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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "A 15-year record (2001–2015) of the ratio of nitrate to non-seasalt sulfate in precipitation over East Asia" *by* Syuichi Itahashi et al.

W. Aas (Referee)

waa@nilu.no

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This study compare observed trends in in-situ observations of sulfate and nitrate in precipitation, and satellite data of NO2 and SO2 with emission estimates of Sox and Nox in East Asia for the last 15 years. This is an important topic since there has been large changes in the emissions in Asia the last decades. The comparison between satellite data with emission, I think is good, but the comparison with in situ data I find a bit shallow. The spatial variability of the emissions and the wet deposition are large, and the site representatvity is a critical question. Are the sites in question able to show the overall trends for the different regions? For South Korea and Japan it is probably

OK, but in China it is too few sites. The authors are aware of the problem and add campaign data in China, but these are only snapshots in time and cannot be used for assessing trends. I do miss more discussion of this. As I understand it, the authors claim that the ratio of NO3/SO4 is a good parameters for assessing the regional trends (better than the individual concentrations), but this is mainly showing that the chemical regime is changing, which is probably correct, maybe not all over the continent though, and does it help us to understand whether the individual trends of NO3 and SO4 are correct?

A critical point is that the paper is the merging all type of sites. In the EANET network, there are many urban sites and (some of) these may not show representative trends for the region. Even though the authors at page 6 line 8-14 discuss this a bit, and claim they (the Chinese urban sites) show similar trends, it is very few sites and only trends for the ratio is presented. I will suggest to separate urban and regional sites in the study, and even better calculate the trends at the individual sites rather than averaging all the sites, which have totally different siting criteria.

I also find the trend calculations a bit too optimistic since you calculate trends from only five years periods, usually one needs at least 7 years (preferably 10) for calculating trends. You have not described how you calculate trends and the significance, except that it is linear.

More specific comments to the text:

* Page 1. The references Endo et al and Ban et al are mainly studying EANET data and not directly with US and Europe. You should rather use US and European references when comparison. Some examples:

EMEP: Tørseth, K. et al. Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972-2009. Atmospheric Chemistry and Physics 12, 5447-5481, doi:10.5194/acp-12-5447-2012 (2012).

CASTNET: Sickles Ii, J. E. & Shadwick, D. S. Air quality and atmospheric deposition in the eastern US: 20 years of change. Atmos. Chem. Phys. 15, 173-197, doi:10.5194/acp-15-173-2015 (2015).

IMPROVE: Hand, J. L., Schichtel, B. A., Malm, W. C. & Pitchford, M. L. Particulate sulfate ion concentration and SO₂ emission trends in the United States from the early 1990s through 2010. Atmos. Chem. Phys. 12, 10353-10365, doi:10.5194/acp-12-10353-2012 (2012).

NADP: Lehmann, C. M. B., Bowersox, V. C., Larson, R. S. & Larson, S. M. Monitoring Long-term Trends in Sulfate and Ammonium in US Precipitation: Results from the National Atmospheric Deposition Program/National Trends Network. Water, Air, & Soil Pollution: Focus 7, 59-66, doi:10.1007/s11267-006-9100-z (2007).

UNECE also has relatively new assessments of trends from Europe and North Americ, which might be relevant as well: http://www.unece.org/index.php?id=42861 and http://www.unece.org/index.php?id=42947

*Page 3 line 13-16. I don't understand what you mean here that "the deposition were centred". with a reference to Pan 2015, who looks at deposition of trace elements in Northern China. I assume the authors are discussion the point I address in the beginning with representativity of the EANET sites, but I don't understand how you can state that "The approach taken here will further promote our understanding of precipitation chemistry for all of China" since the additional sites only cover a short period and cannot be used for trends. If you had looked at one specific year to assess the spatial deposition it would have been different.

*Page 4 line 6. The Ogasawara site was excluded with quite strict criteria. 25% is more appropriate. Further you could have in included the Russian site close to the Korean border, Primorskaya, which is also downwind from the large emission sources in China.

*Page 8 line 13-14: "For the treatment of precipitation amount, months where data were insufficient were the same as when applying the Smirnov-Grubbs test for Ratio calculation." I don't understand this sentence

*Page 8 line 16-17 The sentence "Statistical analysis revealed that, except for the increasing and decreasing trend over China and Korea during Phase III .. there was no clear change in precipitation amount..." is somewhat in contrast to the conclusion later on page 13 line 21: "In spite of the increasing trends of precipitation amount, decreasing trends for nss-SO4 wet deposition amounts over China, Korea, and Japan were seen after 2005–2006". The increase in precipitation amount in China is after 2010 (though the variability is very high) and South Korea has decreasing amount.

*Page 8-9 "The temporal variation found in the NO3 concentration in precipitation did not correspond to the NOx emissions variation". This non-linearity can be due to several factors. E.g.: The non representativity of the sites, the change in atmospheric composition and chemical regimes (changes in base cations and ammonium), oxidation capacity of the atmosphere, all may change the lifetime of NOx and NO3 (course or fine).

*Page 9 line 18. "Contamination". It's a bit misleading word. The satellite measurements are not contaminated they are influence by sources outside Korea (like China)

*Page 9 line 23. Have the volcanic activity changed during the period to influence the trend of the SO2 column data? Should maybe also have been included also in the emission inventories?

*Page 9-10. IMPACTS sites have lower levels compared to EANET since these are mainly regional/rural sites while the BNU site is urban and naturally higher than the average EANET site.

*Page 10: There are some contradicting statements:

1)Over China, NO2/SO2 column ratio were flat during Phase I, sharply increasing during Phase II, and almost flat during Phase III.

2)NO_x/SO_2 emission ratio were well correlated with the variation in Ratio over China

3)Ratio was almost 0.3 during Phase I and subsequently increased.. during Phase II, with a trend of +14.8±1.9%/year and around 0.4–0.6 during 30 Phase III with a trend of +10.1±3.8%/year ($p < 0.05$).

This leads to the conclusion on page 11 . "Ratio observed in EANET network can be a representative dataset of China for the precipitation chemistry"

This is not obvious for me

*Page 12 line 31. Nr. Is this reactive nitrogen? It is not defined. Can also be interpret as reduced nitrogen. I assume reactive nitrogen since you at page 13 line 1 states that Nr can cause eutrophication and this means both NO_3 and NH_4

*Figure 7c. It is not clear how sum NO_3 and SO_4 is calculated Figure C do not add up from fig a and b, even if changing units. Maybe better to look at equivalent and not mass

*Table 2. It would have been nice to indicate how many sites are included in these calculations, and the time period for the different phases should be included in the table so the reader don't need to search in the text. Is it the same number sites in all the phases? In the table there is no unit (kg/ha pr year?)

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