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Memorandum

To: Dr. Alberto Guadagnini, Editor of Hydrology and Earth System Sciences

Subject: Revision of Paper # hess-2022-372

Dear Editor:

Upon the recommendation, we have carefully revised Paper # hess-2022-372 entitled "A General Model of Radial Dispersion with Wellbore Mixing and Skin Effect" after considering all the comments made by the reviewers. The following is the point-point response to all the comments.

Response to Reviewer #1:

1. Scientific Significance

The manuscript presents a model for radial dispersion of solutes injected in wells considering the effect of mixing in the wellbore, the influence of the surrounding skin zone, as well as mobile and immobile regions. The latter, conceptually modeled as two continuums with spatially uniform parameters which co-exist over the entire aquifer, allow simulations of early arrivals and long tailing of the breakthrough curves specific to spatially heterogeneous aquifers. The first-order reactive transport is governed by a system of coupled equations with constant coefficients which can be solved analytically. The analytical solutions derived by the authors in Laplace domain are tested against finite-element numerical solutions and experimental data. It is shown that the new model performs better than partial modes which do not consider simultaneously the mixing, skin, and heterogeneity effects. As an overall evaluation, the manuscript contributes to the scientific progress in the research filed and within the scope of the HESS journal.

Reply: Thanks a lot. We have carefully revised Paper # hess-2022-372.

2. Scientific Quality

(1). The authors present only the solutions in Laplace domain. At page 14 it is mentioned that “the de Hoog method will be employed to conduct the inverse Laplace transform”. A section in the Supplementary Materials with the computation of the inverse Laplace transform or, at least, references for the method and the software used in their study should be included.

Reply: Implemented. Relevant references have been added. See Lines 279-285.

From Eqs. (14) - (15), one may find that it is not easy to analytically invert the Laplace-domain solution to obtain the real-time solution. Alternatively, numerical Laplace transform techniques such as the Fourier series method (Dubner and Abate, 1968), Zakian method (Zakian, 1969), Schapery method (Schapery, 1962), de Hoog method (De Hoog et al., 1982) Stehfest method (Stehfest and Harald, 1970)are called in, where the de Hoog and Stehfest methods perform better for problems related to radial dispersion (Wang and Zhan, 2015).

(2). At page 22 it is mentioned the "genetic algorithm (GA) … employed to search the optimal parameter values", again without any details in Supplementary Materials or references for the algorithm and codes used. These should be included as well.

Reply: Implemented. Relevant references have been added. See Lines 434-439.

In this study, the genetic algorithm (GA) is employed to search the optimal parameter values, such as θ_{m2}, α_1 and ω_1 for CDM of Eqs. (14) - (15), and θ_{m2}, α_0, k and ω_1 for CDM of Eqs. (17) - (18). GA is a stochastic search method, based on natural selection, and it is preferred, due to its efficiency, simple programmability, and robustness. The GA could be implemented straightforwardly in MATLAB to facilitate computation (Katoch et al., 2020;Whitley, 1994;Deb et al., 2002).

(3). Apart from these missing details, the applied methods are valid and the results are discussed in with consideration of related work.

Reply: Implemented. The missing details have been added. See Lines 279-285 and 434-439.

3. Presentation Quality

The results and conclusions are presented in a clear way and in a good English language. The figures and tables included are appropriate and the manuscript contains the relevant references to the literature.

Reply: Thanks a lot.

Response to Reviewer #2:

1. The paper proposes a new analytical solution based on the mobile-immobile framework for redial dispersion within a wellbore that considers mixing effect, skin effect, scale effect, aquitard effect and limited media heterogeneity, as this is considered only in the context of the mobile-immobile as a ratio of conductivities in the aquifer, and not as a spatially varying heterogeneity which is a more realistic pattern. The paper is hard to follow, and generally lacks real clarity, specifically there is no in-depth explanation on the "skin-effect" as they previously did in [Li et al., 2019], and it is hard to understand how the derivation differ from their [Wang et al., 2020] paper which focuses on the transport. Moreover, it is not clear how the model is better than existing models? In line 100 the authors claim that other models, namely MRMT, CTRW, and fADE, are "usually unavailable or difficult to develop" yet a quick search show that there are models that cope with that problem well in CTRW [Dentz et al., 2015; Hansen et al., 2016], fADE [Chen et al., 2017; Soltanpour Moghadam et al., 2022], and even a combination of MRMT and CTRW [Kang et al., 2015]. Also, specifically for reactive transport in radial conditions there are experimental evidence for the scaling of dispersion, mixing, and reaction [Edery et al., 2015; Leitão et al., 1996], which are similar to the scaling in this study. The authors should refer to this literature and explain how their analytical solution differ and why is it better as they claim.

