

Research Paper

# Trichloroethylene-alcohol-water solubility characteristics with implications for partitioning tracer tests at DNAPL - contaminated sites

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## ABSTRACT

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Dense nonaqueous phase liquids (DNAPLs) widely occurred at numerous subsurface sites can act as long-term sources of both vapor-phase and groundwater contamination. Successful remediation and effective risk assessment of DNAPL-contaminated sites is limited by current source zone characterization techniques and DNAPL unique behavior. A relatively new method of DNAPL-contaminated site characterization involved the use of partitioning tracers to provide estimates of the known amount of DNAPL. A new practical continuous flow system was developed in this work to explore the DNAPL's partitioning tracer-water solubility characteristics under pure phase and selected cosolvents conditions which can be crucial for estimate retardation factors of various tracers with implications for partitioning tracer tests at DNAPL-contaminated sites. Trichloroethylene (TCE) was selected as a representative of DNAPL due to its unique properties and solvent effects. Bromide was employed as a non-partitioning tracer, while three alcohols (i.e., iso-propanol, methanol, and ethanol) effluents were determined as a function of time under pure solvent and 30% cosolvent additions. The three alcohols appeared to have been used successfully as a partitioning tracers for detection of potential DNAPL saturation. Moment analysis of breakthrough curves allowed TCE and alcohol mass recovery and retardation factor calculation, and therefore could further estimate apparent DNAPL saturation. Assuming that partitioning to TCE-DNAPL is the only mechanism for retention of alcohols in the system, flow rate and various alcohol fraction additions seemed to have no major influence on retardation factor estimation of partitioning tracers in the system.

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## 1. Introduction

Releases of non-aqueous phase liquid (NAPL) due to improper storage and disposal have resulted in widespread contamination of the subsurface environment (National Research Council, 1994) and posed significant challenges in site remediation and long-term site management. NAPL migrates downward through the saturated zone, light nonaqueous phase liquid (LNAPL) may move laterally within the capillary fringe zone at the water table. For dense nonaqueous phase liquid (DNAPL), the saturation zone may not act as an impediment to vertical migration and DNAPL may continue to move further downward. Upon an infiltrating DNAPL encounters an interface of capillary contrast, it tends to distribute itself along such interfaces in the form of both disconnected entrapped residuals and pools (Wilson et al., 1990; Bradford et al., 1998), referred to as the NAPL source zone.

Extensive and persistent contamination of groundwater occurs as a result of significant but slow partitioning dissolved plumes generated from these DNAPL source zones that vary in size and complexity depending on site characteristics and DNAL properties and distribution. Spatial variability of physical and chemical soil properties can additionally exert a controlling influence on infiltration pathways and organic entrapment, especially for DNAPL. Highly irregular NAPL distributions have been observed frequently in natural subsurface system. Subsurface NAPL contamination is therefore a problem of serious concern at hazardous waste sites around the world.

Trichloroethylene (TCE) is one of the most prevalent contaminants found in soil and groundwater and poses serious health risks even at trace concentrations (NRC 1994). TCE is often discovered as DNAPL phase and much research has been focusing to remediate TCE-contaminated groundwater and soil. Relevant properties of TCE are presented in **Table 1**. Aqueous solubility of 1,000 mg/L and log octanol-water partition coefficient of 2.42 are not as hydrophobic as corresponding values for PAHs and PCBs, but can still be rate-controlling in soil treatment systems. Low aqueous-phase contaminant concentration levels lead to low conversion rates, resulting in longer treatment time and therefore higher treatment cost.

To effectively remediate these contaminated source zone and plume, the resulting NAPL zones must be properly characterized (McKay and Cherry, 1989). A new method of site characterization for NAPL involves the use of partitioning tracers (Jin et al., 1995; Haggerty et al., 2001; Rhee et al., 2006; Ghergut et al., 2012). Partitioning tracers have been employed since the 1970s in the petroleum industry to determine the residual oil saturations.

