

Interactive comment on “Experimental study on retardation of a heavy NAPL vapor in partially saturated porous media” by Simon M. Kleinknecht et al.

Anonymous Referee #1

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General Comments The paper describes experiments designed to measure CS₂ vapor transport/retardation in dry and moist unsaturated porous media, and generally does so in a satisfactory manner. The paper does not provide a compelling motivation for these experiments, however. The introduction briefly discusses the importance of understanding gravity effects on dense vapors, because of the preferential downward flow (i.e., toward aquifers) of such vapors. Density-driven flow is never mentioned again, however; it is neither treated theoretically in the handling of the experimental data nor are the experiments themselves (unlike the first author’s other published work)¹ designed to examine density-driven flow (the experiments examine upward advection, rather than downward density-facilitated flow). Thus, the first stated motivation

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for studying CS₂ vapor transport is left unaddressed, leaving only the vague call for “further (contaminant-specific) investigations. . .to improve the process understanding required to assess the threat to the environment.” Although the experiments appear to be generally well executed, the paper does not deliver on elucidating the contaminant-specific processes that influence CS₂ retardation.

Rather than determining which processes affect CS₂ retention, they made relatively unsupported simplifying assumptions that a single process is important (only dissolution) and then chalked up the discrepancy between their theoretical and measured retardation to the processes they had previously excluded without actually investigating the nature, magnitude, or feasibility of these other processes to close the gap. More specifically, despite its potential importance (which is acknowledged), the authors excluded theoretical treatment of the process of accumulation at the air-water interface because “determining the size of the interfacial areas and partitioning parameters in theoretical approaches is considered a challenge”. The most recent paper they cite regarding this challenge is 18 years old. I encourage the authors to consult more recent literature regarding air-water interfacial area determination and solute accumulation, including those by some of the authors they cite elsewhere (e.g., Brusseau, Costanza-Robinson)²⁻⁹ and others (e.g., Wildenschild, Kibbey)¹⁰⁻¹³ Costanza-Robinson et al.⁹ for example, provide an empirical relationship for sandy materials describing the associated between porous media surface area, moisture saturation, and air-water interfacial areas that could be tailored to the media examined here. With this relationship or others, the authors could assess the potential for interfacial accumulation to feasibly account for the additional retardation experienced most notably on the fine sand.

The authors also summarily excluded sorption of CS₂ to the solid phase from consideration because of its supposed (no numbers are provided) similarity to CO₂ with regard to air-water partitioning and solubility. The correlation the authors are drawing between solubility and/or air-water partitioning and the solid-phase sorption coefficient is unclear. Sorption to the solid phase is more typically correlated to a compound’s

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octanol-water partitioning constant (KOW), which certainly differs substantially for CO₂ and CS₂. Moreover, a saturated phase experiment could readily be conducted and KD measured rather than making such an assumption.

Specific Recommendations a) A revised introduction that provides a more compelling motivation for studying CS₂ retardation and a more accurate framing of the experimental work to follow would allow readers to recognize what aspects of the work are novel and scientifically significant. For example, if CS₂ retardation is really truly understudied (a quick search in a well established database revealed very few CS₂ papers, which, coupled with its prevalence at NPL sites, surprised me) than say so. At several points in the paper, the authors refer to their experimental setup as “novel” (including conclusion #1), but basis of this claim is unclear; what exactly is novel about the setup and what processes/variables/systems does it open to investigation that were previously precluded?

b) Conduct a saturated phase experiment to measure KD and, if not available in the literature, a surface tension experiment to measure KIW before excluding sorption at solid and interfacial phases from consideration.

c) As appropriate, use parameters from (b) in your theoretical model of CS₂ retardation to perform a more complete and rigorous process-based analysis of your experimental findings.

d) The significance of the dispersion/dispersivity parameters derived for CS₂/the porous media is not clear to the reader. If you are going to perform this analysis, what is the important take-home for readers? As it stands, several of the conclusions are underwhelming – moments analysis works (conclusion #2), simple theoretical constructs from 1961 are imperfect (conclusion #3), diffusion effects increase with longer residence time (conclusion #4).

e) The conclusion most directly tied to the goal of the paper and potentially of greater interest to readers is #5, but suffers from interpretations based on assumptions of what

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processes control transport, since those processes were not specifically studied. The experiments and analysis suggested above in (a) would strengthen the conclusions that could be drawn.

f) Conclusion #6 is potentially quite interesting, but needs more discussion and incorporation of more relevant literature. I accept that further experimental investigation of the biodegradation may lie beyond the scope of the current paper, but if the data are going to be presented at all, they should be discussed (e.g., the feasibility of anaerobic degradation to occur at such timescales; if CS₂ is degraded so thoroughly so quickly (recoveries of only 1%!)) then why has CS₂ persisted at so many of the NPL sites for so long? etc.)

g) Conclusion #7 is a bit disorganized, repeating some of #5 and #6 before recommending that SVE be used for CS₂ remediation. This recommendation could be elaborated upon by discussion of what is actually being done and with what degree of success at the many NPL sites contaminated with CS₂. Also, some caveat should be included, given that the volatility and rate of evaporation of CS₂ liquid was not studied.

