

We would first like to thank referee C. Flechard for his very helpful comments, which we think have helped to improve the paper considerably. The comments from referee C. Flechard are in normal font, while the answers are in *italic*.

Reply to referee C. Flechard comments bgd-9-c2123-2012

General Comments

This paper addresses the issues of ammonia (NH₃) exchange modeling between the Earth's surface (including soils, vegetation, water bodies) and the atmosphere, and of how to deal with the bi-directional nature of the exchange, using the compensation point concept, within an atmospheric chemistry and transport model (CTM, here the LOTOS-EUROS model) at the regional (European) scale. The emphasis is placed on the implementation of a new surface/atmosphere scheme within the CTM, on the comparison of modeled concentrations with ground-based observations, and touching upon on sub-grid modeling issues. As such the paper certainly addresses relevant scientific questions within the scope of BG, even if some aspects might be more typically found in atmospheric journals. The regional-scale implementation of the compensation point approach for NH₃ is fairly novel in the CTM community, although by no means unique at the time of writing, and the comparison of the new model outputs with the older, deposition-only DEPAC version is well worthwhile. The paper is straightforward, well written and clearly structured.

The authors argue that accounting for the bi-directionality of NH₃ substantially improves the comparison with ground-based observations of NH₃, although concentrations in receptor (semi-natural) areas are slightly over-estimated while concentrations in emission (agricultural) areas are still underestimated. The inclusion of the compensation point approach in the CTM is undeniably mechanistically more realistic, but I am not entirely convinced that the measurement datasets used to validate the new approach are adequate or comprehensive enough to provide unequivocal evidence of a substantial improvement in modeled NH₃ at the European scale. The authors only use EMEP data (17 sites for NH₃), which are mostly located in North-Central Europe (with 12 sites in Germany, Denmark and Norway alone), which are expected to be biased upwards for NH₃ concentrations (cf section 2.4), and which mostly cover low- to medium-range concentration situations (16 sites out of 17 are under 2.5 µg/m³). The large emission areas (such as The Netherlands, Brittany or the Po Valley, see Fig. 3) are thus under-represented in the EMEP validation dataset, and the lone point above 8 µg/m³ in Fig. 6 drives the whole regression.

It is true that validation datasets are rare, but there exist additional, alternative NH₃ data at the European scale (55 sites) from the NitroEurope project (e.g. Flechard et al., ACP, 2011), which, being based on denuder techniques, do not suffer the potential filter ammonium nitrate evaporation bias of EMEP data, and which cover a wider range of concentrations, especially at the higher end of the concentration spectrum. There are also other data from national monitoring initiatives. The paper would greatly benefit from including such data for a more thorough and comprehensive testing of the model, not only for NH₃ but also for NH₄⁺.

A comparison with NH₃ observations from the NitroEurope network will be included and the EMEP network (Figure 6) will be combined with the NAQMN in the Netherlands (Figure 8) to obtain a wider range of concentrations.

A comparison of the model results with other components (like NH₄⁺) and models is beyond the scope of this paper and is foreseen in an upcoming ÉCLAIRE model comparison. Besides, in the current surface-atmosphere exchange module comparison, a comparison of the model results with NH₄⁺ concentrations is not very useful. Figure 13 shows that the differences in the NH₄⁺ concentrations due to the new surface-atmosphere exchange description are very small over land, where the measurement stations are located. Schaap et al. (2011) also showed that changes in NH₃ concentration do not lead to large differences in NH₄⁺ concentrations, as NH₃ is generally not the limiting component.

Specific comments

p4879, l25: "...bi-directional ammonia exchange with the surface can be simulated rather well nowadays...": this may be true at the field scale provided that model parameters are fitted to local flux observations, but more often than not these parameters are not suitable for other sites, as underlined by the authors. The empirical tuning that is required when dealing with new flux measurements shows that our mechanistic understanding is still far from complete. Perhaps the "rather well nowadays" is still a little too optimistic.

