Review of "Estimating agricultural ammonia volatilization over Europe using satellite observations and simulation data

Summary

This paper sets ambitious goals: to estimate current ammonia volatilization over Europe from satellite data and to predict how it will change as Europe warms. These are interesting ideas, that could potentially provide useful data to the air quality community, due the strong connection between ammonia concentrations and PM2.5 amounts. However, given the many uncertainties in the calculation of the soil emission potential (such as the mass transfer coefficient), the work in this paper is more of a roadmap on how this might be done rather than a set of reliable estimates. Nevertheless, it is still a valuable paper for the community, as it demonstrates the methods and the types of datasets that are needed to achieve its stated goal.

The paper is overall well organized, though a few sections are confusing and need rewriting. Once the suggested revisions are made, the paper should be accepted for publishing.

Technical comments

Section 3.1:
The authors attribute some of the difference between IASI and GEOS-Chem to different sampling times: IASI only measures NH3 at 9:30 am, while the GEOS-Chem output was averaged over an entire month. Wouldn't it be possible to eliminate this disparity by sampling GEOS-Chem only at 9:30 am? Please explain why this was not done.

For the comparison of IASI and GEOS-Chem data, we rerun the same simulation with hourly output and used the GEOS-Chem output between 8:30 and 11:30 UTC, which corresponds to IASI's crossing time above Europe (and what was done in other studies e.g. Viatte et al., 2022). Therefore, the GEOS-Chem data in the latest version of the paper, are spatially and temporally coincident with those IASI measurements. We added the following text (shown below in bold) in the first paragraph of section 3.1 in the manuscript:

"**We compare those to the IASI total columns of ammonia gridded on the same horizontal resolution (0.5° × 0.625°) and over the same month. We applied spatial and temporal coincidence criteria to GEOS-Chem outputs in order to compare them with IASI morning**

observations. For this, we selected data between 8:30 and 11:30 UTC in the GEOS-Chem model output and only considered grid cells where IASI have observations."

Review Figure 1 shows the difference between NH_3 total columns from IASI and GEOS-Chem, during March 2011 in the regions of study. We compare NH_3 total columns from GEOS-Chem where only morning outputs are considered, those range from 8:30 until 11:30 UTC (GC - Morning), and where all hours of the day are averaged to calculate a monthly average of March 2011 (GC - Day), and finally IASI morning measurements are equally shown. If we compare NH_3 from GC – Morning to NH_3 from GC – Day, we can see that the difference is negligible. Most of the NH_3 is generated during the morning hours, and not throughout the whole day, therefore, using GC – Morning or GC – Day, should not make a remarkable difference in the analysis of the results. But, GC – Morning was used since it makes more sense to compare it to IASI morning NH_3 measurements. As such all of the related figures in the manuscript are now updated.
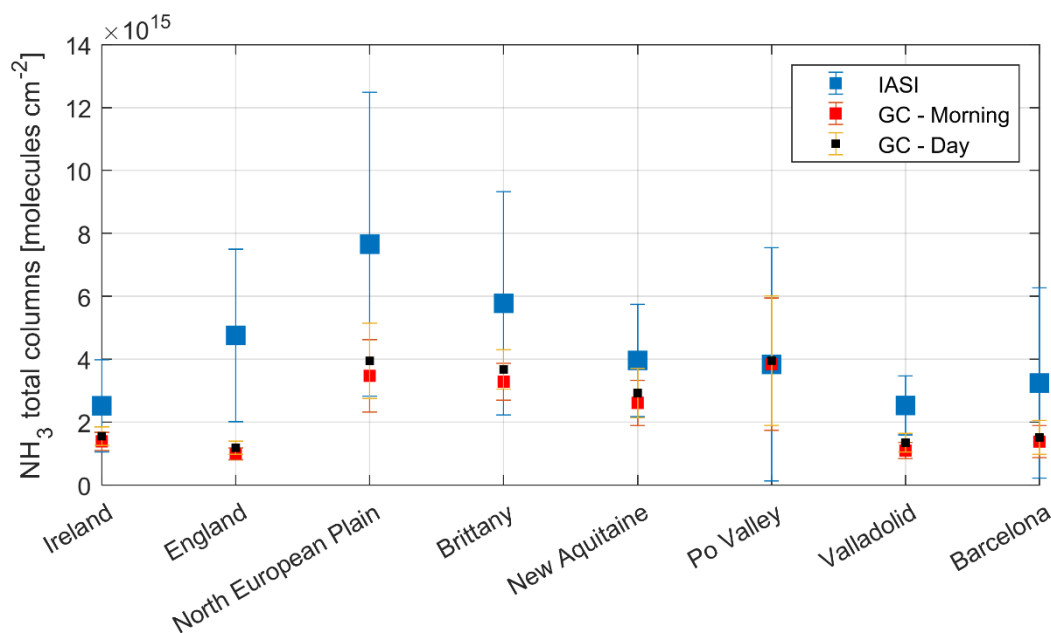
Review Figure 1. NH_3 total columns from IASI and GEOS-Chem, during March 2011 in the regions of study. Blue: IASI NH_3 total columns, red: GEOS-Chem (GC) morning average (8:30 to 11:30 UTC), and black: GEOS-Chem daily average (all hours of the day), with the corresponding standard deviation of each as lines.

