

1,4-Dioxane cosolvency impacts on trichloroethene dissolution and
sorption

Justin Milavec
Geoffrey R. Tick
Mark L. Brusseau
Kenneth C. Carroll

Deposited 2023-09-27

Citation of published version:

Milavec, J., Tick, G. R., Brusseau, M. L., & Carroll, K. C. (2019). 1,4-Dioxane cosolvency impacts on trichloroethene dissolution and sorption. In *Environmental Pollution* (Vol. 252, pp. 777–783). Elsevier BV.
<https://doi.org/10.1016/j.envpol.2019.05.156>



Published in final edited form as:

Environ Pollut. 2019 September ; 252(Pt A): 777–783. doi:10.1016/j.envpol.2019.05.156.

1,4-Dioxane Cosolvency Impacts on Trichloroethene Dissolution and Sorption

Justin Milavec^{1,2}, Geoffrey R. Tick³, Mark L. Brusseau^{4,5}, Kenneth C. Carroll^{1,2,*}

¹Water Science and Management Program, New Mexico State University, MSC 3Q

²Plant & Environmental Science, New Mexico State University, MSC 3Q P.O. Box 30003, Las Cruces, NM 88003, USA;

³Department of Geological Sciences, University of Alabama, Tuscaloosa, AL 35487, USA

⁴Soil, Water and Environmental Science Department, University of Arizona

⁵Hydrology and Atmospheric Sciences Department, University of Arizona, Tucson, AZ 85721, USA

Abstract

Solvent stabilizer 1,4-dioxane, an emerging recalcitrant groundwater contaminant, was commonly added to chlorinated solvents such as trichloroethene (TCE), and the impact of co-disposal on contaminant transport processes remains uncertain. A series of batch equilibrium experiments was conducted with variations of 1,4-dioxane and TCE composition to evaluate aqueous dissolution of the two components and their sorption to aquifer sediments. The solubility of TCE increased with increasing amounts of 1,4-dioxane, indicating that 1,4-dioxane acts as a cosolvent causing solubility enhancement of co-contaminants. The solubilization results compared favorably with predictions using the log-linear cosolvency model. Equilibrium sorption coefficients (K_d and K_p) were also measured for different 1,4-dioxane and TCE compositions, and the findings indicate that both contaminants adsorb to aquifer sediments and TCE K_d values increased with increasing organic matter content. However, the K_d for TCE decreased with increases in 1,4-dioxane concentration, which was attributed to cosolvency impacts on TCE solubility. These findings further advance our understanding of the mass-transfer processes controlling groundwater plumes containing 1,4-dioxane, and also have implications for the remediation of 1,4-dioxane contamination.

Capsule Abstract: 1,4-Dioxane (cosolvent) increased the solubility of TCE and decreases sorption, and log-linear cosolvency model predicted solubility enhancement.

Keywords

1,4-Dioxane; TCE; Groundwater contamination; NAPL; Cosolvent; Sorption

*Corresponding author (kccarr@nmsu.edu).

1. INTRODUCTION

1,4-Dioxane has recently emerged in the environmental remediation industry as an unexpected and recalcitrant wastewater and groundwater contaminant. Toxicological studies have confirmed it is a probable human (B2) carcinogen (e.g., Anderson et al., 2012; Coleman et al., 2007; IARC, 1999; Mohr et al., 2010; Stepien et al., 2014; U.S.EPA, 2013), even though it is not currently classified as a U.S. EPA priority pollutant (McElroy et al., 2019). 1,4-Dioxane has been commonly used as a solvent stabilizer mixed with chlorinated solvents (Mohr et al., 2010), mainly 1,1,1-trichloroethane (TCA) and trichloroethene (TCE) (e.g., Adamson et al., 2015; Anderson et al., 2012; Zenker et al., 2003). Addition to chlorinated solvents in amounts ranging up to several percent by volume reduced solvent volatilization losses, and this two-component mixture has resulted in groundwater contamination through co-disposal (e.g., Anderson et al., 2012; DiGiuseppi and Whitesides, 2007; Mohr et al., 2010; Zenker et al., 2003). Improvements in the analytical detection limits over the last couple of decades for water analysis have revealed the presence of this contaminant at many wastewater treatment and contaminated groundwater sites where 1,4-dioxane was not identified during earlier characterization (DiGiuseppi et al., 2016; DiGiuseppi and Whitesides, 2007; Mohr et al., 2010).

Our limited understanding of 1,4-dioxane transport in the subsurface has been previously inferred from physicochemical properties and usage history (e.g., Mohr, 2001; Mohr et al., 2010; Myers et al., 2018; Stepien et al., 2014; Zenker et al., 2003), which does not entirely explain the observed behavior of groundwater plumes (Adamson et al., 2015; Adamson et al., 2014). 1,4-Dioxane is a semipolar liquid and is considered miscible with water, and due to these properties it is generally assumed to have a low sorption and volatilization potential. Thus, 1,4-dioxane is also assumed to migrate with groundwater, with negligible sorption, retardation, and attenuation. However, at sites with groundwater contaminated by 1,4-dioxane and chlorinated co-contaminants, 1,4-dioxane plumes are frequently smaller than the chlorinated co-contaminant plumes (Adamson et al., 2014), even though 1,4-dioxane plume bulk attenuation rates are comparable to the chlorinated solvents (1,4-dioxane sorption measurements were not included) (Adamson et al., 2015). Given the prevalence of chlorinated-solvent co-contaminants within 1,4-dioxane groundwater plumes, improving our understanding of contaminant-mixture impacts on contaminant transport in groundwater is urgently needed to support plume management and remediation feasibility.

The objectives of this study were: 1) determine the impact of solvent stabilizer 1,4-dioxane on TCE dissolution and solubilization from nonaqueous phase liquid (NAPL) into aqueous solutions; 2) quantify the sorption of 1,4-dioxane and TCE when present as single compounds and as two-component mixtures; and 3) evaluate changes in TCE sorption equilibrium distribution coefficient as a function of variations in 1,4-dioxane concentrations and porous media organic matter content.