We agree with the referee that this might be too optimistic and changed the sentence in:

*"Although inferential models have shown that bi-directional ammonia exchange with the surface can be simulated rather well **at the field scale when using detailed parameter input and some empirical tuning**, the implementation of these parameterizations in CTMs is still difficult (Flechard et al. 2011)."*

p4880, l1-2: "... Especially the representation of the dependency on the pollution regime seems to be important...": this is true for non-stomatal uptake and also to some extent for the apoplastic ammonium content of semi-natural vegetation, but for NH₃ exchange over agricultural crops and (fertilised/grazed) grasslands it should be pointed out that the pollution regime is (much) less relevant than, say, the type of synthetic fertiliser (eg urea vs NH₄NO₃) applied, the type of organic manure, grazing intensity, soil microbial processes, litter decomposition. It is slightly misleading to suggest that, once generic relationships have been derived for stomatal compensation points and non-stomatal resistance (as in Wichink Kruit et al, AE, 2010), "...the new scheme is supposed to be widely applicable because it accounts for the local pollution climate...". There is also a great deal of variation and uncertainty in the soil and leaf litter source (or sink) strength in unfertilised as well as fertilised vegetation, not to mention the strong dynamics of NH₃ volatilisation from applied fertiliser or slurry.

Correct. Text was a little bit misleading. Text changed in:

Especially For the non-stomatal uptake and to some extent for the apoplastic ammonium content, the representation of the dependency on the pollution regime seems to be important (Nemitz et al.,

2001). Wichink Kruit et al. (2010) derived a generic model description for the surface-atmosphere exchange of ammonia for the non-stomatal and stomatal pathway based on the measurement campaigns used in above mentioned studies. This new scheme is supposed to be widely applicable because it accounts for the local pollution climate. Note that the mass balance of NH_3 and thus the local pollution regime over agricultural crops and fertilized/grazed grasslands is strongly determined by the emission of NH_3 , which is treated separately from the surface-atmosphere exchange between the vegetation and the atmosphere. Therefore, local variations in the type of synthetic fertilizer applied, e.g. urea vs. NH_4NO_3 , the type of organic manure, the dynamics of NH_3 volatilization from applied fertilizer or slurry, grazing intensity, soil microbial processes and litter decomposition all cause large uncertainties in the emission strength and consequently the mass balance over these vegetation types.

p4882, l15-16: "DEPAC3.11 assumes that ammonia is present in the vegetation, water surfaces and soils..." : in Wichink Kruit et al, AE, 2010, p947, there is "...no pathway for NH_3 exchange with soil in this model approach, because the canopy is assumed to cover the soil surface completely.", and the RIVM report by Van Zanten et al. (2010) indicates (p15) that "...For the soil compensation point not enough information is known to implement a parameterization, so this variable is currently set to zero. " The soil contribution to the source strength is therefore not accounted for in DEPAC 3.11, and the above sentence should be modified to reflect this, and it should be emphasized in "2.2.2 Description of the "DEPAC3.11" module", lest the text mislead the reader. Further, the argument of a complete soil cover by vegetation is not universally valid, and certainly not throughout the year.

True. Text is changed. Added "for the non-stomatal and stomatal pathway" to the first sentence of the paragraph and changed "assumes that ammonia is present" in "provides the possibility to account for ammonia that is present". In section 2.2.2 we added "The soil pathway is extended with a soil compensation point, χ_{soil} , while the original in-canopy resistance, R_{inc} , and soil resistance, R_{soil} , are maintained. As there is still a lot of uncertainty in the values for soil compensation points and to avoid double counting of emissions from the emission inventory, the soil compensation point is set to zero for the moment. Note that with this setting in 'DEPAC3.11' the soil pathway is effectively the same as in 'DEPACold'. 'DEPAC3.11' is however prepared for including the soil compensation point, although values for R_{soil} might need to be adapted then."

p4883, l27: "weakly dependent": eq. 9 of 2010 AE paper by Wichink Kruit et al indicates an exponential function of temperature, and thus a strong (not weak) temperature dependence related to the NH_3 Henry solubility and protonation constants.

Correct. There indeed is a strong temperature dependence in eq. 9. The sentence was intended to refer to eq. 13, but was formulated incorrect. We changed the sentence in: "The ratio between $[\text{NH}_4^+]$ and $[\text{H}^+]$ in the external leaf surface water, Γ_w , is further weakly dependent on temperature, which accounts for some seasonality."

p4884, l7-8: "...the mean ammonia concentration of the previous month is used as the long-term ammonia concentration...": how critical is the operational definition of the "long term" concentration? Could (should?) the mean (inter-) annual concentration used as a more stable, longer term concentration? Could this be tested in alternative sensitivity runs (requiring perhaps iterative runs to account for circularity between Γ_w and NH_3 concentration)? Importantly, were the parameterisations given in the 2010 AE paper by Wichink Kruit et al derived using the previous

month's concentration relative to the fluxes reported, or using an (inter-) annual mean NH₃ concentration? A discussion of the model sensitivity to this term would be helpful.