Recently, partitioning tracers have been demonstrated successfully to estimate NAPL saturations in environmental systems (Jin et al., 1995; Wilson and Mackay 1995; Haggerty et al., 2001; Rhee et al., 2006; Ghergut et al., 2012). Results to date indicate that transport of partitioning tracer is generally affected by the presence of NAPL contaminants with respect to that of the non-reactive tracers (such as Bromide). To determine the behavior, transport, and fate of the contaminants in the presence of multiphase subsurface system (i.e., water and partitioning tracer phases), and to design proper remediation systems, one must take into consideration the physical and chemical properties of the contaminants as well as solubility characteristics of contaminant-water-partitioning tracer.

The objective of this study therefore is to develop a new practical continuous flow to explore the DNAPL-partitioning tracer-water solubility characteristics under pure phase and selected cosolvents conditions which can be crucial for estimating retardation factors of various tracers with implication for partitioning tracer tests at DNAPL-contaminated sites. TCE was selected as a representative of DNAPL, while Bromide was employed as a non-partitioning tracer, while three alcohols (i.e., isopropanol, methanol, and ethanol) were used as partitioning alcohols and cosolvents with water. Aqueous phase alcohol and TCE in effluents were collected as a function of time under pure cosolvent and 30% cosolvent conditions. Results from this study may be applied to partitioning tracer tests at TCE-contaminated sites as well as to site remediation by combining chemical oxidation and bioremediation with cosolvent-assisted TCE extraction.

## 2. Materials and methods

### 2.1 Experimental setup

Since the objective of current study is to develop a new practical continuous flow to explore the DNAPL-partitioning tracer-water solubility characteristics under pure phase and selected cosolvents conditions which can be crucial for estimating retardation factors of various tracers with implications for partitioning tracer tests at DNAPL-contaminated sites, TCE (99.5%+, Sigma-Aldrich) was selected as a representative of DNAPL due to its unique properties and solvent effects. TCE is known as a suspected carcinogen (National Cancer Institute 1976) and U.S. Environmental Protection Agency priority pollutant (Environmental Protection Agency 1980) and is one of the most commonly detected volatile organic contaminants in groundwater. For TCE, aqueous solubility

of 1,000 mg/L and log octanol-water partition coefficient of 2.42 are not extreme hydrophobic compared to other contaminants, e.g., PAHs and PCBs, but can still be rate-controlling in soil and groundwater treatment systems.

Bromide was employed as a non-partitioning tracer, while three alcohols (i.e., iso-propanol, methanol, and ethanol) were used as partitioning alcohols and cosolvents with water. In addition to the capability to enhance solubility, criteria considered for the selection of these partitioning alcohols were based on their low toxicity, biodegradable ability, high solubility in both aqueous and NAPL phase, low cost, and other favorable factors such as no byproducts formation and biodegradable ability. Methanol was also chosen based on its ability to fairly partitioning into NAPL and thus will not enhance NAPL migration due to swelling of NAPL droplets.

The relevant physical/chemical properties of three alcohols are listed in **Table 2** (MSDS Source: [www.hazard.com/msds2](http://www.hazard.com/msds2)). All the alcohols considered have similar characteristics, which leads one to believe that they will end up giving the similar results. The only major difference is the vapor pressure and boiling point of methanol which means that it will go into the vapor phase before the other alcohols. Methanol, in fact, is a little cheaper but also slightly more toxic and may offset its prices advantage if the toxicity issue has to be addressed.

A schematic diagram of the experimental setup is shown in **Fig. 1**. The reactor was constructed from 12-mL superior quality clear borosilicate glass vial (22.5 mm × 46 mm dimension). The reactor was pre-washed and sterilized to provide sterile conditions at the beginning of the experiment. Magnetic stirrer and stir bars were equipped with the reactor to confirm equilibrium stage of the system. For pure phase system, one gram of TCE was added into each reactor and the rest of the reactor was filled with partitioning alcohol (i.e., either EOH, MeOH, or IPA). For 30% cosolvent case, the system was composed of 1 g TCE, alcohol, and milli-Q water. Sterile milli-Q water was continuously fed into the reactor through reactor inlet using a syringe pump at a constant flow rate of 0.5 and 0.4 mL/min, respectively. Effluents, collected at the outlet as a function of time, were further analyzed for Bromide, TCE, and alcohol concentrations.