2. THEORY, MATERIALS, AND METHODS

2.1. Materials

A Barnstead NANOpure II (Series 550, Dubuque, Iowa) system was used to purify reverse osmosis water to >18 M Ω cm, which was then used (hereafter termed DI water) to prepare all solutions. Reagent grade 1,4-dioxane (99% purity, Sigma Aldrich, St. Louis, MO, US) and TCE (99.5% purity, Sigma Aldrich) organic contaminants were obtained, and used as purchased. 1,4-Dioxane is a cyclic compound (log K_{ow} range -4.0 to 4.49 (Li and Yalkowsky, 1998)) that is semi-volatile, flammable, and relatively miscible in both organic solvents and water.

Aquifer material collected from an alluvial aquifer at Air Force Plant (AFP) 44 in Tucson, Arizona, was used for the experiments. A recent 1,4-dioxane biodegradation study also used AFP44 aquifer material for soil column experiments, but sorption was not investigated (Zhao et al., 2018). Additionally, wastewater biosolids (dry powder) obtained from the waste-water treatment plant in Las Cruces, New Mexico, were added in different amounts to two subsamples of the AFP44 sediment to generate a total of three porous media with increasing amounts of soil organic matter (SOM) (Table 1), as determined by the Walkley and Black titration method (Nelson and Sommers, 1996). Porosity was determined by gravimetric and volumetric methods (Table 1). Sediment pH, cation exchange capacity, textural analysis, and total extracted metals by inductively coupled plasma – optical emission spectroscopy (Perkin Elmer) were also measured.

Subsamples of the porous media were analyzed to confirm the absence of background contamination prior to the experiments. 10 mL subsamples were collected, and placed in 40 mL borosilicate glass volatile organic analysis vials containing 20 mL of methanol (99.9% pure). The subsamples were placed on a Lab-Line Orbit shaker table to equilibrate for 24 hours at 250 RPM after which they were centrifuged at 5,000 RPM for 10 minutes, 2 mL subsamples of the supernatant were then removed from the vials with a gastight syringe (Hamilton Company, Reno, Nevada), and placed into 2 mL auto sampler vials with no headspace. Gas chromatography-mass spectrometry (GC-MS; LECO, Saint Joseph, MI, US) analyses did not detect volatile organic contaminants.

2.2. Organic liquid dissolution

2.2.1 Cosolvency theory—Cosolvents (e.g., alcohols) are typically added to a primary solvent (e.g., aqueous solutions) to increase the solubility of low-solubility chemicals (e.g., hydrophobic organics). The ability of co-solvents to increase the solubility of organic solutes differs depending on the type and strength of the interaction with the solute. The ratio of solute solubilities in a specific organic solvent to that in pure water is defined as “cosolvency power” and is expressed as σ (Li and Yalkowsky, 1998; Yalkowsky et al., 1976):

$$\sigma = \log(S_c/S_w) \quad (1)$$

where S_c and S_w are the solubilities in pure organic cosolvent (subscript c) and pure water (subscript w), respectively. Cosolvency power is a pivotal parameter in a log-linear solubilization model that quantifies the increase in solubility of an organic compound

relative to its aqueous solubility as a function of cosolvent concentration (Li and Yalkowsky, 1998; Yalkowsky et al., 1976):

$$\log(S_m) = \log(S_w) + f\sigma \quad (2)$$

where S_m is the solubility of the solute in the aqueous/cosolvent mixture and f is the cosolvent volume fraction (Li and Yalkowsky, 1998). The cosolvency power can be estimated using the octanol-water partition coefficient (K_{ow}) of the solute by the following expression (Yalkowsky and Roseman, 1981):

$$\sigma = M * \log(K_{ow}) + N \quad (3)$$

Cosolvency power values are specific to the solution dynamics of the solute, cosolvent, and water system, while M and N are empirical parameters specific to the cosolvent and independent of the solute.

In many cosolvent applications, such as contaminant remediation, cosolvency ratios in aqueous mixtures range between a few percent to 50% or more. Although some contaminant remediation applications have used more concentrated solutions (Boving and Brusseau, 2000; ITRC, 2003; Oostrom et al., 2006). Li and Yalkowsky (1998) were able to more accurately predict the solubility at low cosolvent concentrations, by altering cosolvency power (from equation 3) when the cosolvent in the mixture is approximately or less than 50% volumetrically using low-volume range $M_{0.5}$ and $N_{0.5}$ values that they determined for several different cosolvents. These parameters $M_{0.5}$ and $N_{0.5}$ for the calculation of cosolvency power for 1,4-dioxane were determined to be 0.99 (± 0.08) and 1.54 (± 0.21), respectively (Li and Yalkowsky, 1998).

2.2.2 Dissolution experiments—Batch experiments were conducted to measure solubilities of TCE and 1,4-dioxane in water. Experiments were conducted with two-component organic liquid mixtures of various volume ratios of TCE to 1,4-dioxane (i.e., 0.8:0.2, 0.9:0.1, 0.95:0.05, and 1:0) were created by combining measured volumes of each organic liquid, which were equilibrated without headspace. Then, 5 mL subsamples of the organic liquids were placed in 20 mL amber glass vials (Supelco Trace clean 20 mL amber vials with screw open top caps and Teflon-lined septa, Bellefonte, PA) with 15 mL DI water without headspace (i.e., 0.063, 0.032, 0.016, and zero volume fractions of 1,4-dioxane). The vials were placed on an open counter top for 24 hours to achieve equilibrium (as previously determined). Then, 2 mL of the aqueous solution was extracted via pipette (Eppendorf, Hamburg, Germany), and placed in a 2 mL amber vial (Supelco Trace clean, Bellefonte, PA) with screw open caps and Teflon-lined septa (Supelco, Bellefonte, PA) without headspace for immediate chemical analysis. All experiments were conducted at 22 (± 1) °C, experiments were repeated four times for each mixture condition, and both the means and standard deviations are reported. Controls included blank samples without either contaminant and individual (i.e., single compound) solubility experiments.

2.3. Sorption

2.3.1 Sorption theory—The sorption equilibrium distribution coefficient is generally denoted as K_d or K_f (L/Kg) for linear and nonlinear Freundlich isotherms, respectively. The nonlinear isotherm K_f is determined as follows:

$$C_S = K_f C_A^n \quad (4)$$

where C_S (mg/Kg) is the concentration of the solute sorbed, C_A (mg/L) is the concentration of the solute in aqueous solution, and n is the nonlinear Freundlich isotherm exponent. Note that when n is equal to unity, the isotherm becomes linear, and K_d is determined from equation 4 instead of K_f .

