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Final author comments (in red)

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REVIEWER 1

Interactive comment on "Surface water acidification and critical loads: exploring the F-factor" by L. Rapp and K. Bishop

CJ Curtis (Referee)

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General comments

This paper is a valuable contribution to discussions about the validity of critical load model assumptions under the current situation of declining acid deposition across much of Europe. In particular, it develops the definition and interpretation of the mysterious "F-factor" that is a key component of static critical load models and highlights the shortfalls of static SSWC family of models and the assumptions they require. The paper is highly significant because of the major reductions that have been achieved in acid deposition across Europe but the continued exceedance of critical loads in some sites in several countries which require further reductions that are difficult (expensive) to achieve. Hence understanding the uncertainties and reliability of calculated critical loads in these most sensitive unprotected sites is of paramount importance.

The paper is technically very good and the only revisions I would recommend are for further development of some of the discussion, especially regarding the necessary assumptions of static models used for large numbers (thousands) of sites often with only a single spot chemistry sample used for critical loads, compared with the more realistic but much more data intensive dynamic acidification models. In particular, the international critical loads mapping exercise co-ordinated by the CCE for the UNECE CLRTAP has moved towards simple dynamic modelling (e.g. VSD model) and

empirical approaches based on upscaling from sites where data are available for full dynamic model application to sites with only water chemistry and catchment attribute data.

Good point. We will add a sentence about this in the discussion.

Another issue worthy of further discussion is the related issue of critical load exceedance calculated using SSWC or FAB and the steady-state assumptions which mean that current exceedance of critical load does not necessarily indicate current damage. This is again related to the dynamic nature of "F" and is closely linked to the issue of temporally varying critical loads and F. Some of these issues have been discussed in a previous paper on this subject: Curtis, C.J., Reynolds, B., Allott, T.E.H. and Harriman, R. (2001) Critical load exceedance and biological damage: a re-interpretation. Water, Air and Soil Pollution: Focus 1 (1-2), 399-413.

We will work these references into the discussion.

Specific comments

PAGE 3919 Definition of critical load (lines 1-5) is very loose – why not give the full standard definition of Nilsson & Grennfelt?

We have added the full definition with reference to Nilsson and Grenfeldt.
"a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified elements of the environment do not occur according to present knowledge"

Line 6: ambiguous – specify that deposition is declining rather than increasing towards the critical load, i.e. critical loads were exceeded in the past and still are – this provides the introduction to the key point which follows that as exceedance approaches zero, uncertainties become more important especially as further emission reduction become harder and more expensive to achieve.

We appreciate this comment. We now say "Deposition is declining towards the CL", rather than approaching the CL.

PAGE 3921 Line 17: I would go further and say that the term [BC*]0 effectively defines the critical load, as it provides the critical level of base cation leaching to maintain the critical ANC value, i.e. it is the fundamental basis of the SSWC critical load.

We see the point of this comment but [BC*]o (including weathering and deposition and the effect of net uptake of BC) alone does not define the critical load. Critical load can be expressed in several ways but in some way the critical leaching of ANC needs to be included, for example in critical load of actual acidity, CL=BCw – ANCle.crit. Therefore we will not make a change in this part of the text.

PAGE 3922 Line 1: Agree that reference to nitrate may not be necessary in Swedish context but perhaps worth a mention that in other countries e.g. UK, Italy, nitrate may be a major acid anion contributing to acidification.

We see the point of this comment and have added this, as suggested by referee. Nevertheless, the inclusion of nitrogen acts in the same way as sulphur when it comes to critical load of acidity expressed as BC*o – ANClimit (as in SSWC) or expressed as CLmax(S) (as in the FAB model). The key conclusions would not change even with nitrogen included.