## 2.2 Analytical equipment and conditions

For analytical, bromide analysis was performed using a model DX-100 Dionex ion chromatograph (IC) equipped with an Ion Pac AS4A SC 4 mm column and conductivity detector. All samples were analyzed in duplicate injections. Analytical separation of TCE and partitioning tracers (methanol, ethanol, and iso-propanol) was accomplished using Gas Chromatograph (Hewlett

Packard series 6890) equipped with DB-5 column (J&W Scientific; 0.53 mm i.d., 30 m long) and a flame ionization detector (FID). Oven temperature was maintained isothermally at 95 °C and average TCE retention time of 1.45 minutes during a 5 minutes run.

## 3. Results and discussions

### 3.1 For 100% pure phase

Breakthrough curves were prepared by dividing the concentration (C) of each compound in the effluent samples by its initial concentration (C<sub>0</sub>) to obtain a series of normalized concentrations (C/C<sub>0</sub>). These values were then plotted against the number of pore volumes (or time that each sample represented). Normalized breakthrough curves measured for bromide, iso-propanol, and methanol operated under 100% pure solvent conditions are shown in **Fig. 2**. Normalized bromide concentration started off at unity, decreased as a function of time, and finally approached zero within 30 minutes due to the advection process caused by constant feeding of sterile milli-Q water into the system. The relative constant TCE concentration from Br-TCE system detected in the effluents indicated that Br- was not reactive to TCE at all, therefore aqueous TCE concentrations were at its equilibrium solubility limit of approximately 1,000 ppm throughout the experiment. In other words, no TCE solubility enhancement was observed in the system with nonreactive tracer.

Results from this study evidently showed that batch solubility characteristics with alcohols of interests increased the solubility of TCE. Effluent mixtures were analyzed using a gas chromatograph (GC). Unlike Br-, normalized IPA and MeOH concentrations started off around 0.7 and 0.8, indicating that significant portions of alcohols were partitioned to DNAPL phase. IPA and MeOH took longer time (compared to conservative tracer) for the normalized concentrations to approach zero (i.e., within 100 minutes and 60 minutes, respectively), suggesting that there was measurable retardation occurred in both alcohol systems, mainly due to the partitioning between TCE and IPA or TCE and MeOH. A general trend evident from this study is that the partitioning effects of Alcohol-TCE increase with increasing alcohol molecular size. In general, TCE have a relatively low aqueous solubility due to its hydrophobic nature, which is a major barrier to the successful implementation of soil treatment technologies. Very high TCE concentration up to 90,000 ppm, however detected in the effluents from both IPA-TCE and MeOH-TCE systems suggested that TCE concentrations in the reactors were significantly enhanced by the addition of these 2 alcohols. This finding is in good