2.3.2 Sorption experiments—All sorption partitioning experiments were conducted at 22 (± 1)°C using glass vials (Supelco Trace Clean® 20 mL amber vials with screw open top caps and Teflon® lined septa, Bellefonte, PA). Single-component and two-component sorption experiments were conducted with identical methods aside from containing both TCE and 1,4-dioxane together for the two-component. Stock aqueous solutions of TCE and 1,4-dioxane were created in amber vials. The stock solutions were diluted to the desired initial concentration ratios, and 16 mL of solution was placed in the glass vials with the 10 grams of AF-2 porous media (which was the only porous medium used for the single-component experiments), ensuring no headspace existed. Two-component sorption experiments were conducted with each of the three porous media AFP44, AF-1, and AF-2 (Table 1) for evaluation of SOM variations on sorption. The vials were sealed and placed on an Orbit Model shaker table (Lab-Line Instruments, Inc., Melrose Park, Illinois) set to 200 RPM for 24 hours to ensure complete equilibration, which was confirmed from initial testing. The vials were centrifuged (Beckman GP Centrifuge, Palo Alto, CA) at 2000 RPM for 10 minutes to settle suspended solid particles from the aqueous phase, and 1 mL of the aqueous solution was extracted by pipette (Eppendorf, Hamburg, Germany) and placed in a glass vial (Supelco, Trace clean 10 mL amber vials with screw open caps and Teflon® lined septa, Bellefonte, PA) containing 9 mL of DI water for immediate chemical analysis. Contaminant sorption and removal from aqueous solution upon equilibration with porous media was quantified by loss from aqueous solution. All sorption experiments were replicated, and both the means and standard deviations are reported. Controls included blank experiments, and experiments containing porous media with and without either contaminant.

2.4. Chemical analysis

Chemical analyses of 1,4-dioxane and TCE for the dissolution experiments were performed using gas chromatography (GC; Varian 3800, Palo Alto, CA) equipped with a *SPB*TM 624 capillary column (Supelco, 30 m 0.5 mm, 3 mm), a flame-ionization detector (Shimadzu GC-17A, Japan), and a headspace auto sampler (Varian 8200). Splitless direct injection was used with an injector temperature of 200 °C. The temperature program was set to start at 40 °C and then ramped up to 100 °C at 10 °C/min, and the detector temperature was set at 250 °C. Standards were prepared in DI water, analytes were quantified using replicated, linear standard curves, and the lower detection limit was not quantified since the solubility experiments did not approach the method limits.

Chemical analyses of 1,4-dioxane and TCE for the sorption experiments were conducted by GC-MS using a CTC Analytics CombiPal CTC Analytics (Zwingen Switzerland) auto sampler fitted with a 100 μm polydimethyl siloxane (PDMS) SPME fiber (Sigma Aldrich), which was used to collect and deliver samples. Each sample was incubated for 5 minutes at 55 $^{\circ}\text{C}$. After sampling, the fiber had a 4 minute desorption time in the injector, which was fitted with a septaless Merlin Microseal. GC-time of flight (TOF)-MS with the Petro SPME Agitation method was used (Avila et al., 2012). After a 5 minute sample collection, the sample was delivered to a 7890A Agilent (Santa Clara, CA, US) GC fitted with a ZB-5MS column (30 m, 0.25 mm I.D., 0.25 μm film thickness) with Helium as the carrier gas. The inlet was in splitless mode with a constant flow of 1.0 mL/minute over the entire run with a front inlet septum purge of 3 mL/min, and solvent delay of 0.1 minutes was used. The inlet was operated at a constant temperature of 310 $^{\circ}\text{C}$, and the transfer line was constant at 250 $^{\circ}\text{C}$. The oven program started at 50 $^{\circ}\text{C}$ and held for 4 minutes, ramped up to 230 $^{\circ}\text{C}$ at 16 $^{\circ}\text{C}/\text{minute}$, then ramped up to 175 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{minute}$ and held for 2 minutes, and then finished with a temperature ramp-up at 20 $^{\circ}\text{C}/\text{minute}$ to 200 $^{\circ}\text{C}$ and held for 1.5 minutes. The detector was a LECO (Saint Joseph, MI, US) Pegasus High Throughput TOF-MS. We collected masses from 55–550 with an acquisition rate of 10 spectra/second operating at 70 electron volts, and the ion source was heated at 250 $^{\circ}\text{C}$. Analytes were quantified using replicated standard curves based on the experimental matrix. The lower detection limits for both 1,4-dioxane and TCE were approximately 1 mg/L.

3. RESULTS AND DISCUSSION

3.1. Dissolution Experiments

Figure 1 presents the log solubility of TCE in the aqueous phase as a function of volume fraction (f) of 1,4-dioxane within the mixture. The maximum equilibrium concentration of TCE in the aqueous phase (with excess NAPL present) increases as the volume fraction of 1,4-dioxane increases. These results confirm that 1,4-dioxane acts as a cosolvent in the aqueous phase while in contact with excess NAPL phase. 1,4-Dioxane alters the aqueous phase molecular structure, which increases thermodynamic stability for hydrophobic TCE molecules residing within the aqueous phase. The 1,4-dioxane ether functional groups are not capable of hydrogen bonding to each other, however the electronegative oxygen atoms have a partial negative charge capable of interacting with the O-H dipoles of water molecules (Mazurkiewicz and Tomasik, 2006).

Figure 1 also contains a comparison of two approaches for quantifying the cosolvency power of 1,4-dioxane. One approach was through regression analysis of the measured solubility data at various f values, which provides the σ as the slope following equation 2. The experimental solubility of TCE without the presence of 1,4-dioxane (at $f=0$) was 1.2 g/L, which was comparable to literature values (DiFilippo et al., 2010). The second approach used the Yalkowsky and Roseman (1981) model (equation 3) to determine mean, minimum, and maximum σ values using previously published TCE log K_{ow} values (Chiao et al., 1994) (mean of 2.49 ± 0.05 standard error, minimum of 2.29, and maximum of 2.55) along with previously published mean, minimum, and maximum values for empirical parameters $M_{0.5}$ and $N_{0.5}$ (noted above) for 1,4-dioxane (Li and Yalkowsky, 1998). The model-derived

cosolvency was used to predict TCE solubility at various f values following equation 2. Figure 1 confirms that the model prediction, observed data, and the regression results were highly comparable, and there was only a minor difference between the modeled and experimental results over the full range of volume fractions measured. As the model was derived specifically for cosolvency, the comparability of the data and predictive analysis provides further evidence that 1,4-dioxane acts as a cosolvent in aqueous solutions. The slope of equations presented is the “cosolvency power”, or σ , of 1,4-dioxane for TCE solubilization, which was 4.0 and 3.9 for the modeled and experimental regression, respectively.

