Answer to Review by H.H. Gerke (Referee)

Dear Horst H. Gerke,

we would like to thank you for your valuable review and comments regarding our manuscript. All your questions are answered below.

General comments:

The manuscript seems to be written from a hydrologist' point of view, soil hydraulics and soil spatial variability, characterization of soil types, and soil structure as well as soil related references are relatively limited although reactive transport in structured soil is considered.

Answer: There is a lot of information available about the soils and their spatial variability in our study catchment. Although we provided the references, we not explicitly stated that the soil information can be found there (Frey et al. 2009). We plan to provide more specific information about the contributions of the provided references in the catchment description of the revised manuscript. The soil-related model parameter values were already given in the supplementary material.

With respect to testing model hypotheses about the flow pathways, tracer experiments have been carried out first with conservative tracers. The conservative tracers are used to determine the validity of assumptions on flow pathways; a step before testing pathways for the reactive solutes. If simulating reactive transport without a validated distributed water flow model, the matching of solute leaching could be ok, but could result from different reasons. I am not sure but I did not find descriptions of such an intermediate conservative tracer step for calibrating or validating the flow part here.

Answer: We did not perform conservative tracer tests and subsequent model calibration, we only considered a conservative tracer as test substance in the modelling study. Still, even without calibration to conservative tracers, the calibration to three sampling stations for discharge and six solutes instead of the catchment outlet only may be rated as quite sophisticated compared to most modelling studies at catchment scale.

Furthermore, for such large watersheds, studies of spatial heterogeneity at several scales (e.g., fields, the 10m by 10 m grid, the soil horizon, aggregates, or burrows) may be important (e.g., for a drained field, e.g., Gerke, Dusek, Vogel, 2013, Vadose Zone J.) at least to qualitatively characterize the relevance of the various model parameters.

Answer: Spatial heterogeneity is considered in this model by considering 11 different soil types with three soil layers and 12 landuse types. Additionally, drainage areas are separated independently from the soil and landuse types. Compared to the catchment size, we suggest that a 10x10m resolution is sufficient to represent spatial heterogeneity. However, looking at smaller scales, we agree that parameters such as the hydraulic conductivity are rather effective parameters.

Specific comments:

1. Introduction, Methods, Chapter 2.3: Indicate what is different here regarding methods and analyses in comparison to the paper of Gassmann et al 2013 Hydrol Sci J in press? Zin-AgriTra and Zin-Sed 2D needs more explanations.

Answer: In Gassmann et al (in press), Hydrol Sci J, a former version of the model is applied for phosphorus export modelling from an agricultural catchment. Equations for pesticides and TPs are new as well as some hydrological process details. We will include a more detailed differentiation between the model of this paper compared to the former.

2. Chapter 2.31: I did not understand why it was necessary that the soil moisture was assumed to increase within each layer according to an empirical relation (Eq. 1). If the water flow is calculated using Richards' equation as indicated before, the vertical distribution of water contents in all the layers will be calculated automatically according to the numerical discretization. It appears as a highly discretized distributed water balance model combined with some flux model and chemical reaction and sorption components.

Answer: The three soil layers are also numerical layers. Richards equation may lose accuracy due to the relatively low numbers of layers (this was also pointed out by reviewer N. Jarvis). Therefore, we chose to calculate the groundwater table by equations (1) and (2) and to calculate surface infiltration by the Green and Ampt model. Generally, with 40000 cells and 144 timesteps per day, we had to keep the calculation time in arguable ranges. Thus, we restricted the discretization to three numerical soil layers.

3. The use of Hagen-Poiseuille's law for calculating the macropore hydraulic conductivity is a pragmatic possibility that means coupling a pore-scale equation for macropores with a macroscopic scale matrix flow equation. Similar approaches and their usefulness of have been discussed e.g., in Köhne et al. 2009 J Cont Hydrol., Gerke 2006 J. Plant Nutrition & Soil Science.

Answer: Thanks for pointing us to this literature.