The mean concentration of the previous month was chosen as the long-term ammonia concentration because this timeframe corresponds best with the average timeframe of the measurement campaigns that were used to derive the relation for the Gamma_s values. Furthermore, we estimate the timeframe for plants to respond to elevated NH₃ concentrations is in the order of a few weeks to several months. We agree with the referee that further research on the dependency of Gamma_s vs. long-term concentration needs attention from both measurement as well as modeling perspective. Basically, the sensitivity of this relation to the long-term NH₃ concentration should be tested by using the measurement data and sites that were used to derive this relation, which is not available for most of the measurement sites. Furthermore, this is a complicated task, because the duration of measurement periods/campaigns is not equal in most cases. The model sensitivity of this function to long-term NH₃ concentration is shown in figure 19b of Van Zanten et al. (2010) and shows that a doubling of the long-term NH₃ concentration results in a twice as high Gamma_s value and consequently a twice as high stomatal compensation point. We changed the text in this paragraph to explain it a little bit more.

p4885, l7-8: Why is only the dry deposition term used to scale Gamma_w, and not the total wet+dry NH_x deposition, since the NH₄⁺ concentration in water is directly linked to total deposition?

This is a good and very useful comment. We agree with the referee that it is better to scale Gamma_{water} with the total deposition (and we will do that in future studies). However, the gradients of the wet deposition over sea are very similar to that of the dry deposition. This is likely due to the rather homogeneous precipitation amounts over sea and the strong coupling of the wet deposition to the concentration patterns, which match the dry deposition patterns. Therefore the pattern and magnitude of the Gamma_{water} values will be very similar in both cases, because they are scaled based on the measured NH₄⁺/H⁺ ratios. We added the following remark to the text: "Also note that it might be physically more realistic to scale the observed Γ values with the total NH_x deposition instead of the dry NH_x deposition only."

p4885, l22-24: it is not clear further on in the paper where the one-way zoom option and increased resolution were used. For example, p4892, l25, does "...the 7x7 km² grid size resolution of the model..." refers to both Figure 9 and Figure 8 ? It could be useful to indicate in each figure caption the grid resolution used.

We added the resolution of model runs to the figures.

p4886, l18: please say why you consider the evaluation of the model performance to be a challenge: is it because there are too few ground-based monitoring networks and data at the European scale, or because of scale/sub-grid issues, or a combination of both?

Added: ", because there are only few measurement sites where these components are continuously monitored"

The scale/sub-grid/representation issue is explained a few paragraphs further.

p4886, l25: Please explain why you exclude mountain stations in the comparison.

Actually, for ammonia no mountain stations were available, so, the sentence is ambiguous and therefore removed.

p4887, l1-3: The authors make a good point about the representativeness issue, ie that single measured point concentrations in the landscape may not necessarily represent the average concentration of the grid square, so that even if the model is correct, the comparison is doomed to failure. It could be added that this is a problem because the model grid square is much larger than, say, 1 km^2 , and because of the heterogeneity of landscapes. However, the authors appear to argue that the EMEP datapoints shown in Fig. 6 are likely higher than their regional/local background/average, and therefore biased upwards when compared with a modelled grid-square average. However, with 16 data points out of 17 being $< 2.5 \text{ g/m}^3$, the EMEP concentrations can hardly be considered “high” concentrations when compared with those measured in areas of intensive agricultural (for example, the Dutch case in Fig. 8-9, where most concentrations are above 2.5 g/m^3 , and often >5 or $>10 \text{ g/m}^3$). I thus do not find the argument that EMEP stations are overly influenced by local agricultural sources (and thus “over-estimated” from a grid square perspective) entirely convincing.

Added: “These local sources are accounted for in the model, but the emissions are spread over the entire grid cell. Furthermore, the local heterogeneity of landscapes can affect the measurements as well as the model results.”

p4887, l25: the logic for selecting large nature areas ($>500 \text{ ha}$) is sound, but it is not clear to me what grid resolution was used here for the comparison. Is it the zoomed-in option mentioned in Section 2.3 and on p4892, l25 (“... $7 \times 7 \text{ km}^2$...”)?

