Response to Referee #2:

***Interactive comment on* "Quantifying atmospheric nitrogen deposition through a nationwide monitoring network across China" *by* W. Xu et al.**

Anonymous Referee #2

Received and published: 4 September 2015

General comments:

This paper is a useful contribution to the issue of atmospheric nitrogen (N) deposition in China. It presents a 5-year monitoring data of dry and wet N deposition at 43sites across China. However, the methods to obtain deposition fluxes are questionable which can result in large uncertainties to the conclusions made in this study. Some of the uncertainties are not necessary and could be constrained. I explained this in detail below.

Response: The authors appreciate the reviewer for the valuable comments and suggestions that greatly help us improve our work. To reduce uncertainties to the conclusion made in this study, we have optimized the methods for computing dry deposition flux, and have made more clarification on the method of wet/bulk deposition measurement and discussion for wet/bulk deposition fluxes. Detailed responses to the comments are given below.

Specific comments

1. Site locations:

Different from the air quality monitoring networks which focus on the protection of human health, the deposition networks are used to assess the pollutant impacts on sensitive ecosystem and vegetation. Therefore, many networks, for example, CASTNET/NADP in US, CAPMoN in Canada, and IMPACTS in China, locate their sites in rural or protected areas in order to minimize effects from local pollution sources. In this paper, 10 out of the total 43 sites are located in urban areas, which are not homogeneously distributed in China. The comparison of regional averages including results from urban sites may not reveal the real spatial differences. For example, southeast China has two of the largest industrial centres and megacity clusters (the Pearl River Delta region and the Yangtze River Delta region) in China. Severe air pollution has been reported in this region (e.g., Chan and Yao, 2008). But this study shows the mean concentrations of reactive N species in southeast China were 15-25% lower than the national averages (Table 1). I suggest to remove all the urban results in the analysis.

Response: Thank you for your suggestion on site locations. We agree many deposition networks worldwide mainly located in rural or protected areas. But the main objective of our study focuses on a systematic evaluation of dry plus wet deposition along different anthropogenic impacts (with differing reactive N emission intensities) across China. That's why we include ten urban sites in our network. We admit the current monitoring network is not complete and some more sites should be added in the future studies (please see our reply to reviewer #1's comment No. 4). We have noticed that atmospheric reactive N concentrations in southeast China (covering the Pearl River Delta and Yangtze River Delta regions) even lower than the national averages. Two reasons may explain this: 1) reactive N pollutants removed by frequent and high precipitation; 2) only three of total ten monitoring sites located in Pearl River Delta and Yangtze River Delta regions. In addition, our monitoring sites were mainly located at rural areas in southeast China and this could also lead to lower atmospheric N_r concentration and deposition. To avoid misunderstanding, we have deleted Table 1 and related comparison in the revision.

2. The method to derive the dry deposition flux: This paper estimated the dry deposition flux by the inferential method where the modeled dry deposition velocity (Vd) is paired with the measured concentration. Vd results were extracted from the 1-year productions by a global CTM model (GEOS-Chem),which has a horizontal resolution of 1/2 x 2/3 degree. This resolution is in fact too coarse for this study. Many sites (for example, NC1-NC2, NC4-NC5, NE2-NE3, SE9-SE10, SW5-SW6-SW7) are too close from each other and located within the same grid. It means the same Vd values are used for different sites although they may have different surface characteristics. What is the height where the Vds were calculated?70 m AGL? Vd for HNO3 is very sensitive to the calculation of Ra and the values computed at 70 m AGL should be much smaller than that at 2 m AGL. This also applies to the other species at some extend. The Vd calculations highly rely on the landuse types. Did you confirm the landuse map used in the simulation with the actual landuse types of the monitoring sites? They may not be consistent. In this paper, only 1-year simulation (2012) was used to derive Vds for the 5-year (2010-2014) period. This ignored the year-to-year variations in Vd. Several approaches can be taken to improve this. For example, you can run the GEOS-Chem model from 2010 to May 2013 and fill the gap in the period when GEOS meteorological data is unavailable using the means calculated from all the available simulations. Or you may try a single-point dry deposition model which can use the meteorological driving forces from various sources (e.g., field measurements if available, MM5/WRF simulation).

Response: We have re-modeled dry deposition velocities (V_ds) of N_r species at 2 m AGL. Indeed, the V_ds of N_r species computed at 2 m AGL show various degrees of increases compared to those at 70 m AGL. Meanwhile, we have run the GEOS-Chem model from January 2010 to May 2013 for all the 43 sites and fill the gap for the period when GEOS meteorological data is unavailable using the mean values calculated from all the available simulations, as suggested by the reviewer. This approach of dry deposition estimate provides large improvements compared to previous work on nitrogen deposition over China as described below in addressing the Comment No. 6.

