**Responses To Referee #2**

We first acknowledge that many comments from this reviewer are very helpful and have helped us to improve the quality of the paper. We greatly appreciate these comments and we have revised the paper accordingly.

We then like to point out that, after going through carefully all the comments, we have found that quite a few comments from the reviewer are linked to the two key questions: 1) Could the typical stable atmospheric conditions in winter nighttime in Southern Ontario lead to ammonia concentrations as high as the observed? and 2) Should the maximum ammonia concentration observed in summer represent the maximum contribution of local emission in the other seasons at the remote non-agriculture zone sites?

Regarding question 1 above: the stable atmospheric conditions might have played a role causing high winter concentration, but this factor alone cannot explain the differences in seasonal concentration patterns between the agricultural and non-agricultural zones. The high-temporal data collected by denuder as shown below suggest that this factor, while causing concentration accumulation in nighttime in both cold and warm seasons, should not cause big differences between the different seasons in Southern Ontario.

Regarding question 2 above: we do believe it is a safe assumption considering that ammonia emission from natural sources is an exponential function of temperature. The contribution to the observed concentration from local emission in winter is likely less than that in summer.

We do appreciate the additional possibilities provided by the reviewer which we have included in the revised paper. We hope the reviewer will find the conclusions generated from the revised presentation are less speculative than the previous version. We also provide point-to-point responses as detailed below.

*Yao, X.H., Zhang, L. Analysis of passive-sampler monitored ammonia at 74 sites across southern Ontario, Canada. Submitted to Biogesciences, August 2013.*

*Although I am no native speaker, I feel that the text at a few places in this paper could be formulated more clearly, so that misunderstandings can be avoided.*

**Response**: We have revised the paper to present the results in a more logical way to avoid misunderstanding, with the help of the comments provided.

*SOME GENERAL REMARKS*

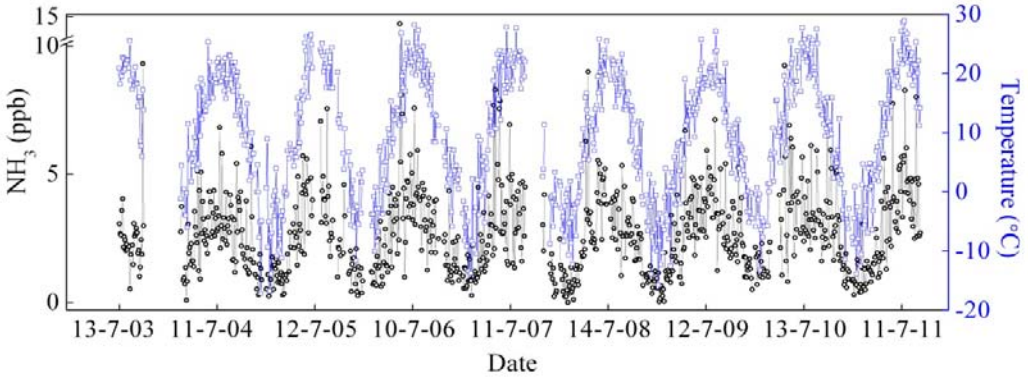
*Ammonia sources are usually low-level sources. For that reason, the concentration decreases*

*rapidly with the distance to the source as the authors have described. During stable atmospheric conditions, which are associated with low wind speeds, the vertical mixing is limited and high concentrations can therefore occur. Stable atmospheric conditions occur typically during the night and are likely to be more frequent during wintertime.*

**Response:** We agree with the reviewer that pollutant concentration can be accumulated due to reduced mixing during the nighttime in both summer and winter, and it is likely true that the inversion happens more often in winter, especially when there is snow cover. However, we think that only this one factor is not enough to explain the higher concentrations in winter than in summer at the remote non-agricultural sites. If the reduced mixing or stable stratification is the dominate mechanism, the same or similar phenomena should have also been observed at the source locations (the agricultural sites). Our data only identified the higher winter concentration at the remote non-agricultural sites.

