Review of *Current, steady-state and historical weathering rates of base cations at two forest sites in northern and southern Sweden: A comparison of three methods* (v3, 1st revision?) by Casetou-Gustafson et al. BG-2019-47 by Michael Velbel

The science

1. This is a paper about weathering rates in forested landscapes on glacial parent materials that only a specialist can love. The slog through under-and mis-referenced statements, mis-numbered Tables, and almost obsessively detailed text was a journey in which not every reader will persevere, but it forced this reviewer to more or less see the whole picture – albeit not without difficulty. The paper will likely be more widely read by novices and other non-specialists who will be drawn to the shiny inter-approach comparison without the benefit of extensive experience interpreting either outputs of individual approaches or comparison of such outputs from multiple approaches. Such readers will either cite the paper for the nuggets they understand from the densely written text or be flummoxed by all the highlighted details and nuances. But that's their problem.

2. Strength (mostly) with some weakness: Some descriptions of pioneering previous work are more correct, and therefore more useful to readers, than others. The "base cation budget" approach as developed in the two papers cited in lines 157-158 is a steady-state linear inverse model. So far so good. However, no aspect of MAGIC is an inverse model (base-cation influx-outflux ("input-output" model). MAGIC – as thoroughly described in the OTHER Cosby et al. 1985 Water Resources Research paper, but not in the Cosby et al. 1985 WRR paper cited in this manuscript – is a forward model in which the (bulk, catchment-averaged) "weathering" rates of the four major base cations are input parameters (see input definitions in the last section of their Table 1).

   Later in the manuscript, lines 559-566 are is well-referenced to several classic references correctly represented, and in that sense invokes insights from (although contributes none to) inter-regional/global literature on weathering rates in forested landscapes on glacial parent materials in general.

   Overall, some misrepresentations and omissions of classic works notwithstanding, this study takes good advantage of pioneering insights of general (global) significance for interpretation of the local weathering rates estimated by diverse means.

3. Weakness: Lines 145-155 - Sensitivity of PROFILE outputs to slight variations in input parameters is correctly acknowledged. What is not discussed is the sensitivity of PROFILE outputs to the mineral dissolution rates and rate laws used in the forward modeling.

4. Strength: Lines 269-286 – The number of profiles rejected for not meeting reasonable acceptance criteria on the one hand suggests reasonable and useful criteria. On the other hand, failure to satisfy many of the numerous assumptions acknowledged disqualifies a distressingly large number of profiles. This suggests that an approach with so many assumptions that so many natural systems (in this case, profiles) cannot satisfy may not

be an approach that reliably produces outputs suitable for comparison with other approaches. Such comparisons being the whole point of this manuscript, this paragraph undermines reader confidence in the entire enterprise. Fortunately, later in the manuscript, precisely these limitations of the assumptions are explicitly addressed and considered in interpreting the core truths hidden amidst the various model outputs.

5. Lines 287-288 – Was bulk density ***measured*** for each soil layer except in some plots where density measurements could not be made below a certain soil depth? Line 287 says estimated. If estimated (as written), then how was the estimation in line 287 different from the estimation in line 288ff?

6. Strength: Section 2.5 – all the components of the base-cation budget seem to be well-constrained. Much good discussion later in the manuscript benefits from this thought and care.

7. Weakness: Lines 438-443 – Using outputs of the other two approaches to constrain uncertainty in the budget approach breaks down the wall of independence, and therefore the validity of comparisons, between the three approaches.

8. Weakness: The treatment of error is confusing. Eight plots were sampled, four in each of two study areas. At each study are, two control plots and two fertilized plots were sampled. Both fertilized plots at Flakaliden were "eliminated from further consideration in calculations of historical weathering rates using the depletion method" (lines 282 - 283). Site mean or average values and their standard errors or combined standard uncertainty were calculated for each of the three approaches. "For the weathering rates based on the depletion method and the PROFILE model, error bars represent the standard error calculated based on four soil profiles at each study site, except for Flakaliden, where the depletion method was only applied in two soil profiles." (Lines 1045-1048, caption for Figure 4). However, error bars are shown for all cations for the depletion approach applied to Flakaliden; the reader is left to infer that these error bars show the range (not the SEs) of the rates estimated for the (only) two Flakaliden profiles.

