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

Simon M. Kleinknecht et al.

simon.kleinknecht@iws.uni-stuttgart.de

1 Comments

We thank the reviewers for their careful observations and important comments. We agree that by providing a revised introduction and conclusion, adding a thorough discussion of all potential contributions to retardation of CS2, and addressing the technical issues raised will improve the quality of our manuscript and hope to get an invitation to do so.

1.1 Rewriting the introduction and conclusions

In a revision, we will change the introduction to give a more compelling motivation for our work in the context of vapor transport in the unsaturated zone, to clarify the reference to density-driven migration, and to underpin the need for the contaminant-specific investigation of CS2. Changing the introduction and addressing the issues/questions will provide a more accurate framing and will emphasize the scientifically important aspects of our work (Review #1: comment a). The conclusions will be restructured focusing on the important findings of our work, the transport processes and retardation of CS2. Minor conclusions such as the discussion of dispersion/dispersivity parameters (Review #1: comment d) will be merged. Effects of density difference on retardation (Review #2: comment 1) were not a goal of our experiments, which aimed at a clear process differentiation between retardation and density-driven migration. Nevertheless, experiments were conducted with bottom-up as well as downward oriented flow showing no impact on the retardation of CS2. Moreover, we will provide a better discussion (Review #1: comment f and g) regarding biodegradation of CS2 (conclusion #6) with input from recent publications as well as our recommendation for soil-vapor extraction (conclusion #7).

1.2 Discussion of potential contribution to retardation of CS2

From a scientific point of view the "retardation issue" is the most critical one (Review #1: comment b and c, Review #2: comment 2). This refers to the "relatively unsupported simplifying assumptions" that adsorption on the solid phase and at the air–water interface may be neglected "because of its supposed similarity to CO2 with regard to air–water partitioning and solubility". We have since carefully consulted publications on the two neglected contributions to retardation. The findings and new insights regarding conclusion #5 (Review #1: comment e) will be included in a revision of the manuscript:

Sorption of a compound on the solid phase is governed by the partitioning co-efficient K_D of that particular compound. The coefficient for CS2 can be estimated with $K_D = K_{OC} \times f_{OC}$, where K_{OC} (L kg^{-1}) is the soil organic carbon partitioning coefficient and f_{OC} the fraction of organic carbon in the soil material. For CS2, the coefficient K_{OC} is 45.7 L kg^{-1} according to the Superfund Soil Screening Guidance, US EPA (1996). Howard (1990) report that "Carbon disulfide in solution would there-fore not be expected to adsorb significantly to soil" due to the relatively low K_{OC}. In our manuscript we introduced the two types of materials used, fine glass beads and Geba fine sand, with a d50 of 162 and 140 um determined from particle-size anal-ysis (Mastersizer 2000, Malvern Instruments Ltd. Worcestershire, United Kingdom). The chemical composition of fine glass beads is given by the manufacturer (Sigmund Lindner GmbH, SiLibeads Typ S 100..200 um) as SiO2 (72.5 %), Na2O (13 %), CaO (9.1 %), MgO (4.2 %) , and Al2O3 (0.58 %) which is soda-lime glass. Geba fine sand (Quarzsande GmbH, Geba weiss, 63..350 um) is composed of SiO2 (99.2 %), Fe2O3 (0.09 %), Al2O3 (1.85 %), and TiO2 (0.24 %), thus a pure quartz sand. Both materi-als contain negligible fractions of organic carbon (f_{OC}) supporting our assumption that sorption of CS2 on the solid phase in our experiments does not significantly contribute to retardation and, hence, may be neglected.

Adsorption on the air–water interface in a partially water-saturated porous medium depends on the air–water interfacial area A_{IA} and the air–water partitioning coefficient K_{IA}. Since we do not have the technical equipment to directly measure the air–water interfacial area in our experiment columns, we used the correlation (Eq. 1) proposed by AUTHOR (YEAR) to estimate it. This correlation is based on X-ray microtomography measurements of glass beads and natural sands.

$$A_{IA} = SA[(-0.9112)S_W + 0.9031] \tag{1}$$

where SA is the geometric surface area according to the smooth-sphere assumption ($SA_{GBfine} = 22.77 \ cm^{-1}$ and $SA_{Geba} = 24.32 \ cm^{-1}$). Figure 1 shows the air–water interfacial areas as a function of water saturation of our materials: fine glass beads

C3

Fig. 1. Calculated air–water interfacial area as a function of water saturation with correlation proposed by AUTHOR (YEAR) for materials used in experiments.