Reply: Thanks a lot. We have carefully revised Paper # 2021WR030815. This comment is divided into the following questions for response:

(1) The paper proposes a new analytical solution based on the mobile-immobile framework for redial dispersion within a wellbore that considers mixing effect, skin effect, scale effect, aquitard effect and limited media heterogeneity, as this is considered only in the context of the mobile-immobile as a ratio of conductivities in the aquifer, and not as a spatially varying heterogeneity which is a more realistic pattern.

Reply: The treatment that media heterogeneity effect is described by MIM might be oversimplified for most cases in reality, while they are inevitable for the derivation of the analytical solution. For a heterogeneity aquifer, the solution presented here may be regarded as an ensemble-averaged approximation if the heterogeneity is spatially stationary. If the heterogeneity is spatially non-stationary, then one can apply non-stationary stochastic approach and/or Monte Carlo simulations to deal with the issue, which is out of the scope of this investigation.

(2) The paper is hard to follow, and generally lacks real clarity, specifically there is no in depth explanation on the "skin-effect" as they previously did in [Li et al., 2019].

Reply: Implemented. More detailed information about skin effects and relevant references have been added. See Lines 63-66 and 78-96.

The skin zone refers to the disturbed region around the well caused by drilling and construction practices or well completion (Yeh and Chang, 2013;Chen et al., 2012; Li et al., 2020;Li et al., 2019;Huang et al., 2019). It is spatially between well screen and aquifer formation zone.

Comparing with aquifer formation zone of interest, the dimension of the skin zone is much smaller, e.g., ranging from 0.1 m to several meters, and it is ignored or included in wellbore. In another word, the effect of the skin zone on radial dispersion (named as skin effect) was negligible. However, numerous previous studies demonstrated that the existence of a skin zone might significantly alter the mechanism of groundwater flow and solute transport around well (Chen et al., 2012;Hsieh and Yeh, 2014;Yeh and Chang, 2013; Li et al., 2020;Li et al., 2019). This is because the physical properties (such as permeability, porosity, dispersivity, and so on) of the skin zone are often vastly different from their counterparts of the formation zone. Previously, studies on the skin effect were mainly concentrated on the groundwater flow process around the well, and much less attention was paid to solute transport processes. To date, few studies considered the skin effect among the above-mentioned analytical models on radial dispersion, such as Chen et al. (2012), Hsieh and Yeh (2014), Huang et al. (2019) and Li et al. (2020). Chen et al. (2012) proposed an analytical solution of solute transport with skin effect to investigate the influences of dispersivity on radial dispersion, soon after, Hsieh and Yeh (2014) extended the model of Chen et al. (2012) by taking into account a third-type (Robin) condition. Huang et al. (2019) demonstrated that the skin effect has a major influence on observed breakthrough curves (BTCs) for radially convergent tracer tests. Recently, Li et al. (2020) developed the analytical model for radial reactive transport with skin effect to investigate the impacts of dispersivity, effective porosity and mass transfer coefficient in skin zone on radial dispersion. The above-mentioned studies demonstrated the skin effects are significant for radial dispersion.

(3) and it is hard to understand how the derivation differ from their [Wang et al., 2020] paper which focuses on the transport.

Reply: Implemented. See Lines 113-114.

Wang et al. (2020) developed a four-stage radial dispersion model with aquitard and wellbore mixing effects under the MIM framework; however, the skin and scale effects were ignored in Wang's model, which were considered in this study. The methodology between these two papers is also different. In Wang et al. (2020), Laplace transform and Green's function methods are used to derive the analytical solution, while only Laplace transform method is used in this study.

(4) Moreover, it is not clear how the model is better than existing models? In line 100 the authors claim that other models, namely MRMT, CTRW, and fADE, are "usually unavailable or difficult to develop" yet a quick search show that there are models that cope with that problem well in CTRW [Dentz et al., 2015; Hansen et al., 2016], fADE [Chen et al., 2017; Soltanpour Moghadam et al., 2022], and even a combination of MRMT and CTRW [Kang et al., 2015]. Also, specifically for reactive transport in radial conditions there are experimental evidence for the scaling of dispersion, mixing, and reaction [Edery et al., 2015; Leitão et al., 1996], which are similar to the scaling in this study. The authors should refer to this literature and explain how their analytical solution differ and why is it better as they claim.