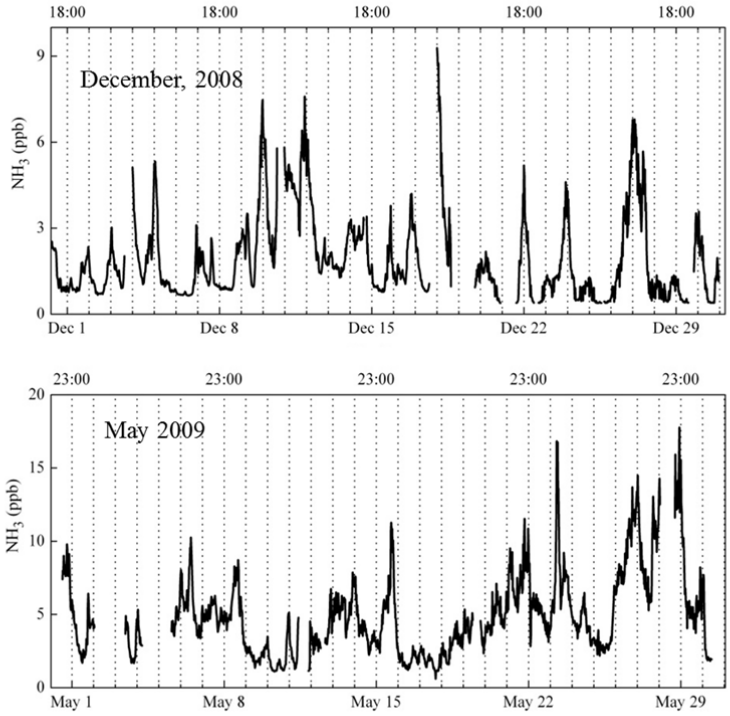
We first like to show a long-term data with high temporal resolution to support the above discussion. Below is the time series of 24-hour denuder samples collected on every third day from July 2003 to September 2011 at an urban site (Downtown Toronto) in Southern Ontario. The data was collected and analyzed as part of the National Air Pollution Surveillance (NAPS, http://www.ec.gc.ca/rnspa-naps/) network, which was established to provide accurate and long-term air quality data of a uniform standard across Canada.

A distinctive seasonal cycle of $NH_3$ mixing ratio can be found. Low mixing ratio of 1.1±0.6 ppb (on average) was observed from December to February of the next year (cold season). High mixing ratio of 3.9±1.6 ppb (on average) occurred from May to August (warm season). March, April, September, October and November were the transient period. The observational results clearly indicate much lower concentrations of $NH_3$ in winter. This seasonal pattern agrees with those observed at the agriculture zone sites shown in the present study.




We then like to show another high time resolution measurement of $NH_3$ also collected in downtown Toronto (unpublished data). The data was collected semi-continuously

using a Dionex Gas Particle Ion Chromatograph (GP-IC) during December 2008 and May 2009. Accumulation of $NH_3$ in mixing ratio was indeed observed at certain nighttime in both cold and warm seasons, and the amplitude of the accumulation was generally higher in May than in December. This data demonstrate the reviewer's point of concentration accumulation due to poor dispersion condition, but the accumulation pattern would not bring winter concentration higher than summer. Thus, other dominate factors exist causing the high winter concentration observed in the present study.




*In Europe in the "good old times", some farmers were applying manure in mid-winter on snow-covered fields. The reason for that was apparently the limited capacity of their storage tanks. This is maybe not occurring in Ontario as many countries have a legislation, which forbids this. Manure and fertilizer are applied to crops when they need it. Different plant species are planted at different times. In case there are spatial differences in coverage by different crops, temporal differences emission peaks resulting from application can be expected. Differences in climate (I do not know whether this plays a role here within the measurement area) might also have an influence on the dates of application of manure and fertilizer. From older data, I can see that about 40% of the crop area in Ontario consists of alfalfa and soybean. These crops do not need manure or fertilizer, but can be sources for ammonia (see e.g. Dabney and Bouldin, 1990).*

**Response**: It is good to know that there was a possibility of manure dumping in mid-winter that might have caused extremely high concentration. However, we do not have any official record if this had happened during our campaign, and it is difficult to find out the truth. Although our official document pointed out that application of

manure and fertilizer across southern Ontario in winter was negligible (Lillyman et al. 2009), we feel that the possibility should be mentioned in the revised paper. Note that this suggestion might help to explain peaks of concentrations in the agricultural zone, but it cannot explain the peaks in non-agricultural zone which has quiet some distance from the potential sources.