1,4-Dioxane has a σ that is similar to other commonly considered cosolvents including alcohols. Ethanol added to gasoline is another example of an additive acting as a cosolvent in groundwater where contaminant dissolution is enhanced by the cosolvent (Powers et al., 2001a; Powers et al., 2001b). Ethanol cosolvency was also previously examined for petroleum hydrocarbons compounds (Corseuil et al., 2004), and the σ values ranged from 0.65 for benzene to 3.14 for pyrene, which are lower than the σ value of 4.0 measured here for 1,4-dioxane dissolving TCE. Additionally, $M_{0.5}$ and $N_{0.5}$ (noted above) for 1,4-dioxane exceed those of methanol and ethanol, and are statistically comparable to 1-propanol (Li and Yalkowsky, 1998). Li and Yalkowsky (1998) present σ values as a function of solute Log K_{ow} values, and the data and function ranges for 1,4-dioxane were comparable to methanol, ethanol, and 1-propanol.

3.2. Sorption Experiments

3.2.1 Single-component sorption experiments—The single-component sorption isotherms are presented in Figure 2 for the medium AF-2 with a SOM of 1.17%. Both linear and nonlinear (i.e., Freundlich or power function) regression analyses were conducted for both TCE and 1,4-dioxane sorption data. For TCE experiment results, the linear K_d and nonlinear K_f values were 5.8 and 11 L/Kg, respectively. Linear regression provided the best match (i.e., larger regression R^2 value) to describe the observed TCE data, and the K_d value was determined as the slope of the regression and/or ratio of equilibrium values for C_S and C_A . Numerous prior studies have indicated TCE exhibits sorption and transport retardation to aquifer sediments and soils (e.g., AllenKing et al., 1997; Benker et al., 1998; Brusseau et al., 2012; Johnson et al., 2003; Russo et al., 2010; Silva et al., 2002; Zhang and Brusseau, 1999). The TCE K_d value is comparable to previously reported values for high organic matter soils and aquifer materials (e.g., Russo et al., 2010).

The nonlinear isotherm equation regression provided the best match (i.e., larger regression R^2 value) to the observed 1,4-dioxane data compared to the linear isotherm (Figure 2). Linear K_d and nonlinear K_f values were 1.6 and 3.8 L/Kg, respectively. The lower magnitude of sorption coefficient for 1,4-dioxane compared to TCE was attributed to its larger polarity relative to TCE. Furthermore, the nonlinear sorption behavior of 1,4-dioxane would not be unexpected due to 1,4-dioxane’s molecular structure. Interestingly, the sorption of 1,4-dioxane was quantifiable as opposed to common assumptions of minimal sorption. There have been very few reports of 1,4-dioxane sorption to soils or aquifers in the literature. Barone et al. (1992) noted a 1,4-dioxane K_d of 0.17 L/Kg that was an order of

magnitude below the value reported herein, whereas the soil considered in Barone et al. had an SOM (0.58%) that was approximately 1/2 of that used in this study, which illustrates the impact of SOM variations on K_d values. A recent water treatment method study reported nonlinear 1,4-dioxane sorption to granular activated carbon with a similar K_f as reported herein (Myers et al., 2018). Another prior study found highly comparable vapor phase to SOM partitioning capacities in peat organic matter for 1,4-dioxane and TCE, which suggests that both contaminants partition to SOM (Chiou and Kile, 1994).

3.2.2 Two-component sorption experiments—The TCE K_d values for the two-component sorption experiments are presented in Figure 3 as determined by the ratio of equilibrium values for C_S and C_A from experiments containing three different molar ratios of 1,4-dioxane and TCE. The experiments were conducted with the three porous media with different SOM (i.e., 1.17%, 0.62%, and 0.22%). Figure 3 contains the data and exponential regression lines and equations for K_d as a function of SOM. Increases in the molar ratio of 1,4-dioxane tended to decrease the K_d of TCE, while increasing the SOM tended to increase the sorption of TCE to sediments. The exponential positive trend of K_d with SOM is typical and generally expected for a hydrophobic organic contaminant. The decreasing K_d is attributed to the cosolvency power of 1,4-dioxane, which increased the aqueous solubility of TCE resulting in a decrease in K_d .

Prior research has found that the presence of cosolvents in aqueous solutions can have significant impacts on both sorption equilibrium and kinetics (Brusseau et al., 1991; Fu and Luthy, 1986; Nkedikizza et al., 1985; Rao et al., 1985; Wood et al., 1990). The equilibrium K_d of a contaminant has been shown to decrease in a log-linear manner with an increase in σ and cosolvent volume fraction (Fu and Luthy, 1986; Nkedikizza et al., 1985; Rao et al., 1985). The activity of the sorbate in the aqueous phase is considered a primary control on K_d (Rao et al., 1985), which explains why the addition of a cosolvent in the aqueous phase alters hydrophobic contaminant sorption. These decreases in K_d for hydrophobic TCE sorption with cosolvent additions are similar to prior observations for different sorbates and solvents (Fu and Luthy, 1986; Nkedikizza et al., 1985; Rao et al., 1985).

The potential impact of 1,4-dioxane transport retardation may be reflected in the study of Adamson et al. (2014), who evaluated plume lengths for sites where 1,4-dioxane and chlorinated solvents co-occur. They observed that 1,4-dioxane plumes are shorter than the chlorinated solvent plumes 62% of the time, whereas 17% of the time the 1,4-dioxane plume is the same length as the chlorinated solvent plume (Adamson et al., 2014). Decreases in TCE K_d with 1,4-dioxane cosolvency (Figure 3) could explain the observed larger chlorinated plume size and transport distance relative to the 1,4-dioxane plume. Thus, the combined impacts of 1,4-dioxane sorption and cosolvency can have a significant impact on the fate, transport, and attenuation of co-contaminants in groundwater.

