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Interactive comment on "Catchment export of base cations: Improved mineral dissolution kinetics influence the role of water transit time" *by* Martin Erlandsson Lampa et al.

Anonymous Referee #1

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It is sometime since I had anything to do with the PROFILE model. I published a series of papers in the 1990s [most notably Hodson et al (1996) Applied Geochemistry 11 835 – 844 and Hodson et al. (1997) Water, Air and Soil Pollution 98 79 – 104] that were critical of the model, not so much in terms of the output, which gives results for weathering rates similar to those determined by other, relevant methods, but the way the model achieves those results. I would argue that any application of the model needs to consider those limitations or at least acknowledge them. I think that this is particular the case in a paper such as this one that: a) involves the original model authors – it is important to acknowledge that researchers independent of the model have raised concerns about it and b) presents an improvement of the model – it is important

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Discussion paper

to understand the context of that improvement, is the model still using incorrect mineral formulae, reliant on input of relative surface area of different minerals (rather than the typically used relative weight % derived from XRD or normative data), reliant on an unproven formula that calculates total mineral surface area on the basis of soil texture, uses reaction orders and rates that are open to question etc. which are issues raised in the above papers about the model. From the opening of the Discussion it would appear that the original form of the model, complete with disputed parameters was used. This is not to say that the paper should be changed extensively, just that published peer-reviewed journal articles from independent groups that raise issues about this model should at least be acknowledged and / or the concerns raised in those papers addressed.

In the abstract it would be good if in the abstract the authors were able to quantify the degree of improvement in model predictions vs. observations rather than simply stating that there is an improvement.

Around line 26 of the abstract it is stated that the PROFILE equations aren't adapted for the unsaturated zone – I think this is a typo for the saturated zone, consistent with the statement in the introduction around line 3 of the third page where it is stated that the equations are restricted to the unsaturated soil domain.

In section 2 the authors indicate the form of various retardation factors used in the model. Given issues with the derivation of some values used in the model raised in the Hodson et al. papers it would be good if the authors, at least in supplementary information, could indicate how these new retardation factors were derived via plots of the data used in their derivation.

Equation 9 – use of texture to calculate mineral surface area should not be used. There are contradictory statements in the publications of Sverdrup regarding the data which were used to develop this equation, in particular whether soils were treated to remove organic material or organic material and sesquioxides (see Warfvinge, P. and Sverdrup,

H.: 1995, 'Critical Loads of Acidity to Swedish Forest Soils'. Reports in Ecology and Environental Engineering 5, Lund University and Sverdrup, H. U.,Warfvinge, P.: 1995, 'Estimating field weathering rates using laboratory kinetics', in White,A. and Brantley, S. (eds.),Weathering Kinetics of SilicateMinerals,Reviews inMineralogy 31. Min. Soc. of Am.) and the inclusion (or not) of an additional fourth term for coarse sand. In addition, despite citing this equation on numerous occasions the publications of Sverdrup et al. have never published the data used to derive the equation. The only data presented to test this equation is in our paper Hodson et al. 1998 (Hodson, ME, Langan, SJ and Meriau, S (1998) Geoderma 83 35 – 54). My recollection is that in Hodson et al. 1998 there are errors in the units but that issue non-withstanding it is the only published test of the relationship and the relationship was found not to stand. The relationship predicts values which are the same order of magnitude as actual measurements but as such, given the accuracy of mineral weathering calculations, it would be more realistic to use a constant for this term. Given the statement in the discussion that the model has a sound theoretical basis in thermodynamics and Transition state theory I do feel it is important to be open and clear about the derivation of variables like the surface area term (and some of the others highlighted in Hodson et al., 1996, 1997). Alternatively (and better) the authors could finally publish the data used to justify their equation (9) – both the data used to generate the equation and the independent data used to validate it.

After the authors write that they use this equation they then go on to write that it gave a number which they felt was too high so they used a lower value similar to values used elsewhere in the PROFILE. To me this seems like having ones cake and eating it. Either the equation is applicable and should be used through out or it isn't applicable and shouldn't be used. By setting the value at an arbitrary level surely surface area is being used as a fitting parameter not an input calculated for the horizon in question.

More generally it would be helpful if a list of the input parameters used in the model were provided in Supplementary information.

As stated in the Discussion (4.3) the proposed modifications are welcome as they help to address the issue regarding chemical affinity where previously mineral phases could continue to dissolve even when the predicted solution concentration was saturated with respect to that mineral. I would suggest that, for the example given for example where the dissolution rate of K-feldspar decreases by an order of magnitude or so after the solution is saturated, this is an improvement but it would be better if the model were modified so as to predict no dissolution (or net dissolution) in a saturated solution which is surely more realistic. That being the case it would be useful if the authors could explain why they chose to modify their model in a way that acknowledges and addresses this issue to a certain extent but not fully.

In the conclusions the authors state that this version of the model is applicable to mineralogically homogeneous hillslopes. This limitation is presumably because of the complexity of considering movement of packages of cation laden water from one mineralogical environment to another where retardation of reactions will change. However it might be useful for the authors to offer an opinion on how “homogeneous” soils have to be for the model to be OK for use. Soils are very inhomogenous on a number of different scales.

In summary, this paper represents a useful advance of the PROFILE model. However, it fails to acknowledge independent, published concerns regarding the parameters used to drive the model. The uncertainty inherent in calculations of this nature do result in the model generally performing quite well when compared to solution chemistry data sets.

In general there are minor typos / issues of grammar that need addressing.

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