*p. 12775. "With the decrease of SO2 and NOx emissions in developed countries, NH3 is increasingly : : :: : :". In Europe the NH3 emissions have also decreased, but the percentage of emission reduction is less than that of SO2 and NOx. For that reason NH3 is in the EU the component that contributes most to potential soil acidification.*

**Response**: We have rewritten the sentence to avoid the misunderstanding: "In the past several decades the decrease of ammonia emission is slower than that of acidifying sulfur and nitrogen species in most developed countries. Thus, the impact of ammonia on ecosystems attracts more attention."

*The measurements are certainly worth to be published, but many conclusions in this paper are highly speculative especially when they are based on correlations only (see below). Without a higher temporal resolution and an appropriate spatially and temporally detailed atmospheric transport model, it is difficult to come up with more certain conclusions. I would therefore welcome a revised version of the article, with much less speculations.*

**Response**: We agree that many conclusions cannot be verified directly due to the low temporal resolution of the data. However, our current understanding on ammonia and ammonium lifetime, deposition rate, and chemical conversion mechanisms coupled with the spatial and seasonal patterns observed from this data set support our conclusions presented in this paper. We do admit that some other factors such as those pointed by this reviewer should be mentioned in the paper.

We also agree that the hypothesis presented in this paper could be verified using a model simulation. We plan to conduct such a study in the near future using a Lagrangian air quality model we recently developed (Wen et al., 2013). Since it takes significant effort and cannot be done in a short time period, it has to be presented in a separate study.

We have revised the paper by including additional possibilities provide by the reviewer, and tried to be less speculative wherever possible.

DETAILED REMARKS

*The abbreviation AAN is sometimes misspelled ANN. This should be corrected.*

**Response: C**orrected.

*p. 12775 last line: "Such a hypothesis (referred to…". It should maybe be noted here too, that it best can be verified if the concentration is measured with a high spatial resolution, but also with a high temporal resolution (which cannot be done with the method employed here). If different hypotheses are investigated it would be better to mention them in the same section and not in the introduction.*

**Response**: We have added this comment in the revised paper and combined all hypothesis together into the methodology section.

*2. Heading: Experiments = Experimental: in this section information should be given on the measurement sites and the methods applied, without any interpretation (as is the case now). A detailed description should be given about the passive sampling method, e.g. construction of the sampler, how it was tested, detection limit, whether e.g. triplicate samples were taken etc.. Very often, the concentrations measured with passive samplers are compared at a few places with more accurate methods, which also have a higher temporal resolution (during the campaign itself). If this were the case, it would be nice to mention it. Information should be given on the sites, or at least on the criteria for the site selection should be given or information on groups of similar sites and a description of each group. Important with this respect is the distance and direction to potential sources. These sources could be permanent fixed sources (housings, storage) or nonpermanent sources (application of manure and fertilizer). Were the samplers placed in the agricultural areas or in adjacent non-agricultural areas? (the last option might make the measurements more representative of a larger area).*

**Response**: A paragraph has been added in the revised paper describing the sampling method and quality control procedure. Some information on site selection and distance between sites have already provided in the first version of the paper.

*p. 12776, line 9 :"The measurements at tens of these sites : : :" It should be mentioned exactly how many sites*

**Response**: Revised. The measurements at eighteen sites started running for consistency check and sampler evaluation.

*p. 12777, line 22: ": : :. with the remaining 20% being associated with fertilizer and pesticide application." It would be nice to have a reference here to the use of ammonia as a pesticide, as this is unusual in other countries.*

**Response:** The information was from Lillyman et al. (2009) and we do not have any other references. To avoid confusion, the word "pesticide" is deleted because we are not sure if this is the real case.