4. CONCLUSIONS

The results of this study demonstrate that as the volume fraction of 1,4-dioxane added to the NAPL phase increases, the solubility of chlorinated solvents (i.e., TCE) in the aqueous phase also increases. The log-linear cosolvent solubility mixture model predicted the observed

TCE solubility data well, confirming 1,4-dioxane acts as a cosolvent for TCE, and the cosolvency power determined herein, along with equations 2 and 3 for other mixture components, may be useful for predictions. Since 1,4-dioxane was added to the chlorinated solvent prior to disposal, 1,4-dioxane would act as a cosolvent to increase the amount of TCE dissolution after release of NAPL as a mixture into groundwater. This effect would have impacted NAPL solubility for any hydrophobic organic contaminants released as NAPL with 1,4-dioxane (e.g., generally TCA and/or TCE) included in the mixture as a solvent stabilizer. As a result, predictions of source-zone mass discharge based on the use of standard aqueous solubilities may be smaller than actual values.

Sorption of TCE was also impacted by 1,4-dioxane cosolvency corresponding with decreasing K_d as cosolvent (i.e., 1,4-dioxane) concentration increased. Thus, 1,4-dioxane co-disposal with TCE may decrease the sorptive attenuation of TCE plumes. The sorption experiments also demonstrated that both 1,4-dioxane and TCE sorb to aquifer sediments, and TCE K_d values increased with increasing SOM content. Groundwater plumes containing 1,4-dioxane and co-contaminants may have enhanced dissolution and decreased sorption behavior due to contaminant mixture cosolvency effects, which influences plume transport as well as remediation efforts. These findings advanced our understanding of the mass-transfer processes controlling groundwater plumes containing 1,4-dioxane and chlorinated solvents within the subsurface, with implications for the remediation of 1,4-dioxane and TCE contamination.

Acknowledgements

This research was primarily supported by the US Department of Defense Strategic Environmental Research and Development Program (SERDP) Project ER-2302. Additional support was provided by the USDA National Institute of Food and Agriculture (Hatch project 1006845) and the Plant & Environmental Science Department at NMSU of which is greatly appreciated. The contributions of Dr. Mark Brusseau were supported by the NIEHS Superfund Research Program (P42 ES04940). We appreciate the assistance of F. Omar Holguin, Adam Dettmer, Naima Khan, Barry Dungan, and Barbara Hunter.

REFERENCES

- Adamson DT, Anderson RH, Mahendra S, Newell CJ, 2015 Evidence of 1,4-Dioxane Attenuation at Groundwater Sites Contaminated with Chlorinated Solvents and 1,4-Dioxane. *Environmental Science & Technology* 49, 6510–6518. [PubMed: 25970261]
- Adamson DT, Mahendra S, Walker KL, Rauch SR, Sengupta S, Newell CJ, 2014 A Multisite Survey To Identify the Scale of the 1,4-Dioxane Problem at Contaminated Groundwater Sites. *Environmental Science & Technology Letters* 1, 254–258.
- AllenKing RM, McKay LD, Trudell MR, 1997 Organic carbon dominated trichloroethene sorption in a clay-rich glacial deposit. *Ground Water* 35, 124–130.
- Anderson RH, Anderson JK, Bower PA, 2012 Co-occurrence of 1,4-dioxane with trichloroethylene in chlorinated solvent groundwater plumes at US Air Force installations: Fact or fiction. *Integrated Environmental Assessment and Management* 8, 731–737. [PubMed: 22492728]
- Avila BMF, Vaz BG, Pereira R, Gomes AO, Pereira RCL, Corilo YE, Simas RC, Nascimento HDL, Eberlin MN, Azevedo DA, 2012 Comprehensive Chemical Composition of Gas Oil Cuts Using Two-Dimensional Gas Chromatography with Time-of-Flight Mass Spectrometry and Electrospray Ionization Coupled to Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy & Fuels* 26, 5069–5079.

- Barone FS, Rowe RK, Quigley RM, 1992 A Laboratory Estimation of Diffusion and Adsorption Coefficients For Several Volatile Organics in a Natural Clayey Soil. *Journal of Contaminant Hydrology* 10, 225–250.
- Benker E, Davis GB, Barry DA, 1998 Estimating the retardation coefficient of trichloroethene for a sand aquifer low in sediment organic carbon - a comparison of methods. *Journal of Contaminant Hydrology* 30, 157–178.
- Boving TB, Brusseau ML, 2000 Solubilization and removal of residual trichloroethene from porous media: Comparison of several solubilization agents. *Journal of Contaminant Hydrology* 42, 51–67.
- Brusseau ML, Russo AE, Schnaar G, 2012 Nonideal transport of contaminants in heterogeneous porous media: 9 - Impact of contact time on desorption and elution tailing. *Chemosphere* 89, 287–292. [PubMed: 22608708]
- Brusseau ML, Wood AL, Rao PSC, 1991 Influence of organic cosolvents on the sorption kinetics of hydrophobic organic chemicals. *Environmental Science and Technology* 25, 903–910.
- Chiao F, Currie RC, McKone TE, 1994 Intermedia Transfer Factors for Contaminants Found at Hazardous Waste Sites: Trichloroethylene (TCE) Risk Science Program, Department of Environmental Toxicology, University of California, Davis, p. 46.
- Chiou CT, Kile DE, 1994 Effects of Polar and Nonpolar Groups on the Stability of Organic-Compounds in Soil Organic-Matter. *Environmental Science & Technology* 28, 1139–1144. [PubMed: 22176242]
- Coleman HM, Vimonses V, Leslie G, Amal R, 2007 Degradation of 1,4-dioxane in water using TiO₂ based photocatalytic and H₂O₂/UV processes. *Journal of Hazardous Materials* 146, 496–501. [PubMed: 17574739]
- Corseuil HX, Kaipper BIA, Fernandes M, 2004 Cosolvency effect in subsurface systems contaminated with petroleum hydrocarbons and ethanol. *Water Research* 38, 1449–1456. [PubMed: 15016521]
- DiFilippo EL, Carroll KC, Brusseau ML, 2010 Impact of organic-liquid distribution and flow-field heterogeneity on reductions in mass flux. *Journal of Contaminant Hydrology* 115, 14–25. [PubMed: 20434229]
- DiGuseppi W, Walecka-Hutchinson C, Hatton J, 2016 1,4-Dioxane Treatment Technologies. *Remediation Winter*, 71–92.
- DiGuseppi WH, Whitesides C, 2007 Treatment Options for Remediation of 1,4-Dioxane in Groundwater. *Environmental Engineer, American Academy of Environmental Engineers* 43, 1–7.
- Fu K, Luthy RG, 1986 Aromatic compound solubility in solvent/water mixtures. *Journal of Environmental Engineering* 112, 328–345.
- IARC, 1999 Re-evaluation of Some Organic Chemicals, Hydrazine and Hydrogen Peroxide, in: *International Agency for Research on Cancer, L., France (1999) (Ed.)*.
- ITRC, 2003 Technical and Regulatory Guidance for Surfactant/Cosolvent Flushing of DNAPL Source Zones. Interstate Technology and Regulatory Council Dense Nonaqueous Phase Liquids Team.
- Johnson GR, Zhang Z, Brusseau ML, 2003 Characterizing and quantifying the impact of immiscible-liquid dissolution and nonlinear, rate-limited sorption/desorption on low-concentration elution tailing. *Water Resources Research* 39, –.
- Li A, Yalkowsky SH, 1998 Predicting cosolvency. 1. Solubility ratio and solute log K_{ow}. *Industrial & Engineering Chemistry Research* 37, 4470–4475.
- Mazurkiewicz J, Tomasik P, 2006 Why 1,4-dioxane is a water-structure breaker. *Journal of Molecular Liquids* 126, 111–116.
- McElroy AC, Hyman MR, Knappe DRU, 2019 1,4-Dioxane in drinking water: emerging for 40 years and still unregulated. *Current Opinion in Environmental Science & Health* 7, 117–125.
- Mohr TKG, 2001 Solvent stabilizers. Santa Clara Valley Water District, San Jose, CA.
- Mohr TKG, Stickney JA, DiGuseppi WH, 2010 Environmental Investigation and Remediation: 1,4-Dioxane and other Solvent Stabilizers. CRC Press Taylor & Francis.
- Myers MA, Johnson NW, Marin EZ, Pornwongthong P, Liu Y, Gedalanga PB, Mahendra S, 2018 Abiotic and bioaugmented granular activated carbon for the treatment of 1,4-dioxane-contaminated water. *Environmental Pollution* 240, 916–924. [PubMed: 29879691]

