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# ***Interactive comment on “Analysis of passive-sampler monitored atmospheric ammonia at 74 sites across southern Ontario, Canada” by X. H. Yao and L. Zhang***

## **Anonymous Referee #2**

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

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

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to be more frequent during wintertime.

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).

p. 12775. “With the decrease of SO<sub>2</sub> and NO<sub>x</sub> emissions in developed countries, NH<sub>3</sub> is increasingly . . . .”. In Europe the NH<sub>3</sub> emissions have also decreased, but the percentage of emission reduction is less than that of SO<sub>2</sub> and NO<sub>x</sub>. For that reason NH<sub>3</sub> is in the EU the component that contributes most to potential soil acidification.

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.

#### DETAILED REMARKS

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

p. 12775 last line: “Such a hypothesis (referred to . . .”. It should maybe be noted

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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.

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 non-permanent 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).

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

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.

p. 12778, line 19: “Hierarchical cluster analysis . . . .”. It should be mentioned here

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which metric was chosen to calculate the distance between pairs of observations.

Fig. 2 (a) text: “in the unit of ktonnes yr<sup>-1</sup> grid<sup>-1</sup>”: 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.

p. 12778, line 22 “Classes” should be “classes”

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.

p. 12779, line 2: “. . . near strong NO<sub>x</sub> emissions”: traffic could also maybe a source for NH<sub>3</sub> in these areas. The formation of NH<sub>4</sub>NO<sub>3</sub> is mentioned, which should lower the NH<sub>3</sub> concentration as well as an increase of NH<sub>3</sub> due to the emission of deposited N-compounds. These effects go into two directions: it is therefore important to know if the NH<sub>3</sub> concentrations relatively high or low. Information should be given on that.

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

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 NH<sub>3</sub> concentration. This seems a bit contradictory. 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

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the dissociation constant of  $\text{NH}_4^+$ ) 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?

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).

Text fig. 5: “but absent of spikes” = but without spikes?

p. 12783, line 1. No significant correlations existed between the concentration of  $\text{NH}_3$  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?

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.

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  $\text{NH}_3$  concentrations on a scale of maybe  $5 \times 5 \text{ km}^2$  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

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peaks are caused by this phenomenon.

p. 12787. Concentrations maybe higher in wintertime due to reduced mixing. So the transport of  $\text{NH}_4\text{NO}_3$  is not the only reason for the observed higher concentrations in low concentration zones.

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.

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.

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

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