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Interactive Comment

Interactive comment on "Air quality and atmospheric deposition in the eastern US: 20 years of change" *by* J. E. Sickles II and D. S. Shadwick

Anonymous Referee #2

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In this work the authors focus on the changes in ambient concentrations and deposition of sulfur and nitrogen species, as well as ozone and wet-deposited H+, measured at 34 sites in the eastern United States for two 5-year time periods, 1990–94 (P1) and 2004–2009 (P4). Changes between the 2000–2004 (P3) and 2005–2009 periods were also examined, though to a much lesser degree. The changes in concentrations over the 20 year period are also associated to the large decreases in SO2 and NOx emissions that occurred during these years. This provides some insights into the response of the measured ambient concentrations and wet deposition rates to these emission changes. In addition, the inclusion of multiple species in the analysis allowed for the

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Interactive Discussion

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exploration of the role of a changing atmospheric composition on the differences in the ambient and deposition levels over the 20-year period. The authors conduct a thorough analysis that helps to document, and provide some important insights into, the changing composition of ambient and deposited sulfur and nitrogen compounds and I recommend its publication, though there are two issues that they should consider.

First, this work builds on previous work by the same authors and uses the same method of analysis and a similar presentation of results as in Sickles and Shadwick (2007, JGR). The earlier work examined changes between P1 and P3, while this work extends the analysis by 5 years and compares P1 to P4. As the authors show, there have been substantial reductions in SO2 and NOx emissions since the early 2000s, and the composition of the atmosphere has also changed. In the context of their previous work, the new information presented here is the changes from P3 to P4. However, since the authors focus on the P1–P4 time period, many of the P3–P4 changes need to be inferred by comparing the new results to the previous results. I think this work would be more valuable if the authors would focus on the P3–P4 time period, with reference to P1–P4 instead of the other way around. If the authors choose to keep the focus on the P1–P4 comparison, then I suggest that they at least provide a similar table to Table 3 but for the difference between the P3 and P4 time periods. This would allow interested readers to examine these differences and draw their own inferences and conclusions.

The ambient particulate ammonium and nitrate concentrations were measured in the CASTNET monitoring program which uses Teflon filters to collect the particulate samples for analysis; however, as shown by Yu et al. (2006, Atm Env), a substantial fraction of ammonium nitrate can volatilize and be lost from a Teflon filter during sampling and handling. In CASTNET the ammonium would be lost, and the nitrate would be collected on the backup filter and be interpreted as nitric acid. This sampling bias is not discussed in the manuscript but could have important implications for the interpretation of results. Specific examples are given below. The authors should discuss this potential bias in the manuscript and incorporate the implication into the discussion of results.

Specific comments: 1) Page 7, lines 3–10: “Recent comparison of concentrations from collocated CASTNET and IMPROVE samplers (with 2.5 μm size cut) indicate CASTNET samplers typically to be biased high at eight non-marine eastern sites by 4 to 7% for aerosol SO4, but ranged between 25% higher and 39% lower for aerosol.” The authors discuss the sampling of the fine tail of course nitrate by the CASTNET sampler which increases nitrate concentrations relative IMPROVE. However, they do not discuss the negative bias due to volatilization of ammonium nitrate from the CASTNET Teflon filter. It is the different contributions of these two biases at the different sites that partially cause the wide variation between the CASTNET and IMPROVE nitrate concentrations.

2) Page 7, line 27: “however, nonideal landscape features (e.g., irregular terrain and/or forested canopies) likely contribute low biases to concentration.” Since the concentrations are measured, why would nonideal landscape features cause low biases to concentrations?

3) The discussion on pages 7 and 8 on biases in deposition estimates is interesting. However, since this work is focused on quantifying differences between P1 and P4, it is not the bias in deposition estimates that is most relevant but rather changes in these biases over time and how this might impact the comparison of time periods that is important. The authors recognize this but only state that they will assume that the biases are constant in time. They should provide some discussion as to why this is a valid assumption. Note, the sampling bias from volatilization of ammonium nitrate from the Teflon filter may not be constant in time and could conceivably enhance or suppress differences between time periods. The authors should discuss this as well.

4) It would be valuable if the discussion of changes in S and N wet deposition in P1 and P4 should be compared to results from Lehmann et al. (2005, Environmental Pollution)

and Lehmann and Gay (2011, PPChem).

5) Page 15, line 5: “Atmospheric OxN concentration is the sum of atmospheric HNO_3 and aerosol NO_3 concentrations (expressed as mass of nitrogen), and almost 60% of the OxN is generally present as HNO_3.” This will be influenced by the ammonium nitrate sampling bias.

6) Page 18, line 15: “Due to the large difference in deposition velocities, 75% of dry N is contributed by dry HNO_3...” This too will be influenced by the nitrate sampling bias. In addition, the exclusion of dry deposition of ammonia highly biases the reported fractions. This should be discussed and potentially illustrated using results from field studies that measured ammonia, such as in the SEARCH program.

7) Page 23, line 26: “when the index, RNO_3 (i.e., the ratio of atmospheric aerosol NO_3 to OxN concentrations), is less than 0.7, then formation of aerosol NH_4NO_3 may be NH_3-limited.” Unfortunately, due to the nitrate volatilization sampling bias, this method cannot be used with these data, and this analysis should be removed.

8) Page 24, lines14–26: As shown by Malm et al. (2007, Atm Env) and Lee et al. (2008, Atm Env), in the eastern United States, some nitrate is in the coarse mode and may be in the form of sodium or calcium nitrate. Therefore, in the neutralization calculation, the ammonium associated with nitrate may be overestimated, thus underestimating the sulfate neutralization. This potential bias should be mentioned.

Minor comments: 1) Page 3, line 14: How are “eastern states” defined? 2) Page 9, line 8: “Five year periods have been chosen to coincide with emission patterns (noted earlier)...” This might have been true in the authors’ first article examining P1 and P2. However, any grouping of emission patterns in P3 and P4 was fortuitous. 3) Page 11, line 1: RD is not in Table2.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 17943, 2014.