Response to the comments of reviewers #3 and #4: Deposition velocity concept does not apply to fluxes of ambient aerosols

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We thank both reviewers and Editor for their constructive comments. Below we address the comments point-by-point.

1 Detailed response to anonymous Referee #3

1.1 Overview

The manuscript "Deposition velocity concept does not apply to fluxes of ambient aerosol" has been submitted to the journal GMD. In general, the manuscript argues that the near-surface aerosol loss process is not related to deposition velocity (Vd), but that chemical decomposition is the primary concern. The present result showed that the Vd/flux/concentration of NH4NO3 was not consistent with those of NH3 and HNO3, particularly near the surface, which is inspiring and highlights the research gap and the challenges encountered in deposition velocity.

Thank you.

The identified gap is, indeed, a lack of the experimental datasets with confirmed proportionality between flux and concentration (in some specific range of conditions). Such datasets could serve as an experimental ground for V_d parameterisation. A corresponding paragraph has been added in Sec 5.4.

1.2 Major concerns

The reviewer has several major concerns

(1) I am not sure if there is any difference between the Vd mechanism in both the model and measurement (Eq. (1) and Eq. (2) in the manuscript). However, Eq. (2) mentioned in the present manuscript is defined assuming there is only one particular surface type.

Strictly speaking, the definition (2) is applicable to a specific observed pair of flux and concentration values.

To make it equivalent to (1) one has to assume the proportionality between flux and concentrations for each specific set of conditions and that the coefficient of proportionality will be the same for all measurements (if one neglects measurement errors).

The corresponding note has been added to the end of Sec 5.4

In fact, Eq. (1) adopts Vd at different surface types represented by vegetation height or surface roughness length. For instance, the grassland/forest/water surface layer has different surface roughness lengths, which can lead to different Vd levels, particularly during long-range transport, resulting in different aerosol and gas concentrations. The results from Fig. 2 were estimated from a forest site in the Netherlands. Could a similar result be duplicated over other surface types?

There seems to be a misunderstanding: V_d is a function of flow, surface, and particle properties as defined in Eq. (1), but it must be independent of aerosol concentrations. In the paper we argue that in a general case (i.e. when non-inert aerosols are present), the flux is not proportional to the concentration of ambient aerosol, which renders measured ratios between concentration and flux basically meaningless, unless the proportionality has been explicitly verified. Similar simulations could certainly be made for other field experiments, it will not change anything: whatever surface type is the near-surface gas-particle partitioning will remain the problem.

(2) NH4NO3 is the major contribution of PM2.5. What about other PM2.5 species such as BC, SO4, dust . . . ? Have you considered other non-volatile compounds and coarse particles to prove non-relation between Vd and the flux? Or the entire manuscript content might not closely align with the title.

As stated in the discussion (section 5.5), the mere *presence* of NH4NO3 in the ambient aerosol is sufficient to break the proportionality between the flux and the concentration of aerosol. Basically, our study shows, by using NH4NO3 as an example, that the process [non-inert aerosol -> conversion to gas -> deposition of the gas] can correspond to a significant net downward flux of aerosol even when the concentration of the non-inert aerosol remains small or seemingly negligible. Figure 5 illustrates that it happens often enough (even when only NH4NO3 is considered and all other non-inert aerosols are ignored) to make the assumption of proportionality invalid for practical use. The section 5.4 suggests a method to check its validity.

If one observes a flux of some specific non-volatile aerosol compound e.g. SO4 as in (Wesely et al., 1985), the deposition velocity could be applied, but a check for proportionality would bring additional confidence. Even in that case the aerosol processes near the surface, such as coating with semi-volatile compounds, could affect the deposition, so the resulting velocity has to be attributed to the right size range, which might differ from the one measured aloft.

(3) I agree that the formulation through wind tunnel studies is not guaranteed for ambient particles in outdoor experiments. Hence, robust observations are vital for model validation. It is suggested to conduct a thorough model comparison with ground observation station data, particularly over a longer period.

Thank you for the suggestion.

The manuscript never said that *formulation* is not guaranteed. We rather show that *proportionality* between flux and concentration is not guaranteed and often violated for ambient particles. Evaluation of a model against particle flux measurements would be an interesting study that deserves a separate paper, and we would be happy to contribute if someone organizes it.

Unfortunately, many experimental studies, instead of reporting fluxes and concentrations separately, report only apparent velocity V_{da}, which makes a quantitative evaluation difficult due to the nature of error propagation through ratios. Therefore, one has to make a qualitative comparison, similar to the one shown in Fig 1. Its purpose is to illustrate the problem and a way to resolve it, whereas the rigorous evaluation of specific models has to be made in dedicated campaigns in the future.

2 Detailed response to anonymous Referee #4

This manuscript addresses the importance of the semivolatile compounds in the determination of apparent deposition fluxes of particles. The authors propose to reconcile the discrepancies between laboratory studies and field studies by considering the importance of ammonium nitrate decomposition during the deposition process. The manuscript is well written, clear and addresses an important problem, especially for the development of chemical transport models for which using relevant parameterizations is critical. I agree with the necessity to account for the gas/particle partitioning during the deposition process. The introduction is especially well written and reintroduced the problematic. I think the manuscript is suitable for publication in GMD and I do not have major comment. I suggest a few modifications to improve the quality of the manuscript.

