Dear Dr Zhang,

Thank you for considering our manuscript for publication in ACP.

We think that the constructive comments from two anonymous referees have led to considerable improvements in the overall readability and clarity of our article. Our revisions include additional discussion on uncertainties originating from the one-layer model structure and possible nocturnal stomatal opening, and clarifications of several minor points in the manuscript. Specific comments are being addressed in the attached point-by-point response, where referee comments are written in blue and our response in black font.

We decided to not replace the introduction of variables in the text with a list of symbols, as suggested by Anonymous Referee #1, as it would only shorten the manuscript by a few lines while at the same time introducing a large table with more than 40 rows. However, we have added such a table as a supplement to the manuscript. Please refer to our reply to Anonymous Referee #1 for a detailed explanation.

A marked-up version of the revised manuscript is attached at the end of this document. All page- and line-references refer to the original manuscript.

Best regards

Frederik Schrader and Co-Authors

Reply to Anonymous Referee #1

The paper compares two alternative models to simulate ammonia fluxes and their comparison with the measured fluxes in five peatland and grassland sites, focusing on the non-stomatal fluxes. The motivation for such more empirical deposition models is the inclusion of bi-directional ammonia fluxes into chemical transport models, which requires few and easily available parameters for the surface resistance. The improvement of such models is needed and the respective analysis here is valuable, specifically as it includes a suffiecient number of sites.

We thank the Reviewer for his/her helpful comments and criticism and for valuing our work. We have implemented most of the suggestions and think they led to a significant improvement of our manuscript. Please refer to the point-by-point response below for a detailed reply to your comments.

Focusing exclusively on nighttime fluxes with sufficiently turbulent condition is a good approach. It should, however, be discussed, if nocturnal transpiration could have confounded these observations.

The assumption of an “infinite” stomatal resistance at night is indeed a strong simplification that is not necessarily physiologically correct, and we should have acknowledged this in the original manuscript. The reason behind it is that it allows modelers to easily differentiate between the stomatal and the non-stomatal pathway, depending on which of the two is assumed to dominate the other one in magnitude of the fluxes. These assumptions allow a very simple inversion of the one-layer model framework to derive R_{w} (and R_{s}) from micrometeorological measurements, without having to explicitly model the other pathway. Consequences of this simplification are that R_{w} derived in such a way may indeed partially integrate stomatal fluxes as well, and therefore the physiological meaning of this variable may be confounded. We will add a discussion of this in the uncertainties sub-section of the results.

Changes to the manuscript: P10L16 (will be moved to “Sources of uncertainty” sub-section; cf. reply to Reviewer #2): Add paragraph: “Explicitly modeling the stomatal pathway with physiologically accurate stomatal conductance models may have the additional benefit of being able to assess bias in the estimation of non-stomatal resistances introduced by nighttime stomatal opening, naturally resulting in a lower contribution of the non-stomatal pathway to the total observed flux. However, note that a distinction between physiological accuracy and the purpose which the derived resistances are used for has to be made. While nighttime stomatal opening is a well-known phenomenon (e.g. Caird et al., 2007), it is rarely respected in modeling studies (e.g. Fisher et al., 2007). A physiologically accurate R_{w} parameterization used in conjunction with a stomatal model that does not account for nighttime stomatal opening would result in biased fluxes. We here derived R_{w} under the assumption that stomata are closed at night to ensure comparability with R_{w} values predicted by the WK and MNS parameterization, respectively, and compatibility with most operational biosphere-atmosphere exchange schemes, but we acknowledge that the physiological meaning may be confounded by stomatal flux contributions at night.“; Add Caird et al. (2007) and Fisher et al. (2007) to list of references.

The parameters included in both models are temperature and, importantly, relative humidity (RH), whereas different ways are chosen regarding the fate of depositing ammonia, either unidirectional (MNS model) or ‘quasi-bidirectional’ (WK model). Based on common patterns of the five test sites, systematic under- and overestimation of fluxes are then diagnosed and empirical improvements are suggested by the authors. Although ultimately I agree with the overall direction of the paper and the interpretation of the results (see few exceptions below), I find it difficult to follow. One of the reasons is the continuous introduction of a multitude of parameters which makes consequent reading sometimes time-consuming and frustrating. Even in case it does not agree with the usual policy of this journal, I therefore suggest a table detailing all used parameters with units and possibly also other abbreviations.

We agree with the reviewer that constantly introducing new variables can interrupt the reader’s flow. A list of symbols, on the other hand, can lead readers inexperienced with the modeling community’s jargon to skip back and forth between pages when new variables appear. Neither variant is very elegant in terms of an uninterrupted reading experience, but we are convinced that we here chose the lesser of two (necessary) evils, and that the manuscript would not benefit from using a list of symbols instead. The majority of all constants and variables are defined ‘in passing’, i.e. we introduce their respective symbols and units in an unobtrusive manner alongside their first appearance in the text (e.g. P3L21: “R_c is further split into a stomatal pathway with the stomatal resistance R_s (s m^{-1}), and […] the non-stomatal resistance R_w (s m^{-1}) […].”). There are only two slightly larger blocks of variable introductions after an equation: P4L10-13 (4 lines) and P5L1-3 (3 lines). All further shortening of the manuscript would be due to removing variable definitions less than one line long and the omission of units in the text. On the other hand, a complete list of symbols would have more than 40 entries, and a shortened list of symbols (e.g. defining only R_x instead of $R_\mathrm{a}, R_\mathrm{b}, R_\mathrm{c}, R_\mathrm{s}, R_\mathrm{w}$) would not be enough to omit variable definitions throughout the manuscript.

Additionally, units may change depending on the circumstances a symbol is used. In the modeling community, (compensation point-) concentrations are often given in µg m^{-3} when they appear in figures, whereas some equations work on with concentrations in mol L^{-1} (a well-known example is the traditional formulation for the conversion from emission potentials to compensation points, as seen e.g. in Nemitz et al., 2000). Explicitly stating or repeating units close to the appearance of a symbol helps avoid confusion in these cases.

As a compromise and as an additional resource for readers unexperienced with the modeling community’s jargon, we have added a list of symbols in the supplementary material.

Changes to the manuscript: P3L13: add “For a list of variables used throughout this article, the reader is referred to Tab. S1 in the supplement.”; add Table S1 (List of symbols) to the supplementary material.

A second and somewhat related reason is the initial explanation of the two models which in some important places is not sufficiently detailed – some examples are given below. I wonder why the effect of RH is so little discussed in the paper - it has an exponential influence on Rw and thus is the most important independent parameter. It could e.g. be included in a analysis similar to Fig. 5.

We agree that RH is the most important parameter. However, we also think it has been sufficiently discussed elsewhere, and a simple exponential decay function does not necessarily need a visualization that goes beyond the relationship shown in Figure 2a. We will highlight the importance of the exponential decay function with minor changes to the text in some parts in the manuscript.

Changes to the manuscript: P2L18-19: Replace “This characteristic behavior is often modeled using relative humidity response functions as a proxy for canopy wetness (e.g. Sutton and Fowler, 1993; Erisman et al., 1994).” with “This characteristic behavior is typically modeled with an exponential relative humidity response function as a proxy for canopy wetness, where a high relative humidity results in low non-stomatal resistances and vice-versa (e.g. Sutton and Fowler, 1993; Erisman et al, 1994).”; P5L3: Add “The exponential decay parameter a was calculated as an average of a values per land-use class reported in the literature”. P5L14: Add “exponential” between “simple” and “humidity”.

I also wonder if the effect of backward-looking moving averages shouldn’t be evaluated together with the RH history. Saturation effects (as mentioned in p.2, l. 20) could play a role at low RH.

Agreed, this is a good idea for further analyses. It is not trivial to find a good balance between a truly dynamic, but demanding (both numerically and in terms of required input-data) representation of the non-stomatal pathway, and a steady-state simplification that can be incorporated easily into existing schemes. We here tried to go the very first step that is more or less as simple as possible (while still respecting site-history in some way), and we found that this is not enough. We hope that this is a valuable piece of information for future analyses, which could (and should) indeed incorporate additional proxies, such as RH or precipitation history, but we deem this beyond the scope of our paper, where the moving-average approach was merely an additional idea about “what could work”, even if it ultimately turned out to not work very well.

Changes to the manuscript: None (but added some explanation as suggested by Reviewer #2).

P. 5, l. 24/25: This is difficult to follow. Can it be supported by a formula? What happens if RH decreases?

We agree that it is not immediately obvious and tedious to show formally from Eqns. (7) and (8) that χ_{w} can only become a fraction of χ_{a}, and we hope a visualization of the solution space over plausible T and χ_{a} ranges (Figure 1 of this response) helps. Similar visualizations for possible Γ_{w} and χ_{w} values can be found in van Zanten et al. (2010, Appendix F, Figs. 17 and 18), which we will refer to in the revised manuscript. A decrease in RH has no direct effect on modeled χ_{w}, only on $R_{\mathrm{w,eff.}}$ due to the exponential decrease in the ‘clean-air’ R_{w} parameterization (Eq. (6)).

Changes to the manuscript: P5L25 add reference “(cf. van Zanten et al., 2010, Appendix F).” at the end of the sentence.

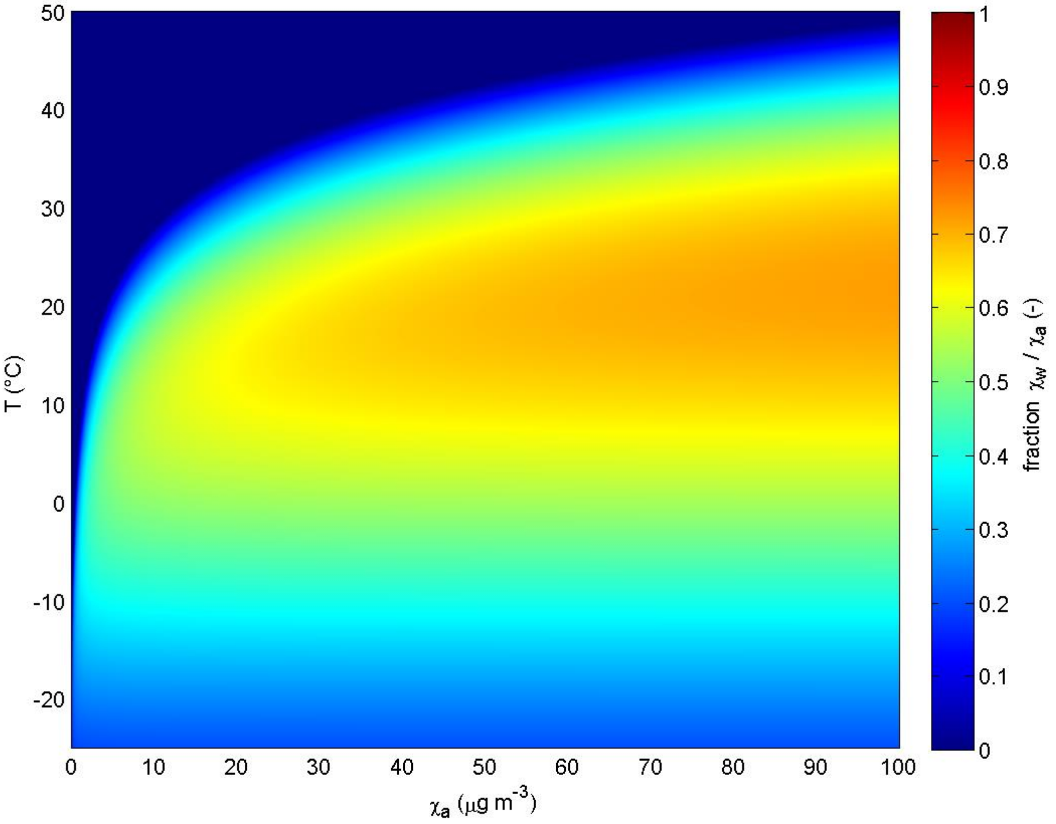

Figure 1: Fractions of the solutions for Eq. (7) of the original manuscript divided by χ_a over a range of plausible χ_a and T values.

P. 8, l. 19-23: This is indeed intriguing, but on the other hand I cannot really believe that MNS works so well in the prediction of fluxes at VK, when looking at the cumulative fluxes in Fig. 3. Even during the flat part, there is an underestimation of 0.3 kg ha-1. The shape of the cumulative fluxes at BM is considerably different from VK, while the shapes of ΔGw differences in Fig. 4 are very similar between BM and VK. Please check if the statement is really correct.

We did not state that MNS predicts the fluxes at VK well. "(…) relatively good predictive capabilities of MNS at BM and WK at VK (…)" (P8L21-22). We acknowledge that ΔG_{w} plots for the MNS model may indeed appear somewhat similar for BM and VK at first glance, but note that at VK we see a larger number of strong underestimations of ΔG_{w} compared to BM. The ratio of negative to positive values of ΔG_{w} for the MNS model is 1.2 at BM versus 2.8 at VK.

