum_{i=1}^{n} \left( \frac{\partial t}{\partial x_i} \right)^2 \delta x_i^2 \right)^{1/2} \]  

(8a)

where \( i = 1, 2, \ldots n \) and \( n \) is the number of variables. Dividing both sides of Eq. (8a) by \( t \) gives

\[ \frac{\delta t}{t} = \sqrt{\sum_{i=1}^{n} \left( \frac{\partial \ln t}{\partial x_i} \right)^2 \delta x_i^2} \]  

(8b)

For our case, \( x_1 = k, x_2 = a, x_3 = b, \) and \( \ln t \) is found from Eq. (7). Carrying out the indicated differentiation and adding terms inside the square root gives

\[ \frac{\delta t}{t} = \left( \frac{\delta k}{k} \right)^2 + \frac{\left( \frac{\delta a}{a} \right)^2 + \left( \frac{\delta b}{b} \right)^2}{(\ln(1 + \frac{a}{b}))^2 (1 + \frac{a}{b})^2} \]  

(9)

The uncertainty in \( \delta k \) derives from two sources: first, the uncertainty in estimating \( k \) from an Arrhenius plot of laboratory data assuming no error in \( T \); and second, the uncertainty in the groundwater temperature \( T \). A corroboring to Eq. (3),

\[ k = k_0 e^{-\frac{E_a}{R T}} \]  

(10)
where \( k_0 \) is the value of \( k \) at temperature \( T_0 \) based on laboratory experiments assuming no error in \( T_0 \). Thus, applying Eq. (8b) for \( k \) instead of \( t \) we obtain

\[
\delta k \over k = \sqrt{\left( \delta k_0 \over k_0 \right)^2 + \left( E_a \over RT \right)^2 \left( \delta T \over T \right)^2} \tag{11}
\]

Combining Eqs. (9) and (11) yields the overall equation for the relative uncertainty in \( t \):

\[
\delta t \over t = \sqrt{\left( \delta k_0 \over k_0 \right)^2 + \left( E_a \over RT \right)^2 \left( \delta T \over T \right)^2 + \left( \ln(1 + \delta V_\alpha) \right)^2 \left(1 + \delta V_\alpha \right)^2} \tag{12}
\]

We now discuss the relative uncertainties in \( k_0 \), the ratio \( k \_C \_F \_C \_k \), \( T \), and the ratio \([\text{DCE}] / [\text{TCA}] \).

**Relative Uncertainty in \( k_0 \)**

The hydrolysis of TCA has been examined by a number of researchers (Walraevens et al., 1974; Pearson and M. Connell, 1975; Dilling et al., 1975; Mabey et al., 1983; Vogel and M. Carty, 1987; Reinhard and M. Carty, 1993), but only one study involved temperatures below 25°C, representative of groundwater conditions.\(^1\) Pearson and M. Connell (1975) recorded a single measurement at a temperature of 10°C. Estimating rate constants at other temperatures requires construction of an Arrhenius plot. For the purpose of estimating the uncertainty in the predicted rate of hydrolysis of TCA at any temperature \( T = T_0 \), we constructed Arrhenius plots from data presented by Haag and Mill (1988), Gerkens and Franklin (1989), Cline and Delino (1989), and Jeffers et al. (1989). We assume that the temperature uncertainty in these experiments is much less than uncertainties encountered in the field. Whatever temperature uncertainty exists in the laboratory is included in the estimates of \( \delta k / k \).

Haag and Mill (1988) studied the hydrolysis of TCA in distilled water and saturated sediment at temperatures ranging from 25 to 60°C. Experiments with distilled water were run in sealed containers with about 5% headspace. Experiments with saturated sediments allowed as much as 30% of the volume as headspace. Both DCE and acetic acid were detected as products of the reaction. The authors concluded that the presence of sediment did not affect the rate of reaction or the ratio of products.