We now state in the text: "For a detailed description of the V_d calculation as well as the estimation of N dry deposition, the reader is referred to the Supplement (Sect. S5), with monthly and annual dry deposition velocities of N_r for different land use types presented in Tables S3 and S4 therein. The model uses the land map of the Global Land Cover Characteristics Data Base Version 2.0 (http://edc2.usgs.gov/glcc/globdoc2_0.php), which defines the land types (e.g., urban, forest, etc.) at the native 1 km × 1 km resolution and is then binned to the model resolution as fraction of the grid cell covered by each land type. The model 1/2° resolution may coarsely represent the local land characteristics at the monitoring sites. Future work using a single-point dry deposition model as for CASTNET (Clarke et al., 1997) would further improve the dry deposition flux estimates, but that requires concurrent *in-situ* measurements of meteorological variables which are not available at present. "

Added reference:

Clarke, J. F., Edgerton, E. S., and Martin, B. E.: Dry deposition calculations for the Clean Air Status and Trends Network, Atmos. Environ., 31, 3667-3678, 1997.

Table S3 has been corrected to show the improved dry deposition velocities over the different land types.

Table S3. Statistics of monthly mean dry deposition velocities of N_r species for three land use types, basing on the modeled hourly values at the forty-three sites during January 2010 and May 2013[a].

Land use type		Monthly mean deposition velocities (cm s^{-1})				
		NH_3	NO_2	HNO_3	pNH_4^+	pNO_3^-
Urban	N	410	410	410	410	410
	Min	0.30	0.01	0.12	0.06	0.06
	Max	1.63	0.44	5.78	0.35	0.35
	Mean	0.45	0.12	1.22	0.17	0.17
	Median	0.34	0.10	1.15	0.17	0.17
	SD	0.29	0.10	1.00	0.07	0.07
Rural	N	902	902	902	902	902
	Min	0.09	0.01	0.05	0.07	0.07
	Max	1.10	0.46	5.78	0.37	0.37
	Mean	0.40	0.17	1.49	0.18	0.18
	Median	0.35	0.16	1.49	0.18	0.18
	SD	0.16	0.12	1.10	0.06	0.06
Background	N	451	451	451	451	451
	Min	0.20	0.01	0.06	0.05	0.05
	Max	1.48	0.57	8.88	0.31	0.31
	Mean	0.47	0.17	1.78	0.16	0.16
	Median	0.43	0.13	1.48	0.16	0.16
	SD	0.22	0.15	1.66	0.06	0.06

[a]The forty-three sites consist of 10 urban, 22 rural and 11 background sites. Among the forty-three monitoring sites, 20 farmland, 5 coastal, 6 forest and 2 grassland sites were included in the rural and background sites.

3. The sampling method of wet deposition: This study utilized a bulk sampler instead of a wet-only sampler to collect the wet depositions. A well-known problem about the bulk sampler is that the wet deposition samples can be contaminated by the dry deposition. This is even worse in the north region of China where precipitation is not frequent and dry deposition may dominate the total deposition. As mentioned in the manuscript, the bulk deposition flux of N can be 20-39% higher than the wet-only deposition. This needs to be emphasized in the conclusion and abstract of the manuscript to remind the readers be careful when comparing your results with previous studies.

Response: We have answered this question in the Reviewer [#]1's similar comment (Response to Reviewer [#]1's Comment No. 3). Briefly we have replaced "wet deposition" by "wet/bulk deposition" in the revision, and have emphasized the difference between bulk and wet-only deposition.

4. P18372: The description of sampling methods is not clear. At the sites without power, how HNO3 was sampled? Was NO2 sampled using Gradko diffusion tubes at all sites? If yes, there is no need to mention this twice in the same section.

Response: Thanks for pointing it out. At the seven sites (i.e., NC2, NE4, NE5, SW5, SW7, TP1

and TP2) without power supply, ambient HNO_3 concentrations were not measured due to lack of passive samplers for HNO_3. Thus, there were no data on HNO_3 concentrations and dry deposition fluxes shown for those seven sites in corresponding Figures (e.g. Figures 2, 3 and 5, Figures S2c). As for total dry deposition fluxes at the seven sites, gaseous HNO_3 was not taken into consideration. At all sites in the network, gaseous NO_2 was sampled using Gradko diffusion tubes. As suggested we have made more clarification on above issues in the revised Sect. 2.2.