- Nelson DW, Sommers LE, 1996 Chapter 34, Total Carbon, Organic Carbon and Organic Matter, in: Sparks DL (Ed.), Methods of Soil Analysis Part 3 – Chemical Methods. Soil Science Society of America and American Society of Agronomy, 677 S Segoe Rd, Madison, WI 53771.
- Nkedikizza P, Rao PSC, Hornsby AG, 1985 Influence of Organic Cosolvents On Sorption of Hydrophobic Organic-Chemicals By Soils. *Environmental Science & Technology* 19, 975–979.
- Oostrom M, Dane JH, Wietsma TW, 2006 A review of multidimensional, multifluid intermediate-scale experiments: Nonaqueous phase liquid dissolution and enhanced remediation. *Vadose Zone Journal* 5, 570–598.
- Powers SE, Hunt CS, Heermann SE, Corseuil HX, Rice D, Alvarez PJJ, 2001a The transport and fate of ethanol and BTEX in groundwater contaminated by gasohol. *Critical Reviews in Environmental Science and Technology* 31, 79–123.
- Powers SE, Rice D, Dooher B, Alvarez PJJ, 2001b Will ethanol-blended gasoline affect groundwater quality? Using ethanol instead of MTBE as a gasoline oxygenate could be less harmful to the environment. *Environmental Science & Technology* 35, 24a–30a.
- Rao PSC, Hornsby AG, Kilcrease DP, Nkedi-Kizza P, 1985 Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation. *Journal of Environmental Quality* 14, 376–383.
- Russo A, Johnson GR, Schnaar G, Brusseau ML, 2010 Nonideal transport of contaminants in heterogeneous porous media: 8. Characterizing and modeling asymptotic contaminant-elution tailing for several soils and aquifer sediments. *Chemosphere* 81, 366–371. [PubMed: 20692012]
- Silva JAK, Bruant RG, Conklin MH, Corley TL, 2002 Equilibrium partitioning of chlorinated solvents in the vadose zone: Low $f(oc)$ geomeedia. *Environmental Science & Technology* 36, 1613–1619. [PubMed: 12004787]
- Stepien DK, Diehl P, Helm J, Thoms A, Püttmann W, 2014 Fate of 1, 4-dioxane in the aquatic environment: From sewage to drinking water. *Water Research* 48, 406–419. [PubMed: 24200013]
- U.S.EPA, 2013. Integrated Risk Information System (IRIS) on 1,4-Dioxane, National Center for Environmental Assessment, Office of Research and Development, Washington DC (2013).
- Wood AL, Bouchard DC, Brusseau ML, Rao PSC, 1990 Cosolvent Effects on Sorption and Mobility of Organic Contaminants in Soils. *Chemosphere* 21, 575–587.
- Yalkowsky SH, Roseman TJ, 1981 Solubilization of Drugs by Cosolvents, in: Yalkowsky SH (Ed.), Techniques of solubilization of drugs. Dekker, New York.
- Yalkowsky SH, Valvani SC, Amidon GL, 1976 Solubility of Nonelectrolytes in Polar-Solvents.4. Nonpolar Drugs in Mixed Solvents. *Journal of Pharmaceutical Sciences* 65, 1488–1494. [PubMed: 978408]
- Zenker MJ, Borden RC, Barlaz MA, 2003 Occurrence and Treatment of 1,4-Dioxane in Aqueous Environments. *Environmental Engineering Science* 20, 423–432.
- Zhang ZH, Brusseau ML, 1999 Nonideal transport of reactive solutes in heterogeneous porous media 5. Simulating regional-scale behavior of a trichloroethene plume during pump-and-treat remediation. *Water Resources Research* 35, 2921–2935.
- Zhao LD, Lu X, Polasko A, Johnson NW, Miao Y, Yang ZM, Mahendra S, Gu BH, 2018 Co-contaminant effects on 1,4-dioxane biodegradation in packed soil column flow-through systems. *Environmental Pollution* 243, 573–581. [PubMed: 30216889]