Changes to the manuscript: None.

P. 11, l. 19: which parameterization?

The MNS parameterization. Thanks for pointing out that this is unclear.

Changes to the manuscript: P11L19-20: Replace "(…) used in this parameterization." with "(…) used in the MNS parameterization.".

Figure 2: Why is Rw lowest at T=0°C?

Cf. P5L7-9: "Contrary to the original formulation of Flechard et al. (2010), Massad et al. (2010) do not use absolute values of $|T|$ (°C), but we chose to do so under the assumption that generally R_{w} increases in freezing conditions (e.g. Erisman and Wyers, 1993)."

We here chose to follow the original formulation of this temperature correction by Flechard et al. (2010), as it seemed physically more plausible to us that ammonia deposition to liquid water is larger than to ice.

Changes to the manuscript: None (already explained in P5L7-9).

Figure 4: Upper row: There seems to be a mismatch between the number of binned values used for MNS and WK comparison, at least for VK. What is the reason?

The number of binned values per bin is of course different, as it defines the shape of the histograms. The bin-width is equal (100 s m^{-1}) for all figures shown in the upper row. Note that we cut-off everything below or above a -1000 or 1000 s m^{-1} difference, respectively, for visual clarity and comparability of the subplots. So indeed the integral over the bars drawn in the figures does not necessarily reflect the total number of data points, if that is the question. The absolute differences can span multiple orders of magnitude, which we would not be able to visualize in a meaningful way. A logarithmic visualization would put more emphasis on the very large differences than necessary (e.g. there is not much difference between a 10^4 and a 10^5 s m^{-1} difference between modeled and measured resistances other than the fact that it is an extremely large mismatch – either modeled or measured fluxes will be close to zero in both of these cases).

Changes to the manuscript: None.

Minor issues P.6, l.11: 'approach', better: 'reach'? (also p. 9, l. 2) P. 6, l. 16: 'compensation point Xw decreases' P. 6, l. 23: why 'moderately'? I would suggest to omit this word P. 7, l. 18: event P. 10, l. 1: omit 'and'

We agree with all corrections, thank you for pointing them out.

Changes to the manuscript: P6L11, P9L2: Replace "approach" with "reach". P6L16: Replace "compensation χ_{w} point" with "compensation point χ_{w}". P6L22-23: Remove "moderately" in both hypotheses. P7L18: Replace "events" with "event". P10L1: Remove second "and" in the line.

Reply to Anonymous Referee #2

General comments

The paper is within the scope of ACP.. The results are correctly presented; the figures illustrate the results in a clear way, but the order should be changed, as detailed in the specific comments. The paper is written in good English. I recommend this paper to be published in ACP, after some major corrections and improvements in the presentation of results. My main remarks concern principally the way results are presented. In my opinion the results could be presented in a more positive way. The reader cannot be convinced if the authors present their results without highlighting the advantages found after the sensitivity tests. This is detailed in the specific comments.

Thank you for your insightful review. Please refer to the specific comments for a detailed answer to each of your concerns.

Some bibliography about how these two models have been used until this study would have been necessary to help the reader understand where the authors want to go and why they have chosen these particular models and not others. Did these models give satisfying results in other studies and why did the authors choose them.

Thank you for highlighting that we missed to give a justification for the choice of the parameterizations. This has been added to the introduction section. There are indeed notable other models, such as the one of Zhang et al. (2010, 2003). The choice of the two particular models compared in this study is based on a number of different reasons: a) they are structurally very similar (the WK parameterization is flexible in terms of its usage within a one- or two-layer model); whereas Massad et al. (2010) and Zhang et al. (2010) exhibit some fundamental differences in their handling of the ground-layer pathway (this is not discussed in particular in this study, but it leads to difficulties in programming comparable model codes); b) the motivation for this study arose from prior experience of the lead author with the MNS and WK parameterizations; and c) the WK parameterization features a unique handling of the non-stomatal pathway with its 'quasi-bidirectionality', and we found it interesting to see how it compares to the traditional deposition-only approach.

Changes to the manuscript: P2L31: Add "The Massad et al. (2010) parameterization has received widespread acceptance in the community, with 53 citations according to the literature database 'Thomson Reuters Web of Science' at the time of writing this article, and variants of it have been applied in numerous studies, e.g. recently in Shen et al. (2016), Móring et al. (2016), Zöll et al. (2016), and others. Wichink Kruit et al. (2010) followed a unique approach by simplifying complex dynamic approaches towards an empirical steady-state formulation of a non-stomatal compensation point model, which is nowadays used within the DEPAC3.11 deposition module (van Zanten et al., 2010) and the chemistry transport model LOTOS-EUROS (Wichink Kruit et al., 2012), and it is structurally compatible with the Massad et al. (2010) model."; Add references for Shen et al. (2016), Móring et al. (2016), Wichink Kruit et al. (2012).

Partial conclusions at the end of each paragraph need to be more clearly assessed. The go home message needs a clearer explaination.

We agree, thank you for pointing out that the conclusions are not clear enough. Please refer to our answers to specific remarks below.

Changes to the manuscript: See below.

Specific comments

Abstract. The abstract gives a clear idea of what is presented in the paper. The sentence line 25 page 1 "The proposed Γ_w parameterization..." needs to be detailed to let the reader know in what way it can be improved.

Agreed, this will be more detailed in the revised manuscript.

Changes to the manuscript: P1L25-26: Replace "The proposed Γ_w parameterization appears to have potential for improvement, but cannot be recommended for use in large scale simulations in its present state due to large uncertainties." with "The proposed Γ_w parameterization revealed a clear functional relationship between backward-looking moving averages of air NH_3 concentrations and non-stomatal emission potentials, but further reduction of uncertainty is needed for it to be useful across different sites."

Page 3 line 13: could you explain how it is realistic or not to switch off the soil/leaf litter layer for natural ecosystems, where it can be an important source of NH3, such as mentioned for example in Wentworth et al., 2014.

Thank you for hinting at Wentworth et al. (2014). We agree with the reviewer about the importance of soil-based emissions.

The decision to use a single-layer framework for unmanaged ecosystems by Massad et al. (2010) was less based on natural conditions, but primarily on data availability of Γ_g for unmanaged ecosystems at the time, as well as methodological issues: Most of the compensation point measurements that they used were based on micrometeorological measurements. The flux measurements used to derive major parts of the parameterization were representative for the ecosystem scale, and the attribution to different conceptual compartments (stomata, cuticula, ground-layer) had to be made based on inverting the resistance model for different environmental conditions (humidity, radiation/time of day). However, this can only be done easily in a single-layer framework due to the relatively straightforward differentiation between stomatal and non-stomatal contributions to measured fluxes (note that we have added discussion on nocturnal stomatal fluxes as suggested by Anonymous Referee #1). Adding a third (ground-layer) pathway severely complicates this approach unless the ground-layer based signal completely dominates the observed fluxes. Ground-layer based emissions are not being ignored, but rather integrated into the stomatal emission potential for unmanaged ecosystems in the MNS parameterization. The model switches to a two-layer formulation after management events, when the contribution of these emissions is strong enough to be more or less unambiguously attributed to the soil. We agree that this is conceptually unsatisfying und should be improved upon in future developments.

Note that this is very similar to our reasoning why we chose to call R_w "non-stomatal" instead of the often used "cuticular" or "external leaf surface" resistance – we cannot be 100 % certain that we do not integrate the influence of other surfaces when we simply invert the model for nighttime conditions (in fact, we most likely do).

Changes to the manuscript: See below (Answer to P10L24-25).

Page 5 line 15: please give the NH3 concentration under which clean conditions are considered.

This goes back to Milford et al. (2001), who concluded that Eq. (6) with a minimum R_w parameter of 2 and an exponential decay constant of 1/12 is valid for conditions without NH_3 saturation at the leaf cuticles (although the term 'clean conditions' was introduced by Wichink Kruit et al. (2010)).

Changes to the manuscript: P5L15: Replace "In this model, a simple humidity response after Sutton and Fowler (1993) is used as an approximation for R_w under 'clean conditions':" with "In this model, a simple humidity response after Sutton and Fowler (1993) is used as an approximation for R_w under low ambient NH_3 concentrations, where saturation of the external leaf surfaces is unlikely (Wichink Kruit et al., 2010; Milford et al., 2001):". Add Milford et al. (2001) to the references.

Page 5 line 24: this term of "pollution climate" is difficult to understand because it is not precise enough. Do you mean "air pollution climate"as mentioned in Wichink Kruit et al. 2007? Is there a value for NH3 concentration to define this threshold of pollution?

Yes, we will change this to “air pollution climate”. There is no threshold for “pollution” here, rather the (admittedly somewhat vague) term is often used throughout the literature to describe the composition of ambient air in terms of different airborne pollutants.

Changes to the manuscript: P4L21, P5L24, P12L17, P12L22: Add “air” before “pollution climate(s)”.

Page 7 line 24 add “with” between “conjunction” and “leaf”.

Thanks, corrected.

Changes to the manuscript: P7L24: Add “with” before “leaf”.

Page 9. The “results and discussion” paragraph needs to be restructured. Uncertainties should be discussed in a specific sub-paragraph. It would be interesting to specify the conditions where these models have been applied, how successful they were, and where they cannot be applied, for example when emission occur instead of deposition.

We agree with the reviewer and have added a sub-paragraph in which we discuss the uncertainties of our methods. Regarding the applicability of the models, please refer to the answer to one comment above (about why we chose these particular parameterizations).

Changes to the manuscript: Move P9L22-P10L26 and related discussion added during the revision process into new sub-section 3.5 “Sources of uncertainty” at the end of the “Results” section.

Page 10 line 1: remove “and” at the end of the line.

Done, thanks.

Changes to the manuscript: P10L1: Remove second “and” in the line.

Page 10 line 10: “a model”: what model exactly are you talking about?

No specific model; N-Input could be derived from any kind of model that is able to predict net annual reactive nitrogen deposition.

Changes to the manuscript: See below.

Page 10 lines 10 to 15: This explanation is not clear. These lines have to be rewritten. Line 11, after the sentence “we do not feel confident...”, is it supposing that only NH3 dry deposition is available? Line 14-15: “A detailed description...” if the investigation is beyond the scope of the paper why then talking about it and give the results of the sensitivity test if you do not give the reasons of why it could not work? Some ideas could be provided to help the reader understand.

Apologies for being unclear here. L11: Yes. L14-15: This statement was primarily given as a justification for why we did not incorporate daytime data by modeling the stomatal pathway, although the flux measurements are less prone to error due to better turbulent mixing during daytime. We believe that this could be a good idea for further studies, where input data for mechanistically satisfying (e.g. photosynthesis-based) models for R_s and reliable estimates of the stomatal emission potential (e.g. via bioassays) are available.

Changes to the manuscript: Rewrite P10L10-15 from: “While this can be estimated from spinning up a model that incorporates more reactive nitrogen species than just NH_3, we do not feel confident estimating total N input from modeled NH_3 dry deposition alone. At sites where total N input is known (e.g. BM, from Hurkuck et al. (2014), or from CTM results), the MNS and WK parameterizations predict such different Γ_s estimates that one model predicts net emission from the stomata and one model predicts a net uptake over the course of the measurement campaign. A detailed investigation on the reasons for this mismatch is, however, beyond the scope of this paper.**”**

to: “While this issue can be overcome by iteratively solving a model with more reactive nitrogen species, so that N input is both a parameter, and a result of the simulation, we here used a model that only predicts NH_3 dry deposition, which we do not consider to provide sufficient information to estimate total N input to our sites. At sites where total N input is known (e.g. BM, from Hurkuck et al. (2014), or from CTM results for other sites), the MNS and WK parameterizations both predict very different Γ_s estimates. The reasons for this mismatch have, to our knowledge, not been investigated to date. We therefore decided to not model the stomatal pathway explicitly and rely on nighttime fluxes only.”

Page 10 line 24-25: What do you mean by “very well”? Do you mean that the assumption of ground layer resistance = infinite is not realistic? And what about weak ground resistance and infinite stomatal resistance? The authors should give some more explanations and overall extract the main positive idea of such sensitivity tests explained in this paragraph. The reader is a bit frustrated not to know if good ideas have to be extracted from that.

$R_\mathrm{g} = \infty$ is more of a technical solution to transform the model into a one-layer model in cases where ground-layer fluxes could not clearly be differentiated from other pathways when parameterizing the model on micrometeorological measurements, not necessarily based on whether or not it is realistic. In principle, it would of course be more realistic to model the ground-layer pathway for all land-use classes, even if weak ground-layer emissions are recaptured by the canopy (modeled via χ_c) but according to Massad et al. (2010) not enough reliable data on ground-layer fluxes and emission potentials were available during the development of the parameterization. Note that one also has to be careful when mixing e.g. R_w parameterizations based on micrometeorological measurements via inversion of a one-layer model together with measurements of $[NH_4^+]/[H^+]$ in the soil solution as an estimate for Γ_g, as the former will already include a contribution of the ground-layer when emission fluxes are large enough to not be completely recaptured by the canopy. Please also refer to our answer to P3L13.

