**Hydrology and Earth System Sciences Discussions**

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# *Interactive comment on* "Parameter identification and analysis of soluble chemical transfer from soil to surface runoff" *by* J. X. Tong et al.

**Anonymous Referee #1**

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In this work the authors present a simplified model of the chemical concentration in the soil surface and its transfer and concentration in overland flow during three stages of the runoff generation process i.e. prior to ponding, between ponding and runoff commencement (presumably as a result of depression storage although this is not stated) and then post runoff commencement. They present observations of the concentration of potassium chloride in overland flow from a simple experimental setup in the laboratory. The authors then fit their model to the observations and derive two unknown model parameters, denoted $\alpha$ and $\gamma$, which they claim describes a combination of: (a) incomplete mixing of the chemical with infiltrating water ($\gamma$); and (b) incomplete mixing of chemical between overland flow and the soil ($\alpha$). Both parameters also reflect gradients in chemical concentration driving diffusive solute transport which are not accounted for explicitly in the mathematical formulation.

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This fitting procedure is repeated between successive observations to derive temporal changes in the two parameters. Not surprisingly, given their methodology, the authors find the model fits the data well. In that respect almost any model could successfully fit the data. For example if I replace their "model" with a linear regression equation for the concentration i.e. $C(t) = C(t^*)(a(t - t^*) + b)$ where $C(t)$ is the concentration at time $t$, $t^*$ is the time of the last observation and $a$ and $b$ are two adjustable parameters then I could guarantee the same level of model performance. Nevertheless, with a "physically" based model instead of a linear regression there is the potential for inferences to made about processes, which offers some appeal. However in this work I did not find the appeal.

The authors base their model upon an instantaneous mixing model with first order kinetics. They assume that during three phases of the infiltration/runoff processes the water fluxes $i$ (infiltration) and $q$ (runoff) are constant. They do not justify nor test these assumptions regarding constant fluxes. Based upon this they derive equations for the concentration $C_w$ in the water phase (they neglect sorption processes) as a function of time. Based upon my own calculations at least one of these equations appears to be in error (I refer to Equation 4, see my derivation in Appendix A of this review). As the authors were not able to measure $C_w$, but only the runoff, it was probably not possible for them to identify this mistake from observations. Additionally, even if they had measured $C_w$, their model fitting methodology probably would not have identified the error either.

There also appears to be another problem with the general derivation of equations. In previous work by the authors, Tong et al., (2010) (as cited in the manuscript) assumed the two fitting parameters $\alpha$ and $\gamma$ were constant with time. The innovation of this HESS submission they argue is that now they relax this assumption and instead consider the temporal variability of these parameters. Therefore, when considering the derivation of the change in $C_w$ with time it would seem appropriate to expand the derivative of multiples of two time dependent variables using the chain rule (see Appendix B of this

review). However, this they do not. If they did then the calibration procedure they conducted to estimate $\alpha$ and $\gamma$ at each time step would also require consideration of their derivatives. It would seem that this would more appropriately allow interpretation of "incomplete" mixing processes.

My major concern is that I am struggling to understand what has been gained by by the work presented. How, for example, can this lead to improved predictions of chemical transport in overland flow? Given that the $\alpha$ and $\gamma$ parameters are determined after the fact, along with their nebulous physical meaning, I fail to see what has been learned. In the experiments where saturated conditions are tested and infiltration apparently limited to constant rates by controlling the outflow, at least one of the parameters looks to take on three distinct values, constant during each of the three stages considered. Therefore one has to question whether it is the nonlinear infiltration process in the other cases which causes the temporal change in mixing parameters, thus violating the basic assumption behind the derivation of the equations. The authors do not provide a basis for us to understand how is it possible to predict these parameters or how they change with time? If we obtain these parameters, what use are they? It seems to me that they are likely to be very specific to the particular experiments and even small changes in rainfall intensity would radically alter the results. Given the equations were derived assuming the parameters were constant in time, how should we interpret temporal changes in the variables from the same equations?

