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Interactive comment on "Assessment of vadose zone sampling methods for detection of preferential herbicide transport" by N. P. Peranginangin et al.

Anonymous Referee #1

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This study adds to the dissemination of well established facts. The authors correctly address the problem by stating that "... practitioner awareness (of preferential flow) lagged ...". Practitioners in this sense probably include not primarily the agronomic consultants and extension specialists, but rather the scientists and administrators involved in pesticide regulation (as for instance, in the OECD). It does make sense to confront a wide segment of readers – as reached by HESS – with another set of experimental results about the sampling problem of chemical transport in soils under partly water-unsaturated conditions. The question is, however, whether those who need this additional lesson actually read HESS. Nevertheless, I advocate to make this informa-

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tion available in a final form (after needed revision) because this contribution adds scientific evidence of the consequences of preferential flow.

Above I picture the positive view on this contribution. One could also argue that almost everything reported in this paper has been said before. I suggest to justify your point more clearly why it is why you sort of duplicate information. The strongest argument is that every new site — characterized in detail relative to its transport properties — is unique and duplication is merely a methodological statement. In addition, adding experimental evidence is one way of scientific verification.

Nowadays, it is getting difficult to write an introduction to a preferential flow paper because the literature got crowded with information regarding this phenomenon. I therefore suggest to primarily compile the review articles that cover the preferential flow problem and refer to the original contributions only when their message is pertinent in this context. I say that because in this paper the number of quoted paper is large but it is not a thorough review of the literature. Some of the original papers are not quoted or misquoted and instead some newer papers are being referenced as THE original contribution.

The experiment described here required quite an effort. Despite this, it was underinstrumented if the authors emphasize the statistics of the sampling problem. For instance, replicating solution samplers (porous cups) only six times is absolutely insufficient to parameterize the underlying distribution of the data. Reporting the coefficient of variation is based on the assumption of a normal distribution of the sampled data population. CV > 100% indicates either insufficient data support or a skewed distribution. The authors acknowledge this shortcoming by reminding the reader to be cautious when only two or three values can actually be used for the analysis. This cautioning action is too cautious because calculating a standard error form two or three or four values contradicts proper use of statistics. I can accept (somehow) the use of CVs in case of the wick pan samplers with eight replicates but even this is a very weak data support. I do not propose to delete the observations obtained with the cup samplers, but to use

this information just as an indication that this study confirms what has been shown before and that this technique has been disqualified – despite its wide use – unless one is willing to come up with a sufficient number of replicates, ... this means many! The same applies to the number of soil cores ... three core samples per depth is little in view of the abundant information about spatial variability of soil variables. These core samples are then analyzed according to the standard procedures, which might be o.k. in case of CI, but definitely not in case of herbicides. The analytical fact that the mass of the applied substance is zero in a given depth region, may mean that the amount being adsorbed might have been raised due to the drastic increase of exposed solid surfaces. This effect is even enhanced in case nonlinear adsorption isotherms. Even when atrazine or 2,4-D, residing in some pores, maybe in the liner of the pores or in the region immediately within the vicinity of the preferential flow path is present, when thoroughly mixed with the entire disaggregated matrix, the concentration will be below the detection limit.

The discussion of the results is quite detailed but educational. Many of the statements have been stated before, but are being recalled for explaining what has been observed. I miss one important fact: preferential pathways may have adsorption and degradation properties which are significantly different from those of the by-passed matrix. The plus minus simultaneous arrival time of conservative and reactive solutes is an extreme evidence of this. This poses a problem, which is difficult to approach and even more difficult to resolve. It is not clear how one should estimate these properties before the experiment has been completed and the preferential flow paths being identified (cat and tail problem). Standard soil analyses are certainly no answer to this.

The editorial quality of the paper is good. The figures and tables are needed and readable, with a few exceptions (see below). It reads well but there are a number of examples where the "precision of language" deserves some attention (" ... " your phrasing/spelling)

"significant flow paths": significant portion of flow paths or of highly conductive flow C3024

soil regions or else but a flow path per se is not "significant"

"non-adsorbed tracers": non adsorbing tracers

"saturated or unsaturated pores": saturated or unsaturated <u>soil</u> or <u>pore regions</u> or what ?

"worse case scenario": probably you mean the worst case scenario

(by the way, it is interesting that the Arkport site exhibits properties, which are not too different form the recommended lysimeter properties for testing pesticide mobility in Europe, considered to be a worst case scenario)

Hyphenation is handled inconsistently and partly incorrectly:

"strongly-structured": strongly structured, no need for a hyphen between an adverb and participle.

"10-yr and 24 h": why hyphen here and no hyphen there, the latter form is more frequently used (SI unit is y for year but yr is tolerated).

There are many examples of this kind in this text.

Table 1:... of the total amount of applied chloride

Table 3: Is this an analysis of the variance between two average values (average of 4 sampling ports per sampler) ... not obvious what you mean. Indicate the number N (of values used for calculating this CV)

Table 4: For chloride there is no column for the mean. Separating the columns for the four columns of Atrazine and 2,4-D using vertical lines would help.

Fig. 1 the "sampling lines" are poorly visible

Fig. 2 here you do not mention that cumulative rain means "rain+ irrigation" why not just defining the amount if "cumulative infiltration"

In summary, I suggest to reposition the main message of the paper or rather the value of the paper's message and to be more considerate in statistical terms.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 6, 7247, 2009.