Responses To Referee #1

We greatly appreciate all the comments, which helped us to improve the paper. Our point-by-point responses are detailed below in italics.

General comments: The manuscript evaluates the ambient ammonia concentrations over southern Ontario as observed with passive samplers and calculated by the STILT-Chem v0.8 model. Three different dry deposition schemes were tested and validated with the observations. Two of the three dry deposition schemes were already present in the STILT-Chem model and were uni-directional. The third dry deposition scheme is bi-directional. For this deposition scheme different values are set for the stomatal and ground emission potentials for different land-use categories and for low-N and high-N canopies. Model results are evaluated using many different types of statistical approaches. However, it is questionable if all these statistics are really necessary and useful in the evaluation of the model results. Simple scatter plots with linear regression statistics are missing in this manuscript. Plots like Fig. 4 in Wen et al. (2013) are desirable in this paper as well (By the way, I can hardly believe that the regression line in the left panel of Fig. 4 of Wen et al. 2013 is correct?). In this way, Figure 3, 4, and 6 can be combined, while much more information is obtained about the spatial correlation between model results and observations. Different symbols could be used for forest and agricultural sites, while different colors can be used for the different model simulations.

Response: As suggested by the Reviewer, scatter plots have been created and added in the paper for forest and agricultural sites for the three schemes. Figures 4 and 6 have been removed. Statistics including correlation coefficients (R), normalized standard deviation (NSD) and centered normalized root-mean-square (NRMS) have been deleted from Tables 2 and 3 as well. Figure 3 remains because it can provide straightforward spatial distributions of observed and modeled NH_3 concentrations and a general transitional trend in the observations from forest sites to agricultural sites. To reflect the above changes,

1) Lines 1-23 on Page 6089, Lines 21-29 on Page 6090, and Lines 1-14 on Page 6091 have been deleted. The following text has been added in Line 1 on Page 6089:

"Figure. 4a shows correlations between observed and modeled mean NH_3 concentrations that are presented in Fig. 3 for the three schemes. The ZBE scheme generally predicted higher NH_3 concentration averages over the entire simulation period than the ZDD and WDD schemes. However, all three schemes produced almost equivalent correlation pattern with the observations. They underestimated NH_3 concentrations at sites with high observed concentrations, while overestimated NH_3 concentrations at sites with low observed concentrations. This phenomenon is more evidently presented in the scatter plots (Figs. 4 b-d) in which weekly measured and modeled concentrations were used. Similar results have been reported by a European study that used the LOTOS-EUROS model (Wichink Kruit et al., 2012), in which NH_3 concentrations in natural areas were slightly overestimated, whereas NH_3 concentrations in agricultural regions were underestimated, with more pronounced underestimations as observed NH_3 levels increased. In terms of statistical values of Ratio-Of-the-Means (ROM) and Mean Fractional Bias (MFB) (Tables 2 and 3), modeled NH_3

concentrations at agricultural sites were overall underestimated by WDD and ZDD in this study, and slightly overestimated by ZBE, but all three schemes significantly underestimated NH_3 concentrations for sites with observed level greater than 6.0 μgm^3, with a tendency to underestimate more with increasing observed concentrations (Fig. 4). The performances of the three schemes at agricultural sites were not obviously different (Fig. 4 and Table 3). All three schemes performed poorly in reproducing observed concentrations at the forest sites, with considerable overestimation and the ineffectively capturing the pattern of observations. This is probably due to much lower emissions strengths and concentration levels at those sites. The same uncertainty in the simulations may lead to more pronounced error/bias in low concentrations than high concentrations. According to the values of ROM, MFB and Mean Fractional Error (MFE) in Table 3, the ZBE scheme performed the best for agricultural sites and for all sites, while the ZDD scheme had the best performance in simulating NH_3 concentrations for the forested sites."

2) all figure numbers after Page 6088 have been adjusted .

We also thank the Reviewer for pointing out the regression line problem in the left panel of Fig. 4 of Wen et al. 2013. We examined it and found out that it should be y=0.83x+0.41, but we accidentally treated as y=0.83x-0.41 when we plotted it.

I doubt whether the bi-directional approach as proposed by Zhang et al. (2010) is the appropriate way to model spatial variations in bi-directional ammonia exchange with the surface. In my opinion, it is wrong to couple the soil emission potential to land-use categories as it is a soil property and not a vegetation property. Therefore, it's not strange that results of the bi-directional dry deposition scheme are not convincingly better than the results of the uni-directional deposition schemes.