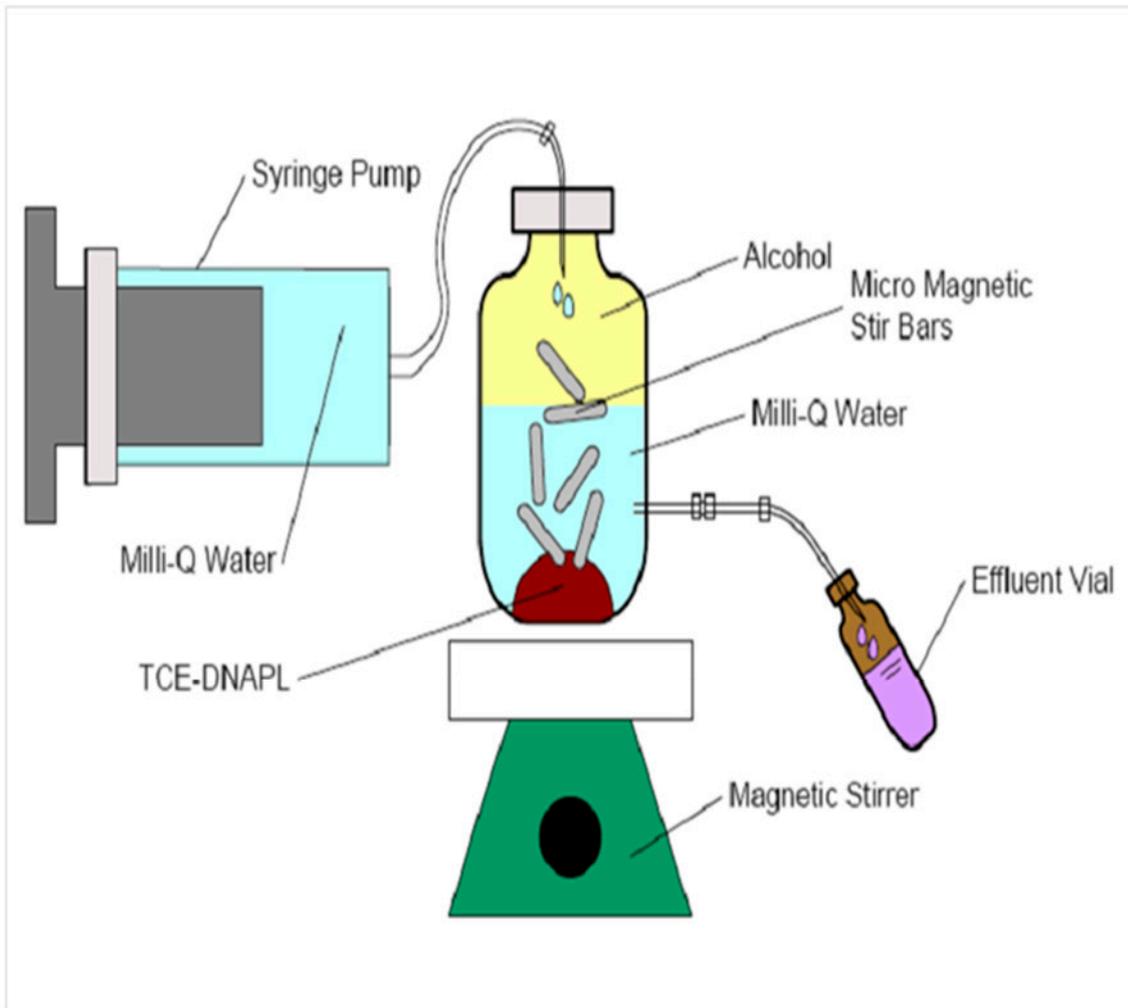


Fig.1. Schematic diagram for continuous batch solubility experiments.

Table 1. Physical/chemical properties of TCE.

Properties	Value
Density (g/mL)	1.46
Water Solubility @ 25°C (mg/L)	1,000
Henry's Law Constant @ 20°C (atm·m <sup>3</sup> /mol)	0.00892
Molecular Weight (g/gmol)	131.4
Boiling Point (°C)	86.7
Log Octanol-Water Partitioning Coefficient, $K_{ow}$ (-)	2.42

agreement with the previous study by Imhoff et al. 1995 who discovered increase NAPL solubility and mobility with increasing methanol cosolvent fraction. TCE mass recoveries were calculated using the trapezoidal rule to

determine the area under each curve. The results indicated that IPA and MeOH flushing could increase TCE mass removal from the reactor by 12% and 8%