Section 3.2:
The authors state that the ammonia lifetime in New Aquitaine is high due to air stagnation. Why is this region prone to stagnation in March?

New Aquitaine is located in Central Europe, this is where the highest number of stagnant days is observed during the spring season (Garrido-Perez et al., 2018). We added this information to the manuscript, now the sentence reads as: "The latter can be related to the high

probability of air stagnation is in that area, especially during spring, in comparison to Northern Europe (Garrido-Perez et al., 2018) […].”

I do not think the authors should state that the GEOS-Chem lifetime estimates agree with the Evangeliou results, since the former range from 1 to 13 hours and the latter from 10 to 13. Please rewrite this statement.

We edited the sentence, now it reads as: “Our results agree with the literature suggesting a residence time between a few hours to a few days (Behera et al., 2013; Pinder et al., 2008). We note that Evangeliou et al. (2021) estimated the lifetime of ammonia over Europe using a different model and the results showed a monthly average ranging from 10 to 13 hours.”

Can the authors explain why the loss to transport in England is lower than in Ireland, even though it is also affected by the Gulf Stream?

Although the gulf stream affects the loss to transport in England, the chemical loss is the dominant one. Acids, such as (HNO_3) and (H_2SO_4), in the atmosphere will react with ammonia (NH_3) since the latter is an alkaline (basic) gas. Therefore, high atmospheric concentrations of NO_2 and SO_2 (from which HNO_3 and H_2SO_4 are derived respectively), induce higher loss of ammonia to chemical reactions. In England, the annual concentration mean of both NO_2 and SO_2 are higher than in Ireland (https://www.eea.europa.eu/themes/air/interactive/no2, https://www.eea.europa.eu/themes/air/interactive/so2). This can explain why the largest proportion of NH_3 is lost to chemistry in England, in spite of the effect of the gulf stream.

We added the following text to the manuscript: “Although the gulf stream also affects the loss to transport in England (region B), the chemical loss is the dominant one. Acids, such as HNO_3 and H_2SO_4 react with ammonia in the atmosphere. Therefore, high atmospheric concentrations of NO_2 and SO_2 (from which HNO_3 and H_2SO_4 are derived respectively), induce higher loss of ammonia to chemical reactions. In England, the annual concentration mean of both NO_2 and SO_2 are higher than in Ireland (European Environment Agency, 2017a, 2017b). This can explain why the largest proportion of NH_3 is lost to chemistry in England, in spite of the effect of the gulf stream.”

Section 4
The text between lines 369 and 390 is extremely confusing, in part because **Figure 5 is referenced before the differences between the four plots are explained.** The calculation of the fixed k is also a bit hard to follow.

This section was re-organized. Now it reads as the following: “Figure 5 illustrates the ammonia soil emission potential Γ_{soil} calculated using Eq. (2-1) and k values presented in Figure 4. After assigning a variable mass transfer coefficient, the remaining variables needed to calculate Γ_{soil} in Eq. (2-1) are ammonia concentration and lifetime, as well as the skin

temperature. Therefore, the emission potential Γ_{soil} shown in Figure 5 is calculated using different configurations:

1- Case 1: GEOS-Chem ammonia and lifetime with MERRA-2 T skin, i.e. simulated Γ_{soil},
2- Case 2: GEOS-Chem ammonia and lifetime and ERA5 Tskin, to check the effect of using ERA5 vs MERRA-2 for skin temperature,
3- Case 3: IASI ammonia, ERA5 T skin and GEOS-Chem ammonia lifetime,
4- Case 4: IASI ammonia, ERA5 T skin and ammonia lifetime from Evangeliou et al. (2021), that were calculated using LMDz-OR-INCA chemistry transport model. The latter couples three models: The general circulation model GCM (LMDz) (Hourdin et al., 2006), the INteraction with Chemistry and Aerosols (INCA) (Folberth et al., 2006), and the land surface dynamical vegetation model (ORCHIDEE) (Krinner et al., 2005).