Response: The scheme of Zhang et al. (2010) is similar in theory to other bi-directional schemes currently used in the community. Two key parameters are needed in the scheme – stomatal and soil emission potentials. Assigning stomatal emission potentials to vary with land use category is a reasonable approach, in our opinion. Because a portion of soil emissions comes from decomposition of the litterfall from previous years, soil emission potentials could also be related to land use category. However, other factors could dominate soil emissions, such as wet deposition at natural areas or fertilization over agricultural lands. In the latter case, soil emission could vary substantially both spatially and temporally, under which conditions the default values in the Zhang et al. (2010) are likely need to be adjusted, as pointed out by this Reviewer and shown in the present study. Thus, a better approach would be to make use of additional information such as the agricultural activities, in the regions where such information is available, while use the model proposed values at location where such information is not available. Such an approach has been adopted by USEPA CMAQ (Pleim et al., 2013, JGR 118, 3794-3806) and a similar approach has also been used in a Wichink Kruit et al. (2010) as pointed out by this Reviewer; but it should be noted that such information is not available in many regions around the world. Thus, evaluating the applicability of the new bi-directional scheme is needed which is the main purpose of the present study. Although the bi-directional scheme is not statistically better than the uni-deposition schemes over the whole region studied here, the bi-directional approach can result in improved results from simple adjustments of emission potentials while the uni-directional schemes cannot because concentrations at some sites were overestimated while at other sites, underestimated.

Specific comments:

p 6076 l 9-10: this is likely due to too high stomatal and soil emission potentials

Response: We agree with the Reviewer that stomatal and soil emission potentials used in the ZBE scheme might be too high for clean forest sites. The uncertainties are mainly caused by using fixed empirically-derived emission potential values for the same land-use category over the entire modeling domain, mainly due to lack of detailed and accurate emission potentials that are specific to each location in the domain. We are working on refinements of emission potentials for different pollution levels as an attempt to improve the accuracy of NH_3 atmosphere/surface exchange modeling.

p 6076 l 16-18: Don't forget that the observations might be influenced by local sources, which means that the observations are probably not representative for the grid size resolution of the model.

Response: The STILT-Chem model is based on Lagrangian framework and does not produce concentrations at gridded scales. Instead, it attempts to resolve sub-grid scale influences and model NH_3 concentrations at point locations where the observations are situated.

p 6077 l 11: 'Wichink Kruit et al., 2012' should be moved to line 16

Response: "Wichink Kruit et al., 2012" in Line 11 Page 6077 has been moved to Line 16 Page 6077.

p 6077 l 15,20: 'Kruit et al., 2010' should be 'Wichink Kruit et al., 2010'

Response: "Kruit et al., 2010" in Lines 15 and 20 has been changed to "Wichink Kruit et al. 2010".

p 6078 l 2: Add reference 'Wichink Kruit et al., 2012' after NH3.

Response: The reference "(Wichink Kruit et al. 2012) has been added after NH_3 in Line 2 on page 6078.

p 6080 l 12-13: How important is this pathway to the lower canopy? It would be more consistent with the other schemes not to account for the pathway to the lower canopy.

Response: We do agree the Reviewer that it would be more consistent with the other schemes if the pathway to the lower canopy in the WDD scheme is not accounted. However, doing so will modify the original WDD scheme, which is a widely used scheme in the community, and thus may not provide the readers a clear picture how the original scheme performs. This is what we tried to avoid in this study because the specific purpose of this study was to evaluate the three dry deposition schemes, not to develop/modify them. The importance of the pathway to lower canopy can be examined by including and excluding it in the simulation, but we do not think it is appropriate to the purpose of this study.

p 6081 l 6: What is meant with improved representation here? Improved compared to what? And why?

Response: The improved representation here in the ZDD scheme means including a newly developed *non-stomatal resistance formulation, a realistic treatment of cuticle and ground resistance in winter and the handling of seasonally-dependent input parameter, which is compared to its earlier version. The improvement is expected to provide more realistic deposition velocities, especially for wet canopies, and to be easily adopted into air quality models.*

p 6083 l 16-24: I doubt whether the bi-directional approach as proposed by Zhang et al. (2010) is the appropriate way to model spatial variations in bi-directional ammonia exchange with the surface. In my opinion, it is wrong to couple the soil emission potential to land-use categories as it is a soil property and not a vegetation property. Especially the overestimation in the low concentration range might be caused by too high emission potentials.

Response: See our responses to the general comments.

p 6087 l 3-6: Why is it reasonable for ammonia emissions to treat all point sources as surface sources? Do you mean that due the small contribution of the point sources to the total emission, the error in the emission estimate is small?