*p. 12778, line 19: "Hierarchical cluster analysis….". It should be mentioned here which metric was chosen to calculate the distance between pairs of observations.*

**Response:** This section was revised for clarification of descriptions of concentration categories and site classes.

*Fig. 2 (a) text: "in the unit of ktonnes yr-1 grid-1": grid should be grid element? It would be nice to see a graph with on the x-axis the emission density of the grid element in which the station is situated and on the y-axis the AAN.*

**Response:** Agree. A figure has been generated and added in the revised paper.

*p. 12778, line 22 "Classes" should be "classes"*

**Response:** Corrected.

*p. 12778 and 12779. It should be discussed into more detail what the differences are between the different groups found in the cluster analysis as this can help with the interpretation.*

**Response**: The differences between the three concentration categories are significant and are the focus of our discussions. The differences between some classes are small (e.g. between classes 1 to 4). The range of AAN for each class have been added in the revised version to demonstrate the differences between groups in concentration levels. Temporal variations can be seen from Figures 4 for classes 1 -4.

*p. 12779.line 2: ": : : near strong NOx emissions": traffic could also maybe a source for NH3 in these areas. The formation of NH4NO3 is mentioned, which should lower the NH3 concentration as well as an increase of NH3 due to the emission of deposited N-compounds. These effects go into two directions: it is therefore important to know if the NH3 concentrations relatively high or low. Information should be given on that.*

**Response:** In our recent paper (Yao et al., Atmos. Environ, 2013, 80, 499-506.), we found that traffic emissions of $NH_3$ yielded a negligible contribution to atmospheric ammonia in southern Ontario. The reference is added in the revised version.

The range of AAN has been added in the revised version.

*p. 12779, line "Long-range transport". The emission areas are not so far away that the transport can be characterized as long-range transport.*

**Response:** "Long-range transport" has been changed into "regional transport" in the revised version.

*p. 12779, line 19. Categories are defined. Apparently, these categories belong also to cluster classes. So it looks like if cluster classes depend on the concentration. On p. 12778 that the classes were based on similar temporal variations in the NH3 concentration. This seems a bit contradictory.*

**Response:** Cluster classes are determined by temporal trends in $NH_3$ concentration. Since high emission zones are concentrated in a small area, the first four classes were thus all below to category 1. Similarly, all low emission zones are concentrated in southeastern Ontario and most of the sites in class 7 had similar temporal trends and belonged to category 3. The rest sites then went into category 2.

*p. 12780. About the remaining 40% of the peaks: Information on mineral fertilizer application could be obtained from agricultural scientists. The report of Lillyman et al. is as far as I can see not on the internet and is therefore difficult to obtain. Maybe the authors could mention the reason that the emissions in the Lillyman et al. emission inventory decrease by 80% in November and December. This is a rather sharp decrease. As the emission rate is increasing exponentially with temperature (caused by the temperature dependence of the Henry's law coefficient and the dissociation constant of NH4+) this could be one effect, but 80% is rather much. Emissions from animal housings and storage facilities will still occur in wintertime, but due to the temperature effect at a lower rate. Did Lillyman et al. already take into account the effect of a snow layer?*

**Response**: We believe the emission reduction of 80% only refers to the anthropogenic emission. The temperature-dependent emission is for natural emission or reemission. We admit that the emission inventory itself also has large uncertainties and may not include sporadic release in winter time. We could not provide more accurate emission estimates to support our analysis, but can only use what is available to us.

*p. 12781, line 7: The high peak concentrations in wintertime can be caused by application on snow or very stable atmospheric conditions (see some of the remarks in the beginning this review).*

**Response**: When we first identified this high concentration narrow zone, we discussed this phenomenon with our colleagues who participated in the field experiment. The possibility of manure dumping was also mentioned during the discussion. However, we have some difficulties to explain the spatial pattern of the high concentration distribution. This is because the high concentration sites distributed at a narrow line extending from southwest to southeast Ontario, a distance of 300 km. Even if the prevailing wind speed was along this path with manure application on the line at the source region, we should at least see some concentration peaks in the receptor areas at neighboring sites.

In the revised paper, we have added this possibility but also pointed out that it could not perfectly explain the observed spatial distribution.

*Text fig. 5: "but absent of spikes" = but without spikes?*

**Response**: Corrected.

*p. 12783, line 1. No significant correlations existed between the concentration of NH3 and RH or T. It should be mentioned here why this could be expected. Did the authors try to calculate the same calculations for stations with high and medium concentrations?*

**Response**: We were not expecting this, but were trying to exclude any unlikely factors. The part has been revised as "20 out of 30 sites were situated at the remote non-agriculture zone where no manure and fertilizer application occurred. The temperature effect cannot explain higher $NH_3$ levels during the six-week period because the highest ambient temperature occurred in the early of August."