Gerkens and Franklin (1989) studied the hydrolysis of TCA in demineralized water, saltwater, and in the presence of undissolved TCA. The authors noted no significant difference between rate constants measured in demineralized water and saltwater at a given temperature. Rate constants were corrected for the fraction of TCA in the headspace in the sealed vials used in the experiments (about 7% of the volume).

Cline and Delino (1989) performed a number of experiments at temperatures ranging from 28 to 70°C and pH levels ranging from 4 to 13. The authors estimated a half-life of 2.0 years at 20°C using an Arrhenius plot of these data and results from earlier analyses. Headspace ranged from about 7 to 13%.

Jeffers et al. (1989) reported hydrolysis rate constants for a number of chlorinated hydrocarbons including TCA. Experiments were carried out in solutions that were less than 10% saturated in TCA at relatively high temperatures ranging from 65 to 116°C and pH levels between 2 and 13. Experiments were conducted in both zero dead volume stainless steel tubes and glass vials with minimal headspace (about 3–4% by volume) but the TCA experiments were conducted in the latter (Jeffers personal communication). The authors estimated a TCA half-life of 1.1 years at 25°C. It should be noted that the authors were unable to detect any DCE in the reaction at any pH but suggest that instrument response may have been insufficient to detect the chlorinated product. Jeffers' results for the individual experiments, which have not been published previously, are given in Table 1.

Only Gerkens and Franklin uniformly corrected their data to account for TCA lost to the vapor phase. They estimated that the fraction of TCA in the liquid phase was 0.92 at 40°C, 0.89 at 50°C, and 0.79 at 80°C. We verified their correction values using the van't Hoff equation and enthalpy and entropy values given by Washington (1996) to calculate the Henry's Law constant at different temperatures. We then applied similar correction factors to rate constants reported by others, assuming 5% headspace in the Haag and Mill experiments, 10% headspace for the Cline and Delino experiments, and 3.5% headspace for the Jeffers data. The correction factor, \( \alpha \), was calculated using Eq. (13) as derived by Gerkens and Franklin:

\[
\alpha = \frac{1}{1 + V_v \_H \_R \_T} \tag{13}
\]

where \( V_v \) is the average fractional vapor phase volume and \( H \) is the Henry's Law constant. The parameter \( \alpha \) is the ratio of

**Table 1. TCA hydrolysis rate constants reported as a function of temperature (Jeffers, personal communication)**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate (×10^{-4} min^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>117</td>
<td>645</td>
</tr>
<tr>
<td>115</td>
<td>564</td>
</tr>
<tr>
<td>112</td>
<td>593</td>
</tr>
<tr>
<td>108</td>
<td>304</td>
</tr>
<tr>
<td>100</td>
<td>173</td>
</tr>
<tr>
<td>87</td>
<td>38.8</td>
</tr>
<tr>
<td>85</td>
<td>31.4</td>
</tr>
<tr>
<td>80</td>
<td>19.5</td>
</tr>
<tr>
<td>67</td>
<td>4.40</td>
</tr>
<tr>
<td>64</td>
<td>2.89</td>
</tr>
</tbody>
</table>
TCA mass in the liquid phase divided by total (liquid and vapor phase) TCA mass. The corrected value of $k$ is $1/\alpha$ times the uncorrected value. The temperature dependence of the Henry’s law constant $H$, as described by Washington (1996), is presented in Eq. (14):

$$\frac{H}{R} = 1.2186 \times 10^8 \exp \left( -\frac{3753}{T} + 8.456 \right)$$ (14)

After applying the appropriate correction factors, an Arrhenius plots were prepared from the corrected data sets for each of the studies as well as the combined data from all four studies. An Arrhenius plot of the data reported by Cline and Delino (1989) is shown in Figure 1. A least-squares fit to the data yields Eq. (15):

$$\ln(k) = -\frac{14768}{T} + 32.1$$ (15)

where $k$ is in seconds and $T$ is in degrees Kelvin. This corresponds to an Arrhenius constant $A = 8.7 \times 10^{12}$ and an activation energy $E_a = 122.8 \text{ kJ/mol-K}$ in Eq. (3).