Response: The reason is the contribution of all point sources to the total emission are small (less than 4%), the error in modeled results caused by treating all point sources as surface sources should be negligible.

p 6087 l 17: 'mode' should be 'model'

Response: The identified "mode" has been changed to "model"

p 6090 l 20: Might this be a meteorology effect?

Response: We agree that this might be a meteorology effect, but this effect cannot be verified in this study. Due to the sharp and significant decrease in NH_3 emissions resulting in about 40% emission reduction from September to November, we strongly believe that the sharp decrease in the estimated NH_3 emissions played a much more important role than meteorology in underestimating NH_3 concentrations after October.

p 6092 l 1: What about the ZBE scheme? An effective Vd (~F/C) can be presented for this scheme.

Response: As suggested by the Reviewer, effective dry deposition velocities from the ZBE scheme were calculated and average diurnal variations for agricultural and forest sites have been added in Fig.7.

The following text regarding this change has been added in Line 8 on Page 6092:

"In order to compare with the other schemes, we divided NH_3 fluxes by corresponding NH_3 concentrations to obtain "effective" dry deposition velocity for the ZBE scheme. Diurnal patterns of effective dry deposition are also presented in Fig. 6. Effective dry deposition velocities from the ZBE scheme clearly show strong NH_3 emission (negative values) from surface to the atmosphere during the daytime for both forest and agricultural sites. During the nighttime, ZBE-calculated effective deposition velocities are almost equivalent to dry deposition velocities estimated by ZDD for forest

sites, but they are small and almost negative for agricultural sites."

p 6092 l 3: What is meant by infinite minimum canopy stomatal resistance?

Response: We thank the Reviewer for pointing out. This statement has not been stated clearly. To make it clear, the following text in Line 3 on Page 6092:

"mainly due to an infinite minimum canopy stomatal resistance assigned in the WDD scheme for the deciduous forest category in the "autumn" season."

has been changed to:

"mainly due to the exclusion of stomatal uptake (through the use of a very large value of 10^{25}s/m for minimum canopy stomatal resistance) for the deciduous forest category in the "autumn" season."

P6094 l 6: How does this figure look for the ZDD scheme?

Response: Modeled results from using ZDD and WDD schemes have been added in Fig. 9. The figure clearly shows that NH_3 concentrations were generally underestimated to a larger extent by ZDD and WDD than by ZBE for sites with strong anthropogenic emission strengths (>6.0 mole/s/gridcell). There is no obvious underestimation or overestimation for ZDD and WDD at sites with low emission strengths.

The following text from Line 8 to Line 15 on Page 6094:

"All data points in Fig. 9 are means for the entire simulation period and the modeled concentrations are from the simulation using the ZBE scheme with minimum emission potentials. It can be seen that the deviations of modeled NH_3 concentrations from observed values were correlated with anthropogenic NH_3 emissions. The model tended to overestimate NH_3 concentrations for sites with low emissions while underestimating NH_3 concentrations for sites with strong NH_3 emissions. Figure 9 also shows that NH_3 concentrations were generally underestimated for most sites where anthropogenic emission strengths were greater than 6.0 mole/s/gridcell."

has been changed to:

"All data points in Fig.8 are averages of the entire simulation period for the 53 sites for all three schemes. Those for the ZBE scheme were the outcome of using minimum emission potentials. The deviations of modeled NH_3 concentrations from observed values obviously show a negative correlation with anthropogenic NH_3 emissions, which is more obvious for ZBE than for the other schemes. When anthropogenic emission strength were greater than 6.0 mole/s/gridcell, all three schemes underestimated NH_3 concentrations. Even for the ZBE scheme which generally predicts the highest concentrations among the schemes, the underestimation can still be significant."

p 6095 l 5: But then also an even larger overestimation of the low concentrations will be obtained, or?

Response: Increasing emission potentials for the locations with emission strengths greater than 6.0 mole/s/gridcell will result in a larger overestimation of the low concentrations. However, the magnitude of the increase for the low concentrations is not expected to be significant for most low *concentration sites because the increase of emission potentials are limited only to a few sites that are met the criteria (>6.0 mole/s/gridcell) and those sites generally are far away from the low concentrations sites.*

p 6095 l 6-20: It looks like there is a general reduction in the deposition in the ZBE scheme, which leads to an overestimation of the low concentration range and a better correspondence in the high concentration range. A coupling of Gamma_s to pollution level in the area (as in Wichink Kruit et al., 2010) could probably improve the ZBE model performance.