Correct. Model resolutions are added to figures.

p4888, l25: “Including the compensation point approach causes the modeled ammonia concentrations to increase...”: it is clear from the Wichink Kruit et al AE paper (2010) and from the Van Zanten et al RIVM report that the change from DEPACold to DEPAC3.11 is not just about including stomatal and leaf surface compensation points, but that there were very significant changes in non-stomatal resistance R_{ns} . What can one say about the respective individual impacts of introducing compensation points and changing resistances? You mention earlier that some of the uncertainty in R_{ns} is transferred onto Γ_{ns} , and this is an important point.

The introduction of the external leaf surface compensation point is coupled to the change in the non-stomatal resistance parameterization and should therefore not be considered separately from each other. In the past, only the non-stomatal resistance determined the non-stomatal flux and the different coefficients in the non-stomatal resistance parameterization were derived in different pollution climates. The low non-stomatal resistances were mainly found in low ammonia or acid (high sulphur) environments, while the high non-stomatal resistances were mainly found in ammonia rich environments. In DEPAC3.11, the non-stomatal resistance only accounts for the wetness of the leaves through its dependency on relative humidity, while the external leaf surface concentration accounts for the pollution climate, through its concentration dependency. It is rather not possible anymore to split the individual impacts of introducing the compensation points and changing resistances. However, the changes for the non-stomatal pathway (i.e. the introduction of the external leaf surface compensation point in combination with the low non-stomatal resistance) are estimated

to be more important than the introduction of the stomatal compensation point in the model. One reason might be that the stomatal flux (and thus a high stomatal compensation point) is still restricted by the stomatal resistance.

p4889, l11 onwards, and Fig.4 : Since this paper concerns itself with surface-atmosphere NH₃ exchange, there should be at least one figure showing the European-scale NH₃ exchange by both models. Figure 4 with NH_x (NH₃+NH₄⁺) exchange is useful, but an equivalent figure for NH₃ only is needed, or perhaps just two additional panels in Fig. 4, above NH_x exchange.

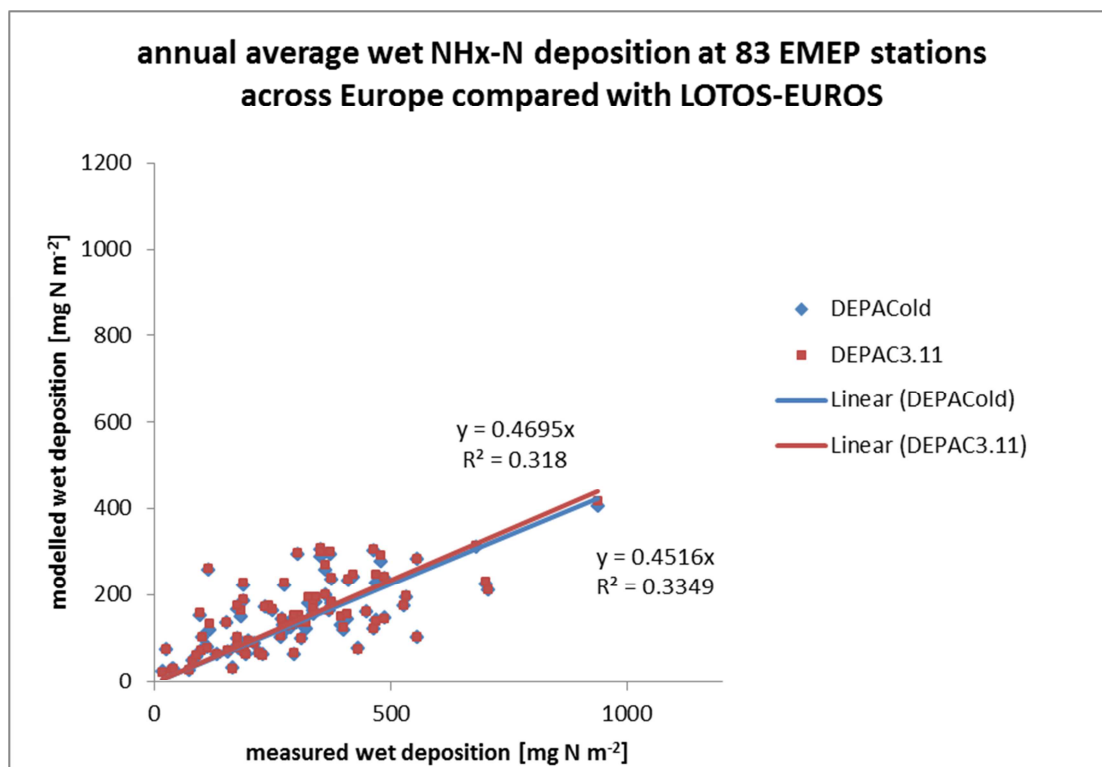
At the time of writing, the model did not yet have the possibility to split between NH₃ and NH₄ exchange. In the new model version 1.8, we changed that and we currently output the individual exchanges. An evaluation of the exchange of individual components is foreseen in the ÉCLAIRE model comparison.