We show in supplementary material Figure S2, the emission potential (similarly to what we show in Figure 5) but from a fixed and averaged k value for all land types. Figure S2 shows the importance of using a variable k that is adjusted to each land type is depicted in supplementary materials (Figure S2). To calculated a fixed k (common to all land types) we assume 14 days of fertilization ($k = 10^{-3}$ m s^{-1}, e.g. croplands), 7 days when k value is reducing ($k = 10^{-5}$ m s^{-1}), and 10 days when k is low ($k = 10^{-6}$ m s^{-1}, e.g. forests) resulting in average of $k = 4.5 \times 10^{-4}$ m s^{-1}. The difference in the emission potential between fixed and spatially variable k is shown in supplementary material Figure S3, where we see that a fixed k might overestimate Γ_{soil} by 10 to 10^3 on a log10 scale (500 – 3000 %), in agricultural areas."

Finally, in the caption for figure S3 it is stated that cases 1, 2 and 3 have identical soil emission potential, which is not true, since case 3 uses IASI rather than GEOS-Chem NH$_3$. Please reorganize and rewrite this section and make it clearer.

Figure S3 shows the difference between using a fixed k value and a variable one. To calculate this difference, we use the following equation: $\frac{\Gamma_{fixed\ k} - \Gamma_{variable\ k}}{\Gamma_{variable\ k}} \times 100$. Using this equation, all other parameters are cancelled out (including the NH$_3$ concentrations from IASI/GEOS-Chem), except for k and τ. The resulting equation is $(\frac{k_v \tau}{k\tau} - 1) \times 100$. Case 1, 2, and 3 use the same τ NH$_3$ lifetime from GEOS-Chem, and case 4 uses τ from Evangeliou et al. (2021). Therefore, the left panel of Figure S3 is not an average of case 1, 2, and 3, but rather the relative difference that is identical for all three cases.

The caption of Figure S3 was changed to: "Relative difference (%) of Γ_{soil} between using a fixed and a variable k value: $\frac{\Gamma_{fixed\ k} - \Gamma_{variable\ k}}{\Gamma_{variable\ k}} \times 100$. Using this equation, all other parameters are cancelled out (including the NH$_3$ concentrations from IASI/GEOS-Chem), except for k and τ. The resulting equation is $(\frac{k_v \tau}{k\tau} - 1) \times 100$. Case 1, 2, and 3 use the same τ

NH₃ lifetime from GEOS-Chem, and case 4 uses τ from Evangeliou et al. (2021). The left panel is the relative difference that is identical for cases 1, 2 and 3 since they use the same τ NH₃."

The comparison between the soil emission potential from **IASI and GEOS-Chem for the cases of England and the Po Valley uses percentages that are not consistent with the values listed in Table 1**. Please explain how they were calculated. And what are the three values of Tskin listed in Table 1?

The MRD shown in Table 1 is calculated in three main steps:

1- A spatial MRD$_{grid\_Europe}$ is calculated for Europe, resulting in what we see in Figure 1d. This is calculated following the equation: $MRD\ (\%) = \dfrac{(GeosChem\ NH_3 - IASI\ NH_3) \times 100}{IASI\ NH_3}$

2- To get an MRD for each of our regions (shown in rectangles in Figure 2a), we then extract the MRD based on longitude and latitude limits specific to each region of focus. The result is a grid of MRD$_{grid\_region}$ (e.g. MRD grid matrix for the Po Valley).

3- The MRD$_{grid\_region}$ is then averaged to give one value for the region of focus (e.g. Po Valley), and the result is shown in Table 1.

It is true that the values for England and the Po Valley do not reflect the difference between the concentrations of IASI and GEOS-Chem, shown equally in the Table 1. We calculated MRD in two additional different ways, and now the new values are more reasonable.

In Review Figure 2, we show on the left panel the NH₃ concentrations from GEOS-Chem (GC) and IASI, and on the right panel the MRD calculated in three different ways:

- In blue: "mean" MRD = the mean of MRD$_{grid\_region}$ (what is shown in Table 1 in the article).