The uncertainty in $\ln(k)$ predicted from the Arrhenius equation can be estimated using regression analysis. The 95% confidence limits (95% C.L.) about the predicted value of $y$ in a standard regression equation of $y = b_1x + b_0$ (where $b_1$ is the slope and $b_0$ is the $x$ intercept) is given in most statistics texts and shown below (e.g., McClave and Dietrich, 1994):

$$95\% \text{ C.L.} = \pm(t_{0.95, n-2})s \sqrt{1 + \frac{1}{n} + \frac{(x_p - \bar{x})^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}}$$ (16)

Table 2. Uncertainty in predicted values of $\ln(k)$ at 15°C and corresponding range of half-life estimates from Arrhenius plots using various data sets

<table>
<thead>
<tr>
<th>Source</th>
<th>Number of data points</th>
<th>Temperature range (°C)</th>
<th>Predicted $\ln(k)$ at 15°C</th>
<th>Half-life (years) (95% C.L.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cline and Delino (1989)</td>
<td>19</td>
<td>28–70</td>
<td>-19.15 ± 0.24</td>
<td>3.59–5.83</td>
</tr>
<tr>
<td>Gerkens and Franklin (1989)</td>
<td>14</td>
<td>40–120</td>
<td>-19.00 ± 0.84</td>
<td>1.70–9.09</td>
</tr>
<tr>
<td>Jeffers (1989)</td>
<td>10</td>
<td>64–117</td>
<td>-19.29 ± 0.28</td>
<td>3.12–8.77</td>
</tr>
<tr>
<td>Combined data set</td>
<td>54</td>
<td>25–120</td>
<td>-19.06 ± 0.49</td>
<td>2.55–6.80</td>
</tr>
</tbody>
</table>

$^a$k in units of seconds$^{-1}$.

$^b$Uncertainty estimates are 95% confidence limits for predicted values of $\ln(k)$.

$^c$95% confidence interval.

The uncertainty in $\ln(k)$, denoted as $\delta \ln(k)$, is approximately equal to the relative uncertainty in $k$, denoted as $\delta k/k$, since $\delta \ln(k) = (\delta \ln(k)/\delta k)\delta k$, which is equal to $\delta k/k$. Thus, the 95% confidence limits reported in Table 2 give direct measures of $\delta k/k$. As shown in Table 2, the Cline and Delino data yield the smallest error in prediction of $\ln(k)$. There are probably several reasons why the uncertainty associated with the Cline and Delino data is the smallest of the studies shown in Table 2. In addition to taking measurements near the temperature range of interest, Cline and Delino have multiple measurements (from 6 to 29) for each temperature and experimental condition. Note that the uncertainty estimate does not improve by combining all the data from the four studies. Therefore, our best estimate of the relative error in $k$ is taken from the Cline and Delino result for the uncertainty in $\ln(k)$, as corrected for headspace and reported in Table 2, about 24% at 15°C. Confidence limits calculated using Eq. (16) for other temperatures show that the error ranges from about 27% at 5°C to 22% at 25°C using the Cline and Delino data set. This illustrates how the error increases as the temperature deviates from the average temperature used in the regression, which was about 50°C for the Cline and Delino data set.

Uncertainty in $k_e/k$

Data presented by several authors for the molar fraction of DCE generated from the hydrolysis of TCA, $k_e/k$, are plotted in Figure 2. The data show a slight increase in the fraction of DCE generated with increasing temperature over the range of 25–80°C. An increase in DCE yield with increasing temperature was also noted by Reinhard and McCarty (1993). This is

Figure 1. An Arrhenius plot of data reported by Cline and Delino (1989) after correcting for headspace effects.
consistent with the SN1/E1 mechanism, where the elimination pathway is favored with increasing temperature (March, 1985).