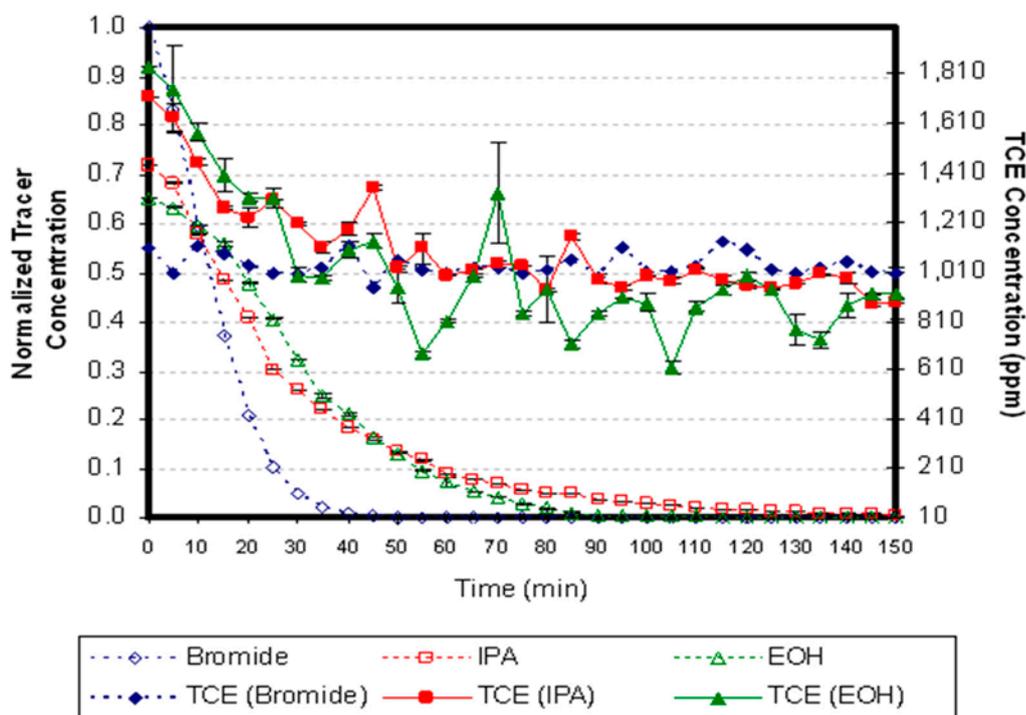


Fig. 2. Effluent TCE and alcohol profiles in partitioning (i.e., alcohol-TCE) and non-partitioning (i.e., bromide-TCE) systems under pure solvent conditions.

Table 2. Alcohol major properties.

Property	Alcohols		
	Methanol	Ethanol	Iso-Propanol
Boiling Point (°C)	65	79	80
Vapor Pressure @ 20 °C (mm Hg)	127	40	33
Melting Point (°C)	-98	N/A	-86
Specific Gravity @ 20 °C	0.791	0.79	0.786
Solubility in Water	100%	100%	100%
Carcinogenicity	No	No	No
Biodegradability in Water	Readily	Readily	Moderately
Biodegradability in Soil	Readily	Readily	Moderately
Half Life in Soil (days)	1-10	N/A	1-10
Environmental Toxicity	Slightly Toxic	Not Toxic	Not Toxic
Bioaccumulation	No	No	No
Price (USD/200L)	672.50	917.80	868.15

respectively, compared to the recovery efficiency from Br-TCE system.

Mass recoveries of partitioning alcohols were also calculated using the trapezoidal rule to determine the area under each curve and comparing this value with the area of the non-partitioning tracer (i.e., Bromide). The mid-point of the area beneath each BTC was defined as the center of mass of the particular tracer. Average retention time for each tracer could be calculated based on the center of mass of the particular tracer as shown in Table 3. In the

simplest case, the retardation factor (R) equals to the quotient of the travel times of the partitioning ( $t_p$ ) and non-partitioning ( $t_{np}$ ) tracers as related by the following equation (Thal et al., 2007; Freeze and Cherry, 1979).

$$R = \frac{t_p}{t_{np}} \quad [1]$$

Retardation factors of partitioning and non-partitioning tracers in each system under pure cosolvent conditions were calculated and the values are also presented in

**Table 3.** The average retention time of nonreactive tracer (Br-) in the system was 7.8 minutes, while both partitioning tracers took longer time in the reactor, resulting in higher retention time and retardation factors. When comparing between MeOH and IPA, the results in **Table 3** revealed that IPA's retardation factor was higher than that of MeOH, perhaps due to the more significant partitioning effects between IPA and TCE in the system under pure cosolvent conditions. A general trend evident from this study is observed that the retardation factors of partitioning alcohols increase with increasing alcohol molecular size and similarly with partitioning coefficients reported earlier (Thal et al., 2007).