*p. 12784. The correlation between the sites TEV and DDK: It is stated that this is partially due to atmospheric transport and/or similar meteorological conditions. I feel that this part is highly speculative and it does not give much information that this correlation can have two reasons. For that reason it cannot be concluded how large the contribution from atmospheric transport is. (what then about the similar meteorology?) . One should remember that contributions from other areas that are 30 km away is usually not that large, because the plume is highly diluted due to vertical mixing when it arrives.*

**Response**: We agree that we do not have an accurate method to identify what factors caused the high correlation between the two sites. We also agree that direct transport may not be the major reason, but the case can set up the upper limit of the contribution of the direct transport from source to receptor. We have made this clear in the revised paper. Our results actually agree with the reviewer suggestion (the last sentence in this comment). We have also added a reference of Theobald et al (2012), to support our conclusion.

*p. 12785. On this page and the following pages the authors are speculating too much about reasons for the (lack of) correlation they observe. What is needed is a model that can calculate the NH3 concentrations on a scale of maybe 5x5 km2 using detailed spatial and temporal emissions. This could maybe exclude part of the speculations.*
*p. 12785. There is no proof that Hypothesis-A would be sufficient to explain the observations. Certainly, some transport will occur, but one cannot conclude that e.g. broad peaks are caused by this phenomenon.*
*p. 12787. Concentrations maybe higher in wintertime due to reduced mixing. So the transport of NH4NO3 is not the only reason for the observed higher concentrations in low concentration zones.*

**Response**: As we responded at the beginning, we plan to use a model simulation to verify the hypothesis presented in this paper, which we hoped to publish in the future. We have revised the conclusion to make the hypothesis a possibility instead of a firm conclusion. We do believe such mechanisms can best explain the phenomena because other known mechanism cannot explain well the observed phenomena. We further

emphasis below.

In our study, the measurements at the non-agriculture sites were used to examine Hypothesis-A. All the non-agriculture sites were situated at remote areas. No manure and fertilizer application occurred at these remote non-agriculture sites because there was no agriculture activity. Thus, the observed $NH_3$ at the remote non-agriculture sites should be either mainly from local nature emissions or regional transport. When the local nature emissions of $NH_3$ at the remote non-agriculture sites were considered alone, soil and plants emissions would be the dominant sources. In this case, the higher mixing ratio of $NH_3$ is widely observed to be associated with the higher ambient temperature. As mentioned by this reviewer, the emission rate of $NH_3$ from the soil is increasing exponentially with temperature. Thus, the observed concentration of $NH_3$ in the summer at the remote non-agriculture sites should represent the maximum contribution of $NH_3$ emitted by local sources because of the highest ambient temperature. Any observed concentration of $NH_3$ in other seasons higher than the observed maximum concentration of $NH_3$ in summer at the remote non-agriculture sites should be associated with the external transport.

If low mixing height (or inversion layer) was the dominant factor, it should have also played similar roles in other seasons at these non-agricultural sites or in winter at the agricultural sites.

*On p. 12784 a good correlation between the stations TEV and DDK is partially explained by atmospheric transport, whereas a good correlation between the stations on p. 12788 is explained (line 27) by local emissions. This does not sound very consequent or at least needs an explanation.*

**Response**: If the two sites are not too far away, then direct transport might play a role, among other factors, e.g., similar temperature and solar conditions could mean similar emission rate if soil and vegetation nitrogen content are also similar. For sites far away, correlation could be mostly caused by similar meteorological conditions which resulted in similar emission rates. We have revised the explanation to make the rationale clear.

*p. 12790. It could well be that one or two figures with the emission density vs. the concentration would give a more clear presentation of the descrepancies between these variables in the different zones.*

**Response**: Agree. A figure has been generated and added in the revised version. Discussions have also been revised accordingly.

*p. 12791. The conclusions about the transport between regions should be left out. They are not proven.*

**Response**: We have revised our conclusions to make the hypothesis a likely possibility instead of a firm conclusion and proposed for more future research on the topic.