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Interactive Comment

Interactive comment on "Transport at basin scales: 1. Theoretical framework" *by* A. Rinaldo et al.

A. Rinaldo et al.

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Reply to Referee #2

All authors feel they have to thank this reviewer for his thorough review work and the interest in the paper.

Detailed answers to the comments offered by Referee #2 are reported below. Italics refer to the reviewer's statements, our comments follow.

> *.. I do not see any need of assuming the further restriction that "the temporal scales relevant for the undergoing advective processes are larger than the characteristic times for the reaction processes". This is indeed the condition under which local chemical equilibrium occurs such that equation (12)*

resembles the linear equilibrium assumption (LEA): $N(\tau, t_0) = k_D C(\tau, t_0)$*. Since the manuscript deals with the linear kinetic reaction (12), which does not entail restrictions on the characteristic reaction time, I wonder why the authors introduce it.*

The statement has been modified as follows: "The temporal scales relevant for the undergoing advective processes are smaller of (or, at most, comparable with) the characteristic times for the reaction processes". The reason for introducing this assumption are explained in Botter el al. (2005), where it is shown that when $k\langle\tau\rangle \leq 1$ (if k is the mass transfer rate and $\langle\tau\rangle$ is the mean residence time), the undergoing spatial gradients in the immobile phase have a negligible effect on the solute response of a heterogeneous system, therefore allowing the well mixed approximation employed by the MRF model. It should be also noted, however, that this assumption is not required when dealing with highly heterogeneous media (e.g. when the variance of the travel time increases). In this case, in fact, the spatial gradients within the immobile phase do not significantly affect the solute response even though the reaction kinetics are relatively "fast" and $k\langle\tau\rangle > 1$. Incidentally, we note that the conditions leading to the Local Equilibrium Assumption (LEA) require that the characteristic time for the reaction processes is negligible with respect to the temporal scales of the undergoing advective processes, that is $k \to \infty$ or $k\langle\tau\rangle \gg 1$. Indeed the previous version was wrong (only in the writing, fortunately - we have subsituted "larger" with "smaller") and we thank the reviewer for pointing this out.

Furthermore, in the second manuscript of this series the authors show clearly that LEA cannot be applied for simulating nitrate leaching from agricultural areas (see Figure 9 of the second manuscript), and that the characteristic time of advection (see Table 2 of the second manuscript) is smaller than that of reaction (see table 3 of the second manuscript). Therefore, I think that the above restriction on the characteristic reaction time is not *needed.*

Correct. In the application of the theoretical framework developed in this paper for modelling the nitrogen transport in the Dese river, the mean ratio between the characteristic time of advection and that of reaction in each geomorphic state is approximately 0.5, therefore allowing the well-mixed approximation. No need for corrections here.

page 1633, line 13, I read: "Notice the difference in the timescale with respect to the travel time f(t) shown in Fig. 2 due to the chromatographic effect... ": I do not see the chromatographic effect invoked by the authors. f(t) and flux concentration peak both around t = 5 h and show a similar tailing, such that the timescales of the two responses are roughly the same.

True. According with the reviewer remarks, the statement "Notice the difference ...reaction kinetics" (page 1633 line 13-14) has been removed. For the specific values of the reaction kinetics and of the mean travel times employed here we do not observe significant chromatographic effects, because the chemical equilibrium between the phases is quickly reached.

All the other recommendations have been met.

Interactive comment on Hydrology and Earth System Sciences Discussions, 2, 1613, 2005.