p4889, l16-17: "...while the largest increases are found in the larger nature areas...": here one could add also in more extensive rural areas, which are not necessarily nature areas.

Added: "the more extensive rural areas"

p4990, l3-11: since there are substantial changes to spatial patterns of wet deposition, can you say whether the new spatial patterns and their magnitude are more consistent with measured wet deposition from monitoring networks across Europe? The validation should be easier for wet deposition than for NH₃, for reasons mentioned above (quantity of available data, spatial variations and representativeness).

As can be seen in the lower right panel in Figure 5, the relative difference in the wet deposition amounts between the two modules over land is small. This is also found if we compare the model results with observations in the EMEP network (see figure below). We have to mention here that the model version that we used here only considered below cloud scavenging explaining the underestimation by the model. In the new model version several improvements were implemented under which in-cloud scavenging (besides the already existing below-cloud scavenging). We think that the results below are not that relevant to present them in the manuscript.

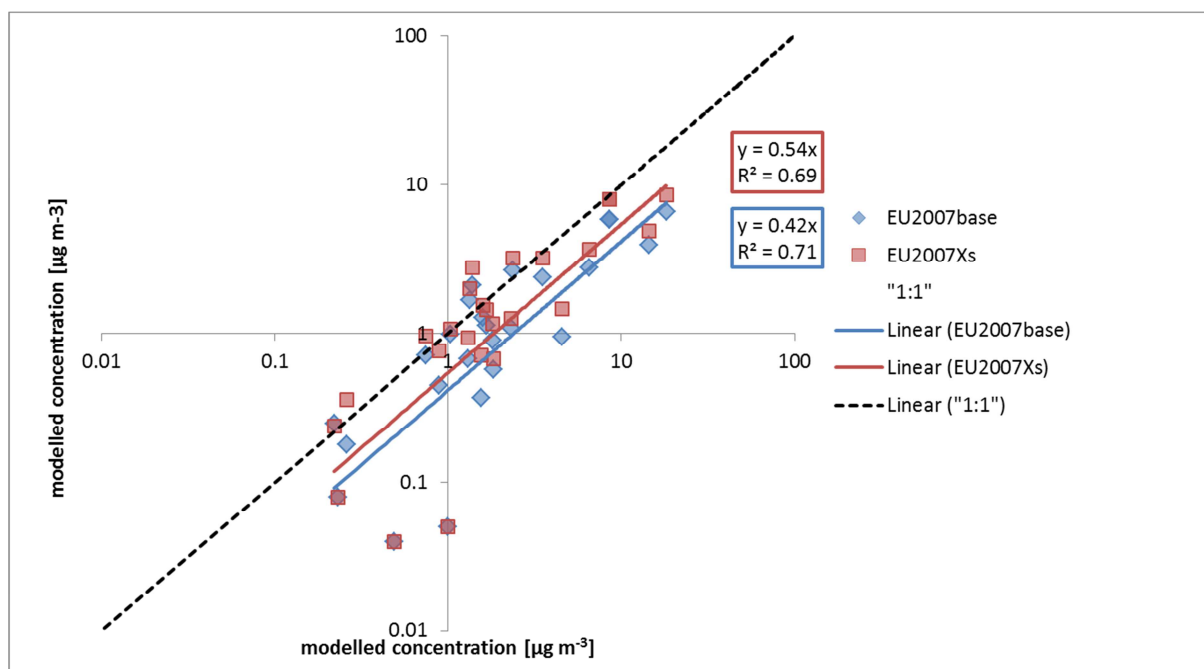
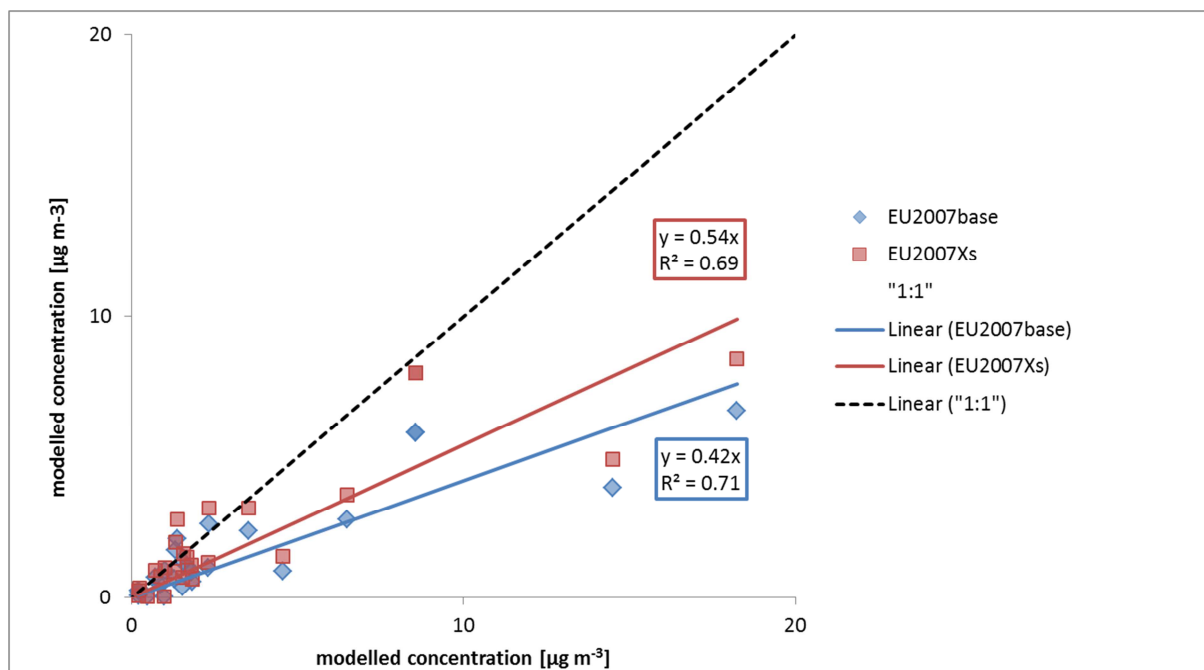


p4890, l21-23: “The slope of the regression between the simulated and measured concentrations is improved from 0.68 to 0.92...”: this is largely driven by one single point at ca 8-9 g/m³ (Eibergen station in the Netherlands). What is the change in slope without this single point? Further, why is this Eibergen data point not shown in Fig. 7? Since N=17 is a subset of N=33, all data points of Fig.6 should also feature in Fig. 7, although clearly other data points are also missing in Fig.7 (compared with Fig.6), such as those in Italy, Hungary and the Czech Republic.

In figure 6 only the stations that report NH₃ to EMEP are shown. In Figure 7 only the stations that report total ammonia (NH₃+NH₄) to EMEP are shown. So, stations in Figure 6 do not have to be a subset of the ones in Figure 7. See also next comment.....