- In red: "median" MRD = the median of MRD$_{grid\_region}$.

- For the third way (in black), we calculated the MRD using directly the averages of NH₃ for the whole region, these are the NH₃ concentration averages shown in Table 1 (e.g. 4.8×10^{15} molecules cm^{-1} for England). The equation is: "MRD$_d$" $= \dfrac{(mean\ GeosChem\ NH_3 - mean\ IASI\ NH_3) \times 100}{mean\ IASI\ NH_3}$.
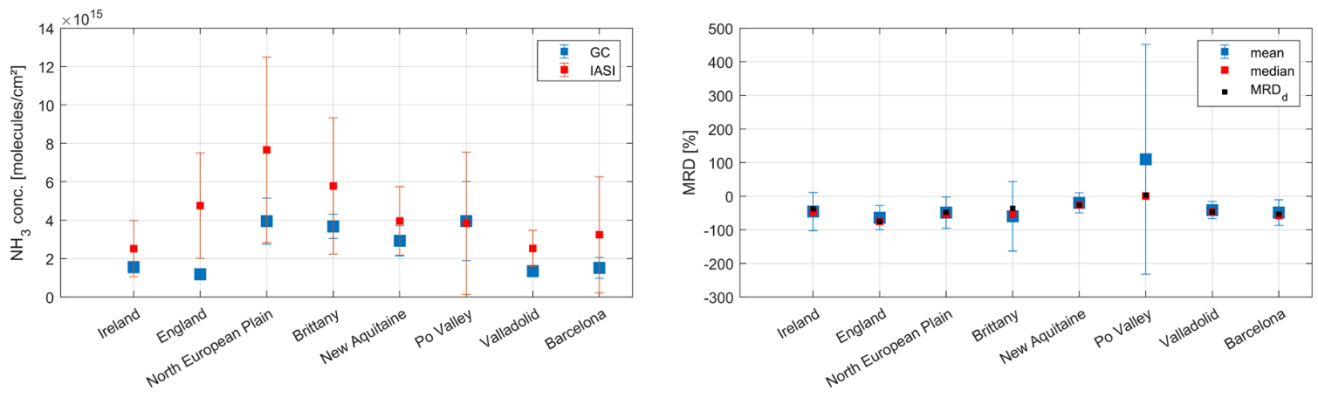
Review Figure 2. Left: NH$_3$ concentrations in the regions of focus from GEOS-Chem (GC) in blue and IASI in red, during March 2011. Right: the mean relative difference MRD [%] as a mean (blue), median (red), and direct MRD$_d$ (black, refer to the text for the details of calculation).

The standard deviation on the mean of MRD shown in blue is greater than 400 % (Review Figure 2, right), therefore it is better to use the median (red) or MRD$_d$ (black) in this case. This huge difference is only seen in the region covering the Alps mountains, where we observe high differences of T skin from MERRA-2 and ERA5. We replaced the MRD values in Table 1 by the median to address this issue.

Table 1. Summary of ammonia average lifetime, emission potential, concentrations and the T skin in selected regions in Europe.

Region	Country	τ_{NH_3} [hours]	T skin [°C]		$\Gamma_{soil} \times 10^4$ [dimensionless]				NH$_3$ concentrations [molecules $\times 10^{15}$ cm^{-2}]		
			ERA5 9:30 UTC	MERRA-2 8:00 to 10:00 UTC	Case 1	Case 2	Case 3	Case 4	IASI	GEOS-Chem	Mean MRD [%]
Ireland	Ireland	3.34	8.74	6.23	0.72	0.44	0.94	0.26	2.5	1.4	− 45
England	England	3.15	8.54	5.73	0.63	0.44	2.06	0.58	4.7	1	− 79.2
North European Plain	Belgium, Netherlands	5.16	7.46	4.57	1.22	0.95	2.51	1.00	7.6	3.5	− 55
Brittany	France	6.93	10.48	8.16	0.98	0.66	1.48	0.70	5.8	3.2	− 43.2
New Aquitaine	France	8.05	11.25	7.47	0.46	0.32	0.49	0.30	4.0	2.6	− 34.1
Po Valley	Italy	7.10	8.95	5.46	0.90	0.86	0.89	0.40	4.0	3.8	+ 0.1
Valladolid	Spain	4.53	11.64	6.93	0.46	0.25	0.62	0.20	2.5	1.1	− 57
Barcelona	Spain	4.94	12.61	9.44	0.31	0.25	0.65	0.28	3.2	1.4	− 57.5

The discussion of Figure 6 (lines 435 to 448) mentions the average temperature and states that in the Po Valley Tskin from ERA5 is twice as high as this average temperature. **Why is this relevant? Don't cases 1, 2 and 3 use very similar temperatures (ERA-5 or MERRA)?** There is no mention of average temperature in description of the cases. Please explain.