Changes to the manuscript: P10L20-21: Replace “(…) the ground layer resistance was set to infinity (Massad et al., 2010) and the model reduces to a one-layer model.” with “the ground layer resistance was set to infinity in order to transform the model structure to that of a one-layer model (Massad et al., 2010).

Page 10 line 28: The reader cannot understand the ideas mentioned in this 3.2 paragraph if the authors do not explain in what purpose they use moving averages of NH3 concentrations. What is the goal of this exercise?

We respectfully refer the reader to section 2.5 (starting on P7L22) of the manuscript, which we will slightly expand in the revised version of the manuscript. However, we would also like to use this discussion forum as a platform to elaborate on them in some more detail:

Most non-stomatal resistance parameterizations found in the literature are steady-state approximations of processes that we know to be dynamic by nature (e.g. Wentworth et al., 2016; Jones et al., 2007a, 2007b; and many others), i.e. they are solved for every moment in time individually, although we are aware that we should keep the history of the site in mind, especially with respect to previous nitrogen deposition and the wetness of the canopy. In the late nineties, Sutton et al. (1998) and Flechard et al. (1999) developed bidirectional cuticular desorption models that model the non-stomatal pathway as a charged capacitor, and they have been successful at modeling e.g. emission events after dewfall at night and subsequent drying of the canopy in the early morning hours. However, it turned out to be difficult to parameterize these models with measurements, e.g. surface pH, or concentration measurements of a number of different atmospheric constituents were needed. Additionally, as these models were naturally also dynamic in a numerical sense, i.e. dependent on the previous state of the system (sometimes with very small time-steps needed for the numerical solution), they had the disadvantage of being computationally expensive, which limited their applicability in spatially explicit transport models. Wichink Kruit et al. (2010) presented an important step towards a balance between mechanistically realistic and computationally efficient models. They tried to simplify the bidirectional parameterization for external leaf surfaces by developing an external leaf surface compensation point model that was dependent on atmospheric ammonia concentrations, thus being capable of modeling saturation effects. While this approach was technically not really bidirectional, due to the fact that the best fit to the data was achieved with an expression which always yields an external leaf surface compensation point that is smaller than the ambient concentration, it led to an improvement in the way that we could now get good estimates for long-term net NH_3 deposition "for the right reasons", i.e. because sometimes there is a significant non-zero external leaf surface emission potential. However, this model only incorporated information about the current state of the system, not about the magnitude of previous deposition events or previous ambient NH_3 levels. In our manuscript, we tried to find a compromise between these two approaches by fundamentally following a similar approach to Wichink Kruit et al. (2010), but making it dependent on the past. We decided to use NH_3 concentration instead of (modeled) fluxes, as it is an easily accessible variable that is directly being measured instead of modeled and therefore available before any model calculations, and a direct driver of NH_3 saturation at humid surfaces. Reviewer #1 correctly pointed out that a logical next step would be to incorporate the "wetness history" of the site into such analyses, e.g. the average relative humidity of the previous day(s), or the days since the last rainfall. We here only presented the very first step towards a conceptually dynamic, but structurally static model of external leaf surface exchange, and while our results are not directly useful for modeling purposes, we believe they are a promising first step for the future treatment of the bidirectional non-stomatal pathway.

Changes to the manuscript: P7L25: Before "We here…" Add: "While it is capable of modeling saturation effects with an ambient ammonia concentration dependent non-stomatal compensation point, it only relies on χ_a at the current calculation step. A compromise between the truly dynamic models of Sutton et al. (1998) and Flechard et al. (1999) and the steady-state simplification of Wichink Kruit et al. (2010) would respect the site's history of reactive nitrogen inputs without falling back to a numerically dynamic model and, consequently, the same difficulties that limit the application of existing dynamic approaches in large-scale models, i.e. it would need to use a proxy for previous nitrogen deposition without relying on the model's flux predictions at an earlier calculation time. "

Page 11 line 2: why this case is not shown? It would have been interesting to see the results?

We opted for a linear horizontal axis in Figure 6 as the majority of the concentration data are in the sub-20 µg m^{-3} region and the fact that there is a functional relationship is still obvious. Additionally, a linear least-squares fit to a log-transformed variable implicitly assumes a multiplicative error-model, the validity of which is unclear in this particular case. Mentioning it in P11L2 was primarily meant to give the reader an idea of the relationship, but there are probably more appropriate statistical models to show this.

The linear fit to the log-log-transformed data is shown in Figure 2 of this response.

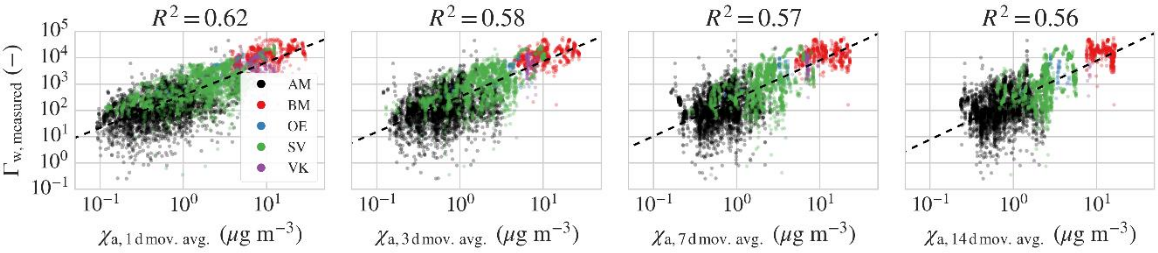

Figure 2: Log-log-relationship between moving averages of air ammonia concentrations with different moving windows and non-stomatal emission potentials derived from flux measurements at five sites.

Changes to the manuscript: None.

Page 11 line 9 :The authors give indications of potential improvements and conclude by writing that no improvement is deduced. What is then the purpose of giving these results if they do not lead to improvement? It should be far better to highlight the advantages instead of giving the disadvantages.

This is probably more of a philosophical issue. The reviewer is correct in stating that the results of this particular attempt are not immediately useful. However, we believe that it is important to avoid publication bias by not exclusively showing polished up positive results, but also by publishing what would be considered 'negative' or 'non-constructive results'. Parameterizing Γ_{w} on some proxy for site history is a logical step in reducing degrees of freedom of more complex, mechanistic models while still being conceptually (albeit not structurally/numerically) dynamic (see answer above). We tested one variant of doing so and arrived at the conclusion that this particular variant is probably not the final answer. By publishing these results regardless, we encourage looking at different approaches and avoid that other researchers unnecessarily try the same, only to arrive themselves at a 'negative', i.e. non-productive finding that they likely won't publish either. We feel that the manuscript at hand can stand on its own feet without this analysis, and if the reviewer and the editor agree that this section should be omitted from the manuscript, we are happy to do so, but we believe it adds some valuable information and gives the reader ideas on how (or how not) to improve Γ_{w} parameterizations in the future.

Changes to the manuscript: None.

Page 11 line 20: same remark as above. The way this paragraph is written does not give a positive issue. The authors should turn it differently to highlight the positive points. This part should follow figure 3.

We have re-phrased the partial conclusion of this paragraph to appear more positive. However, we do not agree that this part should follow Fig. 3, as the motivation to reduce the parameter values of $R_{\mathrm{w,min}}$ and β follows from the left-hand panel of Fig. 5 (see answer below).

Changes to the manuscript: P11L17-20: Replace "While there does not appear to be a comprehensive, generic solution, we assume that there is potential for a significant overall improvement by optimizing these two parameters based on independent data from all four ecosystem types (grassland, arable, forest and semi-natural ecosystems) used in this parameterization." with "This exercise highlights the potential for a significant overall improvement in NH_3 flux predictions by optimizing these two parameters based on independent data from all four ecosystem types (grassland, arable, forest and semi-natural ecosystems) used in the MNS parameterization."

Page 12 line 1: What do you mean by "the impact of this study's main findings are negligible"?

We believe the reviewer might have misread this line (the manuscript says "on" instead of "of"), but we will rephrase this sentence for clarity.

Changes to the manuscript: Replace "(…) the impact on this study's main findings are negligible." with "(…) they do not lead to significant differences in the main findings of this study."

Page 12 line 12: Again what is the advantage of doing this if no solution is going out?

See answer to P11L9 given above.

Changes to the manuscript: None.

Page 12 line 13: the title is not appropriated. Should be "conclusions".

Agreed.

Changes to the manuscript: P12L12: Replace "Conclusions and recommendations for further research" with "Conclusions".

Page 12 line 17: "pollution climate" is not an understandable term. Conclusion needs to be more striking.

Regarding the term "pollution climate", see our reply to your comment on P5L24. We have re-formulated the second sentence to be more to the point.

Changes to the manuscript: P12L17-21: Replace "We tested the potential for an easily accessible improvement of predicted R_w and consequently predicted NH_3 exchange fluxes by using smaller values for the temperature response and minimum R_w parameters and propose to further investigate this route using data from all four ecosystem types represented in the MNS R_w parameterization" with "Adjusting the temperature response and minimum R_w parameters in the MNS model towards smaller values resulted in a better match between modeled and measured NH_3 fluxes at most, but not all sites. We suggest to further investigate the potential of re-calibrating these parameters to flux data from all four ecosystem types represented in the MNS R_w parameterization. Compared to measured values found in the literature (e.g. Massad et al., 2010, Tab. 1), especially the minimum predicted R_w at sites with low atmospheric acid-to-ammonia ratios appear too high."

Page 12 line 27: "We strongly encourage" is not appropriate. Please reformulate.

Agreed, this is probably too subjective.

Changes to the manuscript: P12L27: Replace "strongly encourage" with "suggest".

Changes in the structure are needed. Figure 7 should follow figure 3, figure 8 should follow figure 4. Please adapt the text in function of these figure changes.

We see where the reviewer is coming from, as these figures appear to be very similar visually. However, we respectfully disagree with this suggestion for the following reasons:

Figure 3 and Figure 7 are only similar in the form of the visualization. Figure 3 is a comparison between the two models' predicted fluxes in their original parameterization and marks the first step of our analysis. Figure 7, on the other hand, is the result of changing two parameters in a way that was suggested by the results. It answers a "what if" question that would not have been asked before seeing the left panel of Figure 5; it is not part of the "core" analysis of our manuscript, but more of an outlook, or a suggestion for what parameters to look at in the future. It would therefore not be logical to show it earlier.

Figure 8 is a sensitivity study with the aim to show the influence of some of our decisions and to assess "researcher's bias" introduced by making these choices. This was actually an Appendix in early versions of the manuscript, but since the paper itself is fairly short, we decided to move it to the results section instead. We are happy to move it back to an Appendix section if needed, but we don't think it should be shown earlier, as it is not a fundamental part of the analysis, but rather an addition.

Changes to the manuscript: None.

Technical corrections

Page 6 line 10 and line 26, ibid and i.e. have to be in italics. Throughout the text latin expressions should be in italics.

"Common Latin phrases are not italicized (for example, et al., cf., e.g., a priori, in situ, bremsstrahlung, and eigenvalue)."

From: www.atmospheric-chemistry-and-physics.net/for_authors/manuscript_preparation.html

Changes to the manuscript: None.

Minor changes suggested by the authors

P1L3-10 (list of authors and affiliations): Replace “Undine Richter^{1}” with “Undine Zöll^{1,*}”; add “*née Richter”

P2L3, P7L9, P9L13, P15L30, P18L15 (Tab. 1): Replace citation of discussion paper “Richter et al. (2016)” with citation for final revised paper “Zöll et al. (2016)”.

P3L26: Replace “ug” with “µg”.

P3L27, P4L2: Replace “ng” with “µg” to be accurate within the context of Eq. (2)

P4L3 (Eq. (2)), P6L21: Replace “F_t” with “F_t”.

P5L23 (Eq. (8)): Replace “4 m” with “4 m”.

P9L4, P9L29-32: Replace v_d and $v_\mathrm{d,max}$ with $v_\mathrm{d}\{z-d\}$ and $v_\mathrm{d,max}\{z-d\}$, respectively.

P10L29, P11L1: Replace $\chi_\mathrm{a,mov.avg.}$ with $\chi_\mathrm{a,MA}$ for consistency with Fig. 6.

P13: Add paragraph “Code and data availability” before the Acknowledgments: “Python 2.7 code for the resistance model parameterized after Massad et al. (2010) and Wichink Kruit et al. (2010), as well as the data analysis code can be requested from the lead author via email (frederik.schrader@thuenen.de). Measurement data from AM, BM and OE are property of the respective authors (cf. Tab. 1); for the SV and VK datasets, please contact M. C. van Zanten (margreet.van.zanten@rivm.nl).“

Figure 1 (caption): Replace “(Wichink Kruit et al., 2010)” with “Wichink Kruit et al. (2010)”.

