

6-9-2018

A review of: **Caffeine vs Carbamazepine as indicators for wastewater pollution in a karst aquifer** by Dvory et al.

Summary

The manuscript presents an elegant modeling effort of a sewage spill event in a wash overlaying a dual-domain (rock-blokes and conduits) karstic aquifer. The pharmaceutical Carbamazepine (CBZ) and the mostly beverage sourced (Coffee, Cola etc.) Caffeine (CAF) were used as the sewage tracers. CBZ simulated as a conservative tracer vs. CAF which adsorbs and follows first-order degradation. The pretty unique modeling system of the porous medium that is used in this paper, in which the vadose zone is modeled by 1D (vertical) dual-permeability sub-models, that are linked to the 3D sub-model of the aquifer was described in a previous paper where the conservative transport of CBZ was analyzed. The addition of the calculation of the partition (distribution) coefficient and the first order degradation rate of CAF through calibration of this unique model and a relatively rare field set of data is the main and significant contribution of the paper. The results are K_d for CAF in dual permeability carbonate setting was 0.1 L/kg and the degradation rate 0.09 d⁻¹. Practical conclusions were that CBZ is a good tracer if you can analyze its small concentrations and have relatively sparse data in space and time around the sewage spill, whereas when data around the spill (space and time) exists the more common, zero background, and higher concentration CAF can serve as a good tracer of sewage spill as well.

Recommendation

The paper is in some sense a follow up of Dvory et al., 2018. Nevertheless, the case study is so unique (sewage spill above thick karst system, level of surface and deep subsurface water sampling and monitoring, level of chemical analysis) and the modelling is advanced yet strait forward. And, above all, the added analysis in this work is an interesting and significant contribution to large field-scale reactive transport analysis. The paper is written good and to the point and will be of interest to varying level of karst hydrologist (as well as other flow and transport modelers, soil physicists etc.). Therefore, I recommend publication following minor (some very essential) revisions due to the following specific comments herein.

Specific comments

1) I will start with most annoying discrepancy and then write the comment chronologically as they appear in the manuscript. Perhaps I am wrong, but the authors should check very carefully if typo mistakes in the legend of Figure 4 messed the sensitivity analysis of K_d and λ in section 3.3.

Yo the best of my understanding a breakthrough curve (BTC) of a degrading contaminant down gradient of an instantaneous spill should show a higher peak and a larger width for smaller degradation rates not for higher ones as shown Fig 4a shows. Check if BTC 5 and 3 were switched as well as BTC 2 and 4. The same for distribution coef. and Figure 4b: a BTC of a degrading and adsorbing contaminant will be shorter and retarded for a larger distribution coefficient rather than a smaller one like it is in the figure (e.g. BTC 3). Check.

2) The graphics of figure 4 must be improved by showing a smaller time span so the area below the BTCs will be larger and retardation (fig 4b) and different tails (Fig 4a) will be visualized better.

3) P.1, L.14 - add carbonate before Yarkon-Taninim

4) P. 2 L. 30 – add Fig. 1 after EK11 (or delete EK11)

5) P. 3 L 22 – replace “data logger” with: pressure and temperature probe with data logging capability

6) P. 3 L25 add upstream and downstream from the well head after “stations”

7) Figure 1 the aquifer boundary inset – make it clearer for the fast reader. Add Tel Aviv location and or Mediterranean Sea, a north arrow etc., don’t just send the international readership to lookup where is 35°E and 32°N.

8) P. 5 L. 19 change “pharmaceuticals” to micro pollutants or organic compounds or similar, caffeine is not a pharmaceutical.

9) P. 5 L. 29 – It would be appropriate to mention also Gerke and van Genuchten 1993 for the formulation of the dual permeability model.

10) P. 6 L. 4 – for consistency define qc (like you do for qzm) rather than qi

11) P. 6 L - I think the sentence in the beginning of the row would be better said as: Boundary conditions are of the type of transient head or transient flux.

12) P. 6 L 15 – Delete the sentence starting “Initial ...” Its redundant.

13) P. 7 L. 13 should be parameters were rather than “was”.

14) P 9 L. 29 – Delete “a”

15) P. 10 L. 2 – Delete “around”

16) P. 10 L. 10 change “amongst other” to” in comparison to

17) P. 10 L. 17 or 0.07 – 0.14 or 0.014-0.07 but not as written

18) P. 14 L. 13 “downstream” or downgradient

19) P. 14L. 15 “(2015, 2012b)” there is only 1 reference of Hillebrand et al. in the reference list

20) P. 14 L.18-21. Consider discarding, out of context and does contribute much.