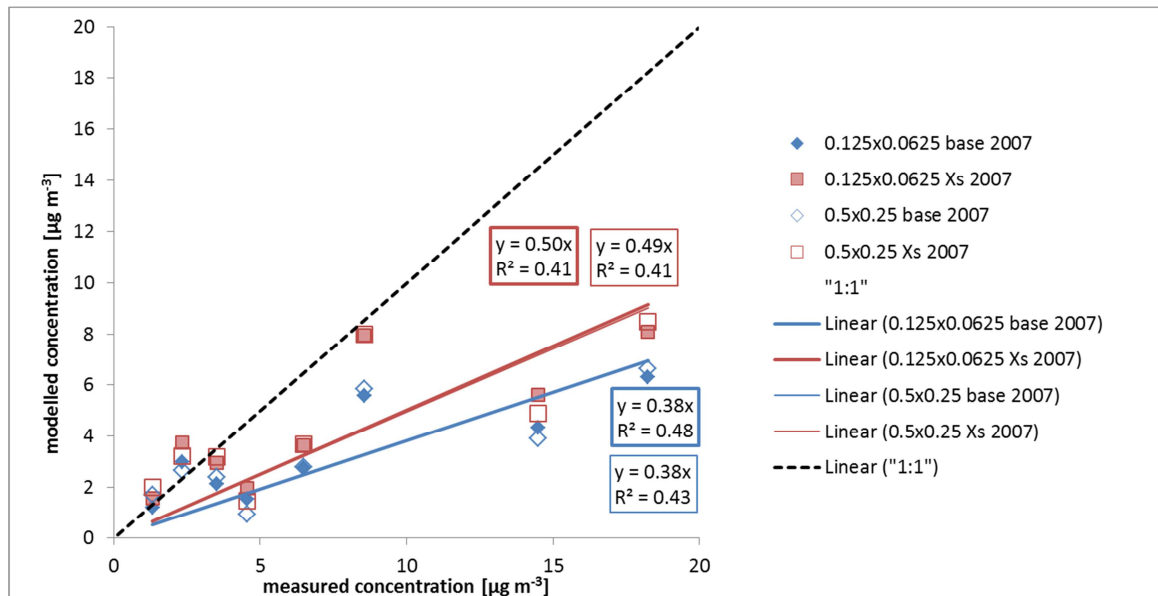
p4891, l5-6: “...in Fig. 7. Again, the largest increases occur in the higher observed concentration range...”: Unfortunately, the data in Figure 7 are medium range and do not extend very far into the high concentration range (only up to 4 µg/m³ for NH_x), so the model cannot be said to be validated for areas of intensive agriculture and emissions. Why not show the data from the Dutch monitoring network NH₃ data (Fig. 8) alongside the EMEP data in Fig.6 (using e.g. different symbols), even if there are grid resolution and representativeness issues, which are discussed in detail anyway ?

Very good idea. We included the data from the Dutch monitoring network in Figure 6 and extended the figure with an additional log-log scale plot which focusses on the low concentration range.



p4891, 117-18: "...we now zoom in on the area with intensive agricultural activity in the Netherlands and compare the modeled concentrations with measurements from the NAQMN in Fig. 8." : please say explicitly whether this model run was done with a different grid resolution ($7 \times 7 \text{ km}^2$?), or whether you are merely comparing the default model runs (European scale , at $25 \times 25 \text{ km}^2$) specifically with a focus on the Dutch monitoring network. In fact it would be very informative to show on the same graph a comparison of measured concentrations from the Dutch network and of modeled concentrations using the high and the low resolution modes of LOTOS-EUROS/DEPAC 3.11. Is there a significant improvement when using a higher resolution, and if not, this points to a parameterization issue rather than a representativeness issue for measured concentrations.

The resolution of the model runs in the comparisons will explicitly be mentioned in the captions. The effect of model resolution is investigated with the NAQMN data in the Netherlands (see below). The results of the higher model resolution does not significantly affect the slope nor the correlation of the regression. It seems that 7x7 km is still too coarse to capture the local sources well or a parameterization issue might still play a role. We consider the results as interesting, but not worthwhile to present them in the manuscript. We will however add some sentences to the manuscript about these findings.



p4891, l27: it seems to me that the bias (offset) in the regression in Figure 8 is not reduced, but increased from 1.39 to 1.92 from DEPAC old to DEPAC 3.11.

Figure 8 is combined with Figure 6.

p4894, l13: "The surface resistance of SO₂ was reduced...": was this harmonization necessary because the NH₃/SO₂ molar ratio increased (cf co-deposition issue) ?

No, this was just a harmonization issue as mentioned in the text. Old value was nowhere documented.

p4894, l26-27: "...The impact on the model performance of LOTOS-EUROS for the SIA components in comparison to measurements is very small...": this statement is not very clear. Do you mean that the improvement of model performance versus measurements is marginal? Please rephrase.

Changed text in: "The changes in the modeled SIA concentrations over land are small and as all measurement stations are located here, the improvement of the model performance of LOTOS-EUROS is marginal over land (not shown)."

p4895, l9: "...require detailed meteorological and plant physiological parameters...": it should also (again) be mentioned that soil sink and source strength is also a major component, although largely unknown and under-studied, and the soil source aspect is absent in this study.