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Non-stomatal exchange in ammonia dry deposition models: Comparison of two state-of-the-art approaches

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Abstract. The accurate representation of bidirectional ammonia (NH_3) biosphere-atmosphere exchange is an important part of modern air quality models. However, the cuticular (or external leaf surface) pathway, as well as other non-stomatal ecosystem surfaces, still pose a major challenge of translating our knowledge into models. Dynamic mechanistic models including complex leaf surface chemistry have been able to accurately reproduce measured bidirectional fluxes in the past, but their computational expense and challenging implementation into existing air quality models call for steady-state simplifications. We here qualitatively compare two semi-empirical state-of-the-art parameterizations of a unidirectional non-stomatal resistance (R_w) model after Massad et al. (2010), and a quasi-bidirectional non-stomatal compensation point (χ_w) model after Wichink Kruit et al. (2010), with NH_3 flux measurements from five European sites. In addition, we tested the feasibility of using backward-looking moving averages of air NH_3 concentrations as a proxy for prior NH_3 uptake and driver of an alternative parameterization of non-stomatal emission potentials (Γ_w) for bidirectional non-stomatal exchange models. Results indicate that the R_w-only model has a tendency to underestimate fluxes, while the χ_w model mainly overestimates fluxes, although systematic underestimations can occur under certain conditions, depending on temperature and ambient NH_3 concentrations at the site. The proposed Γ_w parameterization ~~appears to have potential for improvement, but cannot be recommended for use in large scale simulations in its present state due to large uncertainties~~revealed a clear functional relationship between backward-looking moving averages of air NH_3 concentrations and non-stomatal emission potentials, but further reduction of uncertainty is needed for it to be useful across different sites. As an interim solution for improving flux predictions, we recommend to reduce the minimum allowed R_w and the temperature response parameter in the unidirectional model and to revisit the temperature dependent Γ_w parameterization of the bidirectional model.

1 Introduction

Reactive nitrogen (N_r) deposition can contribute to a number of adverse environmental impacts, including ecosystem acidification, shifts in biodiversity, or climate change (Erisman et al., 2013). Breakthroughs in the measurement of biosphere-atmosphere exchange of ammonia (NH_3), the major constituent of N_r (Sutton et al., 2013), have been made in the recent past with the rising availability of high-frequency measurement devices that can be used within the eddy covariance method (e.g. Famulari et al., 2004; Ferrara et al., 2012; ~~Richter~~ Zöll et al., 2016), and a large body of flux measurements using other measurement techniques, e.g. the aerodynamic gradient method, has emerged from large-scale projects such as NitroEurope (Sutton et al., 2011). These measurements, however, are usually only representative for a specific location and difficult to interpolate in space. Surface-atmosphere exchange schemes that predict ammonia exchange fluxes from measured or modeled concentrations and micrometeorological conditions are used on both the local scale and within large-scale chemical transport models (CTMs). Following the discovery of the ammonia compensation point (Farquhar, 1980), these models are nowadays able to reproduce bidirectional exchange fluxes, i.e. both emission and deposition of ammonia, and typically feature at least a stomatal and a non-stomatal leaf surface pathway. The addition of a soil- or leaf litter pathway by Nemitz et al. (2001) has been recognized as an optimal compromise between model complexity and accuracy of the flux estimates (Flechard et al., 2013), although some uncertainties in the treatment of the ground layer still prevail.

While the representation of the stomatal pathway has received much attention in the literature due to its importance not only for ammonia, but also for a large number of other atmospheric constituents, especially carbon dioxide (CO_2) and water vapor (H_2O) (e.g. Jarvis, 1976; Farquhar and Sharkey, 1982; Ball et al., 1987), modeling non-stomatal exchange is still subject to considerable uncertainty (Burkhardt et al., 2009). Ammonia is highly soluble in water and thus readily deposits to water layers on the leaf cuticle, and on any other environmental surface, following precipitation events, condensation of water vapor, or due to the presence of hygroscopic particles on the surface. This characteristic behavior is ~~often modeled using relative humidity response functions as a proxy for canopy wetness~~typically modeled with an exponential relative humidity response function as a proxy for canopy wetness, where a high relative humidity results in low non-stomatal resistances, and vice-versa (e.g. Sutton and Fowler, 1993; Erisman et al. 1994). A self-limiting effect of ambient ammonia concentrations on the deposition process, due to saturation effects and an increase in surface pH, has been observed in experiments (Jones et al, 2007a,b; Cape et al., 2008) and implemented in some non-stomatal exchange models (e.g. Wichink Kruit et al., 2010). Additionally, re-emission events during evaporation of leaf surface water layers have been measured in the field, which hints at the limits of these classical static and unidirectional approaches (Wyers and Erisman, 1998). Sutton et al. (1998) and Flechard et al. (1999) have successfully reproduced measurements of these events on the field scale by modeling the water films as charged capacitors for ammonia emissions; however, these models need complex dynamic leaf chemistry modules which drastically increase computational expense and necessary input variables and consequently limit their applicability in large scale simulations. Wichink Kruit et al. (2010) developed a static hybrid-model featuring a non-stomatal compensation point approach in order to simplify the model calculations and as an important step towards the use of a bidirectional non-stomatal exchange paradigm within large scale CTMs. In this paper, we compare the performance of two state-of-the-art parameterizations of non-stomatal exchange: The unidirectional approach of Massad et al. (2010) and the quasi-bidirectional approach of Wichink Kruit et al. (2010). The Massad et al. (2010) parameterization has received widespread acceptance in the community, with 53 citations according to the literature database 'Thomson Reuters Web of Science' at the time of writing this article, and variants of it have been applied in numerous studies, e.g. recently in Shen et al. (2016), Móring et al. (2016), Zöll et al. (2016), and others. Wichink Kruit et al. (2010) followed a unique approach by simplifying complex dynamic approaches towards an empirical steady-state formulation of a non-stomatal compensation point model, which is nowadays used within the DEPAC3.11 deposition module (van Zanten et al., 2010) and the chemistry transport model LOTOS-EUROS (Wichink Kruit et al., 2012), and it is structurally compatible with the Massad et al. (2010) model. We highlight strengths and weaknesses of both approaches and apply them to five measurement sites in Germany, the UK, the Netherlands and Switzerland. Predicted (effective) non-stomatal resistances are compared to those inferred from night-time flux measurements, when stomata are mostly closed and the contribution of the non-stomatal pathway to the total observed flux is dominant. In addition, we investigate the potential of parameterizing a bidirectional non-stomatal exchange model by testing backwards-looking moving averages of air ammonia concentrations as a proxy for prior ammonia inputs into the ecosystem, eliminating the need for dynamic or iterative flux-based approaches with the use of a readily available, easy-to-calculate and easy-to-implement metric.

2 Methods

2.1 Bidirectional ammonia exchange models

Ammonia dry deposition is typically modeled using an electrical analogy based on a network of serial and parallel resistances. The two-layer model structure introduced by Nemitz et al. (2001) has been recognized as a good compromise between model complexity, ease of use and accuracy of the resulting exchange fluxes (Flechard et al., 2013), and it is the foundation for the parameterization of Massad et al. (2010) that is used throughout this study. However, in the Massad et al. (2010) formulation, the second (soil / leaf-litter) layer is essentially switched off for semi-natural ecosystems and managed ecosystems outside of management events, because soil emissions are expected to be negligible in these cases. We therefore focus on the one-layer big-leaf model (Fig. 1) in this paper. For a list of variables used throughout this article, the reader is referred to Tab. S1 in the supplement.

In the simplest form, the canopy resistance model (e.g. Wesely, 1989; Erisman and Wyers, 1993), surface-atmosphere-fluxes are limited by three resistances in series: The aerodynamic resistance $R_\mathrm{a}\{z-d\}$ (s m^{-1}) at the reference height $z-d$ (m) (where z (m) is the measurement height above ground and d (m) is the zero-plane displacement height), the quasi-laminar boundary layer resistance R_b (s m^{-1}), and the canopy resistance R_c (s m^{-1}). While $R_\mathrm{a}\{z-d\}$ and R_b are mainly dependent on micrometeorological conditions, surface roughness and chemical properties of the compound of interest, R_c is directly dependent on the characteristics of the vegetated surface. The inverse of the sum of these three resistances is called the deposition velocity, $v_\mathrm{d}\{z-d\}$ (m s^{-1}).

R_c is further split into a stomatal pathway with the stomatal resistance R_s (s m^{-1}), and a non-stomatal (or cuticular) pathway with the non-stomatal resistance R_w (s m^{-1}) (e.g. Erisman et al., 1994; Sutton et al., 1998). Stomatal exchange is usually modeled bidirectionally for ammonia in field scale studies and some CTMs, i.e. it is assumed that there is a non-zero gaseous ammonia concentration χ_s (µg m^{-3}) in equilibrium with dissolved ammonia in the apoplastic fluid. This concentration is often called the stomatal compensation point, although strictly speaking the compensation point is only met when χ_s is approximately equal to the air ammonia concentration at the reference height $\chi_\mathrm{a}\{z-d\}$ (µ~~n~~g m^{-3}) and consequently the net flux F_t (µ~~n~~g m^{-2} s^{-1}) is zero (Farquhar, 1980). The non-stomatal pathway is modeled unidirectionally in many parameterizations, i.e. the gaseous ammonia concentration in equilibrium with the solution on the external leaf surfaces χ_w (µg m^{-3}) is assumed to be zero, although observational evidence indicates that this pathway is in fact bidirectional as well (e.g. Neirynck and Ceulemans, 2008). A canopy compensation point, χ_c (µg m^{-3}), that integrates these two pathways can be calculated as (e.g. Sutton et al., 1995; modified to include χ_w):

$$\chi_\mathrm{c} = \frac{\chi_\mathrm{a}\{z-d\}\cdot(R_\mathrm{a}+R_\mathrm{b})^{-1}+\chi_\mathrm{s}\cdot R_\mathrm{s}^{-1}+\chi_\mathrm{w}\cdot R_\mathrm{w}^{-1}}{(R_\mathrm{a}\{z-d\}+R_\mathrm{b})^{-1}+R_\mathrm{s}^{-1}+R_\mathrm{w}^{-1}}, \tag{1}$$

and the total net flux of ammonia to or from the ecosystem, F_t (µ~~n~~g m^{-2} s^{-1}) as

$$F_\mathrm{t} = -\frac{\chi_\mathrm{a}\{z-d\}-\chi_\mathrm{c}}{R_\mathrm{a}\{z-d\}+R_\mathrm{b}}, \tag{2}$$

where by convention negative fluxes indicate deposition towards the surface and positive fluxes indicate emission. This is typically done on a half-hour basis for consistency with flux measurement practices. $R_\mathrm{a}\{z-d\}$ and R_b are here modeled after Garland (1977) as:

$$R_\mathrm{a}\{z-d\} = \frac{u\{z-d\}}{u_*^2} - \frac{\Psi_\mathrm{H}\left\{\frac{z-d}{L}\right\}-\Psi_\mathrm{M}\left\{\frac{z-d}{L}\right\}}{k\cdot u_*}, \tag{3}$$

and

$$R_\mathrm{b} = u_*^{-1}\left[1.45\cdot\left(\frac{z_0\cdot u_*}{\nu_\mathrm{air}}\right)^{0.24}\cdot\left(\frac{\nu_\mathrm{air}}{D_{\mathrm{NH_3}}}\right)^{0.8}\right], \tag{4}$$

where $u\{z-d\}$ (m s^{-1}) is the wind speed at the reference height, u_* (m s^{-1}) is the friction velocity, L (m) is the Obukhov length, k (–) is the von Kármán constant (k = 0.41), Ψ_H (–) and Ψ_M (–) are the integrated stability corrections for entrained scalars and momentum, respectively, after Webb (1970) and Paulson (1970), z_0 (m) is the roughness length, ν_air (m^2 s^{-1}) is the kinematic viscosity of air, and $D_{\mathrm{NH_3}}$ (m^2 s^{-1}) is the molecular diffusivity of ammonia in air. R_s can be modeled using at least a light and temperature response function (e.g. Weseley, 1989), often with additional reduction factors accounting for vapor pressure deficit, soil moisture and other environmental variables (e.g. Emberson et al., 2000). However, this study focuses on nighttime fluxes when non-stomatal fluxes are assumed to be dominant. If R_{s} is assumed to approach infinity at during nighttime, all terms involving R_{s} in Eq. (1) collapse to zero.