In the updated version of the manuscript we use NH$_3$ hourly concentrations from GEOS-Chem (8:30 to 11:30 UTC). Therefore, to calculate Γ_{soil} from IASI NH$_3$ (case 3 and 4) and GEOS-Chem (case 2), we use T skin from ERA5 that coincides with the overpass of IASI. The new values for Γ_{soil} for cases 1, 2 and 3 compare well in the Po Valley (see Table 1 in the previous answer).

We added the following sentence to highlight this result: "Figure 6 also shows that for cases 1 and 2 (GEOS-Chem) the emission potential in the Po Valley is almost equal to case 3 (IASI), with Γ_{soil} = 0.9 and 0.86 × 10^4 in cases 1 and 2, and 0.89 × 10^4 in case 3 (see Table 1)."

And we added further explanation to the manuscript t: "To calculate Γ_{soil} from IASI NH$_3$ (case 3 and 4), we used T skin from ERA5 that coincides with the overpass of IASI. We used the same T skin values from ERA5 for case 2, in which we use NH$_3$ hourly concentrations from GEOS-Chem (8:30 to 11:30 UTC). The ERA5 T skin are shown in Table 1."

The statement that the inter-variability between the cases does not depend on the lifetime does not seem to be true. Maybe which inter-variability needs to be defined?

This statement was removed.

Section 5

On line 472 the author state that current and future ammonia columns are calculated assuming that the emission potential is unchanged. If the whole point of the future climate modelling exercise is to look at effect of changing temperature on the volatilization of ammonia, and the emission potential is strongly dependent on temperature, this sentence does not make sense.

The Γ_{soil} we calculated in this study (cases 1 to 4) is directly proportional to the soil content of NH$_4^+$. Although, we did not need the concentration of NH$_4^+$ in order to calculate it, the result reflects the amount of fertilizers added (that release NH$_4^+$ from which NH$_3$ is evaporated). Therefore, the statement "the emission potential is unchanged" is not accurate. We change it to "the fertilizer application rate is unchanged", which results in the same soil content of NH$_4^+$.

We changed the title of Section 5, from "**Ammonia under future scenarios**" to "**The effect of temperature change on the volatilization of ammonia**". To better reflect the motives of the work done in Section 5.

Appendix

The referencing of multiple equations in the appendix was wrong. I have corrected them, but please check and make sure my changes make sense. Finally, please also confirm that the

calculation of the first constant in (A-9) (2.75e9) is correct. I was unable to reproduce this value, but that could be an error at my end.

We went through the calculation again, we confirm that this constant is correct. This equation is adapted from Wichink Kruit's PhD thesis (2010), equation A1.4, on p.166.

Minor edits

All the minor comments listed below were addressed one by one. The comments that needed an explanation are also answered below (in blue).

Line 42: … amounted to

Line 43: …a very reactive base, and constitutes …

Line 47: … total ammonia gas is believed …

Line 60: … as shown in the Appendix.

Line 61: …of ammonia in the water in the soil is a function of soil acidity (pH) and temperature...

Line 62: …and controlled by the dissociation …

Line 63: …exists in the gas phase, and therefore Henry's law can be used to describe ….

Line 84: …during the 2003-2019 period …

Line 85: …(2022), leading to increased volatilized ammonia, (due to increase in both nitrogen…

Line 87/88: … Between the years 2008 and 2018, the … columns is estimated to be …

Line 107: … ammonia to provide regional …

Line 116: where

Line 120: …c' is 100

Line 123: … It is a function of the roughness length …

Line 125: The sentence starting with "It can be explained by …" is unclear. Are the authors stating that a resistance model is used to calculate k?

The sentence was changed to clarify the meaning: "It can also be calculated using a resistance model, often used to explain the exchange between the surface and the atmosphere (Wentworth et al., 2014)".

Line 177: … in areas where fertilizers are applied.

Show the emission potential where?

The sentence was changed to clarify the meaning: In addition to croplands, in this study we show the emission potential in forests and grasslands/shrublands for comparison with values in the literature.