PAGE 3927 Line 14: Worth mentioning the long-term increasing trends in DOC observed across much of N Hemisphere here (e.g. Monteith D.T. et al 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450: 537-541.). This is also likely to affect calculations of pre-industrial chemistry even though not directly referred to in SSWC model – affects calculation of alkalinity from ANC (equation 15):

We appreciate this comment. We will add this to the paper, i e, that increasing levels of DOC will increase the acid/base status of the water (Erlandsson et al. 2008, ES&T). This DOC increase has implications for the calculations of pre-industrial chemistry. Equation 15 represents the present time, so an increase in DOC and ANC will be seen in the present sampled chemistry i e, not a problem.

Erlandsson, M., Folster, J., Laudon, H., Weyhenmeyer, G.A., and Bishop, K. (2008) Natural variability in lake pH on seasonal, interannual and decadal time scales: Implications for assessment of human impact. Environmental Science & Technology 42(15): 5594-5599. 10.1021/es8005157.

PAGE 3928 Lines7-8: the restriction of 0<=F<=1 is explicit in some of the original papers describing its calculation and is easy to understand; F=0 implies all S deposition is accompanied by hydrogen ions into surface waters so each unit of sulphate contributes one unit of acidity with no ion exchange in soils. F=1 implies all hydrogen ions are exchanged in soils for base cations with no net contribution of acidity or decline in ANC in surface waters per unit deposition of S. Values of F outside the range 0-1 should not be possible IF the assumptions of the steady-state models are valid? The theoretical implications of computed values outside this range must be discussed further in Section 4.1, especially the meaning of F>1.

We appreciate this comment and we agree on that F values, according to empirical relationships (Falk is an exception) are restricted to 0<=F<=1. However, based on SAFE modeling we calculate the F-factor from time series and then F-values outside 0 and 1 are possible. F < 0 is discussed thoroughly in the paper. When it comes to F > 1 we could add that this happens when $[BC*]_t$ increases more than $[SO4*]_t$ in equation 1. This in turn suggests that the acidity of the precipitation decreased for a time period due to increasing deposition of anthropogenic base cations. Note that increasing DOC

also would push F higher (see previous referee comment) but that is not the reason in this case because DOC is the same for all years in the SAFE modeling.

PAGE 3930 Lines 1-3: this is a key point of the paper, demonstrating the inadequacy of the SSWC model in the context of declining deposition.

Yes, we agree on this.

Section 3.2: More discussion is required here about the limitations of a simple steady state model like SSWC compared with more realistic but data-intensive models like SAFE. It might be construed that a key conclusion from this paper is that the assumptions of the steady-state models are clearly inappropriate for a situation of changing deposition, especially when declining, and this has major controversial implications for the widespread use of critical load models around Europe.

We agree on this. Steady state models works reasonable well when the exceedances in acid deposition are high. Climate change and DOC change need more sophisticated approaches to model but also require much more data. Likely we will still need some very simple approaches too (Erlandsson et al., 2008 Aquatic Sciences, or Filip's MAGIC library).

Erlandsson, M., Fölster, A., Wilander, and Bishop, K., (2008) A metamodel based on MAGIC to predict the pre-industrial acidity status of surface waters. *Aquatic Sciences,* **70**(3):238-247.

PAGE 3932 Lines 15-20: this is a key conclusion from the paper – the assumptions of the steady-state models are not valid during the recovery phase when F can be <0! And yes – the pre-industrial BC concentration is assumed to be constant under a theoretical steady-state.

Yes, _everything_ is assumed to be constant under a theoretical steady-state.

Technical corrections PAGE 3919 Line 17: no capital in "The US"

Ok, thanks!

Lines 18-19: A key component. . ... IS the F-factor in the Steady State Water Chemistry Model. (otherwise current sentence does not make sense)

Ok, thanks!

Line 21: Warfvinge & Sverdrup reference should be 1992a not b in first mention PAGE 3921 Line 5: Hettelingh

Ok, thanks!

Line 20-24: remove extra commas after [SO4*]0 (3 times)

Ok, thanks!