### 3.2 For 30% cosolvent system

Normalized breakthrough curves measured for bromide, iso-propanol, and methanol operated under 30% cosolvent conditions are shown in **Fig. 3**. Normalized bromide breakthrough curve was generally similar to that observed under 100% cosolvent conditions as shown previously in **Fig. 2**, however, it took longer time for the normalized concentration to finally approach zero (i.e., within 40 minutes). This was due to the fact that the milli-Q water was flushed into the system at a slower flow rate of 0.4 mL/min.

Although not as effective as the system operated under 100% cosolvent conditions in terms of solubility enhancement, addition of both partitioning alcohols (IPA and EOH) could enhance TCE concentration in the effluents as the TCE concentrations detected were approximately at 160,000 and 130,000 ppm, respectively. IPA and EOH flushing under 30% cosolvent conditions could increase TCE mass removal from the reactor by 7.5% and 5.25%, respectively.

Average retention time and retardation factors of tracers in each system under 30% cosolvent conditions were calculated and the values are presented in **Table 4** below. The average retention time of nonreactive tracer (Br-) in the system was 9.7 minutes, while both partitioning tracers took longer time in the reactor, leading to higher retardation factors. When comparing between EOH and IPA, the results in **Table 4** revealed that IPA's retardation factor was higher than that of EOH, perhaps due to the more significant partitioning effects between IPA and TCE in the system under 30% cosolvent conditions. It is important to note that the retardation factors of IPA estimated from pure cosolvent and 30% cosolvent systems were similar, suggesting that flow rate and various alcohol fraction addition seemed to have no major influence on TCE-Alcohol-bromide partitioning characteristics. The general trend for retention time as well as retardation factor estimation of partitioning tracers

in the system increase from MeOH to EOH and IPA, respectively.

## 4. Conclusions

Results from this study showed that non-toxic alcohols can be used as : i) partitioning tracers with implications for partitioning tracer tests at DNAPL-contaminated sites to estimate the amount of NAPL; and ii) cosolvents to enhance the solubility of TCE in aqueous phase, which can further remove a major barrier to *in situ* chemical or biological degradation. For the cosolvent ability perspective, it was also discovered from this study that the three alcohols (cosolvents) tested, isopropyl alcohol performed the best by solubilizing TCE-DNAPL in the system, followed by ethanol and methanol. The results are in good agreement with previous work who investigate the effects of alcohol cosolvents on the aqueous solubility of TCE in a different system (Chawla et al., 2001).

In summary, the three alcohols tested appeared to have been used successfully as partitioning tracers for detection of potential DNAPL saturation. Moment analysis of breakthrough curves allowed TCE and alcohol mass recovery and retardation factor calculation, and therefore could further estimate apparent DNAPL saturation at the field scale in the presence of porous media. Assuming that partitioning to TCE-DNAPL is the only mechanism for retention of alcohols in the system, flow rate and various alcohol fraction addition seemed to have no major influence on retardation factor estimation of partitioning tracers in the system. This finding is beneficial for a more cost-effective preliminary test to explore the DNAPL-partitioning tracer-water solubility characteristics under pure phase and selected cosolvents condition which can

**Table 3.** Retention time and retardation factor of pure cosolvent conditions.

Parameters	Br-TCE	MeOH-TCE	IPA-TCE
Retention Time (min)	7.8	15.0	22.1
Retardation Factor (R)	1.00	1.92	2.83

**Table 4.** Retention time and retardation factor of 30% cosolvent conditions.

Parameters	Br-TCE	EOH-TCE	IPA-TCE
Retention Time (min)	9.7	23.0	28.3
Retardation Factor (R)	1.00	2.36	2.90

