

**Reviewer #2 comments on the manuscript “Identification of Parameter Importance for Benzene Transport in the Unsaturated Zone Using Global Sensitivity Analysis” submitted to *Hydrology and Earth System Sciences* (all authors answers are in blue font).**

I have reviewed the manuscript entitled “*Identification of Parameter Importance for Benzene Transport in the Unsaturated Zone Using Global Sensitivity Analysis*,” where the authors analyzed the sensitivity of Benzene transport to various physical and chemical parameters in both homogeneous and heterogeneous vadose zones. The analysis employed various sensitivity methods and addressed issues such as model crashes that can result in missing data and misinterpretation of sensitivity analysis outputs. This manuscript emphasizes a holistic approach to identifying sensitive parameters, which can guide future experimental design by focusing on the identified sensitive parameters. Therefore, it is of great interest for the HESS readers. However, there are some constructive and structural issues throughout the manuscript that must be resolved before publication. My comments and recommendations are below.

**We would like to thank the reviewer for the positive evaluation.**

**1. Line 50: Please provide a more general description of groundwater fuel contamination (not just in Israel).**

Some more information on groundwater fuel contamination can be found in the previous paragraph:

“Petroleum products such as gasoline and diesel are of the most abundant chemicals of ecological concern used nowadays. During petroleum exploration, production, transport and storage, petroleum products often find their way to the environment by accidental leaks and spills (Logeshwaran et al., 2018; López et al., 2008; Nadim et al., 2000). Consequently, groundwater is often polluted from surface sources, posing a substantial potential risk to potable water worldwide (López et al., 2008; Nadim et al., 2000; Logeshwaran et al., 2018; Reshef and Gal, 2017; Kessler, 2022). Since petroleum substances in general, and fuel components in particular, are considered toxic, carcinogenic, and mutagenic (Logeshwaran et al., 2018), strict regulations limit their maximum allowed concentration in groundwater to the parts per billion level (U.S EPA, 2006).”

Following the reviewer’s comment we also expanded this paragraph (line 50) and added more information related to the general context of fuel contamination (**added parts in bold font**):

“Fuel products are usually comprised of different types of hydrocarbons. **Fuel compounds like benzene are among the most commonly found groundwater pollutants (Schmidt et al., 2004; Logeshwaran et al., 2018).** Benzene specifically, is highly soluble and thus of the most mobile fuel constituents in the subsurface (Farhadian et al., 2008). **In the U.S. alone, during 1987–1993 about 0.9 million kg were reported to be released into the terrestrial and aquatic environment by the petroleum industries (Fan et al., 2014).** In Israel, for example, benzene was detected in 60% of all sites monitored for fuel contamination (Reshef and Gal, 2017).”

**2. Lines 59-60: Please add references and discuss what type of models were used. Elaborate on what parameters were used and how natural heterogeneity affects them.**

The following paragraph (lines 59-63 of the original text): “Most models simulating the transport of fuel contaminants in the unsaturated zone use a mechanistic description of the physical, chemical, and biological processes controlling contaminants’ transport and attenuation. These models include many uncertain input parameters, due to the typical heterogeneity of the subsurface environment and the difficulty in obtaining sufficient relevant physical and bio-geochemical characterization of the site (Tartakovsky, 2007)” was changed to include and discuss comments 2 requirements and the studies requested in comment 5 below (lines 63-80 of the revised manuscript):

Since actual water flow and contaminants transport in the subsurface are difficult to measure and predict, mathematical models are used to solve such transport problems (Bear and Cheng, 2010). Many studies have been performed to examine the fate and transport of petroleum hydrocarbons, and specifically of benzene, most in saturated homogeneous porous media (Lu et al., 1999; Brauner and Widdowson, 2001; Choi et al., 2005, 2009). Few studies have also dealt with the movement of benzene in unsaturated porous media (Berlin et al., 2016; Berlin and Suresh, 2019; Troldborg et al., 2009; Ciriello et al., 2017). Benzene transport models typically combine Darcy-type water flow, advective–dispersive transport and a source/sink term considering various physical, chemical and biological processes including sorption, dissolution, and biodegradation (Mohamed and Sherif, 2010). Yet, due to the typical heterogeneity of the subsurface environment and the difficulty in obtaining sufficient relevant physical and bio-geochemical characterization of the site, these parameters entail high level of uncertainty (Ciriello et al., 2017; Tartakovsky, 2007). Soil heterogeneity and layering, for example, was shown to have considerable effect on contaminants transport in some studies (Rivett et al., 2011; Chen et al., 2019), while in others the effect seems to be negligible (Botros et al., 2012; Akbariyeh et al., 2018). This of course depends on the model scale, type of system (natural or irrigated), and type of contaminant tested. Also, the estimation of soil and contaminants parameters can be done in various methods, such as laboratory measurements, scaling and inverse modelling (Botros et al., 2012; Akbariyeh et al., 2018; Berlin et al., 2016; Berlin and Suresh, 2019; Troldborg et al., 2009; Ciriello et al., 2017). This adds another aspect of uncertainty to the model.