We will emphasize throughout the manuscript that in the new module the exchange with the soil is not changed and that the modules do not account for emissions from the soil. We will also make more clear that the module is only supposed to account for non-fertilized conditions. The anthropogenic emissions are accounted for in the emission inventory and including compensation points for soils would result in a double counting of these emissions. An alternative (ideal) method would be to introduce huge Γ values for soils after manure application, but this is too difficult to implement in CTMs which are currently rather tied to the emission inventories.

p4895, l11-13: "The generalization step is often a shortcoming as parameterizations are derived for just one certain land use class, which is located in one certain pollution climate." This may be so, but this paper cannot ignore that there have been other attempts beside the author's to derive and implement generalized parameterizations, e.g. Massad et al, ACP, 2010; Zhang et al., JGR, 2010; CMAQ model, USEPA, cf http://www.cmascenter.org/conference/2010/slides/bash_evaluation_coupling_2010.pdf

We will add a sentence referring to the studies mentioned above.

p4895, l23-27: the co-deposition issue is still a reality, but SO₂ is no longer, or not necessarily, the dominant nor the only source of leaf surface acidity. Rather than take the NH₃ to SO₂ ratio, one should take the NH₃ to the sum of acids (SO₂, HNO₃, HCl, etc) as a scaling factor for the non-stomatal resistance. See Fowler et al, At. Env. Volume 43, Issue 33, 2009, Pages 5193–5267, Fig. 4.5 and comments.

At the moment the effect of co-deposition is not taken into account in the DEPAC3.11 module. We acknowledge that this effect should be accounted for and a new version of the module that accounts for the NH₃-acid co-deposition effect is under development.

p4897, l7: "...is not feasible.": add "for CPU time reasons" ?

Replaced "not feasible" by "computationally expensive".

p4897, l25-27: I do not think this sentence is relevant nor needed here. As mentioned above, the "Nitroeuope" data alluded to (see Table 2 of Flechard et al, ACP, 2011) could easily be added to Figures 6 and 7 without much additional work, adding more weight to this comparison exercise.

We agree. We added a model evaluation with the NH₃ concentrations from "Nitroeuope" and removed the sentence here.

Technical corrections

p 4879, l9: "...It HAS long been known..."

Corrected.

p4879, l13: "...over all KINDS of vegetated surfaces..."

Corrected.

p4879, l28: "...which ARE generally not available TO regional..."

Corrected.

p4882, l25: for clarity, suggest change to : "... an external resistance that represents deposition to non-stomatal leaf and stem surfaces, this sink being especially active when these surfaces are wet." Similarly, on p4885, l19, change "...updated dry deposition..." to "...updated surface exchange..."

Corrected.

p4883, l1: insert "default" between "contains" and "values"

Done.

p4883, l15: change "dry deposition" to "surface exchange", since this (the bi- directionality of fluxes) is precisely what distinguishes DEPAC 3.11 from DEPACold. Also, change "removal" to "exchange" on l16.

Done.

p4883, l21: "...as it WAS derived..."

Corrected.

p4883, l22: Add "In the present study,..." before "The external leaf surface..."

Done.

p4888, l27: "...number OF measurements..."

Added.

p4889, l3: "...amounts TO 1-2 g/m3..."

Added.

p4892, l6 and l9: change "with" to "by"

Changed.

p4892, l14: change "would be" to "was"

Changed sentence.

p4894, l11: change "...in this figure..." to "...in Fig. 13..."

Changed.

p4894, l13: change "synchronized" to "harmonized"

Changed.

p4894, l19: change to: "...OVER the Mediterranean Sea the ATMOSPHERIC NH₄⁺ concentrations..." to dispel any ambiguity (NH₄⁺ "in" the sea might otherwise refer to the aqueous concentration).

Changed.

Figure 1: add distance unit (km) to the x-axis

We added distance unit to the x-axis.

Figure 12: the two panels should be separated (insert a space in the middle, or display maps on two different lines). Also: add scale (km), add a larger situation map of Europe to make it clear where this modelling domain is located. For measured concentrations, if possible : add color-scaled symbols, with black outline and with same colour scale as the modelled map.

The figure will be changed according to the recommendations.

Interactive comment on Biogeosciences Discuss., 9, 4877, 2012.