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Rate-limited Mass Transfer of Trichloroethene

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Rate-limited Mass Transfer of Trichloroethene

BY

Deza Irving

A thesis submitted in partial fulfillment
of the requirement for the degree of

BACHELOR OF SCIENCE
IN
CIVIL AND ENVIRONMENTAL ENGINEERING

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Gwynn R Johnson, Ph.D.

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ABSTRACT

Trichloroethene (TCE) is a volatile and toxic contaminant commonly found in the subsurface. To help reduce the effects of this contaminant, it is important to understand the transport and fate behavior of TCE through the subsurface. As groundwater fills the void spaces of a porous media contaminated with pure-phase TCE, the TCE will dissolve into the water, contaminating the groundwater. It was expected that this dissolution would follow a first-order mass transfer process, suggesting that the rate of dissolution of TCE is dependent on the mass of TCE present in solution. The purpose of this study was to characterize the impact of the initial volume of pure-phase TCE in a porous media on TCE's rate of dissolution, and whether a simple batch experiment can be used to estimate the rate-limited mass transfer coefficient, k_2 . Batch experiments were conducted with different residual TCE concentrations in a natural porous media. Measured k_2 values ranged from 0.001–0.002 min^{-1} , even though the residual TCE concentration of one batch was five times that of the other. This suggests that the residual TCE concentration in the porous media does not affect the mass transfer rates measured in these batch experiments.

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1.0 INTRODUCTION

Trichloroethene (TCE) is a volatile and toxic contaminant that is commonly found in the subsurface and poses a significant risk to groundwater supplies (e.g., Johnson et. al., 2002). Upon being spilled in the natural environment, pure-phase TCE can become trapped in the void spaces of natural soils. As groundwater is exposed to the contaminated subsurface, the TCE dissolves and contaminates the groundwater.

The rate of this dissolution, or the mass flux, of TCE to water can be modeled by the following equation:

$$j = k_a(C_s - C) \quad (1)$$

Where j is the mass flux of TCE to water, k_a is a mass transfer rate coefficient, C_s is the aqueous solubility of TCE, and C is the bulk aqueous-phase concentration of TCE (Imhoff et. al., 1998). The bulk aqueous-phase concentration of TCE represents the resistance to mass transfer of TCE to the water (Imhoff et. al., 1998). As TCE dissolves, there exists a concentration gradient in the water, driven by advection and dispersion. The higher concentration is located near the TCE–water interface and decreases through the water as the distance from that interface increases. If the concentration at the interface reaches the aqueous solubility of TCE, then the dissolution becomes rate-limited by the rate of advection and dispersion of TCE through the porous matrix.

Advection-dispersion for the transport of a solute through porous media can be modeled by the following equation:

$$\frac{\partial C}{\partial t} = \left[\frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_z \frac{\partial C}{\partial z} \right) \right] - \left[\frac{\partial}{\partial x} (v_x C) + \frac{\partial}{\partial y} (v_y C) + \frac{\partial}{\partial z} (v_z C) \right] \quad (2)$$

where C is the concentration of the solute, t is time, D_x , D_y , and D_z are hydrodynamic dispersion coefficients in the longitudinal, transverse, and vertical directions, respectively, and v_x , v_y , and v_z are the average linear velocity in the longitudinal, transverse, and vertical directions (Fetter, 1993). For one-dimensional fluid flow, the governing equation for the dissolution of TCE can be rewritten in the form:

$$\frac{\partial C}{\partial t} = \left[\frac{\partial}{\partial x} \left(D_x \frac{\partial C}{\partial x} \right) - \frac{\partial}{\partial x} (v_x C) \right] \quad (3)$$

This one-dimensional equation describing the transport of TCE in porous media can be combined with the mass flux expression written above to express the rate-limited dissolution of TCE, where:

$$\frac{\partial C}{\partial t} = \frac{\partial j}{\partial x} = \frac{\partial k_a(C_S - C)}{\partial x} \quad (4)$$

Column dissolution studies are typically used to measure this rate-limited mass transfer process. These studies consist of a porous media with a residual pure phase packed into a soil column and flushed with water. The concentration of the contaminant in the effluent is measured and then plotted against time (or nondimensional time, i.e., pore volumes of water). The mass-removal process observed typically shows an initial steady-state stage where effluent concentrations are driven by the maximum aqueous solubility of the contaminant. As the pure phase dissolves, the residual concentration in the porous media decreases and the droplets of the contaminant get smaller. The mass-removal process becomes transient, and the observed relationship shows a rapid monotonic decrease in effluent concentrations (Mahal et al., 2010). Finally, after an extended contact time, another rate-limited steady state stage occurs as the contact area between the advecting fluid (water) and the residual contaminant decreases and elution tailing occurs (see Figure 1 for example).