(GBfine) and Geba fine sand. We estimated the air–water partitioning coefficient K_{IA} of CS2 using the empirical correlation proposed by Valsaraj (1988). He found a corre-lation (Eq. 2) between the interfacial-water partitioning constant K_{IW} ($K_{IW} = K_H K_{IA}$) and the octanol–water partitioning coefficient K_{OW}.

$$K_{IW} = 3 \times 10^{-7} K_{OW}^{0.68} \tag{2}$$

This correlation with $log(K_{OW}) = 2.00$ (US EPA , 1996) and the dimensionless Henry coefficient $K_H = 1.04$ (Lide , 1996) yielded the air–water partitioning coefficient of CS2 $K_{IA} = 6.87 \times 10^{-6} cm$. The contribution of dissolution into the bulk water and of adsorption to the air–water interfacial to the theoretical retardation coefficient (Eq. 3) can calculated using the following equation:

$$R_t = 1 + \beta_w + \beta_{IA} = 1 + \frac{\theta_w}{\theta_a K_H} + \frac{K_{IA}A_{IA}}{\theta_a}. \tag{3}$$

Figure 2 shows the retardation coefficient with air–water interfacial adsorption (green line with triangles) and without adsorption (black line). Since the difference of esti-mated A_{IA} between fine glass beads and Geba fine is marginal, only one theoretical coefficient is plotted in Fig. 2. The ratio between the contributions from dissolution β_w ($\frac{\theta_w}{\theta_a K_H}$) and from air–water interfacial adsorption β_{IA} ($\frac{K_{IA}A_{IA}}{\theta_a}$) at $S_w = 0.162$ yields $\beta_w/\beta_{IA} = 513$. While these calculations indicate that our assumption to neglect ad-sorption on grains and air–water interface is correct, they cannot account for the devi-ation between the retardation coefficient measured for Geba fine sand at $S_w = 0.162$ and the corresponding theoretical value. Since dissolution, which is a function of the Henry coefficient and assumes equilibrium, is already at its maximum and adsorption on the grains may be neglected as discussed above, it is postulated that this increased

C4

Fig. 2. Updated graph of retardation coefficients including contribution of air–water interfacial adsorption in theoretical retardation coefficient (green line with triangles).

Fig. 3. Initial water saturation profiles in fine glass beads and Geba fine sand.

retardation can only be caused by air–water interfacial adsorption. Possible reasons for an underestimation of the adsorption to the air–water interface could be that the inhomogeneous water saturation profile (see Fig. 3), the grain-size distribution, or an underestimation of the specific surface of the Geba fine sand particles lead to an underestimation of the interfacial area. Figure 4 and 5 suggest that the smooth-sphere assumption holds for glass beads but not for Geba fine sand, thus the interfacial area for Geba fine sand might have been significantly underestimated. Moreover, interfacial areas measured with microtomography are significantly smaller than those measured with gas phase tracer experiments (Brusseau , 2006; AUTHOR, YEAR). Costanza (2000) observed the maximum interfacial area for water saturation in the range of 15 to 25 % of water saturation. They also reported the possibility of multilayer adsorption and that the actual adsorption may be significantly underestimated when true A_{IA} values are used.

Ascribing the observed discrepancy in Geba fine sand to air–water interfacial adsorption of CS2, an interfacial area of about $A_{IA,calc} = 6553 \ cm^{-1}$ would be required to obtain retardation factor of $R_{Geba} = 1.31$ (Eq. 3). This is consistent with measured interfacial areas from vapor-phase tracer experiments by Costanza (2000).

In conclusion, the contributions to the retardation based on the parameters, coefficients, and correlations introduced above have shown that for glass beads sorption on

Fig. 4. SEM pictures of fine glass beads.