PAGE 3924 Line 4 remove extra comma

REVIEWER 2

Interactive comment on "Surface water acidification and critical loads: exploring the F-factor" by L. Rapp and K. Bishop

Anonymous Referee #2

Received and published: 20 July 2009

General Comments:

This paper makes an important contribution to the ever evolving acid rain literature and is definitely within the scope of HESS. Its evaluation of the limitations of the F-factor is clear and for the most part complete. The results are well presented and support the paper's central conclusions. The paper is a pleasure to read – clear, concise, generally properly referenced, and the language is almost flawless (there are a few wordy bits). I recommend publication in HESS.

As a widely recognized environmental issue within Europe and North America, "acid rain" has been with us since the 1970s. The scientific rationale behind political action to reduce European and Canadian emissions of acidifying pollutants has been largely based on surface water or forest soil critical loads and exceedances. Much of the early credit for this must go to A. Henriksen (Norway) who developed the Steady-State Water Chemistry Model (SSWC) in the 1980s – a conceptually and computationally simple model that relates an aquatic ecosystem's critical load to the weathering rate of its drainage basin expressed in terms of the base cation flux. Simplicity was achieved through adoption of the F-factor which "corrects" the weathering flux of base cationsfor that proportion of the flux originating from soil leaching. In Henriksen's view of the time, the F-factor should have a value between zero (no soil exchange contribution) and one (all base cations from the soil).

Computationally, the F-factor was the ratio of the change in surface water base cations (relative to pre-industrial conditions) to the change in acid anions, but because little or no information is available for pre-industrial conditions, it has been estimated from contemporary water chemistry information through a number of empirical equations as discussed in the current paper. Using modelled time-series data (1800 to 2100) for Swedish catchments, this paper presents a comprehensive comparison of the different computed values for F and how they very with time, shows how the assumptions that underlay the F-factor's original conceptualization fail under current

conditions of acidification recovery, and point out the implications for continued use of the SSWC in emission reduction policy. Lest the reader thinks this completely refutes the past use of the SSWC to instruct policy development, this paper points out that during the time of its introduction and use to set emission reduction targets in the 1980s and 1990s, the different equations for calculating F gave similar values and hence similar critical load and exceedance values.

Specific Comments:

1) The entire paper depends on using simulated time series data for 0.5 m depth soil water chemistry produced by the biogeochemical model SAFE. The authors offer this as "a plausible time series of annual runoff chemistry". I applaud the author's direct acknowledgement that "use of the SAFE model does not provide us with the real truth". Nevertheless, the "plausibility" of this simulated data should be better supported by comparing them to measured data or at least supplying citations to papers that have demonstrated the goodness-of-fit between SAFE output and measured runoff chemistry. In addition, the version of SAFE used to generate the test data set did not consider SO4 adsorption/desorption in the soils. The authors should note what implications this may have.

We really appreciate this comment. The SAFE model has been applied to soils mostly where the soil depth is limited to the rooting zone. However, there are studies where SAFE has been applied to catchments using estimated average soil depth, vertical water flow as well as lateral water flow through the soil layers thus representing run off chemistry. In Martinson et al (2003a and 2003b), SAFE was applied to the G1 and the F1 catchment at Lake Gårdsjön, Sweden. The focus was to add sulphate adsorption/desorption to SAFE. One of the conclusions was (2003a) that the prediction of the timing of recovery improved when this process was added. The latter study (2003b) concluded that the long-term influence of adsorption on recovery was limited. In an earlier study, (Warfvinge et al (1995), it was reported that SAFE predicted lake pH of the same pattern as reconstructed by paleolimnological investigations in the lake.

References:

Martinson, L., Alveteg, M. and Warfvinge P. 2003a. Parameterization and evaluation of sulfate adsorption in a dynamic soil chemistry model. Environ Pollut., 124, 119-125.

Martinson, L., Alveteg, M., Mörth C-M. and Warfvinge P. 2003b. The effect of changes in natural and anthropogenic deposition modeling recovery from acidification. Hydrology and Earth System Sciences, 7(5), x-xx.

Warfvinge, P., Sverdrup, H., Alveteg, M. and Rietz, 1995. MODELLING GEOCHEMISTRY AND LAKE PH SINCE GLACIATION AT LAKE GARDSJON, Water, Air and Soil Pollution 85: 713-718, 1995.

