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Discussions

Interactive comment on "Model-based estimation of pesticides and transformation products and their export pathways in a headwater catchment" *by* M. Gassmann et al.

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General comments:

This paper describes a fully distributed catchment-scale model of the fate and behavior of pesticides and their metabolites, which accounts for multiple transport pathways to surface water bodies, including macropore flow and subsurface drainage systems. The model is applied to a small catchment in Switzerland in order to elucidate the relative importance of the main transport pathways of three parent compounds and their metabolites. The results are very interesting and quite plausible, even if the predictions

of the relative contributions of the different pathways cannot be directly tested. My only concern is that the model itself is too sketchily described. It would be very helpful to readers if the authors could clarify some aspects of the model, as outlined in the following specific comments.

Specific comments:

1. Page 9853, lines 8-12: It may not be so clear to the reader why you use the Green-Ampt equation for infiltration and Richards' equation for water flow in soil, instead of Richards' equation for both. It would be good if you could clarify this, as it does increase parameter requirements (I presume you can reduce run-times by avoiding Richards' equation during rainfall i.e. high flow periods).

2. Page 9853, line 15: I wonder about these three layers. Are they really numerical layers or are they just used for determining parameter values and then you divide them into a larger number of thinner numerical layers for calculation purposes? Richards' equation would lose numerical accuracy (and therefore it's physical meaning) if it was applied to three such very thick layers.

3. Page 9853, text beginning line 15: This is confusing, because you have just mentioned Richards' equation, which is normally used for calculating water contents, and then you say that water content is calculated according to a given vertical distribution. But I think I understand: Richards' equation is used to calculate flow between the three layers, and equation 1 is only used to estimate water table depth when water content is larger than field capacity. Perhaps, this could be stated on line 15, right at the start of this section, to avoid confusing the reader?

4. Page 9853, line 18: I think z in equation 1 must be a dimensionless depth if the units on both sides of the equation are to match. This should be clarified.

5. Page 9854, line 6: The density of water is missing from this equation.

I am not keen on this way of estimating the saturated hydraulic conductivity of macropores, because the assumptions of the model are never met in reality: macropores rarely flow fully saturated with water (if larger macropores did so, flow would probably be turbulent anyway rather than laminar) and they are not all equal-sized cylindrical tubes. It would be better to allow users to input this parameter rather than estimate it in this way, since K at and near saturation is relatively straightforward to measure with tension infiltrometers.

6. Page 9854, lines 13-16: O.K., but in the model, can water (and solute) flow in the reverse direction, from matrix to macropore? This is a common occurrence in reality, which takes place when conductivity decreases with depth in the soil matrix. It is important to clarify this.

7. Page 9856, equation 10: this equation seems wrong (is it a misprint?).

8. Page 9856, equation 11: This equation seems odd: the root depth must surely be larger than the layer thickness, which would mean that uptake could be larger than the potential rate. It is also not clear to me how the plant uptake is partitioned between the three soil layers. Is it just proportional to their thicknesses? Can these aspects be clarified?

9. Page 9856, line 15: Does the mixing depth also interact with water entering macropores? How does pesticide get into the macropores? Please clarify.

10. Page 9856, line 23 (equation 12): ctotal seem not to be defined, either here or in the following, but it must be the total pesticide mass per volume of soil. This should be clarified.

Later, SSC is defined as the sediment concentration, which may be appropriate for pesticide in water and suspended sediment mixtures, but not in soil. It should be termed the bulk density.

11. Equation 12, 13 and 14: the dissolved concentrations in these equations (csolved and ce,solved) seem to be expressed as mass per volume of soil, which is unconventional. Strictly, they should be expressed as mass per volume of water, and they should then be multiplied by the volumetric water content to give the same units (i.e. mass per soil volume) as ctotal and csorbed.SSC. As a result, you seem to be ignoring the effects of spatio-temporal variations in water content on the pesticide concentration in water (which should in turn control the mass flux of pesticide).

12. Equations 16 and 17: it is not clear to me if the mass fluxes mPC,inf and mTP,inf refer to both macropores and matrix, or only to the matrix? How are both these mass fluxes calculated? Is it just by convection, or do you also account for dispersion? (you will anyway get numerical dispersion if it is the former). More details are needed on this part of the model.

13. Page 9858, line 9: Equation 3 assumes gravity-driven vertical flow, and may not be so appropriate for lateral flow in macropores to tile drains. The text in connection to equation 4 also talks about vertical flow velocities. Some clarification here would be good.

14. Page 9858, lines 16-22: Some more details on the numerical solutions are needed. How are the equations solved (it is not a trivial problem to solve a 3D dual-permeability system)? What are the numerical layer thicknesses (see point 2)? You mention that the time step is adaptable, but what is the maximum time step (presumably 10 minutes, the same as the rainfall?).

15. Page 9860, lines 12-13: What is the lateral connectivity? Unless I missed it, this has not been described earlier?

16. Page 9863, line 26 to page 9864, line 7: it was at first surprising for me that matrix flow to tile drains was apparently such an important loss pathway for pesticides with Koc values of 110 to 300. I had expected that macropore flow would dominate losses so soon after application (< 3 months). But then I read later in the paper (see point 17) that most of these losses arise from residues of applications in previous seasons which were present in the soil at the beginning of the simulation. This seems quite

reasonable, but maybe you could write something about this already at this point in the paper, in order to avoid confusion?

I also wonder if the matrix would contribute any detectable leaching at all if it were not for the presence of macropores? What I mean is that macropores can provide a 'short-circuit' to the subsoil matrix where residues can be stored for some time (because degradation is so slow), and then leach slowly out to the drains. If you ran a simulation without macropores at all (and without any initial residues), I would be surprised if you found any subsoil residues or leaching at all, even in long-term simulations. Have you tried this? Could this be discussed? The potential role of macropores in enhancing matrix leaching like this was discussed by Lewan et al. (2009).

17. Page 9869, line 10: Do you need to assume this? You could just run a simulation without the residues to see their contribution. It would also be valuable to run a simulation without macropores to see their contribution, which can be indirect and delayed as well as direct and immediate (see point 16).

Technical comments:

1. Page 9849, line 5: 'long-term' would be a better word here than 'permanent'.

2. Page 9849, line 10: you should probably add 'occasionally' before 'even more toxic', as this is quite unusual.

3. Page 9849, line 21: you could add a couple of more references here, since many others have previously demonstrated this, for example, Kladivko et al. (1991), Harris et al., (1994), Traub-Eberhard et al. (1994) and Brown et al. (1995).

4. Page 9849, line 24: you could also cite Brown and van Beinum (2009) here (they are already cited elsewhere).

5. Page 9852, lines 14-16: Please add information on the day(s) of pesticide application.

6. Page 9853, lines 12-13: Instead of just 'unsaturated hydraulic conductivity', you should probably refer to 'soil hydraulic functions' here, since the van Genuchten equation is also used to estimate soil water retention.

7. Page 9854, line 12: I think it would be better to use q rather than K to denote a flow rate (the same holds for equation 5 on line 21).

References

Brown, C.D. et al. (1995). Pesticide Sci., 43, 131-140.

Harris, G. L. et al. (1994). J. Hydrol., 159, 235-253.

Kladivko, E. et al. (1991). J. Environ. Qual., 20, 264-270.

Lewan E., et al. (2009). Agric. Water Manag., 96, 1633-1640.

Traub-Eberhard, U. et al. (1994). Chemosphere, 28, 273-284.

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