Line 204 : … we use the ECMWF European Earth Consortium climate model …

Lines 216-219:… two scenarios: the SSPP2-4.5, a "middle of the road" socio-economic scenario with a nominal 4.5W/m2 radiative forcing level by 2100, similar to the RCP-4.5 scenario, and

the SSP5-8.5, the upper edge of the SSP scenario spectrum with a high fossil-fuel development use the 21st century.

Line 238: …2011), which marks …

Lines 239-240: …The differences are likely due to sampling issues: only cloud-free data are used to retrieve ammonia and different sampling times: IASI ….

Line 248: … Therefore, assuming that meteorological …

The sentence was changed to: "Therefore, assuming that meteorological and soil parameters affecting one dataset (e.g. IASI NH_3) are applicable to the other (e.g. model simulation), this is known as the steady-state approximation."

Line 259: What does [not shown here] mean?

It means that we do not show it in this study, but we did the work.

Line 275: The lifetime of ammonia () is shown in Figure 2d.

Line 285: … air stagnation in that area

Line 287: … and (AQEG, 2012), and these PM2.5 particles can dissociate, releasing ammonia

Line 295: … considered the loss …

Line 296: adopted here …

Line 333: … literature. Note that ammonia transfer coefficients are not available for all land types.

Line 335: … in grey in Figure 4

Line 336: … and swine manure, therefore, this value was assigned to croplands…

Line 343: The sentence starting with "These values" should maybe be rewritten as :

These values obtained by using MODIS land cover types and published estimates of k values represent our best effort to realistic mass transfer coefficients, and therefore realistic soil emission potentials.

Line 348: Are the authors extrapolating or aggregating by averaging over each GEOS-Chem grid box? Please make this clear.

We are aggregating several k values and averaging them to match the resolution of GEOS-Chem. We changed the sentence in the manuscript as follows: "We then extrapolate aggregate the array with the k values from 500 m × 500 m to the resolution of GEOS-Chem (0.5° × 0.625° grid box)."

Lines 357-358: Maybe rewrite as: The k value assigned for forests represents the SO2 exchange in high croplands; this value may be very different for ammonia, since NH3 can easily dissolve in the water film on leaves under conditions of high humidity.

Lines 360-363: Again I think the authors mean aggregate not extrapolate. Which several grids?

Isn't the MODIS grid just being aggregated to the GEOS-Chem grid?

The sentence is changed to clarify. Now it reads as: "While changing the resolution of a fine array (500 m × 500 m), several grid points are merged and averaged together in order to construct the coarser grid box (0.5° × 0.625°); the result is therefore an average that might mix croplands with neighboring forests/barelands/grasslands. This leads to a range of different k values that are shown on Figure 4."

Line 365: Using a land type …
Line 392: What is the sentence starting with "Based upon …" supposed to convey?
This sentence was removed.

Line 399: … The emission potential does not agree in value with that of GEOS-Chem
The sentence was changed to: "In case 3, the emission potential agrees spatially with that of GEOS-Chem".

Line 407: … England, northern France, northeastern Spain and Poland….
Line 412: …potential with values ranging from ….
Line 413: Are croplands different from agricultural lands? If not, the sentence starting with "Our values" seems unnecessary.
Yes. This sentence was removed.

Lines 420-423: In this study, lower values than those measured in the field are expected. Therefore, we consider our results to be in good agreement with the values in Personne et al. (2015), since ours reflect a 31 day mean of an average of over a large area (55x70 km2).
Line 433: …soil content of …
Caption of Figure 6: … are explained in the discussion on Figure 5.
Line 485: …more severe in eastern Europe ….
Line 487: …up to +50%...

Line 505: … facing big challenges in air (??) or downwind of large agricultural regions ….
Missing words were added to the sentence, now it reads as: "[…] Europe might be facing big challenges in air quality for regions nearby or downwind agricultural regions, since chemistry and atmospheric transport (Figure 3) drive the loss of ammonia during the growing season in this part of the world."

Line 512: …where there is no ammonia …
Appendix
Line 569: where HNH3 is Henry's constant, which can be …
Line 580: Substituting Eq.(A-7) into (A-8) we get:
Line 586: Since in …
Line 591: … where FluxNH3 …

Line 597: .. Eq. (A-11) can be written as ..

Line 603: … using Eq. (A-9) in (A-13) we get:

References

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Wichink Kruit, R. (2010). *Surface-atmosphere exchange of ammonia*.