

Interactive comment on “A new top boundary condition for modeling surface diffusive exchange of a generic volatile tracer: theoretical analysis and application to soil evaporation” by J. Y. Tang and W. J. Riley

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Received and published: 7 February 2013

Below we put the reviewer's comments as italic. Our reply starts with "response".

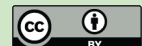
The paper is generally very well written and addresses an important scientific question relevant to the hydrological science community. I believe that the new top boundary condition for exchange of volatile tracers from soil to the atmosphere is a significant improvement over prior formulations. The title clearly represents the content of the

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paper, and the abstract gives a sufficient summary of the paper. The mathematical derivations appear to be correct. I was somewhat confused on the physical meaning of some of the parameters in the derivations. I think that an additional table defining all the symbols including the units used would be of benefit to the reader. The evaluation of the new top boundary condition and comparison to earlier formulations and empirical results was well done and presented. I think that the conclusions reached are appropriate based on the extensive evaluation and comparisons. References are sufficient.

Response: We sincerely appreciate the reviewer's positive comments on our work. We followed the reviewer's suggestion and added a table of symbols to the appendix to ease the reader's understanding of our work.

An additional complicating transport mechanism not considered in this paper that may be significant in the exchange of VOC and pesticide vapors with the soil and the atmosphere is the very large adsorption of these vapors on very dry soil. This is not particularly an issue with water but could be important as the authors move on to other vapors. When the soil surface becomes very dry with only a few molecular layers of adsorbed water, the adsorption of VOC and pesticide vapors on the dry soil increases by orders of magnitude. This effect has been observed in both field and lab experiments.

Response: We thank the reviewer for pointing out this important issue. We added a few words to clarify our treatment for this problem in the revised manuscript (P36, L9-20). In our development, we assumed (1) there is always water in the soil, such that the soil moisture is well defined and all other chemicals can dissolve in the water to form solutions and (2) there is a linear equilibrium between the aqueous and gaseous phases for the chemicals of interest. For very dry soils, the linear partitioning between aqueous and gaseous phase is still a good approximation (Ruiz et al., 1998), provided the VOC concentration is low, which is thus still within the applicability of our theory. However, for such applications, one needs to obtain the linear partitioning parameter (or the solubility coefficient as we used in our development) accurately for different

soils, which is experimentally very challenging (Goss 1993; Ruiz et al., 1998). Further experimental work is required to solve this problem. We have added these points to the revised manuscript.

P 11991. Fig 2. The red line for the curve captions is missing. P 11992, Fig 3. For anyone that is “color challenged”, it is difficult to easily see the differences between some of the colors. I suggest using broken and dot-dash lines for some of the curves and in the other figures.

Response: We revised the figures so that they are more readable.

P 11959, L14-15. Fig 2a seems to be just as good an agreement.

Response: Considering the log10 scale we used for visualization, Fig 2a is not as good an agreement as Figure 2d, though it is better than the other two.

P 11960, L13-14. It is not clear to me that this statement is justified by the curve in Fig. 3c.

Response: The empirical curve missed the constant evaporation stage-I. We have clarified this point in the revised manuscript.

Other editorial comments:

Page 11942, line 21. Data are plural. Thus, “is” should be replaced with “are”. P11945, L11. Define beta here. I did not realize until much later in the paper that beta is simply the ratio of evaporation to potential evaporation. In my opinion, “evaporation efficiency” is not a very descriptive term. Why not use “relative evaporation”?

P 11947, L9. This curve is generally called the “soil-water characteristic” or “soil-water retention” curve.

P 11949, L15. Symbol $C_{g,a}$ is not consistent with C_a in Fig. 1. P11949, L18. Explain where the “2” comes from in Eqns (5) and (6). I assume that this comes about because concentrations and other variables are defined at the center of the top soil control

volume, but this is not clear.

P 11954, Eqn (15). Again beta is not adequately defined.

P 11957, L10. “complicated” rather than “complicate”.

P 11957, L18. remove “the”.

P 11958, L21. Rephrase sentence. How can there be an interaction between an atmospheric conditions and soil physics?

P11959, L3. “what” instead of “that”?

P 11960, L11. Describe the characteristics of the curves that show two-stage evaporation behavior.

P 11961, L10. LP92? P 11961, L27-28. This statement is not apparent from the figure.

P 11964, L25-26. This is the first place that I understood the physical meaning of beta.

P 11968, L12-19. These statements are not clear to me from what is presented in the figure.

P 11993, Fig. 4. r_a rather than g_a in caption?

Response: Following these reviewer suggestions, we carefully corrected typos and grammar problems, and clarified wording where it was confusing.

References Goss, K. U.: Adsorption of organic vapors on ice and quartz sand at temperatures below 0°C, *Environ Sci Technol*, 27, 2826-2830, doi: 10.1021/Es00049a024, 1993.

Ruiz, J., Bilbao, R., and Murillo, M. B.: Adsorption of different VOC onto soil minerals from gas phase: Influence of mineral, type of VOC, and air humidity, *Environ Sci Technol*, 32, 1079-1084, doi: 10.1021/Es9704996, 1998.

Interactive comment on *Hydrol. Earth Syst. Sci. Discuss.*, 9, 11941, 2012.

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