Reply: Implemented. The sentence of 'the analytical solutions associated with radial dispersion are usually unavailable or difficult to develop' in the original manuscript has been deleted, and relevant references have been added. See Lines 101-120.

As for reactive transport in heterogeneous media, the BTCs may exhibit a host of non-Fickian characteristics such as early arrival and heavy tailing (Di Dato et al., 2017;Molinari et al., 2015). Alternatively, many non-Fickian transport models have been developed, such as the multi-rate mass transfer model (MRMT) (Le Borgne and Gouze, 2008;Haggerty et al., 2001), mobile-immobile model (MIM) (van Genuchten and Wierenga, 1976;Zhou et al., 2017;Wang et al., 2020), continuous-time random-walk models (CTRW) (Dentz et al., 2015;Hansen et al., 2016), fractional-derivative ADE models (fADE) (Soltanpour Moghadam et al., 2022;Chen et al., 2017), a combination of MRMT and CTRW (Kang et al., 2015), and so on (Zheng et al., 2019;Lu et al., 2018). Although the models of MRMT, CTRW and fADE perform well in modeling non-Fickian transport, it is not easy to obtain the analytical solutions of these models. Meanwhile, these theories are usually not easy to apply for solving regional-scale transport problems, as pointed out in a recent study (Zheng et al., 2019). MIM is an extension of ADE by considering both flowing and stagnant regions in porous media and mass transfer between them (van Genuchten and Wierenga, 1976;Zhou et al., 2017;Wang et al., 2020), Zhou et al. (2017) and Wang et al. (2020) derived the MIM solutions of radial dispersion. However, the skin effect and the scale effect were ignored in their studies, which will be investigated in this study. Besides the MRMT, MIM, CTRW, and fADE models, another approach to represent the heterogeneity is to use a scale-dependent dispersivity (or dispersion) in the ADE or MIM models (Haddad et al., 2015;Gelhar et al., 1992). Gao et al. (2009a) and Chen et al. (2007) discussed radial dispersion and found that the scale-dependent dispersion effect was not negligible. There are also experimental evidence for the scaling of dispersion, mixing, and reaction (Leitão et al., 1996;Edery et al., 2015).

2. Line 135-137 needs to be clarified

Reply: Implemented. See Lines 148-156.

In this study, we mainly focus on developing analytical solutions of radial dispersion with a Heaviside step source (or step function for abbreviation hereinafter), as solutions of a variety of injection scenarios can be easily obtained on the basis of such a step source solution, as shown in Eq. (A2) in Supplementary Materials, Eqs. (4a) - (4b), or Eqs. (5a) - (5b). Assuming that t_{inj} is the duration of the step source, the solute source concentration (C_0) is $C_{inj}(t)$ when time is smaller than t_{inj}, while it is $C_{cha}(t)$ when time is greater than t_{inj}, in which $C_{inj}(t)$ and $C_{cha}(t)$ represent the solute concentrations [ML^{-3}] in the wellbore before time t_{inj} and after time t_{inj}, respectively; When $C_{cha}(t) = 0$ and t_{inj} approaches zero but the total injected mass remains finite, the model of the step source reduces to the model of the instantaneous injection.

3. Are we defining the asymptotical value for the model in line 137-139, please clarify.

Reply: Implemented. The value of t_{inj} ($t_{inj} = 300$ mim) has been added in Table 5. See Table 5.

4. Line 157-162 defines reaction rate (or radioactive decay, or biodegradation), and retardation factor yet there is no example to using these parameters in the results since R=1, μ is so small it is negligeable, so the sensitivity to these parameters must be small. Can the author comment on the choice of parameters? Also, why is this part in the supplementary and not in the text?

Reply: Implemented. The parameter selection has been added (See Lines 386-395), and the sensitivity of results to R and μ could be seen in Figures 4 and 5.