As noted earlier, for the purpose of estimating a residence time in groundwater, we are generally interested in temperatures between about 5 and 25°C—outside the range of values plotted in Figure 2. The ratio remains relatively constant between 25 and 40°C but appears to increase at temperatures greater than 40°C. It is unclear how this ratio changes at lower temperatures. At the lowest temperatures where \( k_e/k \) was measured, 25 and 28°C, both Haag and Mill (1988) and Cline and Delhino (1989) include estimates of uncertainty with their measured values. Their estimates for the ratio are about 21 ± 2%. Thus, using the authors’ estimates for the lowest temperatures where measurements are available, the relative error in the measured ratio of \( k_e/k \) is about 2/21, or 10% uncertainty in \( k_e/k \). For the purpose of this analysis, we have assumed that this value can be applied at lower temperatures as well.

**Uncertainty in Ratio [DCE]/[TCA]**

For now, we will assume that the uncertainty associated with measurement of the ratio of [DCE]/[TCA] consists solely of errors in sampling and analysis (later in this article we discuss potential chromatographic effects). This uncertainty can be estimated from site-specific field data, e.g., replicate sample measurements from a given well. For the purpose of the present analysis, we have assumed an uncertainty of ±10%.

**Uncertainty in Measurement of Temperature**

Estimating a groundwater residence time from a ratio of [DCE]/[TCA] implicitly assumes that the rate of hydrolysis is constant over time, i.e., that the groundwater temperature is constant over time. In fact, shallow aquifers can show a temperature variation of up to several degrees centigrade over the course of a year. However, because this small seasonal variation is oscillatory in nature, the effect should be insignificant in calculating the uncertainty in \( k \) after a few years. In fact, using a Taylor series expansion of Eq. (3), we estimate the effect of a sinusoidal temperature variation on the effective value of \( k \) is only a few percent, much smaller than the uncertainties in \( k \) discussed above.3

However, depending upon the time of year collected, a single groundwater temperature measurement can differ from the true annual average by about 1°C in shallow aquifers. Therefore, in shallow aquifers it is best to estimate \( k \) based on multiple temperature measurements, taking seasonal effects into account. If no temperature measurements are made, the annual average groundwater temperature can be estimated from the mean annual air temperatures with a correction factor of a 1°C increase for every 40 meters of depth because of the earth’s geothermal gradient (Freeze and Cherry, 1979). Freeze and Cherry note several circumstances in which this approximation may not be valid. However, in general, based on our experience at a limited number of sites, we expect this method will estimate groundwater temperature within at least 0.5°C, and this is what we have assumed for the uncertainty in \( T \).

**Method I Example**

A generalized expression for predicting the residence time in years, assuming that the fraction of DCE formed (i.e., \( k_e/k \)) is 21%, can be constructed by exponentiating Eq. (15) and substituting in Eq. (7):

\[
t(\text{years}) = 3.63 \times 10^{-22} \exp\left(\frac{54.065}{1 + 3.66 \times 10^{-2}T}\right) \\
\times \ln\left(1 + 4.76 \frac{[\text{DCE}]}{[\text{TCA}]}\right)
\]

In deriving Eq. (17), the temperature \( T \) in Eq. (15) has been converted from degrees Kelvin to degrees Celsius and the rate constant \( k \) has been converted from units of s\(^{-1}\) to years\(^{-1}\).