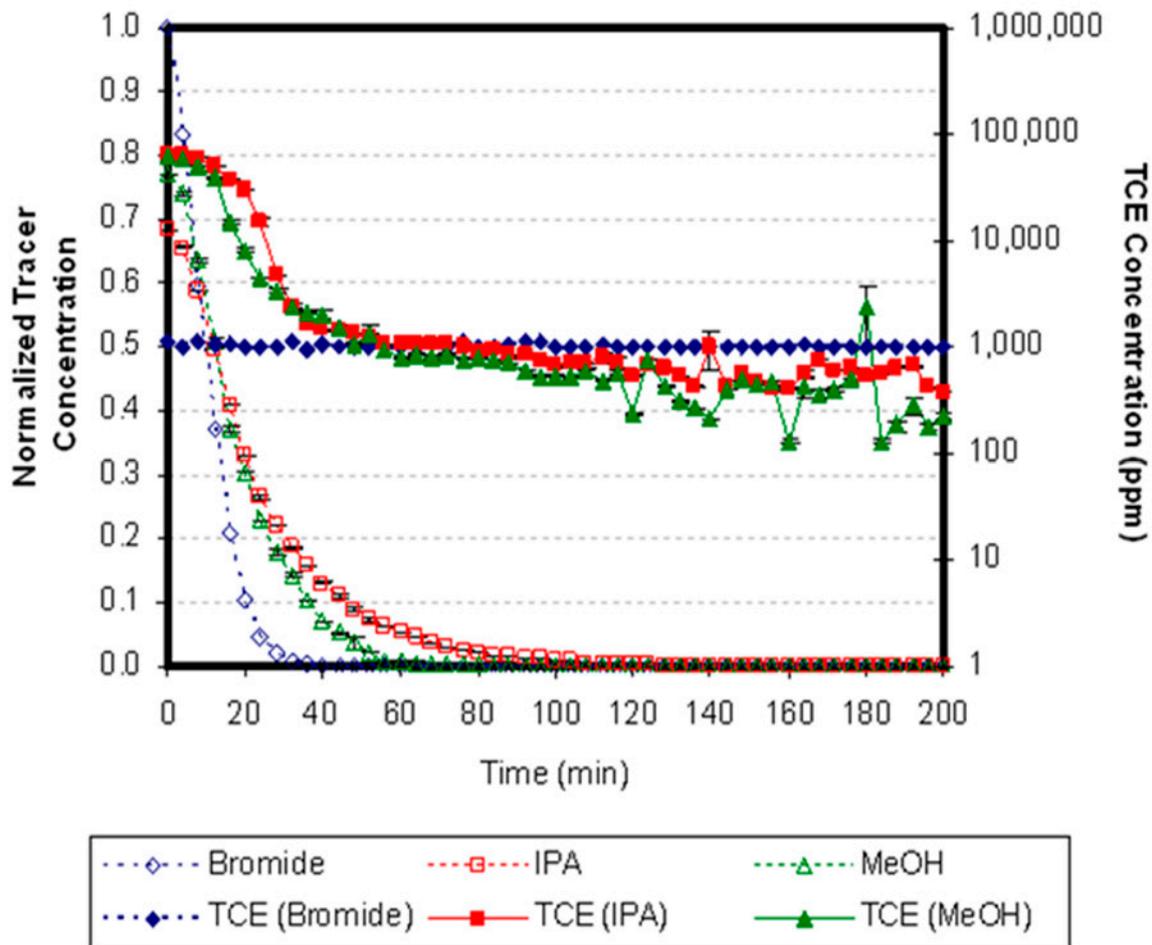


Fig. 3. Effluent TCE and alcohol profiles in partitioning (i.e., alcohol-TCE) and non-partitioning (i.e., bromide-TCE) systems under 30% cosolvent conditions.

be crucial for estimating retardation factors of various tracers with implications for partitioning tracer tests at DNAPL-contaminated sites.

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