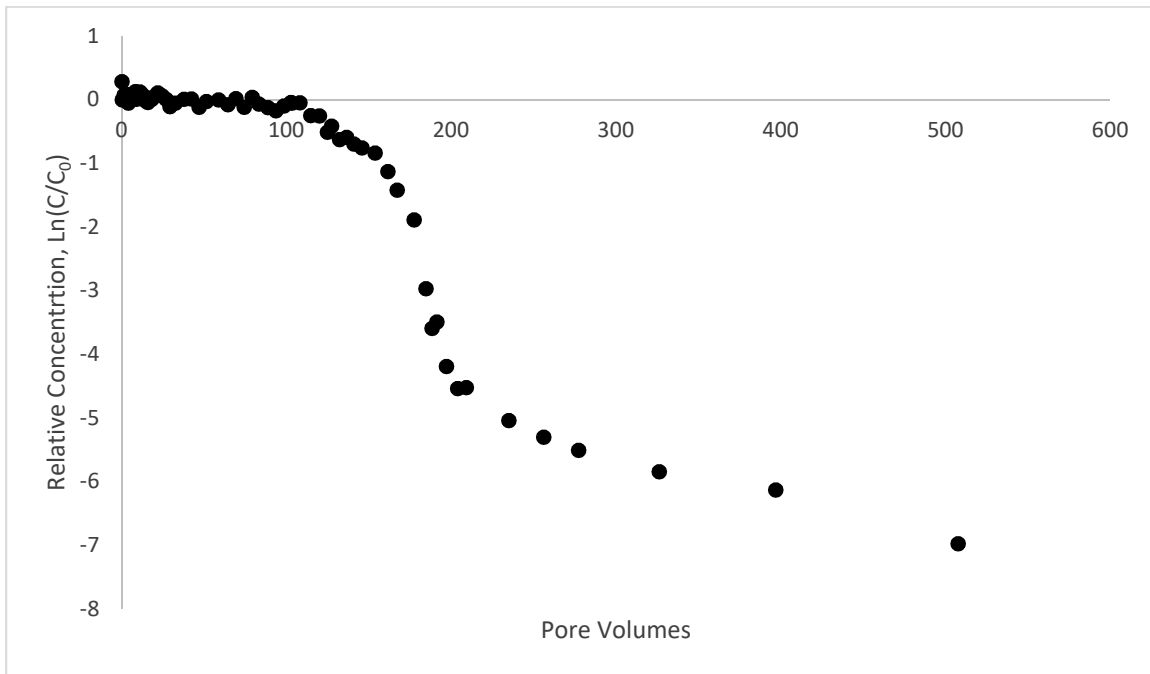


Figure 1. Example of a dissolution study conducted with a uniform homogeneous sand (Mahal et al., 2010; previously measured in our laboratory).

The purpose of this study was to estimate the rate-limited mass transfer coefficient, k_2 , in batch experiments. To reach this stage with a column study typically requires hundreds of pore volumes of advecting fluid. Instead, batch experiments were conducted to estimate the rate-limited mass transfer coefficient, because this may be a faster way to estimate this value successfully. Measured mass transfer coefficients from these batch experiments were compared to those reported in the literature (and as previously measured by our research group).

2.0 MATERIALS AND METHODS

2.1 Reagents

Trichloroethene (TCE), distributed by Aldrich Chemical Company, Inc., was used as the organic liquid contaminant partitioning to water. A 99.5% pure spectrophotometric grade was used. TCE has a density of 1.462mg/ μ L. Nanopure water was used throughout the batch experiments and sample analysis.

2.2 Porous Media

Commercially available 20/30 Accusand (Unimin Corporation) was used. This sand has a porosity of approximately 0.30 and an average bulk density of 1.5g/cm³

2.3 Apparatus

The batch experiments were conducted in 20mL headspace vials. Aluminum caps (20mm) and Teflon-lined butyl rubber septa were used to seal each reaction vial. The TCE was injected into the porous media with a 100 μ L glass micro-syringe.

2.4 Batch Experiment Procedures

Batch experiments were conducted in duplicate. Each reaction vial was filled with approximately 15g of porous media and water was added to saturate the sand to approximately 20%. In batch experiment A (Batch A), 100 μ L of TCE was injected into the wet media of each batch reactor, filled with water and sealed. In batch experiment B (Batch B), 500 μ L of TCE was injected into the wet media, filled with water and sealed.

Controls for each experiment included a water blank and TCE blank. The water blank was created by completely filling with water (i.e., no sand or TCE), followed by capping/sealing of the vial. The TCE blank for each experiment was created by injecting 100 μ L of TCE and 500 μ L of TCE into separate vials, then filling them with water (i.e., no porous media), and sealing. Each batch experiment consisted of fourteen discrete sampling times. These sampling times ranged from approximately 30 seconds to 6 hours. At each sampling time, one discrete batch reactor was sacrificed and three subsamples of the headspace water were collected for analysis of TCE in solution.

2.5 Analytical Instrumentation

An OHAUS Adventurer digital scale with an accuracy of ± 0.0001 g was used to find the mass of the vials, caps, water, porous media, and subsamples throughout the batch experiments. The subsamples were analyzed, using a Hitachi U-1800 UV-VIS Spectrophotometer equipped with deuterium and tungsten lamps at a wavelength of 242.5nm.

To ensure that the maximum absorptivity limit of the spectrophotometer was not exceeded, each subsample was diluted with nanopure water. Subsamples from Batch A were diluted with approximately 4mL of water (and with approximately 1 – 2 mL on replication), and subsamples from Batch B were diluted with approximately 5mL of water. Aliquots of the diluted subsamples were used to fill a 1.7mL

cuvette. This cuvette was placed into the UV-VIS to measure the absorptivity of each subsample. Based on previous research conducted in our laboratory, the absorptivity measured by the UV-VIS for TCE in aqueous solutions is expected to be linearly proportional to the concentration of TCE in the water. In this study, the absorptivity was therefore used as a measure of the relative concentration of TCE that had partitioned to the water.

2.6 Data Analysis

The rate-limited dissolution of an organic solute is typically a first-order mass transfer process, where the rate of dissolution of the solute is dependent on the mass of the solute already present in solution. In other words, the rate of dissolution of the constituent decreases as the concentration of the constituent in solution increases until the equilibrium concentration, or aqueous solubility, is reached. This rate-limited mass transfer process for the dissolution of TCE in the batch reactors can be modeled with a first-order mass transfer differential equation:

$$\frac{dC}{dt} = k_2 C^n \quad (5)$$

where C is the concentration of TCE in the water, t is time, k_2 is the rate-limited mass transfer coefficient of TCE, and n is the order of the reaction, equal to one.