C5

Fig. 5. SEM pictures of Geba fine sand.

the solid phase and on the air–water interfacial area does not significantly contribute to retardation of CS2. An interfacial area of about two orders of magnitude higher would be required to account for the discrepancy observed between the experimental and theoretical coefficient in Geba fine sand. Such areas have been found in vapor-phase tracer experiments but not with microtomography measurements, indicating that the A_{IA} values based on microtomography may not be applicable for the evaluation of retardation on partially water-saturated Geba fine sand. Additional investigations with selected partitioning tracers might yield a better understanding of the different contribution of air–water interfacial adsorption to retardation in fine glass beads compared to Geba fine sand. Nevertheless, we believe that the experiments shown and the (additional) conclusions drawn are conclusive and will substantially strengthen conclusion #5.

2   Technical points/issues

Review #1:

1. We use "irreducible saturation" for water and "residual saturation" for NAPLs. If this is misleading we will replace the term by "residual saturation".

2. The concept of filling the columns will be re-written to improve comprehensibility.

3. The flowchart of the experimental set-up will be simplified and corrected.

4. The choice fell on bottom-up flow due to technical reasons and since no effect of downward oriented flow on retardation has been observed.

5. We will revise the discussion about water saturation and tensiometer measurements. We do trust the measurements at steady state (equilibrium) to derive water saturation profiles prior to the experiments but we are carefully about tensiometer measurements during ongoing vapor injection.

6. We will look into the experimental dispersivity values and their validity and significance.

7. We discussed the impacts of surface area on retardation in the detailed argumentation above. Measurements of specific surface area with BET were below the detection limit of our device.

Review #2:

1. We will revise our statement.

2. Figure 1 will be simplified and corrected.

3. We will carefully revise the manuscript to avoid redundancy

4. and grammatical errors.

5. Correct placement and definitions of mathematical symbols will be checked.

6. First paragraph of "Results and discussion" will be revised.

7. We will provide a more detailed description of Figure 9 and may simplify it.

References

Brusseau, M. L., Peng, S., Schnaar, G., and Costanza-Robinson, M. S.: Relationships among air-water interfacial area, capillary pressure, and water saturation for a sandy porous medium, Water Resources Research, 42, n/a–n/a, doi:10.1029/2005WR004058, http://dx.doi.org/ 10.1029/2005WR004058, w03501, 2006.

Costanza, M. S., and Brusseau, M. L.: Contaminant Vapor Adsorption at the Gas–Water Interface in Soils, Environmental Science Technology, 34, http://pubs.acs.org/doi/abs/10.1021/es9904585, 2000.

Costanza-Robinson, M. S., Harrold, K. H., and Lieb-Lappen, R. M.: X-ray Microtomography Determination of Air–Water Interfacial Area-Water Saturation Relationships in Sandy Porous Media, Environ. Sci. Technol., 42, 2949–2956, doi:10.1021/es072080d, http://pubs.acs. org/doi/abs/10.1021/es072080d, 2008.

Howard, P., Sage, G., Jarvis, W., and Gray, D.: Handbook of environmental fate and exposure data for organic chemicals. Volume II: Solvents, Chelsea, MI (US); Lewis Publishers, Inc., 1990.

Lide, D. R.: CRC Handbook of chemistry and physics, CRC Press, 86 edn., 2005.

US Environmental Protection Agency: Superfund Soil Screening Guidance – Technical Background Document – Part 5: Chemical-Specific Parameters, Tech. rep., Office of Solid Waste and Emergency Response, https://semspub.epa.gov/work/HQ/175235.pdf, 1996.