As an example, consider the situation where the molar ratio of [DCE]/[TCA] is measured to be 1.0 with an assumed relative uncertainty of 10% at a groundwater temperature of 15°C. Using Eq. (17), the residence time in groundwater is estimated to be 11.6 years, and the relative error (95% confidence intervals) is

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3The result of expanding Eq. (3) for \( k \) in a Taylor series about \( T' \) is

\[
k = k(T')\left\{1 + \left(\frac{E_o}{RT'}\right)\left(\frac{T - T'}{T'}\right) + \left[\frac{1}{2}\left(\frac{E_o}{RT'}\right)^2 - \left(\frac{E_o}{RT'}\right)\right]\right\} \\
\times \left(\frac{T - T'}{T'}\right)^2 + \ldots
\]

If \( (T - T') \) is assumed to vary sinusoidally with a period of a year, then when \( k \) is averaged over a year the term proportional to \( (T - T') \) vanishes and \( (T - T')^2 \) has the value \( \Delta T^2/2 \), where \( \Delta T \) is the maximum amplitude of the sinusoidal variation. For \( T = 15 \)°C (288.15 K) and \( E_o = 122.8 \) kJ/mol-K, the value obtained from the Cline and Delhino data (1989), the result is \( k = k(15 \)°C) \( (1 + 0.0076 \Delta T^2) \), showing that a variation of 1°C makes a difference in \( k \) of less than 1%.
given by Eq. (12) with the uncertainty values discussed above:

\[
\frac{\delta t}{T} = \sqrt{(0.24)^2 + (-51.25)^2 (0.0017)^2 + (0.1)^2 + (0.1)^2 (1.75)^2 (1.21)^2} \\
= \sqrt{0.0576 + 0.0076 + 0.0045} \\
= 0.26
\]  

(18)

Thus, the relative error in \( t \) is dominated by, and approximately equal to, the relative error in \( k \) due to uncertainties originating in the laboratory. (Note that if we had assumed an uncertainty of 0.25 in the measurement of \([\text{DCE}]/[\text{TCA}]\) instead of 0.1, the last term inside the square root would be 0.0162 instead of 0.0045, and \( \delta t/t \) would only be increased to 0.28.) For the example of 10% relative error in \([\text{DCE}]/[\text{TCA}]\), the uncertainty in our estimate of \( t \) is \( \pm (0.26)(11.6) = \pm 3.0 \) years.

**Method II—TCA Hydrolysis Rate Constants from Field Data**

If time-series data are available, an alternate approach based on plotting the logarithm in Eq. (7) versus time can be used to estimate the residence time in groundwater. In order to demonstrate this technique, we examine data presented by Wing (1997). Wing investigated the hydrolysis of TCA in a pristine sandy aquifer following a well-documented transient release at a former semiconductor manufacturing facility in Santa Clara, California. Approximately 10–20 gallons of TCA were released over a 4.5–hour period on August 15, 1984. Following commencement of a groundwater pump and treat remedy in 1986, concentrations of TCA and DCE were monitored over time for a period of ten years. 1,1-Dichloroethane (DCA) was also detected in the groundwater, indicating that some biodegradation of TCA was occurring.

The presence of DCA introduces a complicating factor in the interpretation of DCE/TCA ratios, i.e., the loss of TCA via a competing biological process. Vogel and McCarty (1987b) have shown that TCA can undergo reductive dechlorination or hydrogenolysis to form DCA. DCA is also capable of degrading via hydrogenolysis to form chloroethane (CA), although this process occurs at a slower rate (McCarty and Reinhard, 1993). In general, the more highly halogenated compounds are reduced more readily than less halogenated compounds (Vogel and McCarty, 1987b). Thus TCA is transformed more rapidly than DCA, which in turn is transformed more rapidly than CA. Hydrogenolysis reaction rates are greatest under highly reducing, methanogenic conditions but can also occur under less reducing iron-, nitrate-, and sulfur-reducing conditions. The presence of CA may or may not be detected because it will hydrolyze in water at a relatively rapid rate. For example, Vogel et al. (1987) determined a half-life of only 38 days.

Another potential complicating reaction is the loss of DCE. For example, anaerobic dechlorination of DCE to form vinyl chloride has been reported by Barro-Lage et al. (1986). DCE was reduced to vinyl chloride in anoxic microcosms with half-life values of about 3 to 6 months.