2.2 Most recent non-stomatal resistance parameterizations

(i) Massad et al. (2010)

Based on an extensive meta-analysis, Massad et al. (2010) derived a parameterization (henceforth referred to as *MNS*) for a unidirectional non-stomatal pathway model (i.e. $\chi_{\mathrm{w}} = 0$) that models the effect of the air pollution climate by incorporating a so-called acid ratio, AR (–), to scale the minimum allowed R_{w}. It is defined as the molar ratio of average total acid/NH_3 concentrations, AR = (2[SO_2] + [HNO_3] + [HCl])/[NH_3] and is an extension of the classical [SO_2]/[NH_3] co-deposition proxy concept following the decline of SO_2 emissions in Europe during the last few decades (e.g. Erisman et al., 2001). In addition, effects of leaf area index LAI (m^2 m^{-2}) and temperature T (°C) are modeled following Zhang et al. (2003) and Flechard et al. (2010), respectively. With all corrections R_{w} is given as:

$$R_{\mathrm{w,MNS}} = R_{\mathrm{w,min}} \cdot AR^{-1} \cdot e^{a\cdot(100-RH)} \cdot \frac{e^{\beta\cdot|T|}}{\sqrt{LAI}}\,, \qquad (5)$$

where $R_{\mathrm{w,min}}$ = 31.5 s m^{-1} is the ’baseline‘ minimum R_{w}, a (–) is an empirical ecosystem-specific parameter ranging from 0.0318 ± 0.0179 for forests to 0.176 ± 0.126 for grasslands, RH (%) is relative humidity, LAI (m^2 m^{-2}) is one-sided leaf area index, β = 0.15 °C^{-1} is a temperature response parameter, and T (°C) is the temperature. The exponential decay parameter a was calculated as an average of a values per land-use class reported in the literature (Massad et al., 2010). Note that the temperature response was originally derived using temperatures scaled to the notional height of trace gas exchange z_0’ (m). Since sensible heat flux measurements, which are required for this extrapolation (e.g. Nemitz et al., 2009), were not available for all sites, we here used measured air temperatures instead. The influence of using T and RH at the reference height instead of z_0’ is discussed later in this paper. Contrary to the original formulation of Flechard et al. (2010), Massad et al. (2010) do not use absolute values of $|T|$ (°C), but we chose to do so under the assumption that generally R_{w} increases in freezing conditions (e.g. Erisman and Wyers, 1993).

(ii) Wichink Kruit et al. (2010)

Following the bidirectional non-stomatal exchange paradigm introduced in the cuticular capacitance model of Sutton et al. (1998), Wichink Kruit et al. (2010) developed a simplified steady-state non-stomatal compensation point (χ_{w}) model (henceforth referred to as *WK*) using three years of flux measurements over an unfertilized grassland in the Netherlands. In this model, a simple exponential humidity response after Sutton and Fowler (1993) is used as an approximation for R_{w} under ~~’clean conditions’~~low ambient NH_3 concentrations, where saturation of the external leaf surfaces is unlikely (Wichink Kruit et al, 2010; Milford et al., 2001):

$$R_{\mathrm{w,WK}} = 2 \cdot e^{\frac{1}{12}\cdot(100-RH)}\,. \qquad (6)$$

χ_w (µg m^{-3}) is calculated from the temperature response of the Henry equilibrium and the ammonium-ammonia dissociation equilibrium, similar to formulations used for the stomatal compensation point (e.g. Nemitz et al. 2000), as:

$$\chi_\mathrm{w} = \frac{2.75 \cdot 10^{15}}{T+273.15} \cdot e^{\left(-\frac{1.04 \cdot 10^{4}}{T+273.15}\right)} \cdot \Gamma_\mathrm{w} \,, \tag{7}$$

where Γ_w (–) is the non-stomatal emission potential and corresponds to the molar ratio of [NH_4^+] to [H^+] in the leaf surface water layers. Wichink Kruit et al. (2010) derived a functional relationship for Γ_w from measurements of the ammonia air concentration at a reference height of 4 m:

$$\Gamma_\mathrm{w} = 1.84 \cdot 10^{3} \cdot \chi_\mathrm{a}\{4\ \mathrm{m}\} \cdot e^{-0.11 \cdot T} - 850 \,, \tag{8}$$

The WK model is only structurally bidirectional in that the effect of the air pollution climate is shifted from R_w to χ_w. In practice, as χ_w is parameterized as a fraction of χ_a, no emissions can occur (cf. van Zanten et al., 2010, Appendix F).

An effective non-stomatal resistance, $R_\mathrm{w,eff.}$ (s m^{-1}), that produces identical results when used with a unidirectional non-stomatal resistance-only model, can be written as:

$$R_\mathrm{w,eff.} = \frac{\chi_\mathrm{c} \cdot R_\mathrm{w}}{\chi_\mathrm{c} - \chi_\mathrm{w}} \,, \tag{9}$$

or during nighttime conditions, when R_s is here assumed to approach infinity:

$$R_\mathrm{w,eff.,nighttime} = \frac{\chi_\mathrm{a}\{z-d\} \cdot R_\mathrm{w} + \chi_\mathrm{w} \cdot (R_\mathrm{a}\{z-d\} + R_\mathrm{b})}{\chi_\mathrm{a}\{z-d\} - \chi_\mathrm{w}} \,. \tag{10}$$

Note that Wichink Kruit et al. (2010) used surface temperatures estimated from outgoing longwave radiation and the Stefan-Boltzmann law, but in practice the model is routinely run with air temperatures within the DEPAC3.11 code (van Zanten et al., 2010). As with the MNS model, the difference between using air and surface temperatures when the latter was available was investigated in a small sensitivity study.

2.3 Theoretical considerations and generation of hypotheses

The MNS model uses a minimum non-stomatal resistance $R_\mathrm{w,min}$ of 31.5 s m^{-1}, which is further significantly increased when $AR < 1$, $RH < 100$ %, $LAI < 1$ and $T \neq 0$ °C (Fig. 2). For example, at $AR = 0.5$ and $T = 10$ °C, the minimum allowed R_w at 100 % relative humidity lies between 163 and 282 s m^{-1} for an LAI range of 1 to 3 m^{2} m^{-2}. It is evident from Tab. 1 of Massad et al. (2010) that $AR < 1$ is no rare occurrence, but compared to minimum measured R_w (ibid.) predicted values appear to be rather high. It should also be noted that in the MNS model, the deposition velocity can never ~~approach~~ reach the maximum limit allowed by turbulence $v_\mathrm{d,max}\{z-d\}$ (m s^{-1}):

$$v_\mathrm{d,max}\{z-d\} = (R_\mathrm{a}\{z-d\} + R_\mathrm{b})^{-1} \,. \tag{11}$$

The temperature dependent parameterization of Γ_w in the WK model can lead to contrasting effects: When temperatures increase, the exponential decay function in Eq. (8) can completely counter the growth of Eq. (7). In other words, depending on NH_3 air concentration levels, after a certain cut-off temperature the non-stomatal compensation point χ_w ~~point~~ decreases (Fig. 2), although with a constant Γ_w, an equilibrium shift towards gaseous ammonia would be expected to lead to a further exponential increase of χ_w. Consequently, when T is high and χ_w approaches zero, χ_c is canceled out in Eq. (9) and $R_\mathrm{w,eff.}$ becomes equal to the clean air $R_\mathrm{w,WK}$ (Eq. (6)), which at 100 % relative humidity is as low as 2 s m^{-1}.

Based on these considerations, we hypothesize that:

(i) The MNS model has a tendency to overestimate R_w and consequently to underestimate F_t, especially at sites with ~~moderately~~ low acid ratios.

(ii) The WK model has a tendency to underestimate R_w and consequently to overestimate F_t, especially during ~~moderately~~ high temperatures and low air ammonia concentrations.

2.4 Derivation of night-time non-stomatal resistances from flux measurements

Non-stomatal resistance models are parameterized using flux measurements during reasonably turbulent, i.e. near neutral or only slightly stable, nighttime conditions. When stomatal closure is high and therefore $R_\mathrm{s} \gg R_\mathrm{w}$, we can assume that the canopy resistance R_c is approximately equal to R_w based on the single-layer model when the non-stomatal pathway is treated unidirectional:

$$R_\mathrm{w,obs.} \approx -\frac{\chi_\mathrm{a}\{z-d\}}{F_\mathrm{t}} - (R_\mathrm{a}\{z-d\} + R_\mathrm{b}) \,, \tag{12}$$

where $R_\mathrm{w,obs.}$ (s m^{-1}) is the observed non-stomatal resistance, and F_t is in µg m^{-2} s^{-1}. $R_\mathrm{w,obs.}$ values were selected from turbulent nighttime conditions (e.g. Wichink Kruit et al., 2010), when $R_\mathrm{a}\{z-d\} + R_\mathrm{b} < 200$ s m^{-1}, $u_* > 0.1$ m s^{-1}, and global radiation < 10 W m^{-2}.

Existing datasets of flux measurements were used for a comparison of measured and modeled R_w. These measurements were conducted at two peatland sites, Auchencorth Moss (AM) in the United Kingdom, and Bourtanger Moor (BM) in Germany, as well as three grassland sites, Oensingen (OE) in Switzerland, and Solleveld (SV) and Veenkampen (VK), both in the Netherlands. At AM, OE, SV and VK, the aerodynamic gradient and at BM the eddy covariance method was used. For detailed site and measurement setup descriptions, the reader is referred to Flechard et al. (1999) for AM, ~~Richter~~ Zöll et al. (2016) and Hurkuck et al. (2014) for BM, and Spirig et al. (2010) for OE. SV and VK datasets are unpublished as of now. SV is best characterized as a semi-natural grassland and is located in the dune area west of The Hague, NL. NH_3 concentration profiles were measured using a Gradient Ammonia High Accuracy Monitor (GRAHAM, Wichink Kruit et al., 2007) system with inlets at 0.8, 1.7 and 3.6 m above ground. VK is an experimental grassland site used by Wageningen UR for meteorological measurements, where NH_3 was sampled at 0.8 and 2.45 m above ground using Differential Optical Absorption Spectroscopy (DOAS, Volten et al., 2012). A brief overview of measurement conditions at the five sites is given in Tab. 1. LAI and canopy height h_c (m) measurements were available for AM and OE, and the default values proposed in Tab. 6 of Massad et al. (2010) were used at the other sites. Emission events at OE not suitable for this study were filtered out by removing 9 days of measurements after a fertilization event~~s~~, based on the e-folding time of 2.88 days used for fertilizer emission potentials in Massad et al. (2010), which translates into a 95 % ‘extinction time‘ of 8.63 days for the management influence. For VK, no management logs for the measurement site or the surrounding fields were available and only two strong emission periods were removed manually after visual inspection of the dataset.

2.5 Proposal for a semi-dynamic parameterization of non-stomatal emission potentials

The Wichink Kruit et al. (2010) parameterization was developed for frameworks within which the use of dynamic cuticular capacitance models in conjunction with leaf surface chemistry modules may not be practical (e.g. to limit computation time of large scale CTMs). While it is capable of modeling saturation effects with an ambient ammonia concentration dependent non-stomatal compensation point, it only relies on χ_a at the current calculation step. A compromise between the truly dynamic models of Sutton et al. (1998) and Flechard et al. (1999) and the steady-state simplification of Wichink Kruit et al. (2010) would respect the site’s history of reactive nitrogen inputs without falling back to a numerically dynamic model and, consequently, the same difficulties that limit the application of existing dynamic approaches in large-scale models, i.e. it would need to use a proxy for previous nitrogen deposition without relying on the model’s flux predictions at an earlier calculation time. We here additionally investigate the feasibility of a Γ_w parameterization based on backward-looking moving averages of air ammonia concentrations as a proxy for prior NH_3 inputs into the system which might saturate leaf water layers and enhance the compensation points. If such a relationship exists, it can provide an easy-to-use metric that can be calculated from readily available observations without the need for spinning up and iteratively solving a model for F_t estimates, while still allowing the use of a more mechanistic bidirectional approach to non-stomatal exchange. Γ_w values are derived as done by Wichink Kruit et al. (2010), i.e. R_w is parameterized for clean air according to Eq. (6), χ_w is calculated as

$$\chi_w = \chi_a\{z-d\} + F_t \cdot \left(R_a\{z-d\} + R_b + R_{w,WK}\right) , \qquad (13)$$

and finally, Γ_w is calculated by rearranging Eq. (7) to:

$$\Gamma_w = \frac{T+273.15}{2.75 \cdot 10^{15}} \cdot e^{\left(\frac{1.04 \cdot 10^4}{T+273.15}\right)} \cdot \chi_w . \qquad (14)$$

The relationship was investigated for moving-windows of different lengths (1 day, 3 days, 7 days, and 14 days) under exclusion of periods with substantial rainfall (> 5 mm d^{-1}).