Valsaraj, K. T.: On the physico-chemical aspects of partitioning of non-polar hydrophobic organics at the air-water interface, Chemosphere, 17, 875 – 887, doi:http://dx.doi.org/10.1016/0045-6535(88)90060-4, http://www.sciencedirect.com/science/article/pii/ 0045653588900604, 1988.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., doi:10.5194/hess-2016-440, 2016.
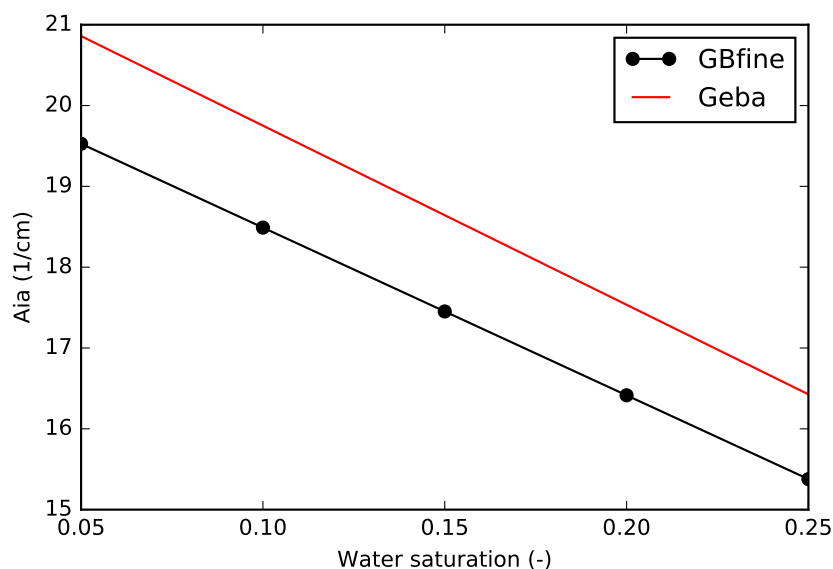
C9

Fig. 6. Calculated air–water interfacial area as a function of water saturation with correlation proposed by Costanza-Robinson (2008) for materials used in experiments.
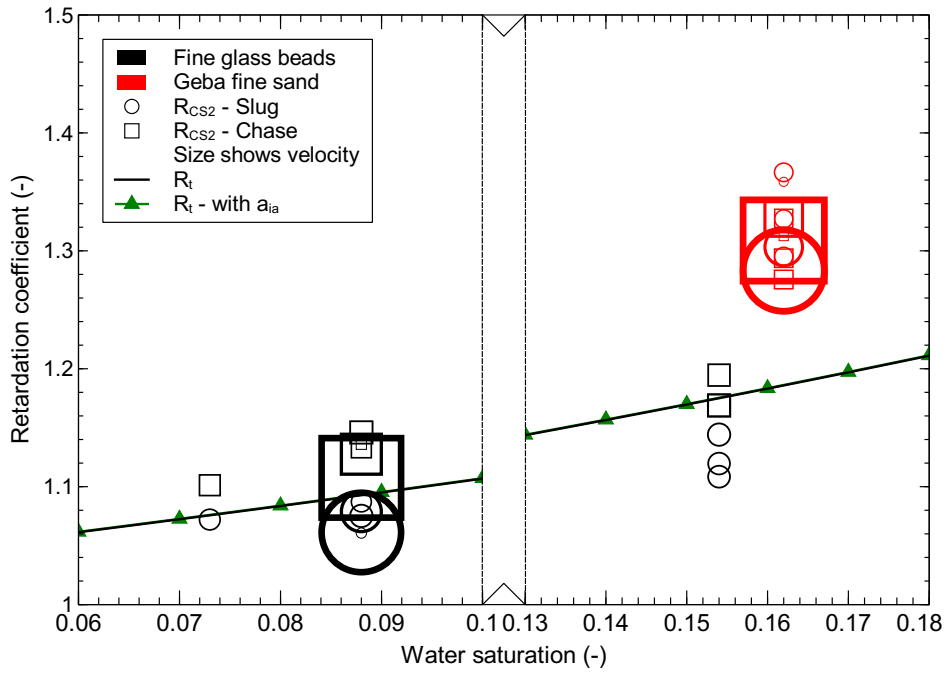
Fig. 7. Updated graph of retardation coefficients including contribution of air–water interfacial adsorption in theoretical retardation coefficient (green line with triangles).
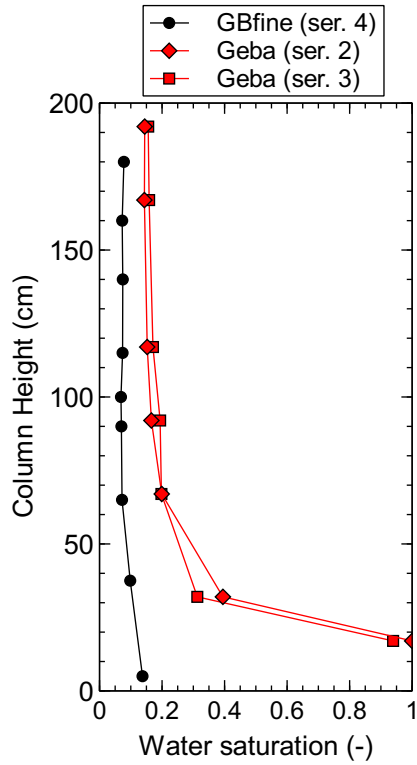
C11