In the present study (this paper) the inclusion of S-adorption/desorption would probably delay the acidification phase and the recovery phase would take longer. Still, the key conclusions would be the same; empirical relationships have difficulties to capture the soil dynamics during recovery.

2) Equation (1) is the simplest possible, albeit most commonly used conceptual formulation for F. Henriksen originally noted that the denominator contains the change in acid anions, but in a time when ecosystems acidification was progressing almost entirely in response to sulphate deposition (i.e., the 1980s), he quickly simplified it to the _SO4 term. The authors should at least acknowledge the existence of a _NO3 term, and given the rapidly changing DOC levels observed in many European and North American surface waters, the possibility of a heretofore unexplored term for changing organic anion.

These two issues are good points. The improved treatment of NO3 and DOC in the manuscript, have already been addressed in earlier comments from Referee 1. Briefly NO3 is now mentioned, and the significance of DOC change will be discussed in the manuscript.

3) Contemporary records of base cation deposition refute the assumption needed to specify Equation (4). The authors should briefly note the implication.

We appreciate this comment. The pre-industrial deposition of BC may not be in the same magnitude as today. We will add this to the paper.

4) Page 3927, line 7: There is no Posch et al. (1993) in the reference list.

Ok, thanks for pointing this out.

5) Section 4.1: I ask the authors to include a short paragraph that discusses what it means to have F-factor values >1. Clearly, something else is influencing _BC beyond _SO4. What are the implications?

Excellent point. We have addressed this in the response to referee 1. We will add this to the manuscript.

6) Page 3934, lines 8 and 9: my immediate response to these two lines was "huh?" On further reflection I think I get it, but a more complete development of this point would be useful.

Thanks, we appreciate this comment. The sentence is wrong and gives the impression that acidification can be expressed as [SO4*]t + [NO3] –[SO4*]o. The sentence has been deleted!

7) Page 3934, line 13: reference to Equation (9) cannot be correct; presumably is should say Equation (11).

Ok, thanks, there was a mistake in the numbering of the equations.

8) Figure 6 (and discussion in Section 4.3): Why has FAB (rather than the SSWC) been used to calculate critical load exceedances? There is an equation for the present day (S+N) exceedance calculated using the SSWC critical load value, i.e., Ex(S+N) = S*dep + Nleaching – CL where Nleaching is the product of the lake NO3 concentration and regional runoff. If Figure 6 is to stand, additions to and extra explanations in the text will be required to deal with the use of FAB.

We appreciate this comment but FAB was used for calculating the official lake critical loads in Sweden that was delivered to CLRTAP. SSWC is included in FAB for the calculation of [BC*]o. The role of F is exactly the same in only SSWC as in SSWC included in FAB.

9) References: Is the journal name in the Curtis et al. citation correct?

Ok, thanks, we will correct this.

REVIEWER 3

Interactive comment on "Surface water acidification and critical loads: exploring the F-factor" by L. Rapp and K. Bishop

General Comments

This is a really well written and carefully argued paper which compares empirical F factor calculations to F factors from the SAFE model. It very effectively describes the derivation and assumptions of the empirical F factor approach and evaluates the dynamics of the F factor through the acidification and recovery. The paper discusses the implications of these dynamics and provides an evaluation of the potential impact on critical loads assessments at the national scale. The authors have been thorough and logical in their approach, and there is some interesting and important analysis with clear implications for the application of F factor approaches. It is a high quality contribution with wide significance to critical load modelling and assessments, and forms an excellent paper for publication is HESS. However, there are some points in the paper where additional clarifications would be useful.

Specific Comments

1. In section 1.2 the authors assume N is negligible, and defend this on the basis that N leaching is small from Swedish catchments. This is not the case in other countries (e.g. UK), and it would be useful in the discussion to pick up this point and briefly outline the implications of the main paper findings for when N leaching is elevated.

This issue has been taken care of in an earlier comment in response to Referee 1.

