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Atmospheric Chemistry and Physics
Discussions

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

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Response to the comments of Referee #2. Thank you for taking the time to examine our manuscript and for providing useful comments.

Response to first general comment. Our study was designed to examine associations between legislated reductions of emissions and changes of monitored air quality and deposition in the eastern US. With a potential data base covering a 20-year period, scoping our study and developing an approach required many choices. These choices involved monitored variables (e.g., ambient concentration, dry deposition and

wet deposition), temporal scales (e.g., weekly, seasonal, annual, and multi-year), and location (e.g., site-specific and regional). The result was a study examining 5-year period mean values from the same sites with data for the complete 20 years. This study approach used the first period as the baseline for most comparisons, because it represented conditions prior to emissions reductions triggered by the Clean Air Act Amendments of 1990 and by other legislated emissions reduction programs. With our current study, we extend a previous study to a fourth 5-year period and focus primarily on P1-to-P4 comparisons of the most recent metrics with their baseline values. Our earlier manuscripts have focused on P1-to-P2 and P1-to-P3 comparisons, emphasizing the latter. Our current manuscript focuses on P1-to-P4 and P3-to-P4, emphasizing the former by maintaining P1 as our baseline. Nevertheless, in some instances, P3-to P4 comparisons are used to provide context and amplify on P1-to-P4 findings. To refocus our study on P3-to-P4 comparisons is inconsistent with our original goal; it would require redefining the baseline period and major re-scoping of our investigation.

Response to second general comment. As noted on page 6, line 21 – page 7, line 11; and in SS07a, use of the CASTNET FP does introduce sampling artifacts into our results, especially those of nitrogen-containing species. Potential biases result primarily from artifacts indigenous to the CASTNET FP sampler: possible loss of aerosol NH4NO3 during sampling; and aspiration of the fine tail of aerosols larger than 2.5 μm by the CASTNET sampler. An expansion of information noted and/or cited in our manuscript is given below.

Possible loss of aerosol NH4NO3 during sampling. Aerosol NH4NO3 collected on a filter may be lost by volatilization into gaseous HNO3 and NH3, driven by a departure from equilibrium and/or by reaction with strong acids. Yu et al. (2006, Atmos. Environ.) focused on the loss of aerosol NH4 from denuded nylon filters in sampling arrangements that differed appreciably from the CASTNET FP. They used a cyclone and annular denuders (coated to remove both HNO3 and NH3) located upstream of FPs containing either two nylon filters in series or a Teflon and a nylon filter in series.

By removing both HNO3 and NH3 before the FP, they likely disturbed the (tendency toward equilibrium) partitioning between gaseous HNO3 and NH3 and aerosol NO3 (present as fine particle NH4NO3) and promoted a maximum amount of volatilization of NH4NO3 into gaseous HNO3 and NH3. They did not report aerosol NO3 loss; however, focusing on only aerosol NH4, they found much larger losses of aerosol NH4 from the nylon-nylon pair than the Teflon-nylon pair at eastern sites (Bondville – 9.5 % vs. 3.5%; Brigantine – 17% vs. 11%; and Smoky Mountains – 18% vs. 5.5%). Chow et al. (2005, JAWMA) have shown that estimation of volatilized aerosol NO3, based on equilibrium considerations when the sample has been completely denuded of HNO3 (but not NH3), grossly overestimates the amount of volatilized aerosol NO3. Sickles and Shadwick (2002, Atmos. Environ.) showed that at Egbert, Ontario ratios of composited weekly daytime and weekly nighttime CASTNET FP samples for aerosol NO3 exceeded paired continuous weekly samples by $\leq$ 2% for winter, spring and fall seasons, but by >20% for summer samples. Further, in a later study Sickles and Shadwick (2008, Atmos. Environ.) report that aerosol NO3 concentrations using the CASTNET FP and IMPROVE sampler (with 2.5 μm size cut inlet and an HNO3 denuder) showed median relative biases ranging between 5 and -10% for all seasons except summer, where the median IMPROVE aerosol NO3 concentration exceeded the CASTNET values by >40% (for more discussion see Reply to specific comment 1, below and Sickles and Shadwick (2008, Atmos. Environ.)). These findings suggest that although loss of aerosol NO3 (present as fine particle NH4NO3) likely does occur, it may be small in non-summer seasons.

Aspiration of the fine tail of aerosols larger than 2.5 μm by the CASTNET sampler. The CASTNET FP sampler is a downward-oriented open-faced integrative filter pack housed inside a larger downward-facing weather shield, each with no additional particle sizing inlets (e.g., cyclone or impactor) (SS07a). Post-SS07a findings from Sickles and Shadwick (2008, Atmos. Environ.) as well as unpublished wind tunnel and modeling studies of particle sampling characteristics of the CASTNET FP inside its weather shield at wind speeds of 0.4 – 8 ms-1 suggest appreciable collection of both fine ($\leq$2.5

μm) and larger (2.5-10 μm) particles on the first filter (Teflon) of the FP. Thus, collection of particles containing SO4, NH4, and NO3 and/or collection of the fine tail of larger particles, may provide high biases to CASTNET aerosol concentrations in comparison to their PM2.5 contribution but low biases in comparison to their contribution to total PM. Aerosol SO4 and NH4 occur mainly as fine particles (e.g., Wolff, 1984, Atmos. Environ.; Lefer and Talbot, 2001, JGR; Zhang et al., 2008, ACP) and are unlikely to offer appreciable high bias to CASTNET PM relative to their PM2.5 contributions. As noted in our current manuscript (page 7, lines 8 – 10) and in Sickles and Shadwick (2008, Atmos. Environ.), co-located sampling at 10 eastern sites showed good agreement, with CASTNET aerosol SO4 concentrations 4-7% higher than IMPROVE (with 2.5 μm size cut inlet).