Response: Due to the general insufficiency or unavailability of measured or explicitly calculated data of emission potentials that are required by a NH_3 atmosphere/surface exchange model for all locations in a domain, emission potentials are assumed to be the same in the ZBE scheme and a fixed empirically-derived value of stomatal emission potential and a fixed value of soil emission potential are used for each land-use category. This assumption, on one hand, makes the scheme applicable to a regional-scale air quality modeling, but on the other hand likely leads to the inaccuracy of modeling results because emission potentials vary with many factors that could not be included in the current approach. We do agree with the Reviewer that refining emission potential to pollution levels is important for the ZBE model performance, and we will implement the improvement in the future work. Also see our responses to the general comments.

p 6096 l 2: What about the effect of local sources on the observations?

Response: Local sources greatly affect the observations of NH_3. The effect of local sources on the observed NH_3 concentrations can be roughly seen from the comparison of NH_3 concentrations between agricultural sites and forest sites (Figs. 3 and 5) where higher local sources generally lead to higher NH_3 concentration observations. The observations generally can reflect well the effect of local sources, however, modeled results are in most cases unable to reflect all those effects reasonably due to uncertainties and incompleteness in representing all local sources in the modeling.

p 6096 l 13-16: I totally agree.

p 6106 Table 4: Why is this so different from the values for agricultural sites in Table 3?

Response: The reason is the statistics in Table 4 only represent the results of five agricultural sites with strong anthropogenic NH_3 emissions that were particularly selected for a sensitivity test, while the statistics in Table 3 represent the results of all agricultural sites (39) for a benchmark simulation.

p 6109-6112: scatterplots similar to Fig 4 in Wen et al. (2013) would be useful. See also General comments.

Response: Scatter plots between observed and modeled NH_3 concentrations for 53 sites have been added.

p 6113: add effective Vd for ZBE.

Response: Effective dry deposition velocities of NH_3 from the ZBE scheme have been added in Fig.7. The following text regarding this change has been added in Line 8 on Page 6092:

"In order to compare with the other schemes, we divided NH_3 fluxes by corresponding NH_3 concentrations to obtain "effective" dry deposition velocity for the ZBE scheme. Diurnal patterns of effective dry deposition are also presented in Fig. 6. Effective dry deposition velocities from the ZBE scheme clearly show strong NH_3 emission (negative values) from surface to the atmosphere during the daytime for both forest and agricultural sites. During the nighttime, ZBE-calculated effective deposition velocities are almost equivalent to dry deposition velocities estimated by ZDD for forest sites, but they are small and almost negative for agricultural sites."

p 6115: add the other two schemes to this figure.

Response: Modeled results from WDD and ZDD schemes have been added in Fig. 9. To reflect this change in the paper, the following text from Line 8 to Line 15 on Page 6094:

"All data points in Fig. 9 are means for the entire simulation period and the modeled concentrations are from the simulation using the ZBE scheme with minimum emission potentials. It can be seen that the deviations of modeled NH_3 concentrations from observed values were correlated with anthropogenic NH_3 emissions. The model tended to overestimate NH_3 concentrations for sites with low emissions while underestimating NH_3 concentrations for sites with strong NH_3 emissions. Figure 9 also shows that NH3 concentrations were generally underestimated for most sites where anthropogenic emission strengths were greater than 6.0 mole/s/gridcell."

has been changed to:

"All data points in Fig.8 are averages of the entire simulation period for the 53 sites for all three schemes. Those for the ZBE scheme were the outcome of using minimum emission potentials. The deviations of modeled NH_3 concentrations from observed values obviously show a negative correlation with anthropogenic NH_3 emissions, which is more obvious for ZBE than for the other schemes. When anthropogenic emission strength was greater than 6.0 mole/s/gridcell, all three schemes underestimated NH_3 concentrations. Even for the ZBE scheme which generally predicts the highest concentrations among the schemes, the underestimation can still be significant."