5. P18378L23: annual precipitation -> annual precipitation amount?

Response: Yes, we have changed "annual precipitation" to "annual precipitation amount"

6. P18387L8: According to the references given, I think it means this study made improvements compared with previous work in China. It is better to clarify this.

Response: Thank you for this suggestion. We have revised the corresponding sentences in the Section 4.4 to clarify this.

"In previous work, dry deposition flux was inferred from atmospheric N_r concentrations and a literature-based annual mean deposition velocity (Shen et al., 2009), or reported by Luo et al. (2013) which did not consider the different dry deposition velocities of various N_r species among different land use types. Clearly, in this study we have greatly improved the estimation of dry deposition, but further work is still needed to increase the reliability and accuracy of N dry deposition values."

References:

Luo, X. S., Liu, P., Tang, A. H., Liu, J. Y., Zong, X. Y., Zhang, Q., Kou, C. L., Zhang, L. J., Fowler, D., Fangmeier, A., Christie, P., Zhang, F. S., and Liu, X. J.: An evaluation of atmospheric N_r pollution and deposition in North China after the Beijing Olympics, Atmos. Environ., 74, 209–216, doi:10.1016/j.atmosenv.2013.03.054, 2013.

Shen, J. L., Tang, A. H., Liu, X. J., Fangmeier, A., Goulding, K. T. W., and Zhang, F. S.: High concentrations and dry deposition of reactive nitrogen species at two sites in the North China Plain, Environ. Pollut., 157, 3106–3113,doi:10.1016/j.envpol.2009.05.016, 2009.

7. P18387L20-25: The organic N species have been found as important contributors tothe N dry deposition. For example, Turnipseed et al. (2006) reported that PAN accounted for 20% of the daytime NOy flux at a forest site. This should be included in the uncertainty discussion (section 4.4).

Response: Thank you for this valuable suggestion. We have added the following sentences to discuss this issue in the revised Section 4.4.

"On the other hand, the total dry deposition flux in this study may be underestimated due to omission of the dry-deposited organic N species in our network and missing HNO_3 data at very few sites as noted earlier (Sect. 2.2). The organic N species have been found as important contributors to the N dry deposition. For example, PAN accounted for 20% of the daytime, summer time NO_y ($NO + NO_2 + HNO_3 + NO_3^- + PAN$) dry deposition at a coniferous forest site (Turnipseed et al., 2006). However, the contribution of PAN and other known atmospheric organic nitrates to total N_r inputs must be minor on the annual time scale, as reported by Flechard et al. (2012)."

References:

Flechard, C. R., Nemitz, E., Smith, R. I., Fowler, D., Vermeulen, A.T., Bleeker, A., Erisman, J. W., Simpson, D., Zhang, L., Tang,Y. S., and Sutton, M. A.: Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network, Atmos. Chem. Phys., 11, 2703–2728,doi:10.5194/acp-11-2703-2011, 2011.

Turnipseed, A. A., Huey, L. G., Nemitz, E., Stickel, R., Higgs, J., Tanner, D. J., Slusher, D. L., Sparks, J. P., Flocke, F., and Guenther, A.: Eddy covariance fluxes of peroxyacetyl nitrates (PANs) and NOy to a coniferous forest, J. Geophys. Res., 111,D09304, doi:10.1029/2005JD006631, 2006.

8. Supplement section S5: As stated in the manual of GEOS-Chem(http://wiki.seas.harvard.edu/geos-chem/index.php/Dry_deposition), the dry deposition for particles followed Zhang et al.(2001) scheme, instead of Wesely (1989),which is a dry deposition scheme for gases.

Response: Yes, we now state in both the Section 2.5 and Section S5 "The model calculation of dry deposition of N_r species follows a standard big-leaf resistance-in-series model as described by Wesely (1989) for gases and Zhang et al. (2001) for aerosols."

Added Reference:

Zhang, L. M., Gong, S. L., Padro, J., and Barrie, L.: A size-segregated particle dry deposition scheme for an atmospheric aerosol module, Atmos. Environ., 35 (3), 549-560, doi:10.1016/s1352-2310(00)00326-5, 2001.

Technical corrections:

9. P18372L3: Sutton et al. (2001) -> Sutton et al. (2001))

Response: Revised as suggested.

10. P18372L11: delete "produced by"

Response: Deleted as suggested.

11. Supplement section S1: South China (SC) -> Southeast China (SE)

Response: Revised as suggested (changed "South China (SC)" to "Southeast China (SE)".