The solution to this differential equation is:

$$\int_{C_0}^C \frac{dC}{C} = \int_{t=0}^t k_2 dt$$

$$\ln\left(\frac{C}{C_0}\right) = k_2 t$$

where C_0 is the initial concentration of TCE in the water.

This equation can be linearized to follow the form $y = mx + b$:

$$\ln C = k_2 t + \ln C_0 \quad (6)$$

If the $\ln C$ is plotted against t , the slope of the resulting regression line is k_2 and the y-intercept is $\ln C_0$. The purpose of these experiments is to determine whether the initial volume of TCE in the porous media (i.e., the initial residual saturation of TCE) affects the rate-limited mass transfer coefficient, k_2 , and whether a batch reaction can be used to successfully model this mass transfer. The slope of the regression was used to determine the mass transfer coefficient for each batch.

3.0 RESULTS

The following sections will describe the data gathered throughout each batch experiment, the linearization and regression results of each batch experiment. Additionally, a comparison of the measured rate-limited mass transfer coefficient to those reported in the literature (and previously measured in our laboratory) follows.

3.1 Data Gathered

Each batch experiment included 14 reaction vials plus controls. For example, a portion of the data collected in preparation for Batch A has been provided in Table 1. The ‘WB’ in the excerpt denotes the water blank and the ‘TB’ denotes the TCE blank, as controls.

3.1.1 Preparation Data

To prepare for each experiment, the tare mass of each reaction vial and its cap was determined. A mass of porous media was added and measured accordingly. Finally, a volume of water was added to discrete batch reactors and recorded (Table 1). Approximately 15g of sand was added to each vial, then 2–3g of water, saturating the sand to approximately 20%.

Table 1. A portion of the data gathered during the preparation stage of Batch A.

	WB	TB	1	2	3	4	5
Vial (g)	14.9219*	14.7482	14.8710	14.9627	15.9003	15.0533	14.9806
Vial & Cap (g)	16.6191	16.5833	16.5812	16.7202	17.6910	16.7611	16.7565
Cap (g)	1.6972	1.8351	1.7102	1.7575	1.7907	1.7078	1.7759
Vial & sand (g)	-----	-----	29.9665	30.0334	30.8910	30.0281	30.0181
Sand (g)	-----	-----	15.0955	15.0707	14.9907	14.9748	15.0375
Vial, sand & h ₂ O (g)	-----	-----	32.1950	32.0779	33.1965	32.3324	32.1083
h ₂ O (g)	-----	-----	2.2285	2.0445	2.3055	2.3043	2.0902

*Measured using OHAUS Adventurer digital scale with an accuracy of ± 0.0001 g

3.1.2 Residual TCE Concentration Data

The initial residual saturation of TCE is the volume of TCE in the voids of the porous media. For Batch A, that initial residual saturation was created by injecting 100 μ L of pure-phase TCE into the porous media with an initial $\sim 20\%$ moisture content. For Batch B, 500 μ L of pure-phase TCE was injected into the porous media (also at $\sim 20\%$ moisture content).

Using the mass of sand found in the preparation stage, and the average bulk density of 20/30 Accusand, the volume of sand in each reaction vial was calculated. The volume of the sand in each vial was multiplied by the porosity of the sand, which was approximately 0.30, to find the volume of the voids. The volume of TCE is consistent throughout each experiment: 100.0 μ L or 0.1000cm³ for Batch A and its duplicate, and 500.0 μ L or 0.5000cm³ for Batch B and its duplicate. The residual concentration of TCE was calculated as the volume of TCE divided by the volume of voids in the porous media used. The

reaction vials in Batch A had an average residual TCE concentration of 3.3%, and the vials from Batch B had an average residual of 16.6% (Table 2, for example).

Table 2. A portion of the residual TCE concentration calculations for Batch A.

	WB	TB	1	2	3	4	5
Mass of Sand (g)	-----	-----	15.0955	15.0707	14.9907	14.9748	15.0375
Volume of Sand (cm³) ($\rho_{\text{media}} = 1.5\text{g/cm}^3$)	-----	-----	10.0637	10.0471	9.9938	9.9832	10.0250
Volume of Voids ($\eta * V_{\text{sand}}$)	-----	-----	3.0191	3.0141	2.9981	2.9950	3.0075
Volume of TCE (cm³)	-----	-----	0.100	0.100	0.100	0.100	0.100
Residual [TCE] (%) ($V_{\text{TCE}}/V_{\text{voids}}$)	-----	-----	3.31	3.32	3.34	3.34	3.33

3.1.3 Sampling Data

Once the TCE was injected into the sand of a vial, the vial was filled with water and capped. The time each vial was capped was recorded, and its mass was measured. After the estimated time interval for a vial had elapsed, the discrete batch reactor vial was sacrificed. The time each vial was sacrificed was recorded and three subsamples of the headspace water were collected and placed in cold storage. The total contact time for each vial was then calculated in seconds, minutes, and hours (Table 3, for example).

Table 3. A portion of the data gathered and calculations during the sampling stage of Batch A.

	WB	TB	1	2	3	4	5
Vial, cap, sand, h₂O & TCE (g)	37.9039	38.1129	47.0171	47.1802	47.9469	47.2892	47.4148
TCE (g) [1.462g/cm ³ *100 μ L]	0.000	0.146	0.146	0.146	0.146	0.146	0.146
Time crimped (hr:min.sec)	12:28.06	12:30.39	12:33.34	12:36.08	12:38.49	12:41.54	12:44.55
Estimated Interval	[END]	[END]	(6h)	(5h)	(4h)	(3h)	(2h)
Time opened (hr:min.sec)	18:35.18	18:36.33	18:33.34	17:36.23	16:38.50	15:42.11	14:44.57
Contact Time (hr:min.sec)	6:07.12	6:05.54	6:00.00	5:00.15	4:00.01	3:00.17	2:00.02
Time (sec)	22032	21954	21600	18015	14401	10817	7202
Time (min)	367.20	365.90	360.00	300.25	240.02	180.28	120.03
Time (hr)	6.120	6.098	6.000	5.004	4.000	3.005	2.000

3.1.4 Sample Analysis Data

Subsamples from each discrete batch reactor were analyzed by UV-VIS spectrophotometry within 7 days of sample collection. Each subsample needed its own vial and cap, so the tare masses of each were recorded. These vials were not crimped; the caps were used to reduce the amount of TCE lost to the air. The amount of water used to dilute each subsample for Batch A was approximately 4mL. Starting with subsample 3, the absorptivity dropped to 0.008, which is close to the lower absorptivity limit of the spectrophotometer. The amount of water used to dilute each subsample in the Batch A duplicate was therefore dropped to between 1–2mL.

The measured absorptivity values had to be adjusted according to the amount of nanopure water used to dilute each subsample. It was assumed that any variation in the density of water in each subsample due to the presence of TCE was negligible, and a dilution factor was calculated by dividing the volume of each subsample by the volume of added dilution water. Dividing the measured absorptivity by the dilution factor gave a relative absorptivity, assumed to be linearly proportional to the concentration of TCE in each subsample (Table 4, for example).

Table 4. A portion of the data collected and calculated during the sample analysis stage for Batch A.

	WB	TB	1	2	3	4	5
Sample vial (g)	14.7406	14.7475	14.7834	14.7385	14.9700	14.9770	14.8888
Vial & cap (g)	16.4800	16.4621	16.5114	16.5370	16.7833	16.7500	16.6971
Cap (g)	1.7394	1.7146	1.7280	1.7985	1.8133	1.7730	1.8083
Vial & h₂O (g)	18.9816	18.9076	19.1214	19.0397	19.1150	18.9044	19.1903
h₂O (g)	4.2410	4.1601	4.3380	4.3012	4.1450	3.9274	4.3015
Vial, cap, h₂O, & sample (g)	22.6496	22.4831	22.7156	22.6889	22.7806	22.5105	22.8202
Sample (g)	1.9286	1.8609	1.8662	1.8507	1.8523	1.8331	1.8216
Absorptivity (Abs)	0.003	0.013	0.010	0.019	0.008	0.007	0.008
Dilution Factor (V_{sample}/V_{h2O})	0.4548	0.4473	0.4302	0.4303	0.4469	0.4667	0.4235
Relative Abs	0.007	0.029	0.023	0.044	0.018	0.015	0.019
Time (min)	0	365.90	360.00	300.25	240.02	180.28	120.03

3.2 Batch Linearization

The results of Batch A and its duplicate are presented in Figure 2. The overall shape of the temporally variable concentrations measured for TCE is reproducible between the two batch experiments. As the contact time between the residual pure-phase TCE and water increases to a maximum of 6 hours, the concentrations of TCE measured in the aqueous phase approaches a steady state, equilibrium concentration.

Analysis of this temporal data using Equation 6 resulted in a rate-limited mass transfer coefficient, k_2 , of 0.002min^{-1} (Figure 3). The duplication of Batch A produced a k_2 value of 0.001min^{-1} (Figure 4).

Batch B and its duplication also resulted in TCE concentrations trending to a long-term steady state, equilibrium concentration (Figure 5). The rate of dissolution shown by the data starts out steep as concentrations of TCE rise and as contact time increases measured TCE concentrations level off/plateau.

When linearized and regressed, Batch B resulted in a rate-limited mass transfer coefficient, k_2 , of 0.002min^{-1} (Figure 6). The duplication of Batch B produced a k_2 value of 0.001min^{-1} (Figure 7).

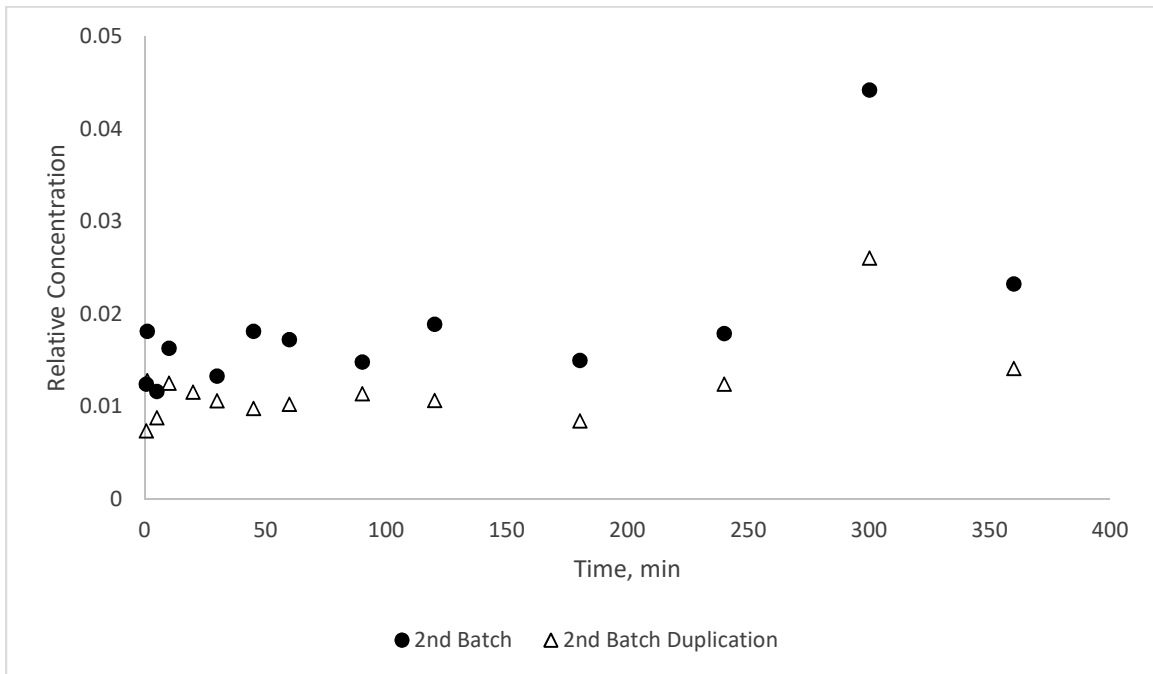


Figure 2. Relative absorptivity data from Batch A and its duplication.

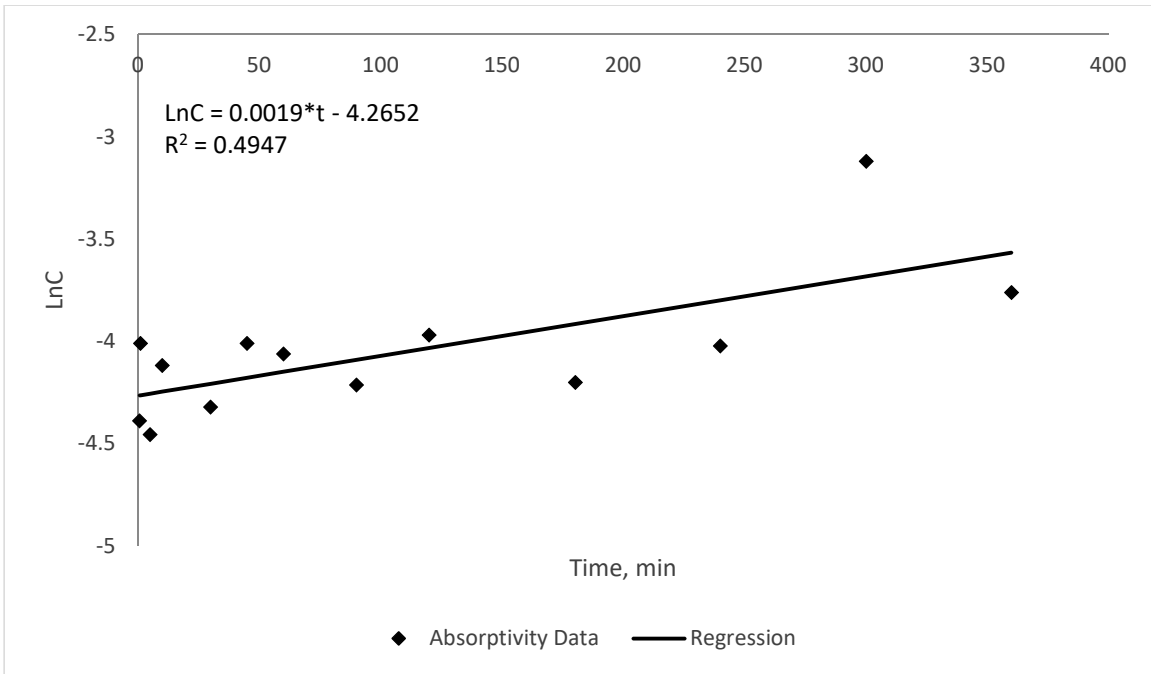


Figure 3. Regression analysis results for Batch A.

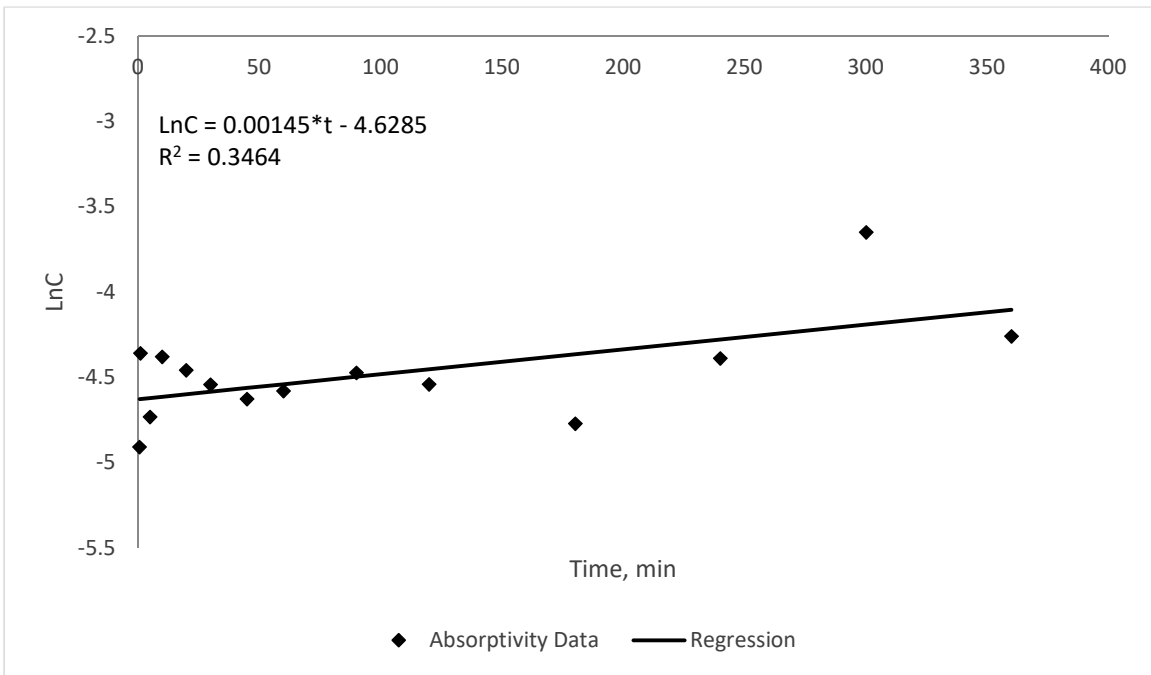


Figure 4. Regression analysis results for the duplication of Batch A.

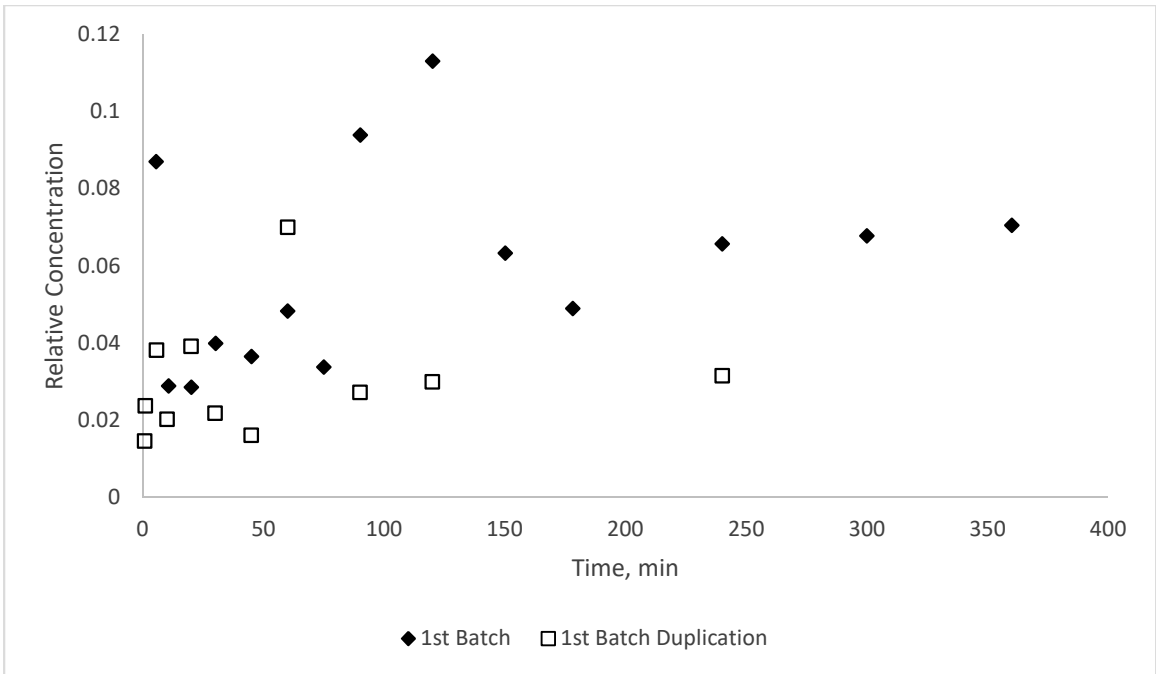


Figure 5. Relative absorptivity data from Batch B and its duplication.

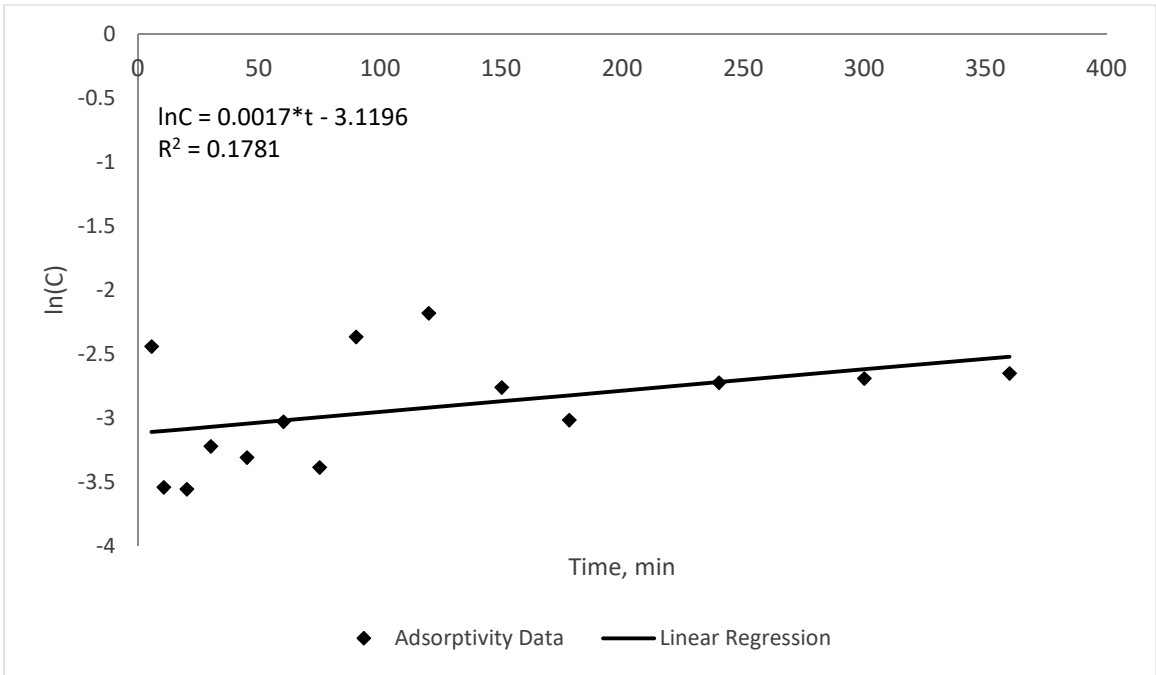


Figure 6. Regression analysis results for Batch B.

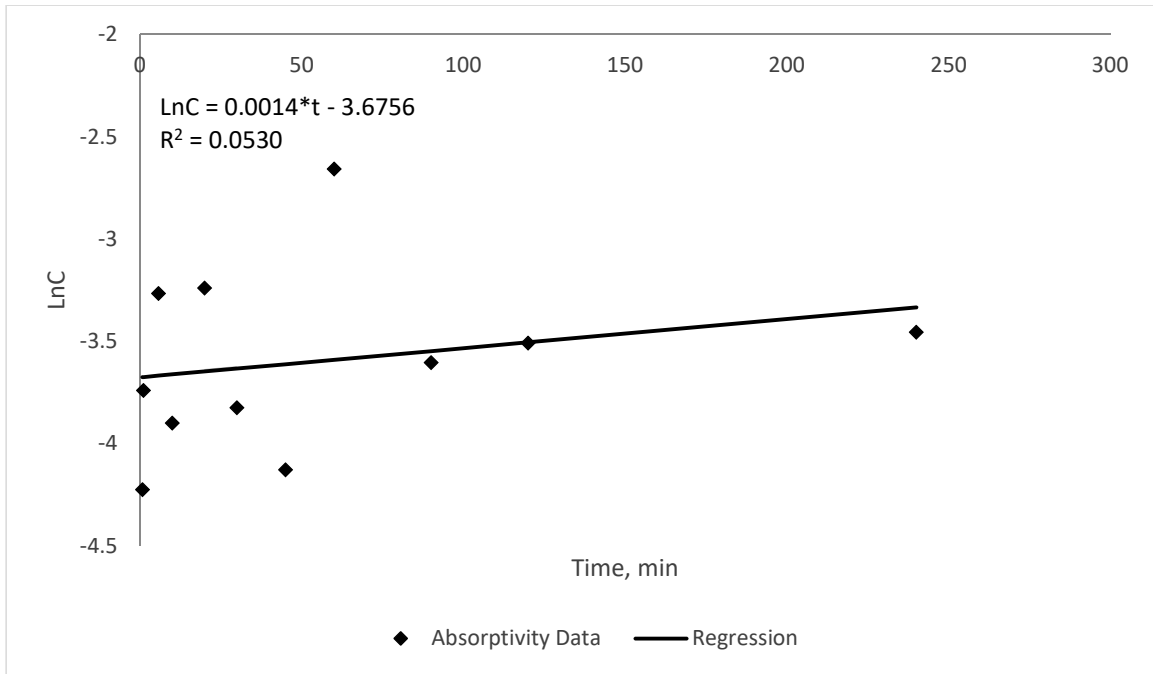


Figure 7. Regression analysis results for the duplication of Batch B.

3.3 Column Experiments for Comparison

Four column dissolution studies (published in the literature and previously characterized in our laboratory), each with a different porous media and initial residual saturation of TCE, were used to compare the measured rate-limited mass transfer coefficients. An example of the complete dissolution of residual TCE in a natural porous media was previously presented (see Figure 1). Figure 8 shows the percent mass recovery achieved over time (nondimensionalized in terms of flushing volumes of fluid, i.e., pore volumes) for these representative dissolution experiments. The Mix is a mixed media, where different porous media were mixed under laboratory conditions in order to simulate a heterogeneous surface soil. Eustis media is a sandy agricultural soil. The last data set was from the same quarried uniform soil, 20/30 Accusand, used in the batch experiments.

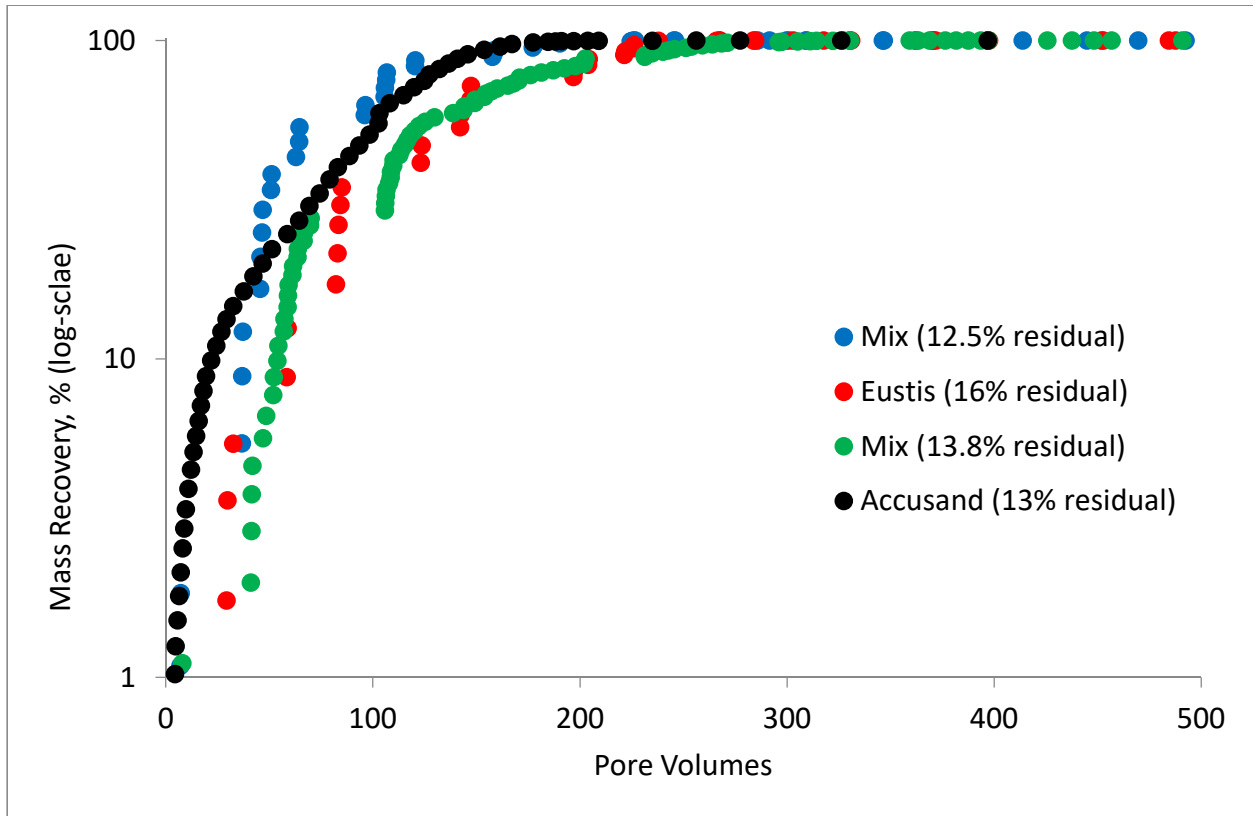


Figure 8. Regression analysis results for the duplication of Batch B.

The data from the secondary steady state stage of the dissolution studies were isolated. These were linearized and regressed in a similar fashion as the batch experiment data. The measured rate-limited mass transfer coefficients compared to those measured in this study (from batch experiments) are reported in Table 5 where the magnitudes of k_2 measured per min in the batch experiments were converted to nondimensionalized time assuming an effective average flowrate of 0.5mL/min and approximately 11mL of water per total volume of porous media.

Table 5. A summary of the rate-limited mass transfer coefficients and residual TCE concentrations for each column and batch experiment.

	Residual %	$k_2(\text{min}^{-1})$	k_2	R^2
Mixed Media 1	12.5%		2.4e-7	0.90
Eustis Media	16.0%		1.9e-7	0.92
Mixed Media 2	13.8%		1.1e-6	0.91
20/30 Accusand	~13%		5.3e-6	0.85
Batch A	3.3%	0.002	9e-5	0.50
Batch A Duplicate	3.3%	0.001	4e-5	0.35
Batch B	16.6%	0.002	9e-5	0.18
Batch B Duplicate	16.6%	0.001	4e-5	0.05

4.0 DISCUSSION AND CONCLUSION

From the results of the batch experiments, the rate-limited mass transfer coefficient, k_2 , ranged from $4\text{e-}5$ to $9\text{e-}5$ ($0.001\text{--}0.002\text{min}^{-1}$) for Batch A and B at approximately 3% and 17% residual saturations, respectively. Batch B had five times as much TCE injected into the media than Batch A, and the measured mass transfer coefficients for both batches are similar. This suggests that the initial residual saturation of TCE in the batch reactors does not affect the overall rate-limited mass transfer of TCE to water. In contrast, the mass transfer coefficients reported for the column experiments (in the literature and as previously measured in our laboratory) ranged from $0.2\text{e-}6$ – $5\text{e-}6$ for similar magnitudes of residual saturation of TCE (between 12 and 16%). It may be of interest to note that these batch experiments were conducted using 20/30 Accusand and a comparison of measured k_2 between batch and column studies for that media equaled $7\text{e-}5$ (on average) versus $5\text{e-}6$, respectively.

The k_2 values from the column experiments are consistently lower than those measured in the batch experiments. This could be something that needs some further investigation. For example, the difference could be due to the column studies having dynamic flow and the batch experiments having static flow. Alternatively, future batch experiments may include batch studies using samples of these other porous media (e.g., mixed media and Eustis media) for better comparisons.

If the batch experiments described in this report were replicated, some experimental design components should be addressed. First, the sample size should be increased to at least 30 reaction vials, instead of 14, because larger sample sizes typically produce more normalized results, or trends that are more obvious. With a larger sample size, the range of time intervals can be wider and greater accuracy toward a long-term steady state concentration of TCE in solution may be achieved. For example, the sample times can range from 1 minute to 10 hours. The minimum sample time should be no less than 1 minute, because that gives enough time to crimp the vial, measure its mass, then open it and collect the subsamples. Additionally, when analyzing the subsamples, it would be beneficial to conduct the sampling and sample analysis on the same day, which reduces the potential for TCE mass loss to the air. Also, since the measured absorptivities for Batch A almost fell below the lower detection limit of the spectrophotometer, and the Batch B absorptivities did not exceed 0.100, it seems unnecessary to dilute the subsamples before

analysis. Finally, during Batch B, after injecting the TCE and filling the vials with water, each vial had a pool of TCE on top of the sand. The vials in Batch A did not have this pool of TCE. Unless the batch experiments are replicated with a larger amount of sand in each vial, it is recommended that no more than 100–200 μ L of TCE are used for 15g of 20/30 Accusand.

If more evidence is gathered that suggests that a batch experiment can successfully be used to estimate the rate-limited mass transfer coefficient, k_2 , of organic contaminants, these values can be used in risk assessment applications. The estimated values of k_2 can be applied to dissolution models to determine whether they can predict the transport of an organic through a porous media. These models can also be used to predict how many pore volumes are required to flush a contaminated site.

5.0 REFERENCES

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