2. SAFE is used to provide F factors for soil water at 0.5m depth, whereas the empirical F factors relate to lake water chemistry. The authors should provide a fuller explanation and defence of this

approach to re-assure general readers that the two sets of modelled data are comparable, and that the differences are not simply a function of processes causing soil – lake water differences.

These issues have been taken care of in response to a similar concern of Referee 1. We have added new references to when SAFE has been applied to surface water chemistry.

3. The authors state that SAFE does not include S adsorption/desorption. Again, the authors should provide a fuller explanation of the implications of this to re-assure general readers that this is not significantly impacting on the analysis.

This issue was dealt with in Referee 1 by citing earlier work that specifically considers the effect of including S-adsorption in SAFE when predicting surface water responses. The adsorption term altered the timing of changes.

4. In section 2.2 it would be useful if the authors could briefly outline how each of the empirical equations was derived. Given the thoroughness in which the concept of the F factor is outlined in the rest of the paper, this would provide useful context.

We appreciate this comment and it would be interesting. However, we do not think this is within the scope of this paper and our conclusion would not change.

5. The point made at lines 1-3 on page 3930 (section 3.1) (depletion of soil store of BC then S deposition decline) is a key point explaining the dynamics of the F factor and is crucial to the point the paper makes. As such it should be more clearly stressed in the conclusion, and possibly also in the abstract.

Ok, this will be stressed more in the manuscript i e, the dynamics of F when recover starts.

6. At section 4.2 page 3933 lines 14-15 the authors could usefully clearly state the direction of difference in CLs.

We agree on this. A sentence about the negative F´s influence on CL during recovery will be added.

7. In section 4.3 the authors use scenarios of F factor change to assess implications for CLs assessments. They should more clearly defend the chosen scenarios, with particular reference to the findings of sections 3.1 and 3.2 (i.e. are the chosen scenarios realistic in the light of the observed differences between empirical and SAFE F factors).

Our point is to show what happens when F´s are modified in the direction of the findings from SAFE modeling. The chosen scenarios are indeed reasonable in the light of the SAFE results, even though Scenario 4 is a bold one, as stated in the text as "an extreme scenario".

We do not intend to exactly show what the "errors" are in F, but rather there will be errors. We have added references to earlier work with SAFE on surface waters. This provides a better basis for the scenarios presented..

8. Section 4.3 would also benefit from a slightly more complete description of the changing CLs with the different scenarios. For example, for the 50% F factor decrease scenario the point is made that the proportion of exceedances falls compared with the standard scenario, but the paragraph goes on to state that "The pattern is that high exceedances decrease and low exceedances. . . do not change". The latter suggests changes in the amount of exceedance rather than the absolute number of exceedances. I think a data table here might help to clarify the changing distribution of CLs with the different scenarios.

We appreciate this comment. As the reviewer points out, a table might be useful. The table could be arranged like this:

Scenarios	Proportion of Exc, %	Exc, eq/ha/yr
Standard case		
-50%		
-0,3		
-0,6		

where "Amount of Exc", is the sum of all exceedances

9. In the conclusion it would be useful to more clearly and systematically state how estimates of F and CLs would change through the acidification and recovery phases i.e. don't just say there are errors, say in what direction these are. This is a really important aspect of the paper and needs to be clear at this point.

We appreciate this comment. The direction of the expected error will be stated explicitly in the discussion and conclusion..

10. The abstract could also usefully emphasise this point by more clearly stating what the directional errors are in using F factors and CLs from contemporary (recovery phase) water chemistry samples.

Good point! There is greater specificity in the abstract as well.

Technical corrections

This is extremely well presented, and I only spotted a couple of phrasing errors:

1. Section 1 page 3919 lines 17-19: "is the. . . is the"

2. Section 4.3 page 3934 line 4: erase the s on depends

In Figures 3-5 the figure titles could make clearer what the sites in the North and South represent (i.e. low and high cumulative deposition). We all know that folk look at the diagrams without reading the full text. The words 'North' and 'South' could also be placed next to the graphs on Figs 4 and 5. (like in Figure 3.