9. Strength (good inferences) and weakness (text is under-referenced w.r.t. relevant past work elsewhere): Lines 500-501 – "The closest resemblance between methods was found between $W_{depletion}$ and W_{budget} for Na." No surprise here; Taylor and Velbel (1991) showed that diverse approaches (in their case, excluding versus including biomass) yielded more similar weathering rates for Na-hosting minerals than for the mineral hosts of other base cations, because (as is also noted in this manuscript in lines 504-505 and 657-658), the independent variables (input terms to the inverse model) for Na budgets are the least influenced by variations and uncertainty for biomass stocks and flows relative to the corresponding terms for any other base cations. This enables intersite comparisons of weathering rates for Na-host minerals more readily than for the mineral hosts of any other base cations (Price and Velbel, 2005). Similarly, Taylor and Velbel (1991) and Velbel (1995) showed that estimated weathering rates of K-hosting minerals are the most influenced (relative to the hosts of other base cations) by the large role botanical demand for K and the corresponding large sensitivity of calculated rates to quantification of

biomass-related concentrations and fluxes. Lines 504-506, 657-658, and 664-666 of the present manuscript rediscover this phenomenon effectively and concisely. This correspondence between the work presented in this manuscript and (unfortunately uncited) long-known previous work inspires reviewer confidence in this manuscript's results from using the cation-budget approach.

10. Strength (good inferences) and weakness (text is under-referenced w.r.t. relevant past work elsewhere): The case that solute budgeting is the most reliable approach has been previously made (Velbel and Price, 2007). The sound results of the cation budget approach in the present manuscript, and the weak correspondence between the results of the other two approaches with the cation budget results (Fig. 5 in the present manuscript), both appear consistent with this previously articulated argument insofar as consideration of weathering rates is concerned.

11. Strength: In light of the previous several comments, I find Discussion section 4.1 Comparison of conceptually different methods (lines 522-540) an honest statement of how all approaches have their individual limitations, and a sound (although I cannot vouch for pioneering or up-to-date) assessment of the state-of-the-science regarding how to use the different approaches for scientific investigation. The rest of the Discussion expands successfully on section 4.1 in considerable detail. (The implications of all this for using such approaches for decision support in land-use management is another matter entirely.)

12. The effort to detect a pulse in PROFILE is both charming and valiant.

13. Weakness (text is under-referenced w.r.t. relevant past work elsewhere): The depletion method rests weightily on the assumption of Zr immobility. The assumption of Zr immobility is well-justified on crystal-chemical grounds, and consistent with observations and consequent inferences in many studies. However, unfortunately, Zr immobility may be an actual extant limiting condition in fewer weathering profiles than the number to which the assumption has been applied. In addition to the parent-material (glacial till) heterogeneity and redistributive processes in plow-layers and by earthworms that are invoked in this manuscript (lines 607-633), there exist papers (albeit only a handful) over the past four decades or so demonstrating both corrosion of zircon in soil grains and physical translocation of fine-grain zircon through soil-regolith pore networks. Unfortunately, I have not yet worked systematically on Zr as a mobile versus reference element and have thus not had to recover this literature, and in some of the papers the relevant observations are incidental to the main point of the paper, so I would be able to put my hands on only one of these papers at present.

14. Strength: The comparisons of estimated total depletion that would follow from the weathering rates determined by the various approaches with the measured total depletion over the duration of pedogenesis since deglaciation (Figure 6) is novel, and is only possible because so much work has been done at the study sites in support of the work reported in this manuscript and the related papers in the same volume.

15. Strength (good inferences) and weakness (text is under-referenced w.r.t. relevant past work elsewhere): Attributing the differences between the three approaches to changes in the exchangeable cation pool is well-considered, and well supported by this study's multiple measurements of cation exchange pools one to two decades apart (lines 361-364). The suggestions for not-yet-measured sources of Ca and K are well-considered, at least to the extent that they conform with this reviewer's experience with how complicated the mass budgets for these specific elements can be (e.g., Taylor and Velbel, 1991; Velbel, 1995; Price et al., 2005).

16. The data, observations, evidence, and inferences presented in this manuscript support a for the most part persuasive case for the stated interpretations, conclusions, and modest implications for similar work in similar landscapes.

17. If I ever get to teach my graduate-level "weathering" course again (increasingly unlikely as my career careens toward an untimely collision with retirement), I would assign this paper as either an introduction to the three approaches or, after the three approaches had been individually introduced from older pioneering studies, as the starting point for a treatment of their inter-comparability, relative scholarly merits, and relative utility.

The manuscript

18. The work as presented appears to be sound but the presentation of the work needs to be improved by better explanation of observations, relations between observations, how the observations support the inferences and interpretations, *<u>and their implications for the literature</u>*. Revisions of the manuscript are required before further review and an editorial decision.