3 Results and discussion

3.1 Comparison of existing parameterizations with observations

The MNS model tends to underestimate nighttime F_{t} at all five sites, whereas the WK model overestimates F_{t} for BM, OE and SV, underestimates it for VK, and only very slightly underestimates it for AM (Fig. 3). Note that total cumulative F_{t} in Fig. 3 is by no means representative for an estimate for total NH_3 input during these times, but based on non-gap filled nighttime fluxes only. Additionally, a mismatch between modeled and measured flux densities early in the time series propagates through the whole time series of cumulative fluxes. For example, at BM the MNS model performs very well after a mismatch during the first week, whereas the WK model fits the observations closely until mid-March 2014. Similarly, the strong measured deposition event early in the VK time series is not reproduced by either of the models. Comparing differences in modeled and measured nighttime R_{w} (Fig. 4, upper row) supports these observations: While using the MNS model leads to an overestimation of the majority of observed R_{w} at all sites, as hypothesized, the picture is not as clear for WK. Here, the majority of modeled R_{w} values lies below the observations for BM, OE, SV and VK, however, for AM and VK both frequent over- and underestimations of R_{w} canceled each other out, thereby leading to fairly reasonable predicted net fluxes at these two sites. The inverse of these resistances, the non-stomatal conductance $G_{\mathrm{w}} = R_{\mathrm{w}}^{-1}$ may be a better predictor for the resulting fluxes, as very high resistances have a negligible effect on fluxes. Differences between modeled and measured G_{w} are shown in the lower row of Fig. 4 and generally lead to similar conclusions (note that here underestimations of G_{w} directly lead to underestimations of F_{t}), but emphasize the relatively good predictive capabilities of MNS at BM and WK at VK during most times, which may not immediately be obvious from looking at cumulative fluxes (Fig. 3).

We attribute the mismatch of the MNS model results and measurements to the relatively high baseline minimum allowed R_{w} and the strong response of the temperature correction function (Fig. 5, left panel). Note that AR at all sites is lower than 1, ranging from 0.1 at BM to 0.7 at AM, which results in minimum R_{w} of 315 and 45 s m^{-1} before LAI and T correction, respectively. For example, at OE with an AR of 0.4 and an average LAI of approximately 2 m^2 m^{-2}, even under conditions highly favoring deposition towards the external leaf surface in the MNS model (RH = 100 %, T = 0 °C), deposition velocity is restricted to an upper bound of 1.8 cm s^{-1}, although observations regularly exceeded this threshold. In their comprehensive literature review, Massad et al. (2010) themselves report $R_{\mathrm{w,min}}$ between 1 and 30 s m^{-1} for grassland and between 0.5 and 24 s m^{-1} for semi-natural ecosystems. In their parameterization of R_{w}, on the other hand, the actual deposition velocity can never approach the theoretical limit allowed by turbulence (Eq. (11)), although this case was regularly observed in the field. This is of course true for all unidirectional R_{w} parameterizations of the commonly used $R_{\mathrm{w}} = R_{\mathrm{w,min}} \cdot e^{a\cdot(100-RH)}$ form, however, in the WK model a small minimum R_{w} of 2 s m^{-1} allows $v_{\mathrm{d}}\{z-d\}$ to approach $v_{\mathrm{d,max}}\{z-d\}$ closely. Regarding the temperature correction, the parameter β = 0.15 °C^{-1} translates into an increase of R_{w} by a factor of 4.5 with a T increase of 10 K. Equation (7), however, only predicts an increase of the compensation point χ_{w} by a factor of approximately 2.8 to

4.1 for a T increase of 10 K, depending on the starting temperature, which translates into a significantly smaller factor for $R_{\mathrm{w,eff.}}$ considering the influence of other variables in Eq. (9) and / or Eq. (10). Note, the relatively good agreement with measured fluxes at BM, despite the very low AR.

Reasons for strikingly diverse performance of the WK model are not straightforward, but may be explained based on the combined effect of T and χ_{a} on the Γ_{w} parameterization, as depicted in Fig. 2. For example, at BM the model performs relatively well until mid-March 2014 (Fig. 3), when measured fluxes decrease, whereas modeled fluxes remain at a similar level and later even increase. This observation corresponds to an increase in both T and χ_{a} at the site (cf. ~~Richter~~ Zöll et al., 2016), leading to a decrease in effective R_{w} and therefore an increase in modeled F_{t}. In fact, with all sites pooled into one combined dataset, two interesting characteristics of the parameterization emerge from a plot of differences in modeled and measured R_{w} against χ_{a} (Fig. 5, right panel): (i) The underestimation of R_{w} does indeed increase with rising temperatures and χ_{a}, as hypothesized. (ii) There is an additional tendency to actually overestimate R_{w} when temperatures are relatively low, which strongly responds to increasing χ_{a} and may be an indication of a too high modeled Γ_{w} under these conditions. These two contrasting effects may explain the good agreement of net modeled and measured cumulative fluxes e.g. at AM, where concentrations were relatively low during most times and both low and high temperatures without extremes were measured.

3.2 Semi-dynamic Γ_{w}

Estimated non-stomatal emission potentials Γ_{w} appear to have a strong dependency on backward-looking moving averages of measured air ammonia concentrations $\chi_{\mathrm{a,}\cancel{\mathrm{mov.avg.}}\mathrm{MA}}$ (µg m^{-3}) (Fig. 6). While this may indicate some potential as an easy-to-use and readily available proxy for prior NH_3 inputs without the need for more complex and / or computationally intensive mechanistic models, estimated Γ_{w} values are extremely noisy and span multiple orders of magnitude in the < 5 µg m^{-3} range. An increase in the moving-window length from 1 day (Fig. 6a) to 14 days (Fig. 6d) does not lead to a substantial decrease in the magnitude of the noise. There is a very clear linear relationship when log-transforming both Γ_{w} and $\chi_{\mathrm{a,}\cancel{\mathrm{mov.avg.}}\mathrm{MA}}$ (R^2 = 0.62 for the 1 d moving average case; not shown), however, the strong variability of the data, especially in the low-concentration region, leads to a best fit that predicts large Γ_{w} even at concentrations as low as 1 µg m^{-3} ($\Gamma_{\mathrm{w}} \approx 380$), which eventually ends in unreasonably high emission fluxes. Without further noise reduction, this approach appears unfeasible as an alternative to more sophisticated dynamic models (e.g. Flechard et al., 1999) or those featuring additional dependencies as the one of Wichink Kruit et al. (2010). Making the moving-window width dependent on time since the last substantial precipitation event might help reduce this noise and lead to a more realistic representation, but in turn complicates the implementation and increases the degrees of freedom in this approach, thereby reducing its advantage over mechanistically more accurate models.

3.3 MNS with updated parameters

Since we hypothesized the reasons for the mismatch between modeled R_w with the MNS model and measured $R_\mathrm{w,obs.}$ to be based on two easily accessible parameters with relatively obvious effects on modeled resistances ($R_\mathrm{w,min}$ and the temperature response parameter β in Eq. (5)), we additionally investigated the effects of adjusting them towards smaller values. Figure 7 shows the effects of simply halving both $R_\mathrm{w,min}$ and β on predicted nighttime fluxes. Even though there still remains significant scatter, doing so decreases the mismatch between modeled and measured fluxes in most cases. However, in one case (BM) predicted fluxes actually turn out to fit the measurements worse than with the original parameters, and in another case (VK) this only leads to a marginal improvement. This exercise highlights the potential for a significant overall improvement in NH_3 flux predictions by optimizing these two parameters based on independent data from all four ecosystem types (grassland, arable, forest and semi-natural ecosystems) used in the MNS parameterization.~~While there does not appear to be a comprehensive, generic solution, we assume that there is potential for a significant overall improvement by optimizing these two parameters based on independent data from all four ecosystem types (grassland, arable, forest and semi-natural ecosystems) used in this parameterization.~~

3.4 Sensitivity of the main findings

Parts of both models used in this study were developed using an estimate of surface temperatures, either by extrapolating T from the reference height $z-d$ to the notional height of trace gas exchange z_0' using sensible heat flux H (W m^{-2}) measurements, or by estimating $T\{z_0'\}$ from outgoing long wave radiation measurements and the Stefan-Boltzmann law. Additionally, the temperature response function of Flechard et al. (2010), which is used within the MNS model, was fitted using surface level values of relative humidity, $RH\{z_0'\}$ which were derived using measured latent heat fluxes LE (cf. Nemitz et al., 2009). Since H and LE measurements were not available at all sites and introduce an additional source of uncertainty, especially during moderately stable nighttime conditions, and the WK model is routinely being used with air temperatures within the DEPAC3.11 code, we here used both T and RH at the reference height as input data. Figure 8 (upper row) illustrates the effects of using T and RH at different conceptual model heights for AM. While there are of course numerical differences, ~~the impact on this study's main findings are negligible~~they do not lead to significant differences in the main findings of this study. Generally, the WK model appears to be less sensitive to these choices than the MNS model.

For both SV and VK, no measurements of [HNO_3] and [HCl] were available. We estimated AR for the MNS model based on the observations of Fowler et al. (2009), that across NitroEurope sites, [SO_2] makes up around 40 % of the sum [SO_2]+[HNO_3]+[HCl] to be approximately 3.5 times the ratio of [SO_2]/[NH_3]. From the definitions AR = (2[SO_2]+[HCl]+[HNO_3])/[NH_3] and SN = [SO_2]/[NH_3], a lower bound of $AR \geq 2 \cdot SN$ is obvious. Using a symmetrical range around our initial estimate of $AR \approx 3.5 \cdot SN$, we set an additional upper bound of $AR \leq 5 \cdot SN$ and tested the effects of using these values on R_w differences for both affected sites (Fig. 8, lower row). Again, there are apparent numerical differences, but they do not affect the main observations made here (i.e. they neither change the sign of the differences in modeled and measured R_w, nor do they change the general magnitude of the differences e.g. from a strong overestimation to an insignificant one).

3.5 Sources of uncertainty

Nighttime $R_\mathrm{w,obs.}$ are affected by (i) the uncertainty in the flux measurements, which can be high due to insufficient turbulent mixing, and (ii) uncertainty in modeled $R_\mathrm{a}\{z-d\}$ and R_b, which results from increasingly high stability corrections ($\Psi_\mathrm{M}\left\{\frac{z-d}{L}\right\}$ and $\Psi_\mathrm{H}\left\{\frac{z-d}{L}\right\}$) under increasing atmospheric stability, possible inaccuracy of estimated z_0 and d, and possible inadequacy of the R_b model for some surfaces. We therefore emphasize that the results of this study are to be interpreted qualitatively and can only reveal overall tendencies in the models' accuracy, not provide a precise quantification of the mismatch between models and measurements. Propagation of these uncertainties through the analysis resulted in some negative values of $R_\mathrm{w,obs.}$. There are generally two possible reasons for negative canopy resistance values to occur: (i) emission (i.e. positive fluxes), or (ii) ’overfast‘ deposition ($v_\mathrm{d}\{z-d\} > v_\mathrm{d,max}\{z-d\}$) that is not compatible with the resistance modeling framework used here. As a rule of thumb, we set an upper tolerance threshold for $v_\mathrm{d}\{z-d\}$ of $1.5 \cdot v_\mathrm{d,max}\{z-d\}$, considered to be within the limits of night-time flux measurement uncertainty and representing perfect sink behavior, and consequently set $R_\mathrm{w,obs.}$ to zero in these cases. Measurements where $v_\mathrm{d}\{z-d\} > 1.5 \cdot v_\mathrm{d,max}\{z-d\}$ were discarded and assumed to be either resulting from incompatibility with the atmospheric resistance ($R_\mathrm{a}\{z-d\}$, R_b) model or from measurement error. During emission events, $R_\mathrm{w,obs.}$ was set to infinity. Ranges from 2 to 16 % invalid values, 63 to 93 % deposition and 4 to 29 % emission ~~and~~ were observed across the five sites during near-neutral nighttime conditions. The latter especially highlights the importance of further research towards a truly bidirectional paradigm for non-stomatal exchange (i.e. cuticular desorption, ground-based emissions, or emission fluxes from other environmental surfaces).

An additional investigation of daytime non-stomatal exchange would be beneficial in terms of a significant reduction of uncertainty in the observations and in order to cover a much wider range of temperatures and humidity regimes. However, comparisons based on daytime flux estimates were not made in this study in order not to introduce an additional source of bias via the stomatal pathway. Both Massad et al. (2010) and Wichink Kruit et al. (2010) also presented parameterizations for the stomatal emission potential, Γ_s (–). However, for MNS information about annual total (dry and wet) N input into the system is necessary. While this issue can be overcome by iteratively solving a model with more reactive nitrogen species, so that N input is both a parameter, and a result of the simulation, we here used a model that only predicts NH_3 dry deposition, which we do not consider to be sufficient information to estimate total N input to our sites. At sites where total N input is known (e.g. BM, from Hurkuck et al. (2014), or from CTM results for other sites), the MNS and WK parameterizations both predict very different Γ_s estimates. The reasons for this mismatch have, to our knowledge, not been investigated to date. We therefore decided to not model the stomatal pathway explicitly and rely on nighttime fluxes only.

