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Comparative meta-analysis and experimental kinetic investigation of column and batch bottle microcosm treatability studies informing in situ groundwater remedial design

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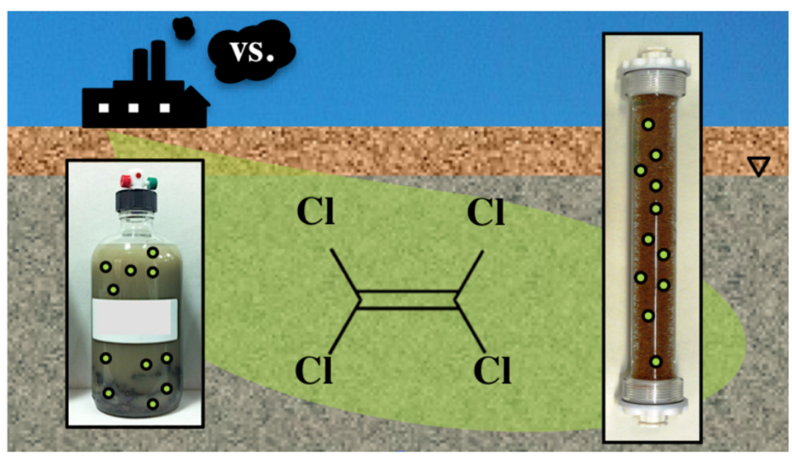
HIGHLIGHTS

- Literature revealed an industry preference for batch kinetics over column kinetics.
- Generally, observed rate constants were higher (faster rates) for continuous systems.
- Greater data density in columns creates more reliable estimates for sustained rates.
- For controlled-release carbon sources, batch data may overestimate in situ results.
- Unified framework for data use and reporting in treatability studies is necessary.

GRAPHICAL ABSTRACT



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ABSTRACT

A systematic comparison was performed between batch bottle and continuous-flow column microcosms (BMs and CMs, respectively) commonly used for in situ groundwater remedial design. Review of recent literature (2000–2014) showed a preference for reporting batch kinetics, even when corresponding column data were available. Additionally, CMs produced higher observed rate constants, exceeding those of BMs by a factor of 6.1 ± 1.1 standard error. In a subsequent laboratory investigation, 12 equivalent microcosm pairs were constructed from fractured bedrock and perchloroethylene (PCE) impacted groundwater. First-order PCE transformation kinetics of CMs were 8.0 ± 4.8 times faster than BMs (rates: 1.23 ± 0.87 vs. 0.16 ± 0.05 d^{-1}, respectively). Additionally, CMs transformed 16.1 ± 8.0-times more mass than BMs owing to continuous-feed operation. CMs are concluded to yield more reliable kinetic estimates because of much higher data density stemming from long-term, steady-state conditions. Since information from

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BMs and CMs is valuable and complementary, treatability studies should report kinetic data from both when available. This first systematic investigation of BMs and CMs highlights the need for a more unified framework for data use and reporting in treatability studies informing decision-making for field-scale groundwater remediation.

1. Introduction

Despite significant remediation efforts over the last few decades by the United States and other developed nations, the number of hazardous waste sites remains considerable. Assessments conducted by the United States Environmental Protection Agency (US EPA) concluded that 294,000 hazardous waste sites exist across the United States, with projected remediation costs amounting to more than $209 billion [1]. With some of the easiest to remediate sites now closed, a large number of challenging sites remain, estimated to require greater than 100 years for cleanup, and containing recalcitrant or comingled contaminants, typically in hydrogeologically complex environments [2]. In the US, the largest category of recalcitrant contaminants is halogenated volatile organic compounds (VOCs). This contaminant class comprises the highest percentage of sites on the US EPA's National Priorities List (sites eligible for remedial action under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) or Superfund program), and the largest class of organic contaminants detected at Department of Defense installations [1]. Chlorinated solvents, which are the prime contributor to this category, are particularly challenging to remediate because of their pronounced recalcitrance to (bio)transformation and ability to form difficult to locate dense non-aqueous phase liquid (DNAPL) point sources [2].