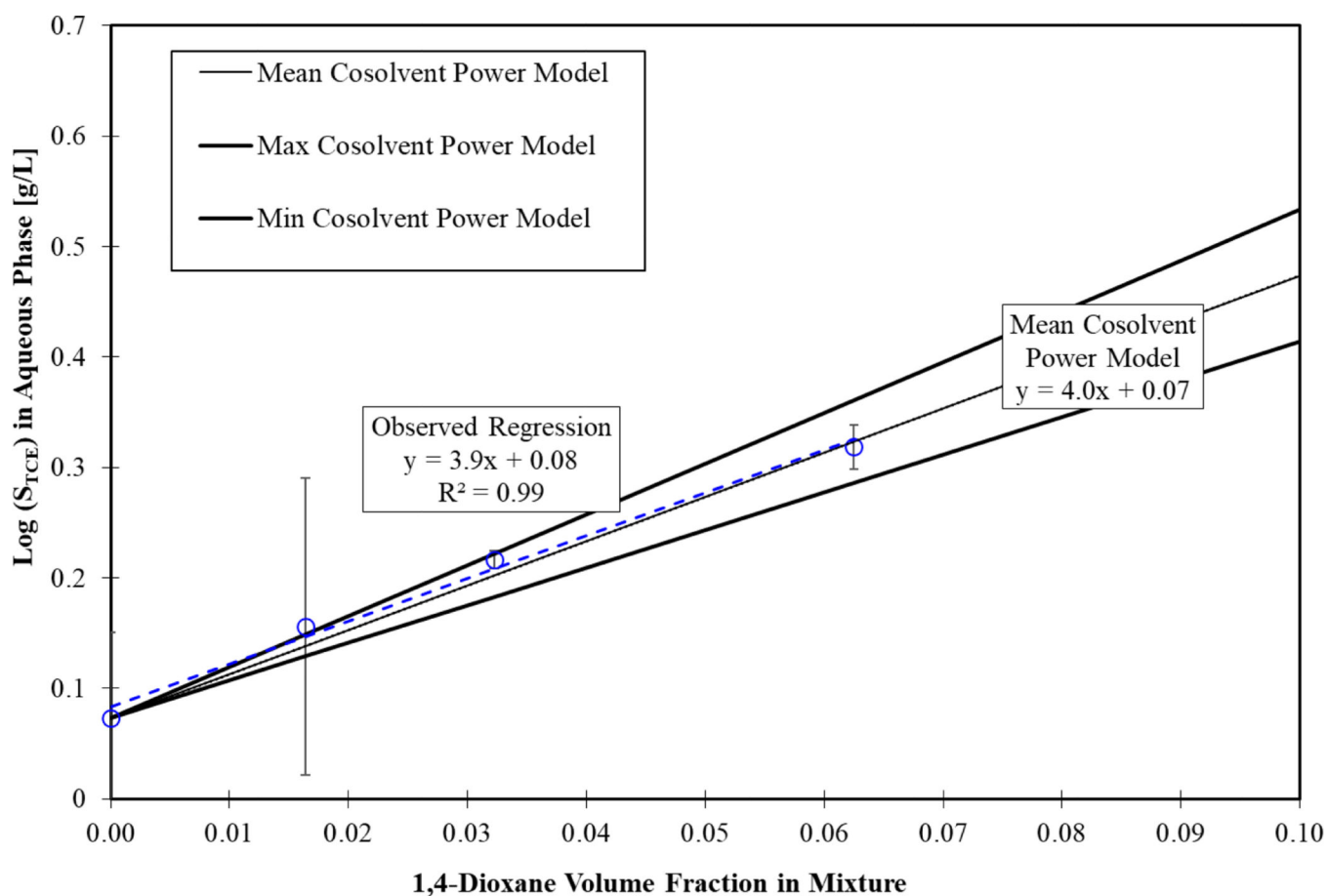


Figure 1. Observed TCE solubility (S_{TCE}) in aqueous solution as a function of 1,4-dioxane volume fraction ($f_{1,4-D}$) of the mixture compared to the mean and range of predicted values using the log-linear mixture solubility model (solid lines). Regression is plotted for the observed data (dashed line), and error bars represent one standard deviation about the mean for quadruplicate experiments.