Thank you!

2.1 Comments:

1. I was a bit puzzled at first by the title “Deposition velocity concept does not apply to fluxes of ambient aerosols”. The title seems to indicate that the “deposition velocities” cannot be applied to particles. However, the authors show that this concept can be interpreted in different ways (Eq. 1 or 2) and states that “The concept of deposition velocity (in a sense of Eq. 1) can reduce the complexity of dry deposition schemes in models. However, it should be accompanied with phase conversion calculations to make the scheme applicable under ambient conditions, where semi-volatile species break the aerosol mass conservation, and where the observed vertical fluxes cannot”. I therefore understand that the concept can be applied if the gas-particle partitioning is properly represented. However, it cannot be applied to measure the effective deposition velocities. If possible, I suggest finding a title that reflects this subtility.

Thank you! We adjusted the title, which now says "ambient aerosol", i.e., directly referring to the ambient aerosol in-bulk. We also reformulated the abstract to highlight this detail.

2. “Non-conservative substance” felt weird in the abstract. I understood after reading the study that the authors “non-conservative” means here that due to gas-particle that the whole particle is not conserved and that part of it may evaporate. I would suggest giving a rapid explanation of what non-conservative refers to in the abstract and the first time this notion is employed.

We reformulated the abstract to avoid the confusing statement.

3. P4, l115: “bi-directional gas-particle partitioning” I would remove bi-directional that may be confusing. I think it refers to the partitioning (that implies that there is evaporation and condensation) and not to a bi-directional deposition/emission flux.

Thank you! Corrected.

4. P4, l116: "NH4NO3 is formed when NH3 and HNO3 are in abundance, and it decomposes back to the gaseous constituents when the product of their partial pressures drops below a t emperature-dependent threshold (Mozurkewich, 1993)." Only temperature is mentioned. Is the effect of relative humidity not accounted for in SILAM?

Yes. Clarification added.

5. P5, l145-148: "we have performed a series of the simulations". Replace "a series of the simulations" by "a series of simulations".

Fixed.

6. A short summary of the parameterizations of Kouznetsov and Sofiev (2012) in the method section could be useful to better understand the study.

We have added a paragraph describing the scheme.

7. P6, l182. I think the term "partitioning" is better than "fractionation"

Fixed.

8. P12, l303: "One of plausible explanations" -> "one plausible explanation"

Fixed.

9. In the conclusions, it would be nice if the authors could provide additional recommendations on the use of deposition parameterization in 3D models. If the authors recommend not to use parameterizations derived from apparent measurements of deposition fluxes in field experiments, it should appear in the conclusions (along with a list of widely used parameterizations that cause problems).

We have added a paragraph that explicitly lists a few well-known publications on the schemes fitted to outdoor observations of apparent deposition velocities. It also summarizes the Recommendations section. Thank you for pointing out this omission.

3 Editor's comments

I now have another set of reviews for your article but again they give opposing reviews, with one requesting a major revision. Can you respond to the comments of both referee's after which I need to look at the amended manuscript. I think that one referee does have a point regarding the ambiguity of your title in that you refer solely to 'ambient aerosols' and not the chemical precursors which form such aerosols, where the referee also highlights "The paper highlights the concern with chemical decomposition rather than particle deposition, offering a different perspective from previous studies." I am not sure this is true but you need to change the title such that is reads "... due to inadequacies in simulating gas-aerosol partitioning." or something similar.

Thank you for your suggestion. We amended the title to correct the ambiguity pointed out by the reviewer: "ambient aerosol" (a mixture of volatile and non-volatile compounds) rather than "ambient aerosols" (all aerosol components). The message of the paper is that the concept postulates proportionality, which does not hold for ambient aerosol mixture, and therefore is inapplicable. Indeed, even with perfectly simulated partitioning, the dry deposition velocity concept still cannot be applied to the aerosol mixture as a bulk.

In both critical reviews provided thus far (both suggesting a major revision) there is an issue of confusion regarding the definition of Vd between model and measurement which indicates a more definitive and/or clear response on this is necessary.

This is, indeed, a complicated part. We have amended the text near equations 1 and 2 trying to make it more transparent for readers. However, we also tried not to lose what reviewer #4 supported in the introduction as "especially well written".

The second round of reviewers are different from the first due to a lack of response to a request as to whether your changes you made to the first submission were acceptable and addressed concerns.

We now tried to address the critical comments more precisely.

4 Concluding remarks

In the end we would like to thank Editor and all reviewers for the comments. We hope that the revised manuscript can be accepted for publication in GMD.

References

Wesely, M. L., Cook, D. R., Hart, R. L., and Speer, R. E.: Measurements and Parameterization of Particulate Sulfur Dry Deposition over Grass, J. Geophys. Res., 90, 2131–2143, https://doi.org/10.1029/JD090iD01p02131, 1985.