**3. Lines 67-68: Please add References. Many disciplines are using these methods. Do they all use it the same? Are they all reporting similar challenges as in the current study?**

References Saltelli and Annoni, 2010; Razavi et al., 2021 were added (lines 88-89 of the revised manuscript).

Regarding the use of GSA in different disciplines, we believe a detailed discussion of the subject is beyond the scope of this specific research and of the introduction section. However, we have added text regarding the main challenges in the application of GSA in hydrological modelling as identified by Song et al. (2015) (lines 110-118 of the revised text):

“In his review, Song et al. (2015) identifies three main “hot spots” in GSA application with hydrological modelling, though these are relevant to many other disciplines. The three “hot spots” are: (1) Computational cost and subsequent meta-modelling used instead of running

the models multiple times, where the reliability and goodness-of-fit of meta-models should be explored, (2) GSA method selection, convergence and reliability - selecting an appropriate GSA method, monitoring the convergence, and estimating the uncertainty of the GSA results are important for hydrological models, (3) GSA methods involve many hypotheses or have other limitations, including the independence of input variables, where in practice, the parameters employed by hydrological models usually have interactions or correlations that needs to be considered.”

**4. Line 86: replace the ‘papers’ by ‘studies’**

Done, thank you (line 114 of the revised manuscript).

**5. Line 94: There are studies on transport in heterogeneous media that should be discussed.**

1. Akbariyeh, S., Bartelt-Hunt, S., Snow, D., Li, X., Tang, Z., & Li, Y. (2018). Three-dimensional modeling of nitrate-N transport in vadose zone: Roles of soil heterogeneity and groundwater flux. *Journal of contaminant hydrology*, 211, 15-25.
2. Botros, F. E., Onsoy, Y. S., Ginn, T. R., & Harter, T. (2012). Richards equation-based modeling to estimate flow and nitrate transport in a deep alluvial vadose zone. *Vadose Zone Journal*, 11(4).
3. Chen, N., Valdes, D., Marlin, C., Blanchoud, H., Guerin, R., Rouelle, M., & Ribstein, P. (2019). Water, nitrate and atrazine transfer through the unsaturated zone of the Chalk aquifer in northern France. *Science of the Total Environment*, 652, 927-938.

Added, see comment 2 above.

**6. Lines 95-96: What does it mean ‘individual impact of multiple parameters’?**

It means how much each parameter of the set of parameters tested affects the model. For clarity purposes the sentence was rephrased to: “The objective of this study was to assess the specific impact of each of the multiple parameters that affect benzene transport in the unsaturated zone“ (line 125 of the revised manuscript).

**7. Lines 96-108: The objectives should be concise. You can elaborate on the choice of a specific method in the method section.**

It is true. Yet, the other reviewer had asked us to elaborate more in this paragraph on the GSA methods tested. Therefore we prefer to leave it this way with a comment that more details can be found in the method section – so as to have it somewhere in between the two requests of the two reviewers (line 125 of the revised manuscript).

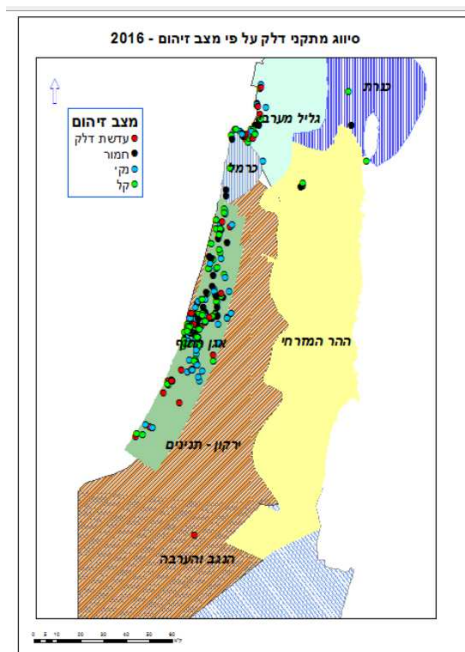
**8. Lines 167-171: 1. Is there a chemical/biological reason? 2. I didn't understand the range issue (why not analyze using a logarithmic scale?)**

1. No chemical or biological issue here, merely an issue of sensitivity. As stated in the text, high values of  $\lambda_k$  always resulted in concentration and flux of 0, which lowered the overall sensitivity and analytical strength of the GSA.