Technical Points a) If I understand the intended meaning correctly, “irreducible saturation” is more typically termed “residual saturation” b) I didn’t understand the concept of filling the porous media columns “each with an overfill of around 30 cm”. c) I found the schematic of the experimental system to be overly detailed to the point that it limited reader comprehension. I believe the He tank should be Ar instead? Several items in the figure weren’t in the legend. The purpose of the Tedlar bags was not clear. I would dramatically simplify the figure. d) The rationale for bottom-up flow was never provided and seems to counter the stated motivation of examining density-driven flow. e) The paragraph containing lines 1-10 on p 6 seemed particularly disorganized, jumping around from the N₂ chase to the gas mixture, back to the chase. f) Although 7 experiments are described (series 1-4 for glass beads; 1-3 for fine sand), only a fraction of these had full data – no saturation profiles for 3 of the 7; and poor mass recovery for series 3 fine sand. Because the saturation was at the heart of arguments regarding

CS2 retardation, the missing saturation profiles for these experiments is noteworthy. That said, the accuracy of the saturation profiles was called into question on p 9. The validity of basing arguments on profiles that are simultaneous dismissed as misleading due to the small size of the tensiometers was confusing. Moreover, column mass had been measurement throughout the experiment and supposedly provided an independent measure of moisture saturation that was more reliable. Why weren't these data shown instead of the tensiometer data (e.g., in Figure 3)? I don't mean to imply you should only show data you agree with, but if you fundamentally do believe that the tensiometer data are inaccurate, why present them to readers? g) As the authors note, it is not uncommon for compound-specific behavior to get lumped into dispersivity values, and also common for dispersivity values for nonreactive tracers to be considered more reliable. The authors might therefore consider using the non-reactive tracer data to arrive at a dispersivity value and fix this as an input parameter in the dispersion fitting of the CS2. h) The authors repeatedly mention grain-size distribution as a variable potentially influencing retardation. Presumably some of the grain-size effect is through its relationship to surface area (and therefore would affect solid-phase sorption and air-water interfacial accumulation). Some discussion and theoretical handling of the surface area impacts on retardation is needed.

1. Kleinknecht, S. M.; Class, H.; Braun, J. Density-driven migration of heavy NAPL vapor in the unsaturated zone. *Vadose Zone J* 2015, 14, 10.102136/vzj2014.12.0173.
2. Brusseau, M. L.; El Ouni, A.; Araujo, J. B.; Zhong, H. Novel methods for measuring air-water interfacial area in unsaturated porous media. *Chemosphere* 2015, 127, 208-201310.1016/j.chemosphere.2015.01.029.
3. Brusseau, M. L.; Janousek, H.; Murao, A.; Schnaar, G. Synchrotron X-ray Microtomography and Interfacial Partitioning Tracer Test Measurements of NAPL-water Interfacial Areas. *Water Resources Research* 2008, 44, W0141110.1029/2006WR005517.
4. Brusseau, M. L.; Peng, S.; Schnaar, G.; Costanza-Robinson, M. S. Relationships among air-water interfacial area, capillary pressure, and water saturation for a sandy porous medium. *Water Resources Research* 2006, 42, W03501.
5. Brusseau, M. L.; Peng, S.; Schnaar, G.;

Murao, A. Measuring air-water interfacial areas with X-ray microtomography and interfacial partitioning tracer tests. *Environmental Science and Technology* 2007, 41, 1956-61. 6. Costanza, M. S.; Brusseau, M. L. Contaminant vapor adsorption at the gas-water interface in soils. *Environmental Science and Technology* 2000, 34, 1-11. 7. Costanza-Robinson, M. S.; Brusseau, M. L. Air-water interfacial areas in unsaturated soils: Evaluation of interfacial domains. *Water Resources Research* 2002, 38, 1195-211. 8. Costanza-Robinson, M. S.; Carlson, T. D.; Brusseau, M. L. Vapor-phase transport of trichloroethene in an intermediate-scale vadose-zone system: Retention processes and partitioning-tracer-based prediction. *Journal of Contaminant Hydrology* 2013, 145, 82-89. 10.1016/j.jconhyd.2012.12.004. 9. Costanza-Robinson, M. S.; Harrold, K. H.; Lieb-Lappen, R. M. X-ray microtomography determination of air-water interfacial area-water saturation relationships in sandy porous media. *Environmental Science and Technology* 2008, 42, 2949-56. 10.1021/es072080d. 10. Culligan, K. A.; Wildenschild, D.; Christensen, B. S. B.; Gray, W. G.; Rivers, M. L.; Tompson, A. F. B. Interfacial area measurements for unsaturated flow through a porous medium. *Water Resources Research* 2004, 40, W12413. 10.1029/2004wr003278. 11. Chen, L.; Kibbey, T. C. G. Measurement of air-water interfacial area for multiple hysteretic drainage curves in an unsaturated fine sand. *Langmuir* 2006, 22, 6874-80. 12. Chen, L.; Miller, G. A.; Kibbey, T. C. G. Rapid pseudo-static measurement of hysteretic capillary pressure-saturation relationships in unconsolidated porous media. *Geotechnical Testing Journal* 2007, 30, 474-82. 13. Kibbey, T. C. G.; Chen, L. A pore network model study of the fluid-fluid interfacial areas measured by dynamic-interface tracer depletion and miscible displacement water phase advective tracer methods. *Water Resources Research* 2012, 48, W10519. 10.1029/2012WR011862.

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