4. The Green-Ampt approach was used for simulating the "infiltration" (i.e., water transfer) of macropore water from macropores in to the soil matrix. How that coupling with the present layer model worked in detail here, I could not figure out. This simplification provides probably relatively stable solutions; however, transfer can be limited in just one direction; that means transfer from the matrix into the macropores for relatively saturated conditions is not considered?

Answer: In the model, we suppose that macropores are only filled by overland flow, which is generated in this region mainly by saturation excess overland flow, i.e. during saturated topsoil conditions. Saturated conditions are also needed for an initiation of matrix flow to macropores. Thus, we suppose that the error is not too large and may probably be overlain by other uncertainties. In this case, we sacrificed the level of process detail for the model applicability at catchment scale. Details on the implementation of the Green and Ampt method for macropores are given in the reference provided in the manuscript (Weiler 2005).

5. In chapter 2.4.1, the cell grid size of 10 m was mentioned, which is of course still small compared to the size of the catchment. It is clear that with increasing cell size, the use of soil hydraulic properties and geometries will be more problematic, because of the internal heterogeneities within cells.

Answer: We agree that it may be problematic to account for theses heterogeneities in larger cells. However, it is a common approach in catchment scale modelling to delineate cells (or hydrotopes) with same soil properties. In most studies the cells (or hydrotopes) are even larger than in this study.

6. The macropore numbers and sizes are probably crucial for the outcome of this model. The parameters maybe regarded as "effective"; the question is whether these simplifying assumptions (number-diameter-conductivity-Green-Ampt mass transfer) are compensating for other unknown effects that occur in the field. Recent studies (soil) showed that earthworm burrows are not uniform, a drilosphere exists, and burrow walls are coated with casts; older burrows are often used by roots such that the hydraulic properties and exchange can differ in a wide range. Furthermore the wall coatings because of higher organic matter contents can have sorption properties that strongly differ from those of the matrix (such literature has not been discussed or included here). Of course, transformation product sorption along macropore walls is largely unknown.

Answer: Thanks, we agree. With respect to heterogeneities and unknown or not implemented processes, one may refer to all considered soil parameters as 'effective', even at smaller cells than in our study. We will mention this in the discussion along with a short discussion about interactions between macropores and solute transport.

7. Model calibration: For such a complex model system consisting of several models, each should in principle be calibrated independently and interactions separately. This can probably not be achieved using discharge and effluent concentration curves only but with additional observations in soils, drainage waters and other spatial compartments. It is interesting to have a tool for separately calculating discharge components such as e.g. tile drain via macropore; the question is how these separate components can be experimentally validated, how they may be compared with observations (which here was probably not yet possible).

Answer: Thanks. We will add a short discussion about possible procedures for the validation of the export pathways and the difficulties associated with it at page 9868, l. 10.

8. What is the strategy here to address the problem of equifinality?

Answer: As stated in the text and given in the supplement, we took most of the hydrological model parameters from a former sampling and modelling study (Frey et al., 2009), i.e. these parameters we not calibrated. Sorption and transformation parameters were calibrated in relatively narrow ranges as found in the literature (Table 1). The narrow ranges restrict the freedom of choice of parameter values and thus lower the probability for equifinality.

The results and conclusions of this modelling study are in line with the hypotheses suggesting the important role of different pathways and physico-chemical characteristics of pesticides and transformation products. Nevertheless, it would be interesting to see how the results were affected by assumptions and calibrations of flow and transport in macropores, the exchange, or effects of the drainage network on discharge and leaching.

Answer: We already showed the influence of sorption kinetics on event export and the parameters for water table calculations in the supplement. We will add model runs without soil residues from former pesticide applications in order to quantify the effect of residues on export pathways. Thus, the assumption can be ruled out. However, it is beyond the scope of this paper to perform a full parameter sensitivity analysis (considering the model runtime and the amount of parameters).

References cited in the answer:

Frey, M.P., Schneider M. K., Dietzel A., Reichert P., Stamm, C. Predicting critical source areas for diffuse herbicide losses to surface waters: Role of connectivity and boundary conditions. J. Hydrol. 365 (1-2), 23–36, 2009.

Weiler, M.: An infiltration model based on flow variability in macropores: development, sensitivity analysis and applications, J. Hydrol., 310, 294–315, 2005.