Regarding the organization of the scientific content in the manuscript: Specific matters relating to this manuscript are highlighted in the following numbered items and the subsequent line-index list.

19. Clear identification of scientific novelty in Introduction (Statement of Purpose): A successful manuscript must identify the novelty of the work reported in terms of advancing the frontiers of forest-soil weathering. A successful manuscript should clearly identify what is new and scientifically significant about the work presented. The authors should clearly state the aim of this study (i.e., what problem you want to solve, etc.). This will help readers to understand the scientific novelty of this study. The authors need to show (state clearly) how this study differs from past studies of similar soils. The Introduction of the paper should define the scope of the problem to be solved by the work presented. The Introduction should provide background explaining what problem is being solved, or what gap in existing scientific-community understanding as reported in the literature is being filled, by the work reported in the paper. The Introduction should briefly explain why this problem is not already solved or why the solution in this manuscript is better than previous solutions in some specified important way.

The Introduction section makes a number of good and promising points:

Lines 114-117 - "Differences in input data can be attributed to different time scales used when acquiring different input data, challenges determining accurate mineralogical compositions and the use of field data compared with laboratory data (Van der Salm, 2001; Futter et al., 2012). Thus, they recommend that at least three different approaches be applied per study site to evaluate the precision in weathering estimates."

Lines 120-121 - "The choice of methods is primarily based on the fact that rates of weathering may vary over time (Klaminder et al., 2011; Stendahl et al., 2013)."

Lines 140-142 - "Since the rate of weathering may vary over time (Klaminder et al., 2011; Stendahl et al., 2013), the average 'historical weathering' rate may differ from the present-day weathering rate. The depletion method is most widely used in Sweden to estimate weathering rates, specifically at the regional scale (Olsson et al., 1993)."

Lines 162-164 – "The base cation budget approach is most reliable when based on long-term data from well-defined systems, although even then estimated weathering rates suffer from large uncertainties, as errors in the sinks and sources accumulate in the mass balance equation (Simonsson et al., 2015)." The case has already been made elsewhere that solute budgeting is the most reliable approach (Velbel and Price, 2007).

Lines 165-167 – The manuscript is correct in observing that "The base cation budget approach has mostly been applied under conditions where accumulation in biomass were not directly measured but estimated to be small, or base cation stocks in the soil were assumed to be at steady-state (e.g. Kolka et al., 1996; Sverdrup et al., 1998; Whitfield et al., 2006)."

Lines 173-178 – "The base cation budgets were estimated at the period of stand development when nutrient demand was expected to peak. In combination with access to highly accurate data on biomass production, these conditions also provided opportunities to relate weathering to base cation accumulation in biomass at high nutrient uptake rates, and possible simultaneous depletions of extractable base cation stocks in the soil. Furthermore, input data to PROFILE were characterised by high quality quantitative mineralogical data, measured directly by X-ray powder diffraction (XRPD), as previously discussed by Casetou-Gustafson et al. (2018)."

So far, so good.

20. If the purpose is primarily to describe a local phenomenon, then either the paper belongs in a local or regional journal or the manuscript needs to better explain the scientific novelty of the work. Does this study of these phenomena and models at these places have significant potential to change our understanding about such phenomena and the application of these models elsewhere, or does it only confirm that it is much like others that have been similarly characterized and modeled and it is just adding information about this particular occurrence? How does the detailed study of these two field sites

advance scientific understanding beyond merely characterizing this locally important land-use type? If there is no larger scientific significance, then specifically how does the work reported improve the management and use of the forest resource? A study of sites and with methods that do not have international or global significance for understanding that type of deposit is not self-evidently sufficient for an international journal. Is the work reported an ensemble of measurements and tasks that has significant potential to change scientific or applied approaches to this kind of landscape? What is distinctive or unique about the reported work relative other published approaches to the same problem? What can the community do better after the work reported here than it could do without this work? Specifically how does the work reported in this manuscript improve upon prior art? I look forward to further explanation about this, and especially for this to be very clearly stated in the Introduction and Abstract of the revised version.

21. The Introduction should set the stage for the Discussion and Conclusions sections: Once the Introduction and statement of purpose have been written (as discussed above), the Discussion and, especially, the Conclusions, should clearly and explicitly link the outcomes of the research with the identified gap in community understanding as identified in the Introduction. The present manuscript as written does not accomplish this. The mere fact that specific sites have not been previously examined for the reported phenomenon, or a specific combination of characterization methods and modeling approaches has not been previously applied, does not by itself justify publication in an international journal, and Conclusions that do not link the Results and Discussion back to the literature on a larger scientific problem are not enough to justify publication in an international journal.