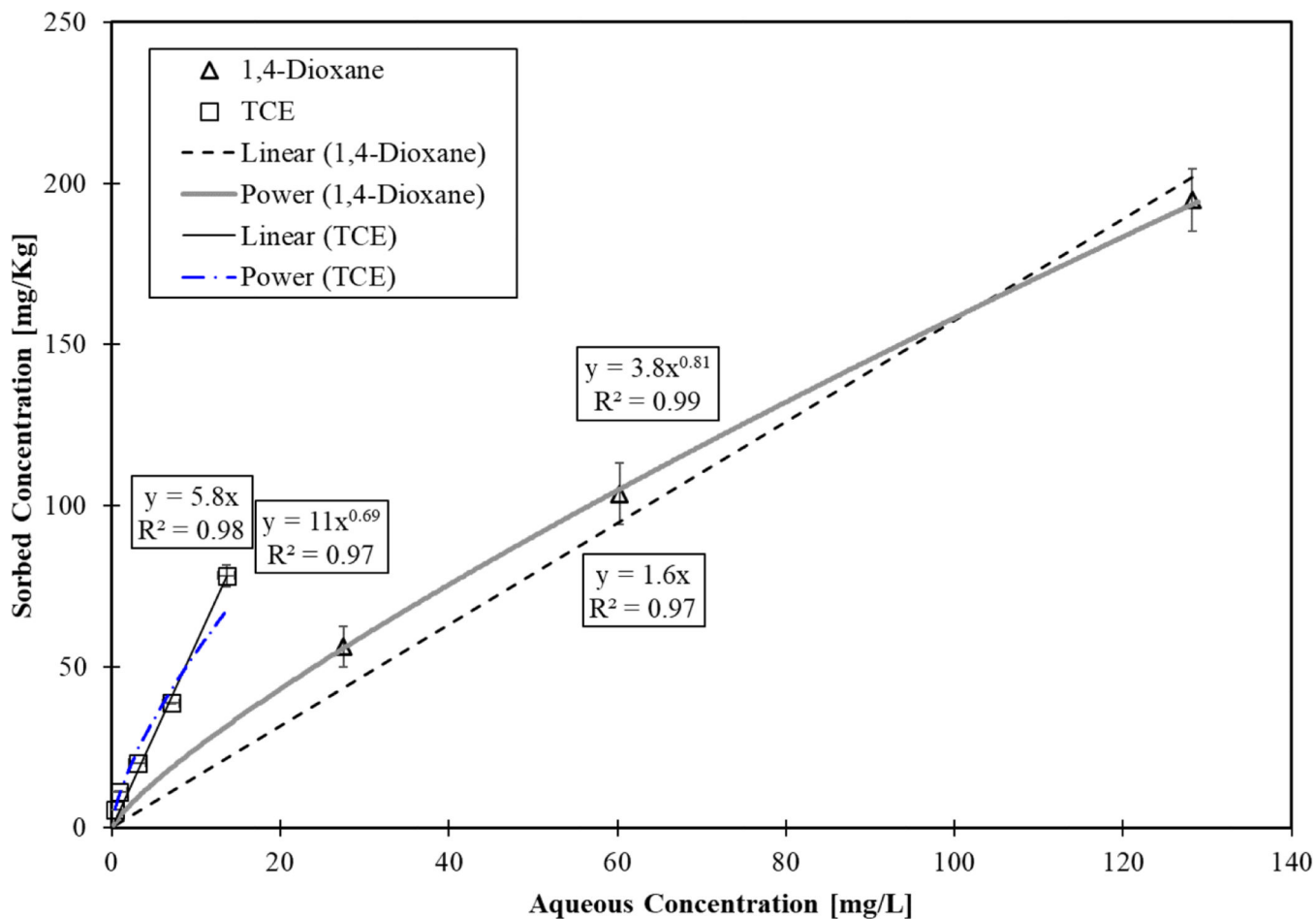


Figure 2.

Single contaminant sorption isotherm relationships between equilibrium sorbed-phase concentration (C_S) and aqueous-phase concentration (C_A) in contact with AF-2 porous media for contaminants TCE and 1,4-dioxane. The linear and power (i.e., Freundlich) regression lines and equations were used to determine the K_d and K_f values. Error bars represent one standard deviation about the mean for measured replicate experiments.

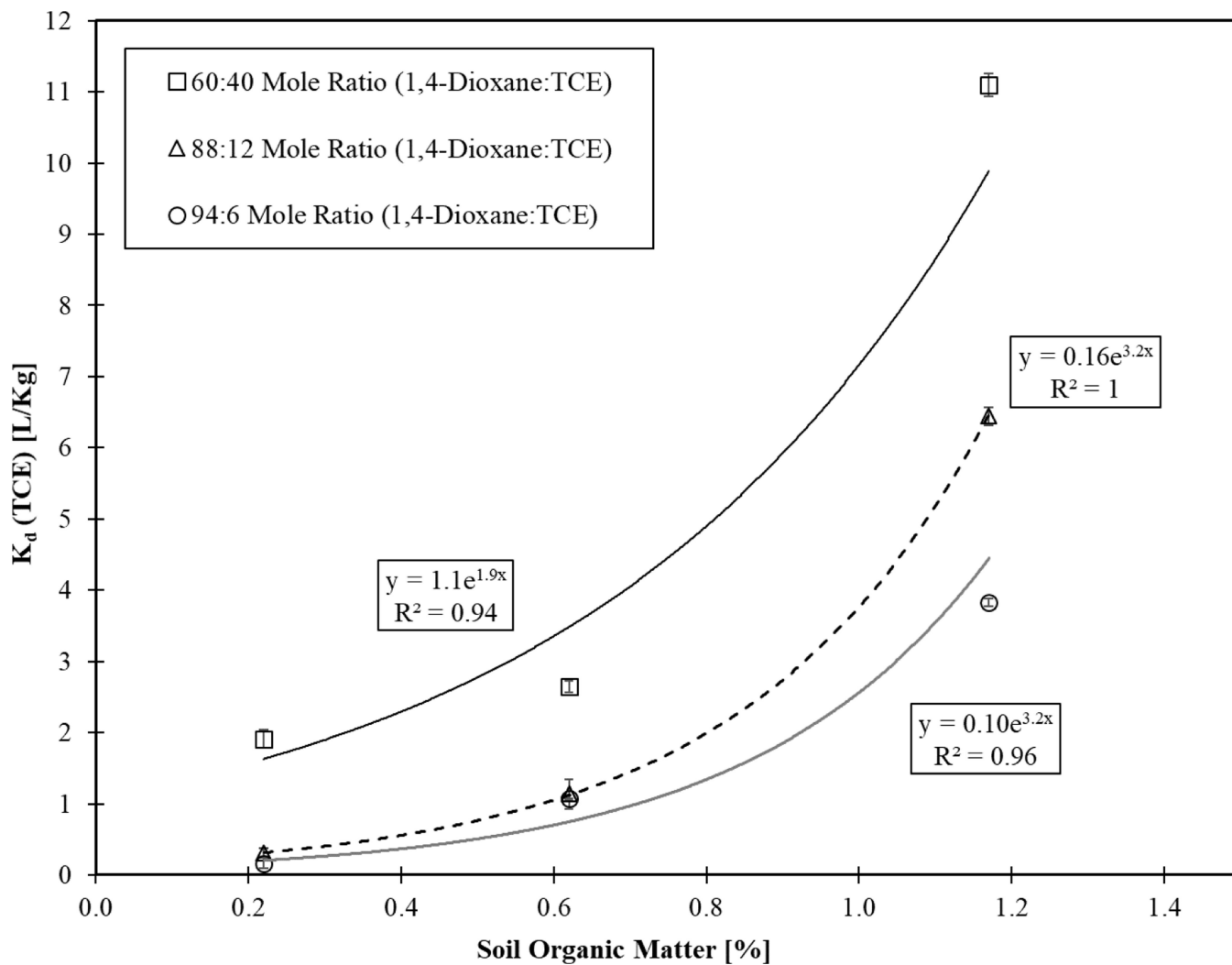


Figure 3. Two-component sorption K_d values as a function of SOM content for contaminant TCE. The regression lines and equations quantify the relationships at three different mixture molar ratios. Error bars represent one standard deviation about the mean for measured replicate experiments.

Table 1.

Characteristics of AFP44, AF-1, and AF-2 porous media (aquifer) sediments.

Site Media	AFP44	AF-1	AF-2
Texture	Clay Loam	Clay Loam	Clay Loam
SOM (%)	0.22	0.62	1.17
Cation Exchange Capacity (meq/100g)	20.6	23.4	26.6
pH	8.27	7.54	7.46
Porosity	0.652	0.56	0.55
Bulk Density (g/cm ³)	0.88	0.96	1.0

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript