Quantifying Impacts of Microcosm Mass Loss on Kinetic Constant Estimation

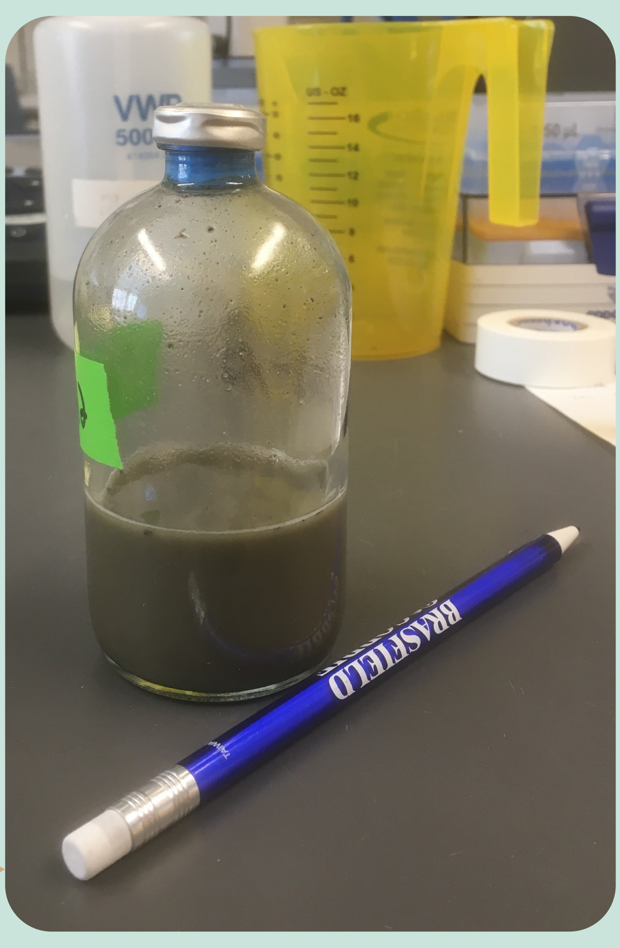
www.jackelsey.com
elsey.jack@gmail.com

Jack L. Elsey Tufts University | **Linda M. Abriola** Brown University | **John A. Christ** S&B Christ Consulting, LLC.

All microcosms experience contaminant mass loss, but almost no studies include mass loss in their models. This oversight can greatly bias the best-fit kinetic constants of those models.

Introduction

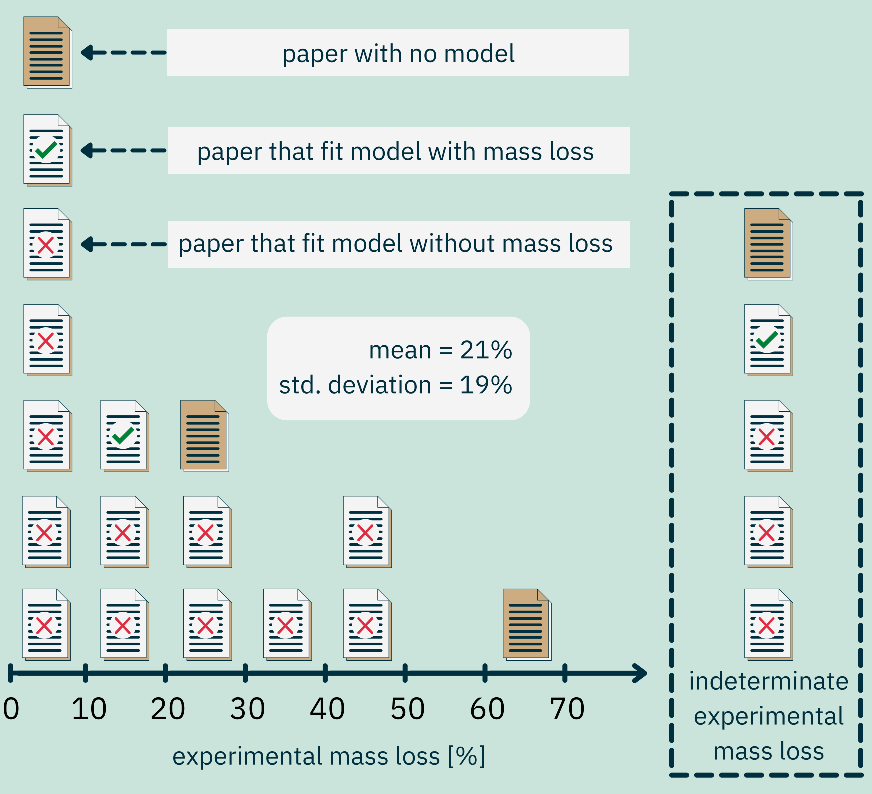
Before full-scale application of in situ bioremediation at sites contaminated by chlorinated solvents, the efficacy of the microbial reductive dechlorination (MRD) process is often first evaluated in laboratory microcosm experiments, where groundwater, soil, contaminants, and microbes are sealed in a small glass bottle with an anoxic headspace. Every few days a syringe is used to extract small water samples through the butyl rubber septum that seals the mouth of the microcosm bottle, and MRD models are then fit to the measured contaminant concentrations. Contaminant mass loss from the bottle inevitably occurs when the water samples are taken and it can also occur when contaminants sorb into the septum[1][2][3], but most literature MRD models fail to account for this mass loss. The primary purpose of this study is to explore potential bias in best-fit kinetic parameters that can result when mass loss is neglected from the model formulation.



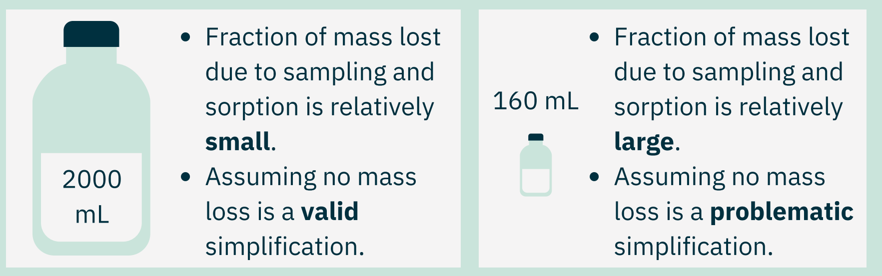
a typical microcosm experiment
Photograph by Sheng Dong at Auburn University.

Literature Review

A total of 22 microcosm papers studying MRD of tetrachloroethylene (PCE) and/or its daughter products were reviewed. Plotted data from these papers were extracted with WebPlotDigitizer[4] and used to (1) estimate experimental mass losses if they were not quantified by the study authors and (2) evaluate whether a paper's model fitting method accounted for these mass losses (i.e. determine if model values for total contaminant moles in the bottle decreased over time). As can be seen in the histogram, experimental mass losses were often substantial but the model formulations that were used usually assumed that no mass loss occurred.



The earliest paper[5] in this literature review did use a model with mass loss. The authors' subsequent paper[6] however described a spreadsheet-based model fitting technique that was widely adopted but required assuming no mass loss. This assumption was confirmed to be valid for their 2-liter microcosms but later papers that used similar models with smaller 160-mL microcosms did not reevaluate this assumption.



Methods

Fit an MRD model that accurately accounts for mass loss to a microcosm experiment[7] from the literature to determine "true" values for four Monod kinetics parameters:

- cis-1,2-dichloroethene (cis-DCE) u-max
- cis-DCE K_s
- vinyl chloride (VC) u-max
- VC K_s

Monod Kinetics

$$\text{MRD rate} = \frac{u^{\max} C X}{K_s + C}$$

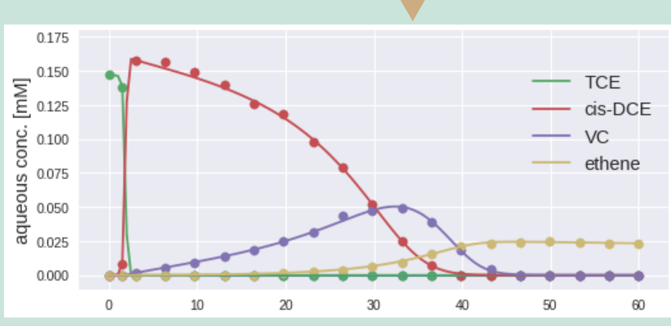
$u^{\max}$: maximum substrate utilization rate; X: dechlorinator biomass concentration; K_s: half-saturation constant; C: contaminant concentration

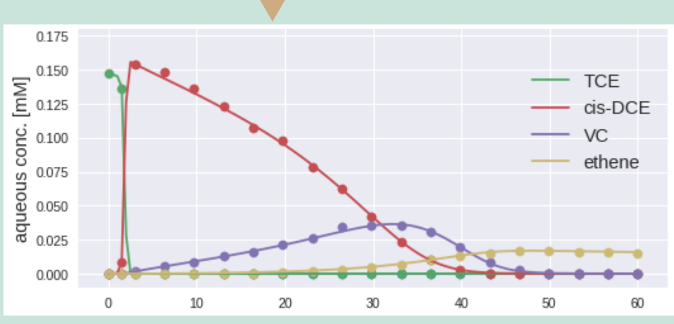
Using the previously determined "true" parameter values, generate synthetic concentration data for a hypothetical microcosm experiment with **10% experimental mass loss**.

Using the previously determined "true" parameter values, generate synthetic concentration data for a hypothetical microcosm experiment with **40% experimental mass loss**.

Fit a model that assumes 10% mass loss (LML).

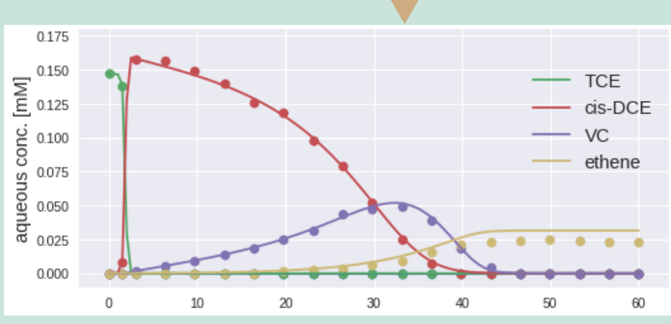
Fit a model that assumes 40% mass loss (HML).

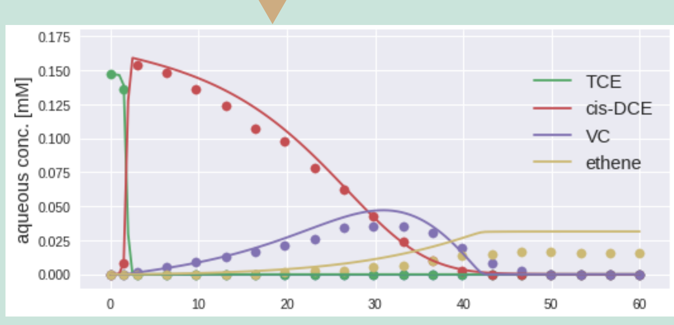




Fit a model that assumes no mass loss (NML).

Fit a model that assumes no mass loss (NML).