22. A description of a new soil-weathering case study must thoroughly compare the data from the new deposit with data from the literature (primary papers are best, but review papers may suffice) on similar landscape/land-use types elsewhere. This allows the reader to appreciate the paper's inferences about what is new or unusual about the study area, and what is familiar and common about it. The present manuscript as written does not accomplish this, which may be OK considering that it appears not to be intended to. The first comparative assessment (lines 548-557) and much of what follows in section 4 is local-regional comparison with other Swedish studies back at least as far as 1995. This content comes across to a reader unfamiliar with recent studies in Sweden as detailed and thorough, albeit perhaps not especially exciting. The second comparative assessment (lines 559-566) is well-referenced to several classic papers, and in that sense invokes insights from (although contributes none to) inter-regional/global literature on weathering rates in forested landscapes on glacial parent materials in general. This study takes good advantage of such pioneering global insights for interpretation of the local weathering rates estimated by diverse means. However, the work reported appears to be of local-regional significance only. It provides no major new insights for forested landscapes on glacial parent materials in general. If the purpose of the paper is primarily to describe a local deposit without such a comparison with other similar deposits, then the paper may be more appropriate for a local or regional journal, economic geology journal, or trade journal that publishes local resource-evaluation work, rather than an international journal.

23. A locality map is a near-universal courtesy to readers. This manuscript requires one. The fact that it lacks one sadly reinforces the perception created by the rest of the manuscript, that it is directed mainly to readers who already know where the study sites are and why they should care.

24. Why is Fig. S3 the first Figure cited (even before S1 and S2)? All Figures should be numbered in the order they are first referred to in the text, and referred to in the text in their numbered order. The manuscript as written is poorly organized in this regard. Please make the necessary adjustments so that all Figures are cited in their numbered order, and numbered in their cited order.

25. All Tables should be numbered in the order they are first referred to in the text, and referred to in the text in their numbered order. The manuscript as written is poorly organized in this regard. For example, Table 1 is cited in line 204, but the information described in the corresponding text is on Table 4a. Please make the necessary adjustments so that all Tables are cited in their numbered order, and numbered in their cited order.

26. This manuscript is seriously under-referenced. Numerous statements are made in such a way that the reader cannot distinguish statements about common knowledge among Swedish forest-soil scholars from statements that ought to refer the reader back to an authoritative primary reference. Also, pioneering primary references, the original sources of ideas, should be cited, rather than citing more recent derivative papers that apply the same concept or say the same thing (e.g., regarding use of Zr vs. Ti as a reference element).

27. Supplemental information: To the extent that the large tables (e.g., Tables S1 and S2) are essential to the paper, the Editor and authors might consider making the same tables available in Excel or .csv form as supplemental online material. Data available in a directly usable format (not requiring transcription or OCR from the printed/pdf version) might wind up being widely used by the community.

Regarding the English, I commend the authors for a rather well written manuscript. I did note, however, that the English style and format does not quite adhere strictly to expectations. I have listed below some specific points to which attention should be directed (e.g., typographical and grammatical errors, word choices, punctuation, capitalization, sentence structure, subject-verb agreement, paragraph organization, &c.).

28. Generally speaking, use “since” only when referring to time rather than as a conjunction in place of “because.” Several occurrences (line 140, 2nd occurrence; 147, 387, 516, 536. 560, 630, 666, 668, 673, and 690) require correction in this regard.

29. Use “by” or “by way of” or “by means of” rather than “via” (“via” connotes a spatial, geographic pathway or route, and is not to be used metaphorically) or “through” (which Lalso has spatial connotation). Line 599 requires correction in this regard.

30. Replace “frequent(ly)” with “commonl(ly)” in lines 107 and 168.

31. “Data” is plural; “datum” is singular. Data are/were, not data is/was (lines 401-2, 433); many other occurrences are correct.

32. The concept of “stability” is not used with sufficient rigor in this manuscript. Any phase (or assemblage) or state is either stable (at equilibrium with one or more specified other phases) or unstable *with respect to a specific alternate phase assemblage or state under a given set of conditions*. This specific state must be explicitly stated (e.g., stable with respect to dissolution in dilute acidic solutions at Earth-surface conditions). A mineral that survives for a long time because it reacts slowly is persistent, not stable (Velbel, 1999). Line 137 requires attention, consideration, and rewriting in this regard.