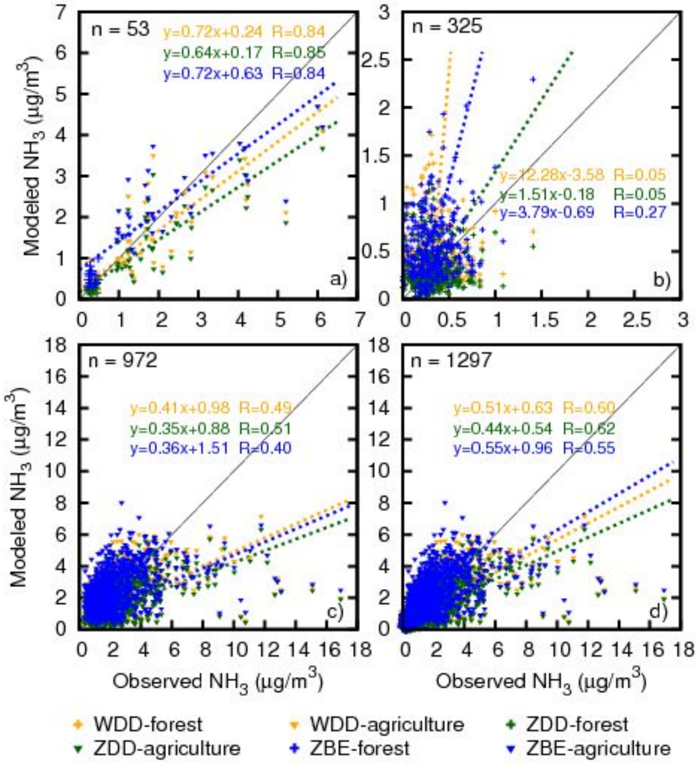

Fig. 4. Correlations between measured and modeled NH_3 concentrations for the WDD (yellow), ZDD (green), and ZDD (blue) schemes, respectively, including: (a) for all 53 sites using mean concentrations over the entire simulation period; (b) for forest sites (+) using weekly concentrations; (c) for agricultural sites (▼) using weekly concentrations; (d) for all 53 sites using weekly concentrations. Solid black lines represents 1:1 lines.

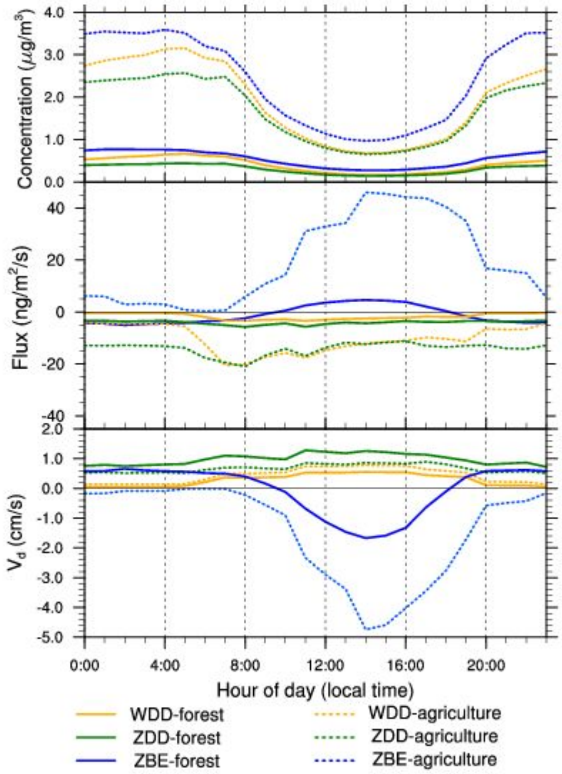

Fig. 6. Diurnal variations of modeled dry deposition velocity (bottom), surface exchange flux (middle), and NH_3 concentration using WDD (orange), ZDD (green), and ZBE (blue) schemes respectively, averaged over the entire simulation period for forest sites (solid lines) and agricultural sites (dashed lines). Negative fluxes represent downward movement out of the atmosphere whereas positive fluxes represent emission from surface to the atmosphere. Dry deposition velocities for ZBE represent its effective dry deposition velocities, where negative values indicate emissions from surface.

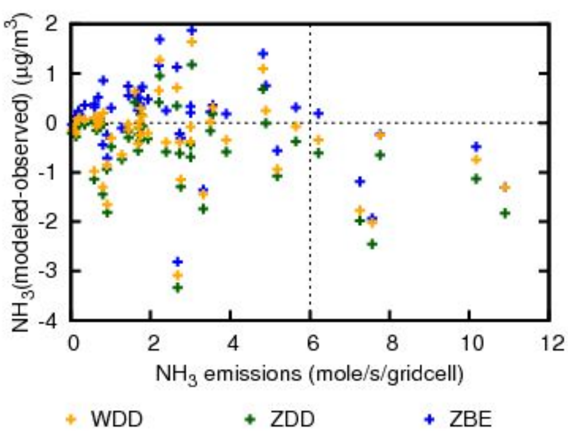

Fig. 8. Scatterplot for deviations of modeled NH_3 concentrations from observed values vs. Corresponding mean anthropogenic emission strengths for the three schemes for each test sites. All data points are means for the entire simulation period.