~~While this can be estimated from spinning up a model that incorporates more reactive nitrogen species than just NH_3, we do not feel confident estimating total N input from modeled NH_3 dry deposition alone. At sites where total N input is known (e.g. BM, from Hurkuck et al. (2014), or from CTM results), the MNS and WK parameterizations predict such different Γ_s estimates that one model predicts net emission from the stomata and one model predicts a net uptake over the course of the measurement campaign. A detailed investigation on the reasons for this mismatch is, however, beyond the scope of this paper.~~

Explicitly modeling the stomatal pathway with physiologically accurate stomatal conductance models may have the additional benefit of being able to assess bias in the estimation of non-stomatal resistances introduced by nighttime stomatal opening, naturally resulting in a lower contribution of the non-stomatal pathway to the total observed flux. However, note that a distinction between physiological accuracy and the purpose which the derived resistances are used for has to be made. While nighttime stomatal opening is a well-known phenomenon (e.g. Caird et al., 2007), it is rarely respected in modeling studies (e.g. Fisher et al., 2007). A physiologically accurate R_w parameterization used in conjunction with a stomatal model that does not account for nighttime stomatal opening would result in biased fluxes. We here derived R_w under the assumption that stomata are closed at night to ensure comparability with R_w values predicted by the WK and MNS parameterization, respectively, and compatibility with most operational biosphere-atmosphere exchange schemes, but we acknowledge that the physiological meaning may be confounded by stomatal flux contributions at night.

Another source of uncertainty lies in the fact that R_w models are often developed as 'cuticular resistance' models with only leaf surface exchange in mind. However, in the one-layer resistance framework used here it is not possible to clearly differentiate between deposition towards or emission from wet leaf surfaces, leaf litter, the soil, stems and branches, and any other environmental surface. In fact, the MNS model was originally developed on the basis of the two-layer model of Nemitz et al. (2001), but outside of management events, the ground layer resistance was set to infinity in order to transform the model structure to that of a one-layer model (Massad et al., 2010)~~ and the model reduces to a one-layer model~~. While it is indeed conceptually unsatisfactory to ignore the source / sink strength of the ground-layer, an unambiguous identification of multiple non-stomatal pathways' flux contributions by simply inverting the model and inferring resistances from meteorological measurements is not possible, unless there is a signal that can confidently be attributed to originate from e.g. the ground layer (for instance after fertilizer application). Therefore, due to these methodological limitations, both the parameterizations and the measurements of R_w discussed in this paper may very well integrate exchange fluxes with not only wet leaves, but also e.g., the the soil, stems and branches, or other surfaces.

4 Conclusions ~~and recommendations for further research~~

We presented a semi-quantitative assessment of the compared performances of two state-of-the-art non-stomatal resistance parameterizations for ammonia biosphere-atmosphere exchange models, supported by flux measurements from two semi-natural peatland and three grassland sites.

The unidirectional R_w-only approach of Massad et al. (2010), which, in addition to the classical humidity response, reflects the effects of the air pollution climate, vegetation via the leaf area index, and an empirical temperature response, was found to overestimate R_w during nighttime at all five sites. Adjusting the temperature response and minimum R_w parameters in the MNS model towards smaller values resulted in a better match between modeled and measured NH_3 fluxes at most, but not all sites. We suggest to further investigate the potential of re-calibrating these parameters to flux data from all four ecosystem types represented in the MNS R_w parameterization. Compared to measured values found in the literature (e.g. Massad et al., 2010, Tab. 1), especially the minimum predicted R_w at sites with low atmospheric acid-to-ammonia ratios appear too high. ~~We tested the potential for an easily accessible improvement of predicted R_w and consequently predicted NH_3 exchange fluxes by using smaller values for the temperature response and minimum R_w parameters and propose to further investigate this route using data from all four ecosystem types represented in the MNS R_w parameterization.~~

The quasi-bidirectional model of Wichink Kruit et al. (2010) shows a more complex response to varying air pollution climates and meteorological conditions, with both a tendency to underestimate R_w, as initially hypothesized, during warm conditions and moderately high ambient NH_3 concentrations, and a tendency to overestimate R_w during colder conditions, with an even stronger response to increasing χ_a. While there is likely no simple solution as may be the case for the MNS model, the WK parameterization with its non-stomatal compensation point approach appears to be conceptually more compatible with field observations (e.g. morning peaks of NH_3 emission due to evaporation of leaf surface water). We ~~strongly encourage~~suggest revisiting the Γ_w parameterization with additional data from other ecosystems and investigating alternative approaches to model the effects of seasonality in Γ_w, e.g. by using a smoothed temperature response instead of an instantaneous one. An extension of the model with an SO_2 co-deposition response is currently being researched.

A simple alternative approach to dynamic models for the non-stomatal emission potential revealed a clear response of Γ_w to backward-looking moving averages of χ_a. These findings may turn out to be promising for CTMs, as they provide a first step towards a simplification of computationally intensive mechanistic model. However, further noise reduction, especially in the low concentration region, is needed for it to be useful for predicting NH_3 exchange fluxes.

Code and data availability

Python 2.7 code for the resistance model parameterized after Massad et al. (2010) and Wichink Kruit et al. (2010), as well as the data analysis code, can be requested from the lead author via email (frederik.schrader@thuenen.de). Measurement data from AM, BM and OE are property of the respective authors (cf. Tab. 1); for the SV and VK datasets, please contact M. C. van Zanten (margreet.van.zanten@rivm.nl).

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Tables

Table 1: Summary of the five datasets. AGM = Aerodynamic gradient method; EC = Eddy covariance, MNS = Massad et al. (2010). Measurement period is the period during which flux measurement were available after final data filtering. T and χ_a ranges are minimum and maximum values during the measurement period and values in parentheses denote the 5 %, 50 %, and 95 % quantiles.

ID	Site name	Ecosystem type in MNS	Measurement period	Measurement technique	T (°C)	χ_a (µg m-3)	avg. AR (–)	Reference
AM	Auchencorth Moss (UK)	semi-natural	02/95 – 02/96 05/98 – 11/98	AGM	-7.8 – 26.9 (0.0, 9.4, 17.3)	0.0 – 32.9 (0.1, 0.4, 2.9)	0.7	Flechard et al. (1999)
BM	Bourtanger Moor (DE)	semi-natural	02/14 – 05/14	EC	-4.4 – 22.3 (0.7, 7.3, 17.8)	1.6 – 62.0 (3.2, 9.0, 26.6)	0.1	~~Richter~~ Zöll et al. (2016)
OE	Oensingen (CH)	grassland	07/06 – 10/07	AGM	-3.0 – 33.1 (1.2, 12.3, 23.8)	0.0 – 24.7 (0.4, 2.2, 8.0)	0.4	Spirig et al. (2010)
SV	Solleveld (NL)	grassland	09/14 – 08/15	AGM	-1.5 – 31.7 (3.4, 11.6, 20.4)	0.1 – 15.6 (0.2, 1.2, 6.6)	0.5	unpublished
VK	Veenkampen (NL)	grassland	01/12 – 10/13	AGM	-5.4 – 31.6 (4.0, 15.2, 26.2)	0.3 – 116.9 (2.5, 8.8, 27.7)	0.3	unpublished

Figures

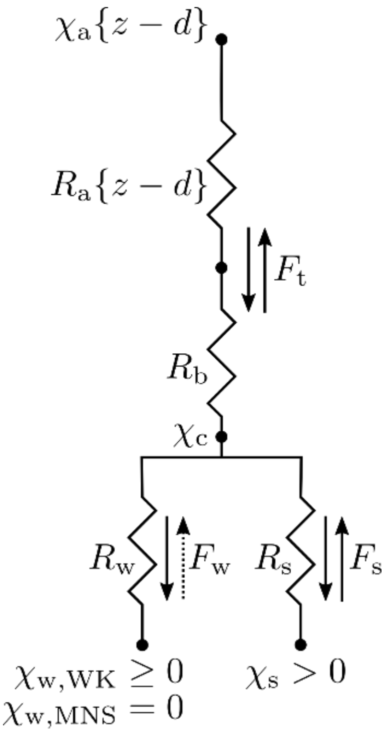

Figure 1: Structure of the single-layer model of NH_3 surface-atmosphere exchange used in this study. The non-stomatal pathway can be treated either uni- or bidirectionally, depending on the specific parameterization. MNS = Massad et al. (2010); WK = ~~(~~Wichink Kruit et al.~~,~~ (2010).

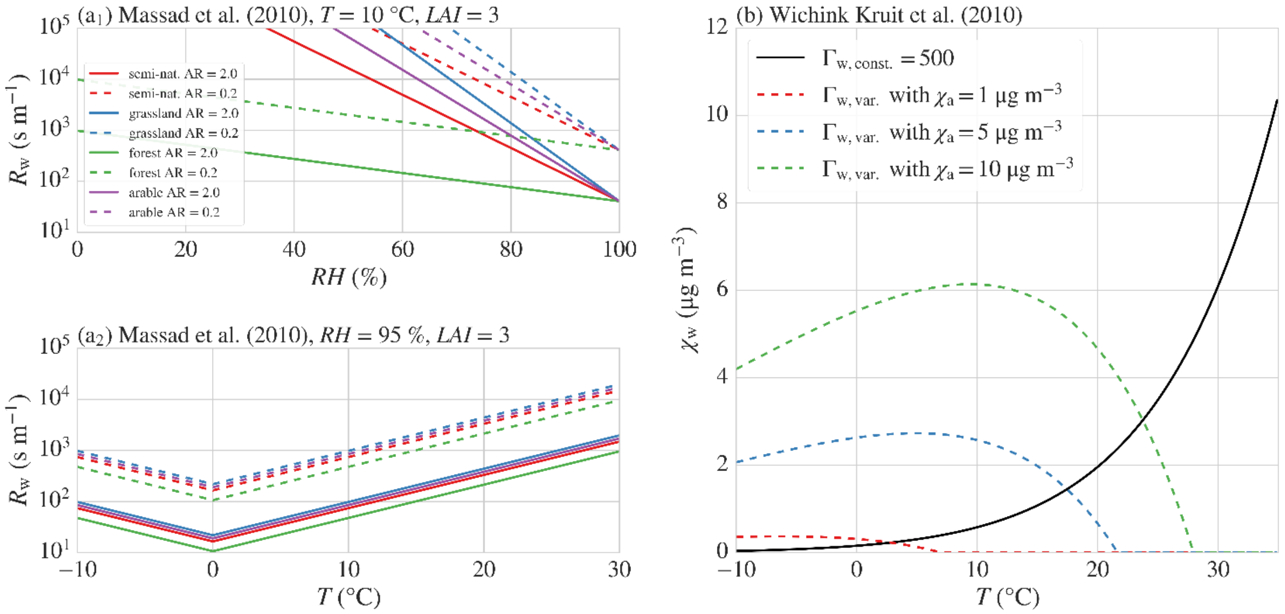

Figure 2: Theoretical considerations about the non-stomatal resistance parameterizations' response to changes in micrometeorological conditions. (a) Non-stomatal resistance (R_w) as a function of (a_1) relative humidity (*RH*) and (a_2) temperature (*T*) for different ecosystems and pollution climates according to the Massad et al. (2010) parameterization. (b) Non-stomatal compensation point (χ_w) as a function of air ammonia concentration (χ_a) and temperature (*T*) in the Wichink Kruit et al. (2010) parameterization.

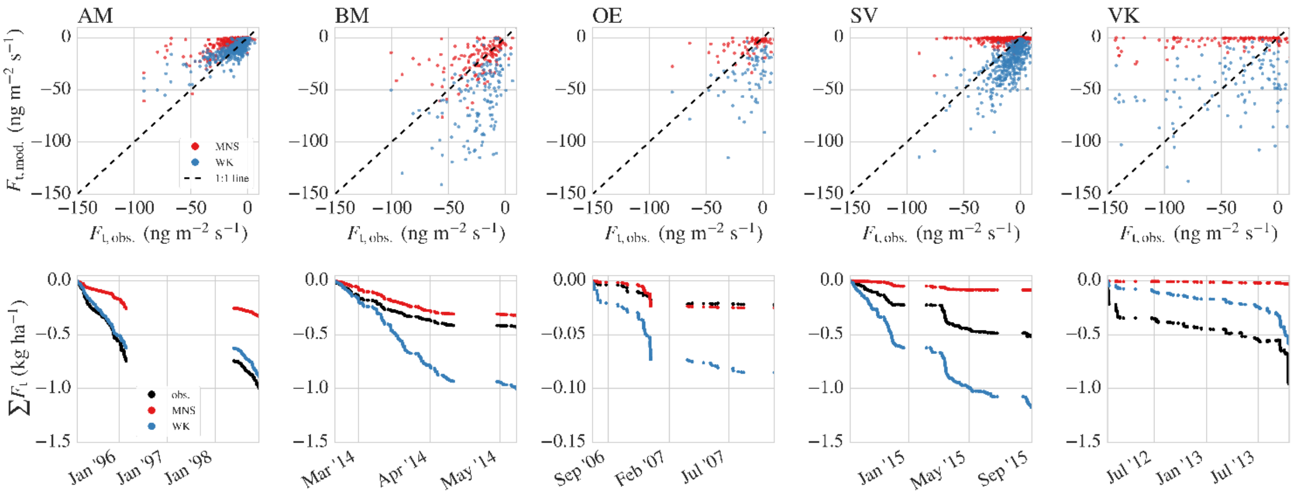

Figure 3: Measured and modeled ammonia dry deposition fluxes (F_t) during near-neutral or slightly stable nighttime conditions. Upper row: Modeled vs. measured 6 h median flux densities. Lower row: Cumulative fluxes. obs. = observations; MNS = Massad et al. (2010); WK = Wichink Kruit et al. (2010). Refer to the text for site descriptors. Note the different scaling of the axes.