The parameters used in the numerical simulation are: $r_w = 2.5$ cm; $r_s = 12.5$ cm; $Q_{inj} = Q_{cha} = 100$ ml/s; $t_{inj} = 300$ s; $\alpha_1 = 2.5$ cm; $\alpha_2 = 2.5$ cm; $\theta_m = 0.30$; $\theta_{im} = 0.01$; $\omega = 0.001$ d^{-1}; $R_{m1} = R_{im1} = R_{m2} = R_{im2} = 1$; $B = 50$ cm; $\mu_{m1} = \mu_{m2} = \mu_{im1} = \mu_{im2} = 10^{-7}$ s^{-1}, and $h_{w,inj} = h_{w,cha} = B$. These parameters are from the experimental applications of Chao (1999), Chen et al. (2017), Wang et al. (2018) and Wang et al. (2020), in which Wang et al. (2020) summarized the values of reaction rate, retardation factor, dispersivity, porosity, and first-order mass transfer coefficient for sandy and clay used in numerous investigations, as shown in Table 4 of Wang et al. (2020). In addition, the values of retardation factor and reaction rate represent that the chemical reaction and sorption are weak for the tracer of KBr in the experiment of Chao (1999). It is not surprising since KBr is commonly treated as a "conservative" tracer.

5. As the COMSOL solution was based on equation 14, which is the basis for the analytical solution equation 20-23, it is not surprising that the match between them in figure S4 is good, yet why do they differ so much from the observation in Chao et al 1999? Moreover, can the authors supply an R-square or quantify how well the analytical solution performs for all figure, and not just figure 3, where the COMSOL solution is very different? Please, add the error to the figure caption as it is confusing to switch between the figure to the table?

Reply: Implemented. This comment is divided into the following questions for response:

(1) As the COMSOL solution was based on equation 14, which is the basis for the analytical solution equation 20-23, it is not surprising that the match between them in figure S4 is good, yet why do they differ so much from the observation in Chao et al 1999?

Reply: Implemented. The COMSOL solution is a numerical solution, and it is used to test the new analytical solution of this study. The models used to interpret the observation in Chao et al 1999 are analytical solutions, not numerical solutions. Meanwhile, New Figures S4a and S4b have been added in *Supplementary Materials*. Figure S4 in the original *Supplementary Materials* has been changed into Figure S5. See Lines 396-401, Figures 1 and S4.

(2) Moreover, can the authors supply an R-square or quantify how well the analytical solution performs for all figure, and not just figure 3, where the COMSOL solution is very different? Please, add the error to the figure caption as it is confusing to switch between the figure to the table?

Reply: Implemented. See Lines 452-458, Figures 1 to 3 and Figures S4 and S5, Table 6.

The COMSOL solution is only used to test the accuracy of the new models of this study, as shown in Figures 1 and S4. The R-square (R^2) has been added in Figures 1 and S4 representing fitness between analytical solution and numerical solution, and the R^2 has been added in Figures 2, 3 and S5 representing fitness between computed and observed BTCs. The error (E_r) form Table 6 have been added to Figures 2, 3 and S5.

6. Another point is that there is no explanation as to why the error is so big, and why the analytical solution is better than the numerical one with respect to the error.

Reply: Implemented. See Lines 445-451 and Figures 2, 3 and S5.

In this study, the models used to interpret the observation in Chao et al 1999 are analytical solutions, not numerical solutions.

Figure 2 shows the fitness of observed BTC by the solution of Chen et al. (2007) which considers the scale effect but ignores the mixing and skin effects. One might find that the fitness between computed and observed BTCs was obvious. We found that it was probably due to the following two reasons. Firstly, the model of Chen et al. (2007) used to best fit the data is an instantaneous slug test model, which was a rather gross approximation of the injection which lasted about 5 hours. A more proper way is to treat the 5 hours injection as a step source. Secondly, the solution of Chen et al. (2007) only considered the scale-dependent dispersivity, but ignored the mixing effect and the mass transfer between the mobile and immobile domains.

So, we used the new analytical solution of this study to re-interpret the observed data, as shown in Figures 3 and S5.

7. To summarize, the paper seems like an important contribution as it considers many physical aspects for radial dispersion (reaction, retardation, conductivity change in the skin area), and provides an analytical solution that considers these aspects. However, at the moment the advantage of the analytical solution, when compared to experimental data and even to the numerical solution is not clear enough. The paper is not approachable, as the figures need to be combined with the error while all the details of the modeling and results need to be ordered and clarify. Lastly, there is a bulk of literature that need to be added to put this work in the right context. I believe that addressing these comments will make the paper more approachable, provide the right context and make a stronger case for the analytical solution presented here.

Reply: Implemented. We have carefully revised the manuscript after considering all of the above-mentioned comments. Thanks a lot for such valuable comments.

If you have any further questions about this revision, please contact me.

Sincerely Yours,

Quanrong Wang, PhD, PG.

Professor and

Holder of Endowed CUG Scholar in Hydrogeology