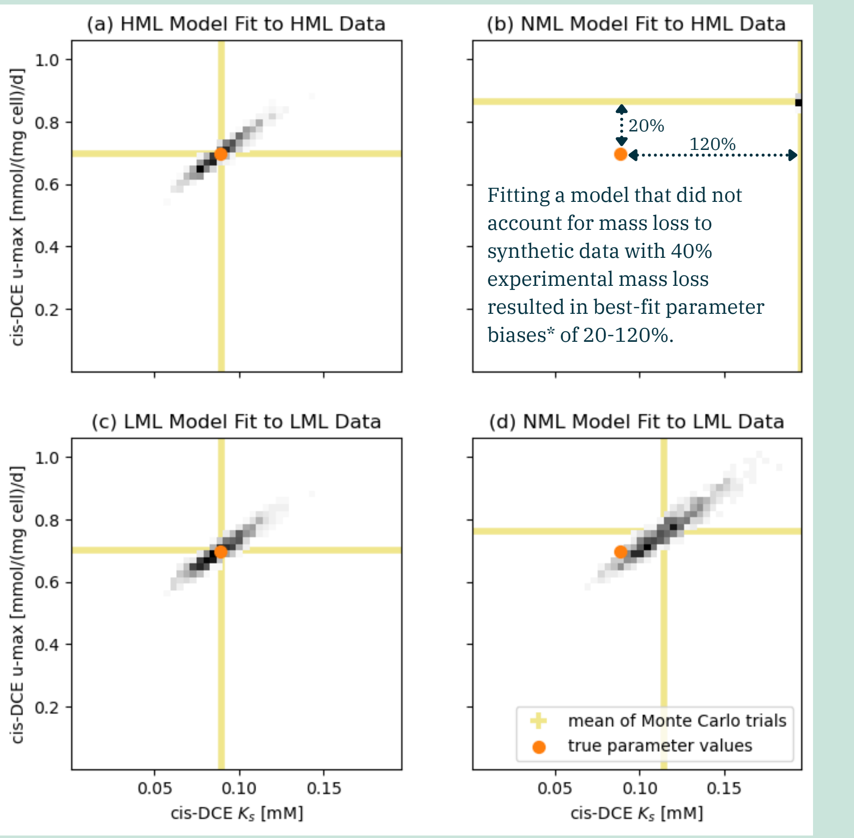




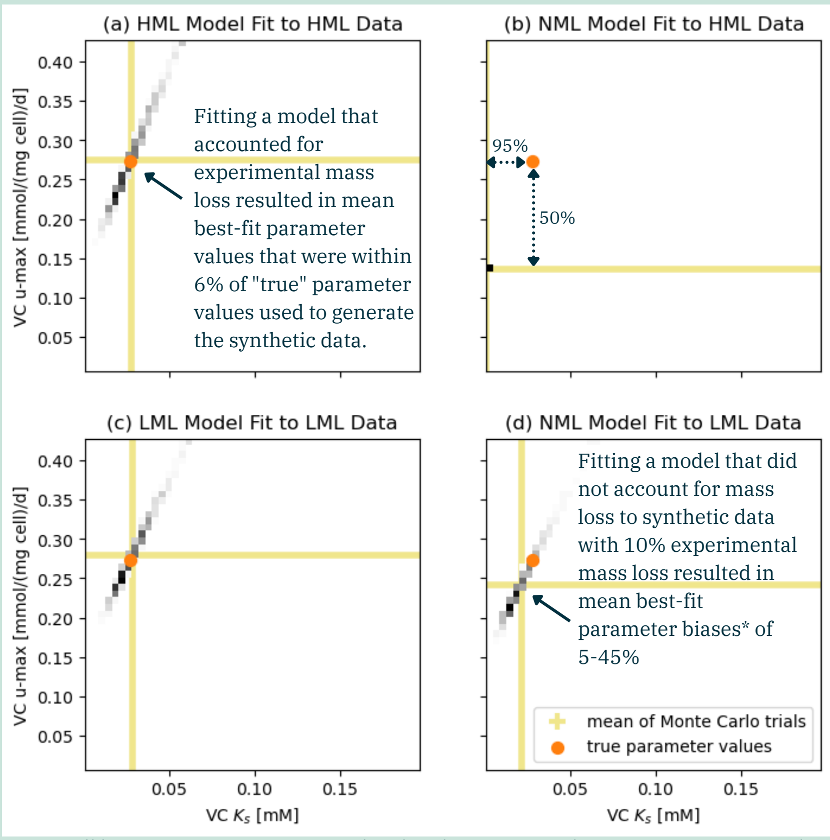
Compare model fits to see if models that account for mass loss yield best-fit parameter values that are closer to the "true" parameter values used to generate the synthetic data than model fits that neglected mass loss.