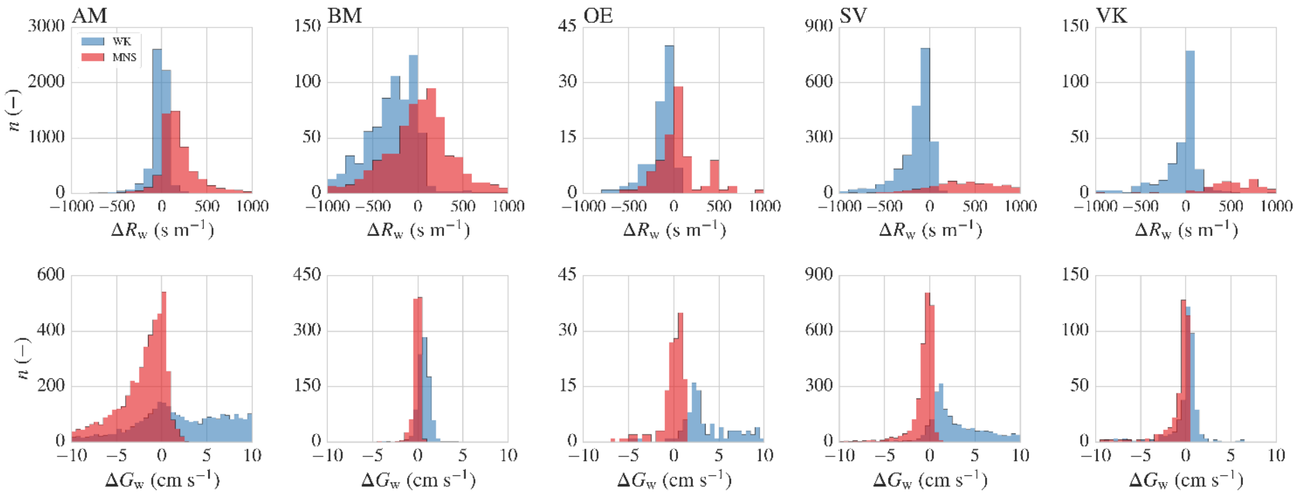

Figure 4: Differences in measured and modeled 30 min nighttime non-stomatal resistances (R_w, upper row, 100 s m^{-1} bins) and conductances (G_w, lower row, 0.5 cm s^{-1} bins). $\Delta R_\mathrm{w} = R_\mathrm{w,modeled} - R_\mathrm{w,observed}$ and $\Delta G_\mathrm{w} = G_\mathrm{w,modeled} - G_\mathrm{w,observed}$, i.e. positive values indicate an overestimation and negative values indicate an underestimation by the models. Note that an overestimation of R_w leads to an underestimation of fluxes F_t, whereas an overestimation of G_w leads to an overestimation of F_t.

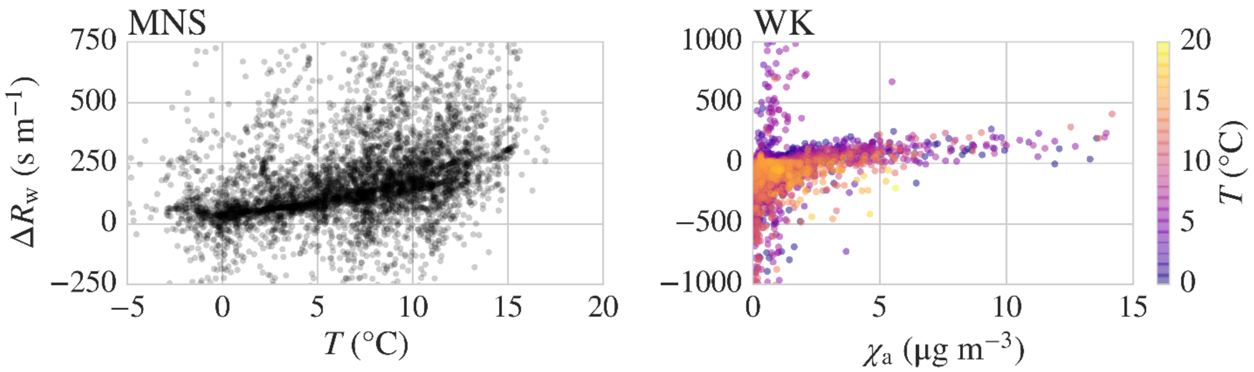

Figure 5: Differences between modeled and measured 30 min nighttime non-stomatal resistances (ΔR_w) as a function of T and/or χ_a. Left panel: Increasing mismatch of measured and modeled R_w in the MNS model due to a too strong T response. The line-shaped pattern emerges from times when observed R_w is zero and is equal in magnitude to the minimum allowed R_w in the parameterization. Right panel: The WK model reveals a tendency for both stronger over- and underestimation of observed R_w with increasing χ_a, where overestimation occurs more frequently during colder and underestimation during warmer conditions.

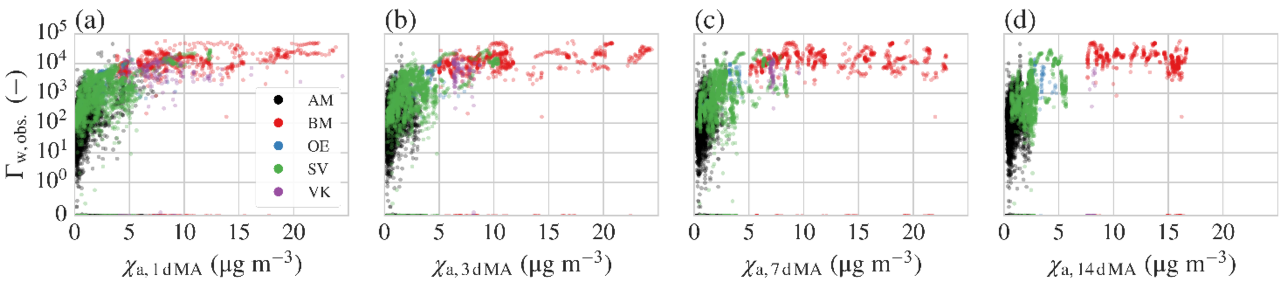

Figure 6: Non-stomatal emission potentials inferred from measurements (Γ_w) as a function of backward-looking moving averages of measured air ammonia concentrations (χ_a). (a) 1 day, (b) 3 day, (c) 7 day, (d) 14 day moving window. Periods with substantial precipitation were removed from the analysis.

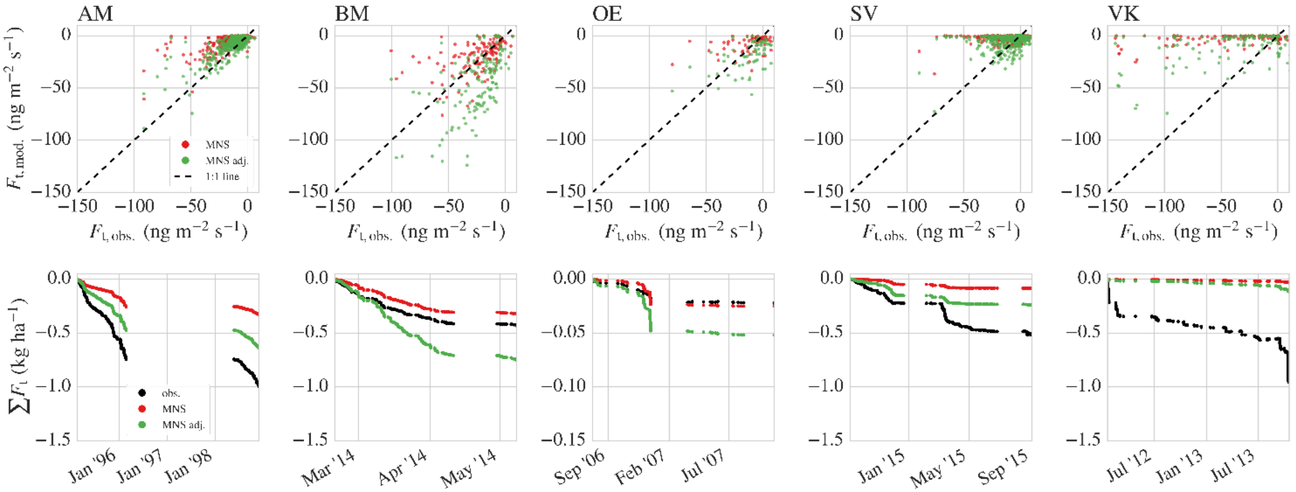

Figure 7: Measured and modeled ammonia dry deposition fluxes (F_t) during near-neutral or slightly stable nighttime conditions. Upper row: Modeled vs. measured 6 h median flux densities. Lower row: Cumulative fluxes. MNS adj. = MNS with halved minimum R_w and temperature response parameter β.

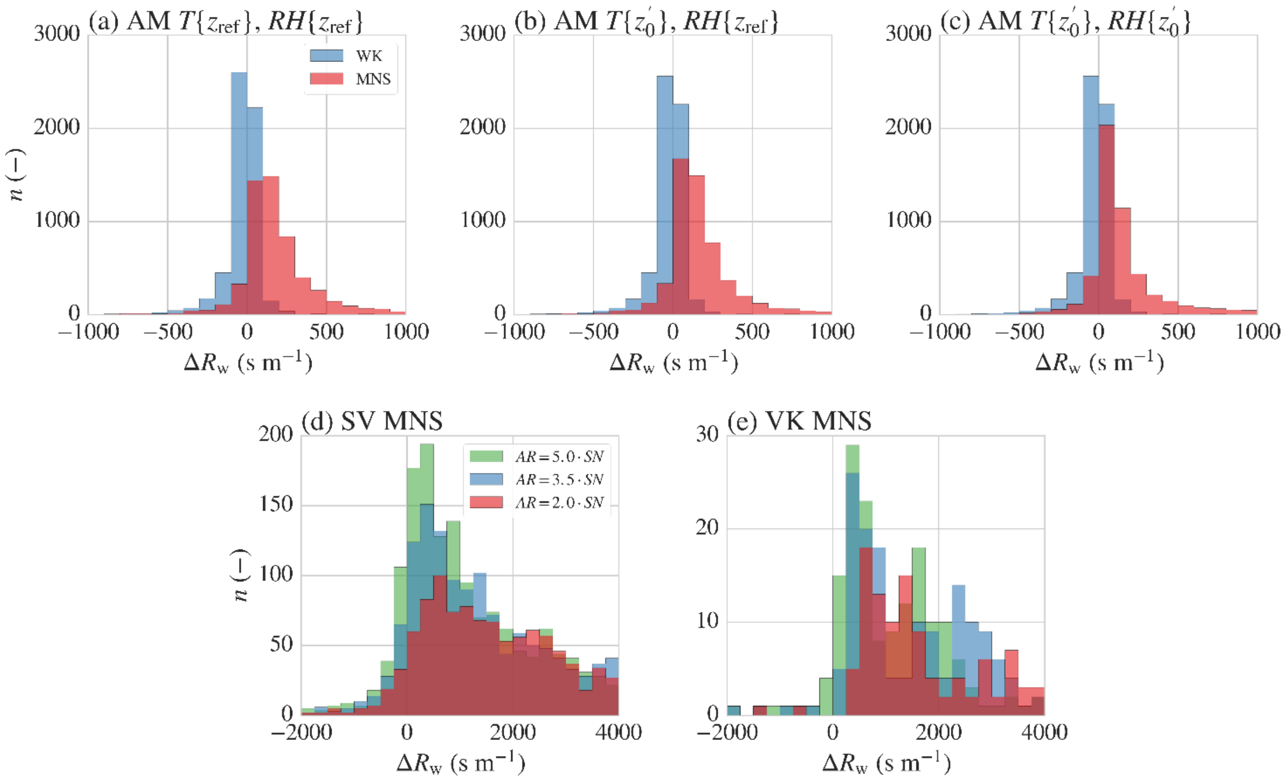

Figure 8: Sensitivity of differences in measured and modeled non-stomatal resistances to the use of measured air vs. surface temperature and relative humidity estimates. Upper row: Exemplary calculations for AM with (a) *T* and *RH* at the reference height, (b) *T* at the notional height of trace gas exchange (z_0'), and (c) *T* and *RH* at z_0'. Lower row: AR estimated as 2.0, 3.5 and 5.0 times the [SO_2]/[NH_3] ratio SN for (d) Solleveld and (e) Veenkampen. Note the asymmetric horizontal axis in (d) and (e). Data are binned into 100 s m^{-1} bins for (a-c) and 250 s m^{-1} bins for (d-e) to ensure visual clarity.