2. The Morris method always takes the range tested and divides it in a very simple manner to several equal parts, it does not use a logarithmic scale.

**9. Lines 180-184: You should plot the range of profiles and the map, if there is one, of all the locations. Put in supporting information.**

Unfortunately we cannot plot the range since only a general range of 2-50 m groundwater depth was stated in the report for the 236 contaminated sites tested (Reshef and Gal, 2017). The below map is given in the report. It shows the distribution of monitored fuel facilities and the state of contamination on site. The map was added to the supporting information section (Figure S1).



Distribution of monitored fuel facilities and the state of groundwater contamination in circles (red – fuel plume, black – severe contamination, blue – clean, green – minor contamination)

**10. Line 200: There shouldn't be a single-line paragraph.**

Thank you. This paragraph was combined with the paragraph below (line 225 of the revised manuscript).

**11. Line 204: Only clay layers. How do you define Clay? by texture percentage?**

Following comment 15 below, the details regarding clay layers definition and distribution were moved from results to the methods part section 2.2 where the answers to the above mentioned question are given (line 243 of the revised manuscript).

**12. Lines 211-212: Delete**

Deleted.

**13. Lines 332-336: Delete**

Deleted.

**14. Lines 339-346: Move to ‘Methods’**

We believe this part is important and appears at the beginning of the results for each GSA performed, since it gives general information on the GSA itself and how much of the runs were converged. This has important implications on the results.

**15. Lines 442-464: Move to ‘Methods’**

Moved to line 251 of the revised manuscript.

**16. Line 482: replace ‘adress’ by ‘address’**

Replaced – thank you very much.

**References**

Akbariyeh, S., Bartelt-Hunt, S., Snow, D., Li, X., Tang, Z., and Li, Y.: Three-dimensional modeling of nitrate-N transport in vadose zone: Roles of soil heterogeneity and groundwater flux, 15–25 pp., <https://doi.org/10.1016/j.jconhyd.2018.02.005>, 2018.

Bear, J. and Cheng, A.: Modeling Groundwater Flow and Contaminant Transport, <https://doi.org/10.1007/978-1-4020-6682-5>, 2010.

Berlin, M. and Suresh, K. G.: Numerical Experiments on Fate and Transport of Benzene with Biological Clogging in Vadoze Zone, *Environ. Process.*, 6, 841–858, <https://doi.org/10.1007/s40710-019-00402-w>, 2019.

Berlin, M., Vasudevan, M., Kumar, G. S., and Nambi, I. M.: Numerical modelling on fate and transport of coupled adsorption and biodegradation of pesticides in an unsaturated porous medium, *ISH J. Hydraul. Eng.*, 22, 236–246, <https://doi.org/10.1080/09715010.2016.1166073>, 2016.

Botros, F. E., Onsoy, Y. S., Ginn, T. R., and Harter, T.: Richards Equation–Based Modeling to Estimate Flow and Nitrate Transport in a Deep Alluvial Vadose Zone, *Vadose Zo. J.*, 11, <https://doi.org/10.2136/vzj2011.0145>, 2012.

Brauner, J. S. and Widdowson, M. A.: Numerical Simulation of a Natural Attenuation