While the paper is short, it is quite difficult to read. There is little context as to why experiments were conducted in a particular way. It is difficult to identify a coherent scientific objective. The conclusions do not seem to be able to be generalized beyond the individual experiments conducted. Given my concerns with the equations and calibration procedure I doubt that the results, showing a good fit of the model to the data, can be scientifically justified. There are also numerous gaps in the description of the methodology including: measurement of concentrations; optimization procedure used in the calibration; measurement of soil properties such as hydraulic conductivity and

porosity; which makes it difficult for another scientist to reproduce the results. The "calibration procedure" looks to have omitted several spurious points with high concentrations later in the experiment, however, this is not discussed. Readers are left to refer to the table and figures to attempt to identify what particular "cases" were. There is essentially no discussion to place the results in the context of work previously conducted. There are also numerous grammatical errors present, which appear to be of secondary importance to the points just raised.

## Appendix A: Re-derivation of Cw in the period from commencement of ponding and prior to runoff beginning

Repeating the same definitions and assumptions as stated by the authors the mass in the mixing zone (of depth $h_{mix}$) and free water on the surface (of depth $h_p$) is given by:

$$M_w = C_w(\alpha h_p + h_{mix}\theta_s) \tag{A1}$$

where $M_w$ is the chemical mass, $\theta_s$ is the saturated volumetric water content and $\alpha$ is one of the incomplete mixing parameters.

During this period the ponded water depth is assumed by the authors to increase at a constant rate such that:

$$h_p(t) = (p-i_p)(t - t_p) \tag{A2}$$

where $p$ is the precipitation rate, $i_p$ is the infiltration rate, and $t_p$ is the time at which ponding commenced.

The resulting change in mass during this period is given by

$$\frac{\mathrm{d}M_w}{\mathrm{d}t} = -\gamma i_p C_w \tag{A3}$$

i.e. $q = 0$.

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Substituting Eq. (A1) and Eq. (A2) in Eq. (A3) I get:

$$\frac{\mathrm{d}\left(\left(\alpha(p - i_p)(t - t_p) + h_{mix}\theta_s\right)C_w\right)}{\mathrm{d}t} = -\gamma i_p C_w \tag{A4}$$

Evaluating the derivative, assuming $h_{mix}$, $\alpha$, $\theta_s$, $p$ and $i_p$ are constant, as the authors did, gives:

$$h_{mix}\theta_s\frac{\mathrm{d}C_w}{\mathrm{d}t} + \alpha(p - i_p)(t - t_p)\frac{\mathrm{d}C_w}{\mathrm{d}t} + C_w\alpha(p - i_p) = -\gamma i_p C_w \tag{A5}$$

and rearranging gives:

$$\frac{\mathrm{d}C_w}{\mathrm{d}t} = \frac{(-\gamma i_p - \alpha(p - i_p))C_w}{(h_{mix}\theta_s + \alpha(p - i_p)(t - t_p))} \tag{A6}$$

with the boundary condition, $C_w(t_p)$, given by the authors as Eq. 3.

If I solve this first order ordinary differential equation I get:

$$C_w(t) = C_w(t_p)\left(\frac{\alpha(p - i_p)(t - t_p) + h_{mix}\theta_s}{h_{mix}\theta_s}\right)^{(-\gamma i_p - \alpha(p - i_p))/(\alpha(p - i_p))} \tag{A7}$$

which differs from Eq. 4, as given by the authors, in the numerator of the exponent. I note this same equation was previously published elsewhere (Tong et al., 2010) and apparently, by my calculations, in error. I checked my calculations using Mathematica 6.0 and have supplied this file to the editor.

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## Appendix B: Consideration of time dependent parameters $\alpha$ and $\gamma$

If we begin from Eq. (A4) but now consider that both $\alpha$ and $\gamma$ are time dependent then expansion of the derivative gives:

$$(p-i_p)(t-t_p)C_w\frac{\mathrm{d}\alpha(t)}{\mathrm{d}t}+\alpha(t)(p-i_p)C_w+(\alpha(t)(p-i_p)(t-t_p)+h_{mix}\theta_s)\frac{\mathrm{d}C_w}{\mathrm{d}t}=-\gamma(t)i_pC_w \tag{A8}$$

An analytical solution of this equation however looks to require the definition of physically meaningful constitutive equations for $\alpha$ and $\gamma$. However a finite difference methodology with an appropriate optimization procedure to estimate how $\alpha$ and its derivative as well as how $\gamma$ change in time, using experimental data, looks as if it could estimate how $\alpha$ and $\gamma$ change with time. Given the not insignificant contribution to such a discretization from the $\alpha(t)$ and $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ terms the impact upon the results seem to be profound.

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