33. Replace “stable” with “constant” or “uniform” in lines 274, 631, and 633.

34. Strata (or beds) are produced by sedimentological superposition of layers of physically mobilized grains deposited from a fluid medium under the influence of gravity. Horizons are produced by the pedogenic equivalent of chromatography. If the origin of discrete depth intervals of great lateral extent is uncertain or indeterminate, neither term should be used. All references to “layers” should be changed to “horizons” or “intervals”.

35. Please replace “x”s used as multiplication signs with the multiplication sign (“×”) in lines 194 and 375.

36. Be careful to match the number (singular vs. plural) of articles, subjects, and verbs. Several occurrences (e.g., line 707) require correction in this regard.

37. This reviewer did not check the references for accuracy or style, or for conformity between references cited in the text and those listed in the bibliography.

General comments:

There are many places in the text where, alone or in concert, insertion or redeployment of commas and semi-colons may make long sentences easier to read.

Specific comments:

Line 101 – replace “if” with “whether”

Line 170 – replace “on” with “to”

Line 353 – replace “ar” with “is”

Line 416 – Delete close paren.

Line 481 – Replace “as opposed” with “in contrast”.

Line 580 – Replace “were possible to reconcile” with “could be reconciled”

Line 648 – delete the duplicate period.

Line 832 – “Sedimentologists” is plural.

Line 864 – Journal title should be in title case (all major words capitalized).

Figure axis labels should be in the format “Label (units)”. The experienced reader presumes that elemental “concentration (%)” in Figure 2 means weight %, but, because it could be atomic or molar %, (“wt. %”) would eliminate the possibility of misunderstanding by non-specialists and novice readers. The labeling of axes for all other Figures is excellent.

Tables S1 and S2 are not useful as formatted. Graphical representation of the sensitivity analysis is required if it is intended to be understood by readers.

Tables S3 and S1b contain similar data for the two field areas; the numbering of these tables does not make sense.

Table S4 – Reporting model-input soil bulk densities and exposed mineral surface areas to 15 significant figures is not justified by anything explicitly stated in the text.

These comments, above and below, are intended to help improve the effective presentation of the work done and the scientific impact of the revised manuscript.

References

Cosby, B. J., Wright, R. F., Hornberger, G. M., and Galloway, J. N., 1985. Modeling the effects of acid deposition: Estimation of long-term water quality responses in a small forested catchment. Water Resources Research, v. 21, p. 1591-1601.

Price, J.R., Velbel, M.A., and Patino, L.C., 2005. Rates and timescales of clay-mineral formation by weathering in saprolitic regoliths of southern Appalachian Mountains from geochemical mass balance. Geological Society of America Bulletin, v. 117, no. 5, p. 783-794.

Taylor, A.B. and Velbel, M.A., 1991. Geochemical mass balance and weathering rates in forested watersheds of the southern Blue Ridge. II. Effects of botanical uptake terms. In: Pavich, M.J. (editor), Weathering and Soils. Geoderma, v. 51, p. 29-50. (In the same issue as the Brimhall paper)

Velbel, M.A., 1995. Interaction of ecosystem processes and weathering. In Solute Modelling in Catchment Systems (Trudgill, S., editor), John Wiley & Sons, pp. 193-209.

Velbel, M.A., 1999. Bond strength and the relative weathering rates of simple orthosilicates. American Journal of Science, v. 299, p. 679-696.

Velbel, M.A., and Price, J.R., 2007. Solute geochemical mass-balances and mineral weathering rates in small watersheds: Methodology, recent advances, and future directions. Applied Geochemistry, v. 22, p. 1682-1700.

If other even older papers made the same points as those listed above, the bibliographies of the listed papers may help locate the true pioneer papers.

A Table I produced for my own use in this review.

	Asa site base-cation weathering rates mmol$_c$ m^{-2} yr^{-1}				**Flakaliden site base-cation weathering rates mmol$_c$ m^{-2} yr^{-1}**			
Method	Ca	Mg	K	Na	Ca	Mg	K	Na
Historical depletion	4.7	3.1	0.8	2.0	11.0	12.9	3.2	7.0
Steady-state forward model	8.9	3.8	5.9	18.5	11.9	6.7	6.6	17.5
Base-cation budget	65	23	40	6.6	35	14	22	2.2
Fertilizer (F) (kg ha^{-1} yr^{-1})	10	8	45		10	8	45	