Because there are a number of factors that can affect the rates of biotic processes (e.g., availability of electron donors, nutrients, and microbes) they are difficult to predict. Nevertheless, when DCA is present, and the loss of DCA to CA as well as biodegradation of DCE can be neglected, an equation analogous to Eq. (7) can be derived where \( k_T \) is the rate constant for the total rate, which includes biodegradation.

\[
t = \frac{1}{k_T} \ln \left( 1 + \frac{k}{k_T} \frac{[\text{DCE}]/[\text{TCA}]}{[\text{DCA}]/[\text{TCA}]} \right) 
\]  

(19)

This equation comes about as follows. Eqs. (5) through (7) are still valid with \( k \) replaced by \( k_T \). Substituting \( k_T = k + k_s \), where \( k_s \) is the biodegradation rate constant, and \([\text{DCA}]/[\text{DCE}] = k_s/k_T \), Eq. (7) yields Eq. (19). The second term in the argument of the logarithm in Eq. (19) contains the factor \( k/k_s \), because it accounts for both DCE and acetic acid. Because the third term only accounts for the single chemical DCA, no similar factor occurs.

A plot of the logarithm term in Eq. (19) on the \( y \) axis versus time on the \( x \) axis gives a slope equal to \( k_T \) and an \( x \) intercept equal to the estimated date of release. Using this approach, with an assumed DCE yield of 25%, Wing (1997) was able to estimate a date of release within one week of the actual release using the first five of ten years of reported data. No uncertainty was reported for his estimate.

For the purpose of demonstrating Method 2, we estimated \([\text{DCE}]/[\text{TCA}]\) and \([\text{DCA}]/[\text{TCA}]\) ratios measured in two groundwater monitoring wells from Figures 1 and 3 presented by Wing (1997) and plotted the natural log expression in Eq. (19) versus time using all ten years of data (Figure 3). The \( x \)-intercept of a least-squares best-fit straight line is equal to the estimated date of release.

For this example, according to Wing, we know the exact date that the spill occurred—August, 1984. Our estimated spill dates, based on data interpolated from graphs presented by Wing for Wells E-7 and E-13, are November, 1983, and November, 1982. The estimated uncertainty in these predictions can be obtained from regression analysis. For the equation \( y = b_1(x) + b_0 \), the standard deviation on a calculated \( x \) value is \( \sigma = \frac{s}{\sqrt{b_1}} \sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(y - \bar{y})^2}{b_1^2 \sum (x_i - \bar{x})^2}} 
\]  

(20)
where \( y \) is the value of \( y \) at \( x \) (in this case, \( y = 0 \)), \( n \) is the number of measurements, and \( m \) is the number of replicates (in this case \( m = 1 \)). The 95% confidence limits about \( x \) are \( \pm t_{0.95,n-2}(s_x) \). For Well E-7, the 95% confidence limits about our predicted value of \( x \) result in estimated release dates of April 1981 to June 1986, an uncertainty range of about \( \pm 2.5 \) years. This range of estimates includes the actual date of release. The latest sample date for Well E-7 is December 1993. The length of time between the estimated release date and last sample date is about 10 years. Thus, the relative uncertainty is about \( \pm (2.5/10) \) or \( \pm 25 \)%, which is comparable to Method I. For Well E-13 (which has a latest sample date of September 1995) we estimate the 95% confidence limits in the release date to be October 1978 to December 1986, which also includes the known release date. However, in this case the relative uncertainty is about \( \pm 36 \)%, which is slightly higher than Method I. Note, however, that the Method II uncertainty estimates include the uncertainties in both [DCE]/[TCA] and [DCA]/[TCA], whereas Method I only included the uncertainty in [DCE]/[TCA].