Repeat process hundreds of times.

Results



HML = high (40%) mass loss LML = low (10%) mass loss NML = no mass loss



* All bias percentages are normalized to the corresponding "true" parameter value.

Conclusions

- MRD microcosms in the literature exhibited mean experimental mass losses of 21%, but very few studies fit models with formulations that incorporated mass loss.
- In a numerical experiment, models that failed to consider mass loss resulted in significant fitted parameter bias, ranging from 5-45% or 20-120% of the parameter magnitude for synthetic microcosm datasets with low (10%) or high (40%) mass loss, respectively.
- The inverse problem of fitting MRD models to microcosm data is inherently challenging due to the large number of model parameters and high correlation between some of these parameters. Neglecting mass loss in the model formulations simply adds to the uncertainty and limits the applicability of the best-fit kinetic constants obtained when modeling microcosm data.

This work was supported by the Strategic Environmental Research and Development Program (SERDP) Project ER-2311 (contract #W912HQ-13-C-0011).

The authors would like to thank SiREM for providing the KB-1® culture used in the microcosm experiment.

References

1. S. Prager and F. A. Long, "Diffusion of hydrocarbons in polyisobutylene," Journal of the American Chemical Society, vol. 73, no. 9, pp. 4072–4075, 1951.
2. R. Göbel, R. Krska, R. Kellner, R. W. Seitz, and S. A. Tomellini, "Investigation of Different Polymers as Coating Materials for IR/ATR Spectroscopic Trace Analysis of Chlorinated Hydrocarbons in Water," Appl Spectrosc, vol. 48, no. 6, pp. 678–683, Jun. 1994, doi: 10.1366/000370294774369054.
3. R. Göbel, R. W. Seitz, S. A. Tomellini, R. Krska, and R. Kellner, "Infrared attenuated total reflection spectroscopic investigations of the diffusion behaviour of chlorinated hydrocarbons into polymer membranes," Vibrational Spectroscopy, vol. 8, no. 2, pp. 141–149, Jan. 1995, doi: 10.1016/0924-2031(94)00045-I.
4. A. Rohatgi, WebPlotDigitizer. San Francisco, California, USA, 2019. https://automeris.io/WebPlotDigitizer
5. L. H. Smith, P. K. Kitanidis, and P. L. McCarty, "Numerical modeling and uncertainties in rate coefficients for methane utilization and TCE cometabolism by a methane-oxidizing mixed culture," Biotechnol. Bioeng., vol. 53, no. 3, pp. 320–331, Feb. 1997, doi: 10.1002/(SICI)1097-0290(19970205)53:3<320::AID-BIT11>3.0.CO;2-O.
6. L. H. Smith, P. L. McCarty, and P. K. Kitanidis, "Spreadsheet Method for Evaluation of Biochemical Reaction Rate Coefficients and Their Uncertainties by Weighted Nonlinear Least-Squares Analysis of the Integrated Monod Equation," Appl. Environ. Microbiol., vol. 64, no. 6, pp. 2044–2050, Jun. 1998.
7. L. Yang et al., "Exploration of Processes Governing Microbial Reductive Dechlorination in a Heterogeneous Aquifer Flow Cell," (in press) Water Research, 2021.

www.jackelsey.com
elsey.jack@gmail.com
(313)410-6362
Tufts University Department of Civil and Environmental Engineering
200 College Avenue, Medford, MA 02155