The methodology for hazardous waste site characterization and remedial determination, known as Remediation Investigation/Feasibility Study (RI/FS), is outlined in CERCLA [3]. Integral to this framework is the use of treatability studies (often referred to as *feasibility studies*), intended to evaluate the performance, design and cost of potential remediation strategies before implementation [4]. Treatability studies require site geologic materials and groundwater to be tested with the proposed remedial technology, most commonly at the bench-scale. Although the US EPA offers treatability guidance documents designed to outline basic experimental parameters, a specific roadmap from inception to completion is not explicitly defined [5–7]. Thus the approach taken and data required to satisfy treatability study goals are open for interpretation.

Bench-scale treatability studies commonly use batch bottle or continuous-flow column designs to characterize and quantify contaminant changes in an experimental system as a proxy for in situ site conditions [8–10]. Batch microcosms (BMs), usually comprised of glass bottles with a narrow neck and orifice, are filled with geologic materials, site groundwater, amendments, and sealed with a gastight septum closure (closed systems). Batch bottle studies are the least expensive alternative in treatability studies and are the simplest to conduct [11–13]. Continuous-flow column microcosms (CMs) are commonly fabricated from glass or plastic cylinders, with sampling ports located at the inlet and outlet, and sometimes along the length of the column [14–16]. Columns are constructed with geologic material, solid amendments (optional), and groundwater is pumped through the column at a specified flow rate, typically in up-flow mode to remove trapped gases (open systems). Continuous-flow column experiments, although more expensive and challenging to operate, are known to be more representative of field conditions, by including the simulation of groundwater flow extant in the subsurface [17].

Data obtained from feasibility studies include the degree of removal (or sequestration) of the contaminant of interest, and are used to develop an understanding of the transformation kinetics [18–20]. In studies where the contaminant is chemically or biologically transformed, kinetic data are often presented in the form of rate constants, specifically as first-order rate constants (k) and corresponding, concentration-independent half-lives ($t_{1/2}$) [21–23]. Often, these calculated parameters are directly compared to those of other studies with similar experimental designs, in an effort to further substantiate the feasibility of the tested technology [24–26]. First-order rate constants are often used to populate projection models, which are integral in determining the fate and transport characteristics of the contaminants of interest [27–30]. A kinetic analysis is arguably the most valuable calculated parameter because this approach supplies the time necessary for cleanup, which largely dictates overall remediation costs. However, the experimental design, type of data extracted, calculations completed, and the manner in which data are presented is not stipulated, thereby rendering it subject to considerations of time, money or other issues.

In this study, a meta-analysis of the scientific literature was performed to determine common approaches to the use and reporting of BM- and CM-derived kinetics. In addition, an experimental investigation was conducted to better understand fundamental differences in reaction kinetics derived from batch and column treatability studies. Experimental treatability studies were conducted using bedrock and groundwater impacted by perchloroethylene (PCE), one of the most frequently encountered recalcitrant groundwater contaminants in the US and around the world [31]. The fate of PCE in the environment is a function of prevailing physical, chemical and biological conditions at the cleanup site [32,33], thus necessitating remedial design that is customized on a case-by-case basis informed by feasibility studies. Literature findings and original experimental data on combined batch and column BMs and CMs treatability studies were completed to elucidate the benefits and limitations of each.

2. Materials and methods

2.1. Literature meta-analysis

A literature review was conducted using Arizona State University's OneSearch, which includes Web of Science, JSTOR, RefWorks and other sources (Table S1), to determine the number of combined batch and column chlorinated solvent treatability studies published in peer-reviewed sources. Search criteria included an aggregate of the following keywords and phrases: batch; column; dechlorination; and 'rate constant.' Search results were refined by excluding the following subject terms: atmospheric protection/air quality control/air pollution; limnology; soil science and conservation; waste-water; wastewater treatment; sludge; water purification; and water purification methods. Publication dates included only those articles published from 2000 to 2014. Of the total number of search results (sorted by relevance); 30% of the