**Qualitative Discussion of Additional Uncertainty Factors**

We now examine two other factors that arise in applying the DCE/TCA ratio method to date groundwater plumes. First we examine the effect of the presence of a pure phase and how this alters interpretation of the time, \( t \) in Eq. (7). Second, we examine the effects of sorption and how this (1) may affect the rate of hydrolysis and (2) can lead to bias in estimating \( t \) from field data.

**Effect of a Pure Phase**

Experiments performed with TCA present in a separate nonaqueous phase clearly show that only the dissolved phase undergoes hydrolysis. For example, Gerken and Franklin (1989) noted that varying the organic/aqueous volume ratio from 0.04 to 25 did not appreciably change their calculated rate constants. From this they concluded that hydrolysis of TCA occurred only in the aqueous phase.

A Archer and Stevens (1977) conducted experiments with TCA concentrations exceeding the solubility limit and found that \( 69.1 \times 10^{-4} \) moles of chloride ion were formed per mole of TCA per hour at 80°C, implying a rate constant for TCA degradation of 0.21 h\(^{-1}\). This is essentially identical to the result 0.216 h\(^{-1}\), given by Eq. (15) and thus is also consistent with only the dissolved phase participating in reactions described in Eqs. (1) and (2).

The implication is that if a dense nonaqueous phase liquid (DNAPL) is introduced to groundwater, hydrolysis begins with dissolution at the fringe of the DNAPL, which is also when transport in the groundwater begins. The bulk of the DNAPL is neither hydrolyzing nor being transported. Thus DCE/TCA ratios measured in the plume can only represent a travel time from the DNAPL source region to a downgradient well rather than the date when the DNAPL spill occurred. In this case \( k \) can no longer be determined by time series data from a single well unless that well is at the plume front. In contrast, for a release of TCA in the dissolved phase, from a wastewater discharge, for example, measurement of the DCE/TCA ratio at any location or time should be representative of the single date when hydrolysis began.

**Effect of Sorption**

It is unclear whether or not hydrolysis of TCA occurs when the TCA is bound to sediment. Several authors have measured hydrolysis in the presence of sediment and concluded that there was no significant effect (Haag and Mill, 1988; Reinhard and McCarty, 1993). However, at least in the case of the Haag and Mill experiments the magnitude of the effect is expected to be small and might not have been readily observable. To demonstrate this, consider what the situation would be if only the dissolved phase were available for hydrolysis. The fraction of TCA in solution, \( f_s \), can be estimated as:

\[
 f_s = \frac{1}{1 + \frac{\delta_b}{\delta_w} \frac{k_d}{k_d}} = \frac{1}{Re} \tag{21}
\]

where \( \delta_b \) is the soil bulk density (g/cm\(^3\)), \( k_d \) is the soil/water partition coefficient (cm\(^3\)/g), \( \theta_w \) is the water-filled porosity (unitless), and \( Re \) is the retardation coefficient.

With the given assumptions, the rate of hydrolysis would be decreased by a factor of \( 1/Re \). Haag and Mill (1988) performed TCA hydrolysis experiments with sediments but found no effect. However, the sediment contained only 0.02% carbon and the authors measured only minimal (7%) sorption to the sediment. Assuming 93% of the TCA is dissolved, this would correspond to a retardation coefficient of \( 1/0.93 = 1.08 \) and the hydrolysis rate constant would be decreased by only a factor of 1.08. Thus, it would not be surprising if the authors had been unable to detect this small effect.

The Haag and Mill (1988) data are not inconsistent with TCA degradation being less in the presence of an absorbed phase. At
60°C the value of $k$ for sediment pore water is about 19% less than the value in distilled water. At 25°C, the value of $k$ in pore water was about 18% less than the average of the other three values at that temperature. At 40°C, a run with clay had a value of $k$ that was about 19% smaller than the run with distilled water. At 25°C and 40°C the difference is well within the experimental uncertainty, but at 60°C the two values would only be equal if both were near the 95th percentile confidence value.