- Experiment with a Petroleum Hydrocarbon NAPL Source, *Groundwater*, 39, 939–952, <https://doi.org/10.1111/j.1745-6584.2001.tb02482.x>, 2001.
- Chen, N., Valdes, D., Marlin, C., Blanchoud, H., Guerin, R., Rouelle, M., and Ribstein, P.: Water, nitrate and atrazine transfer through the unsaturated zone of the Chalk aquifer in northern France, *Sci. Total Environ.*, 652, 927–938, <https://doi.org/10.1016/j.scitotenv.2018.10.286>, 2019.
- Choi, J.-W., Ha, H.-C., Kim, S.-B., and Kim, D.-J.: Analysis of benzene transport in a two-dimensional aquifer model, *Hydrol. Process.*, 19, 2481–2489, 2005.
- Choi, N. C., Choi, J. W., Kim, S. B., Park, S. J., and Kim, D. J.: Two-dimensional modelling of benzene transport and biodegradation in a laboratory-scale aquifer, *Environ. Technol.*, 30, 53–62, 2009.
- Ciriello, V., Lauriola, I., Bonvicini, S., Cozzani, V., Di Federico, V., and Tartakovsky, D. M.: Impact of Hydrogeological Uncertainty on Estimation of Environmental Risks Posed by Hydrocarbon Transportation Networks, *Water Resour. Res.*, 53, 8686–8697, <https://doi.org/https://doi.org/10.1002/2017WR021368> Received, 2017.
- Farhadian, M., Vachelard, C., Duchez, D., and Larroche, C.: In situ bioremediation of monoaromatic pollutants in groundwater: A review, *Bioresour. Technol.*, 99, 5296–5308, <https://doi.org/10.1016/j.biortech.2007.10.025>, 2008.
- Logeshwaran, P., Megharaj, M., Chadalavada, S., Bowman, M., and Naidu, R.: Petroleum hydrocarbons (PH) in groundwater aquifers: An overview of environmental fate, toxicity, microbial degradation and risk-based remediation approaches, *Environ. Technol. Innov.*, 10, 175–193, <https://doi.org/10.1016/j.eti.2018.02.001>, 2018.
- Lu, G., Clement, T. P., Zheng, C., and Wiedemeier, T. H.: Natural Attenuation of BTEX Compounds Model Development and Field-Scale Application, *Ground Water*, 37, 707–701, <https://doi.org/10.1111/j.1745-6584.1999.tb01163.x>, 1999.
- Mohamed, M. M. A. and Sherif, N. E. S. M. M.: Modeling in situ benzene bioremediation in the contaminated Liwa aquifer (UAE) using the slow-release oxygen source technique, *Environ. Earth Sci.*, 61, 1385–1389, 2010.
- Razavi, S., Jakeman, A., Saltelli, A., Prieur, C., Iooss, B., Borgonovo, E., Plischke, E., Lo Piano, S., Iwanaga, T., Becker, W., Tarantola, S., Guillaume, J. H. A., Jakeman, J., Gupta, H., Melillo, N., Rabitti, G., Chabridon, V., Duan, Q., Sun, X., Smith, S., Sheikholeslami, R., Hosseini, N., Asadzadeh, M., Puy, A., Kucherenko, S., and Maier, H. R.: The Future of Sensitivity Analysis: An essential discipline for systems modeling and policy support, *Environ. Model. Softw.*, 137, <https://doi.org/10.1016/j.envsoft.2020.104954>, 2021.
- Reshef, G. and Gal, H.: Summary of actions to prevent pollution of water sources from fuels 2016, 2017.
- Rivett, M. O., Wealthall, G. P., Dearden, R. A., and McAlary, T. A.: Review of unsaturated-zone transport and attenuation of volatile organic compound (VOC) plumes leached from shallow source zones, *J. Contam. Hydrol.*, 123, 130–156, <https://doi.org/10.1016/j.jconhyd.2010.12.013>, 2011.
- Saltelli, A. and Annoni, P.: How to avoid a perfunctory sensitivity analysis, *Environ. Model. Softw.*, 25, 1508–1517, <https://doi.org/10.1016/j.envsoft.2010.04.012>, 2010.
- Schmidt, T.C., Schirmer, M., Weiß, H., Haderlein, S. .: Microbial degradation of tert-butyl ether and tert-butyl alcohol in the subsurface., *J. Contam. Hydrol.*, 70, 173–203, 2004.
- Song, X., Zhang, J., Zhan, C., Xuan, Y., Ye, M., and Xu, C.: Global sensitivity analysis in

hydrological modeling: Review of concepts, methods, theoretical framework, and applications, *J. Hydrol.*, 523, 739–757, <https://doi.org/10.1016/j.jhydrol.2015.02.013>, 2015.

Tartakovsky, D. M.: Probabilistic risk analysis in subsurface hydrology, *Hydrol. L. Surf. Stud.*, 34, 2007.

Troldborg, M., Binning, P. J., Nielsen, S., Kjeldsen, P., and Christensen, A. G.: Unsaturated zone leaching models for assessing risk to groundwater of contaminated sites, *J. Contam. Hydrol.*, 105, 28–37, <https://doi.org/10.1016/j.jconhyd.2008.11.002>, 2009.

X. Fan, L. He, H.W. Lu, J. L.: Environmental and health-risk-induced remediation design for benzene-contaminated groundwater under parameter uncertainty: A case study in Western Canada, *Chemosphere*, 111, 604–612, 2014.