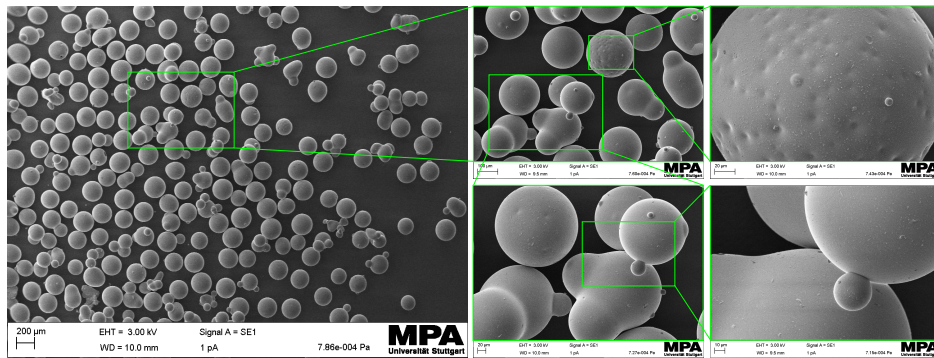**Fig. 8.** Initial water saturation profiles in fine glass beads and Geba fine sand.

C12

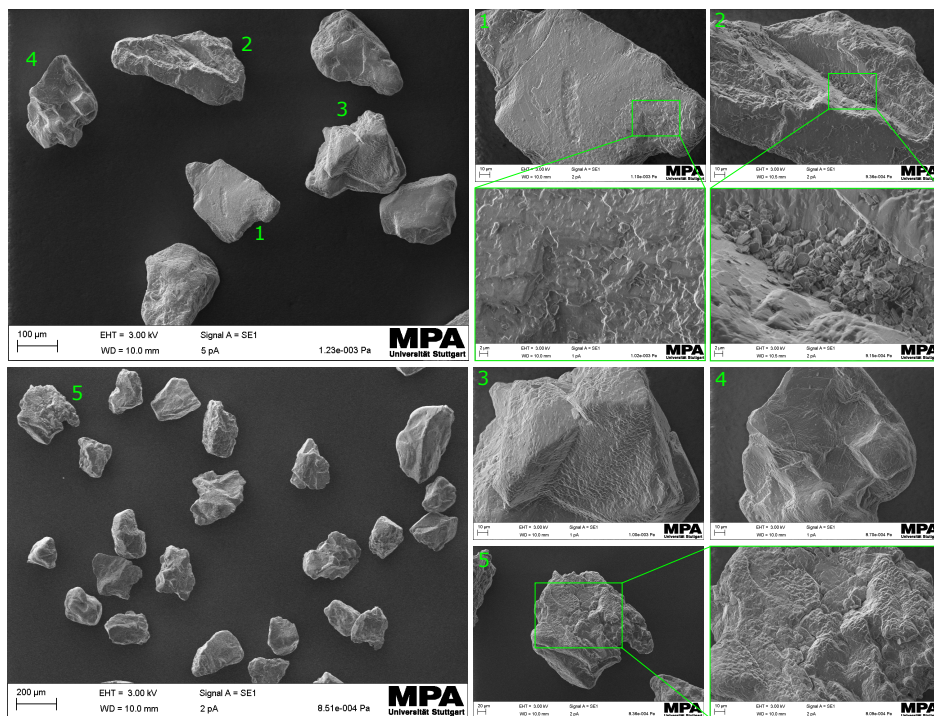**Fig. 9.** SEM pictures of fine glass beads.

Fig. 10. SEM pictures of Geba fine sand.