On the other hand, Reinhard and M Carty (1993) also found no apparent effect of sorption on the rate of hydrolysis. The mean half-life for autoclaved sediment slurry was about 25% less than mean half-lives for both filtered groundwater and nonautoclaved sediment slurries. The 95% confidence levels for half-lives overlapped for all three conditions.

In principle, sorption processes can also affect the DCE/TCA ratio detected in a well because of differences in the DCE and TCA groundwater velocities. These contaminant velocities differ from the groundwater pore velocity by the factor $1/Re$. The soil/water partition coefficient introduced above depends upon the fraction of organic carbon ($\text{foc}$) in the sediment, as described by Eq. (22).

$$k_d = K_{oc} \cdot \text{foc}$$

where $K_{oc}$ is the partition coefficient normalized to the fraction of organic carbon in the soil. Using $K_{oc}$ values for TCA and DCE of 110 ml/g and 65 ml/g (U.S. EPA, 1994) and assuming a soil/sediment bulk density of 1.6 g/cm$^3$ and a water-filled pore space of 0.4 (typical for a sandy aquifer), calculated retardation coefficients will vary as a function of $\text{foc}$ as indicated in Table 3.

As indicated in Table 3, if the $\text{foc}$ in the aquifer is greater than say about 0.1, there could be a significant difference in retardation factors and hence in contaminant velocities. The effect is less than it would be if one were considering an initial spill of two chemicals with differing groundwater velocities since the rate of DCE generation is always greatest at the location of maximum TCA concentration. In any case, at higher $\text{foc}$, it is possible for the DCE plume to “outrun” the TCA plume and affect the DCE/TCA ratios.

If the DCE plume outruns the TCA plume, DCE/TCA ratios can be greatly enhanced in front of the TCA plume and diminished behind the front of the TCA plume. Similarly, the greatest effect on ratios will be at the plume lateral fringes. For this reason analysis is best conducted using data from locations where $[\text{TCA}]$ or $[\text{TCA}] + [\text{DCE}]$ is largest. Except for the fringes of the plume, this chromatographic effect should not greatly affect the estimated time since the molar ratio occurs in the logarithm in Eqs. (7) and (19). To the extent that there is a bias in estimating the time from Eqs. (7) or (19), using data from behind the plume front will tend to underestimate the time.

**Conclusions**

Measurements of the DCE/TCA ratio can be used to indicate how long hydrolysis has been occurring and age date a release of dissolved TCA. The rate of formation of DCE from TCA follows first-order kinetics and can be described by an Arrhenius equation. Estimating the rate of hydrolysis at groundwater temperatures from an Arrhenius plot based on laboratory experiments involves significant uncertainty. When estimating the time since hydrolysis began, under favorable conditions, this uncertainty, together with other parameter uncertainties, results in 95% confidence limits of about ±25%. We find that the uncertainty in $t$ is dominated by the uncertainty in estimating $k$ using laboratory data and the Arrhenius equation.

The rate of DCE formation can also be determined directly from time-series field data. One analysis of time-series field data indicates that use of these data, instead of laboratory-based hydrolysis rate constants, can result in time estimates with comparable uncertainty levels. If there is a DNA PL source present, [DCE]/[TCA] ratios represent a travel time rather than a date of release because hydrolysis does not occur in the pure phase. Therefore, data must be obtained near the plume front in order to determine the age of a spill. It is best to determine DCE/TCA ratios at the centerline, behind the plume front, in order to minimize potential bias from chromatographic effects.

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**References**


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Table 3. TCA and DCE retardation coefficients and relative velocities as a function of fraction of organic carbon

<table>
<thead>
<tr>
<th>Fraction of organic carbon (%)</th>
<th>Retardation coefficient</th>
<th>Ratio of DCE velocity to TCA velocity</th>
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<tr>
<td></td>
<td>TCA</td>
<td>DCE</td>
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<tr>
<td>0.01</td>
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