During summer at eastern non-urban non-marine sites Wolff (1984, Atmos. Environ.) showed that aerosol SO4 exists primarily in the fine ($\leq$2.5 μm) fraction and aerosol NO3 exists mainly as larger particles. Lefer and Talbot (2001, JGR) report similar findings (MA, summer 1991-1996; aerosol SO4 and NH4 <1 μm; aerosol NO3 >4 μm), and they associate larger aerosol NO3 with coarse alkaline (Ca+2) soil particles. Studies at 8 sites in Canada (in various seasons, 2001-2005) by Zhang et al. (2008, ACP) suggest that aerosol SO4 and NH4 particles are unimodal (<0.6 μm), that aerosol NO3 exists mainly as larger particles (>4 μm) during the warm seasons, and that during the cold seasons aerosol NO3 is bi-modal, existing mainly (78-90%) as fine particles (<0.6 μm, presumably NH4NO3), with the remainder as larger particles (>4 μm). Similar findings were reported by Lee et al. (2008, Atmos. Environ.) where 85% of total aerosol NO3 occurred as fine particle NH4NO3 in cold season sampling an eastern US (Bondville) site; whereas, only 2% occurred as fine particle NH4NO3 in the warm season sampling at a different eastern site (Smoky Mountains). Thus, there is evidence suggesting that the size distribution of aerosol NO3 is often multimodal, and that >75% may exist as fine particles in non-marine environments during cooler seasons.

Evans et al. (2004, Atmos. Environ.) and references therein have shown the importance of partitioning ambient gas phase HNO3 into larger size range particles by reacting with coarse sea salt (NaCl) and mineral dust (CaCO3) constituents present in ambient air. Alkaline particles (e.g., soil/mineral dust, road salt, sea salt) may contain aerosol NO3 (possibly formed by scavenging HNO3 while airborne (e.g., Evans et al., 2004, Atmos. Environ.)), and to the extent that they are collected, these larger particles may provide a high bias to CASTNET aerosol NO3 concentration relative to its PM2.5 contribution. Some of these alkaline particles (if unreacted and retained on the Teflon filter of the CASTNET FP) may also scavenge airborne HNO3 from sampled air during week-long sampling periods, leading to a high bias of CASTNET aerosol NO3 concentration and to a low bias of CASTNET HNO3 concentration (e.g., enhanced retention of HNO3 through reaction with co-collected NaCl on a Teflon-coated aluminum cyclone sampling inlet has been demonstrated by Li-Jones et al., 2001, Atmos. Environ.). Although some of the above discussion is referenced in the text, it will be revised where needed to clarify the potential impacts of these sampling artifacts.

Reply to specific comment 1): Several factors can contribute to the variations between CASTNET and IMPROVE aerosol NO3 concentrations reported in Sickles and Shadwick (2008, Atmos. Environ.), and many are noted in that article. One is the relatively high variability of CASTNET aerosol NO3 measurements. Duplicate, co-located CASTNET sampling has shown weekly CVs for aerosol SO4 and NO3 concentrations of 2.3% and 8.1% (Sickles and Shadwick, 2002, Atmos. Environ.). Here, variability of aerosol NO3 concentration was highest among CASTNET species, with median absolute relative differences <12%. Another likely contributor to variations between CASTNET and IMPROVE samples reported in Sickles and Shadwick (2008, Atmos. Environ.) is the comparison of non-simultaneous samples (i.e., seasonally aggregated IMPROVE samples collected every third day were compared with seasonally aggregated continuous weekly CASTNET samples). In addition, samplers in this study were co-located within 0.1 km; however, the locations included a range of elevations, climates, and environments (e.g., inland versus marine). For example, although with CASTNET and IMPROVE showed mixed comparisons at inland sites, CASTNET sites

showed consistently higher median aerosol NO3 concentrations at marine-influenced sites. (Here, the fine tail of coarse sea salt-containing aerosol NO3 could have been captured, and/or the fine tail of coarse sea salt-containing aerosol could have been captured and retained HNO3 during subsequent sampling). Seasonally, CASTNET and IMPROVE aerosol NO3 concentrations showed median relative biases ranging between 5 and -10% for all seasons, except summer, where the median IMPROVE aerosol NO3 concentration exceeded the corresponding CASTNET values by >40% (but this was at very low concentrations, $\approx 0.25\ \mu$g m-3). These observations are consistent with loss (via volatilization and/or reaction with strong acids) of NH4NO3 from the Teflon filter of the CASTNET FP during warm season sampling and minimal loss during cooler seasons.

Reply to specific comment 2): Information about the impacts of non-ideal landscape features on concentration is given in the citations noted on page 7, line 28 – page 8, line 1 and in SS07a. For example, SS07a (and references therein) suggest that dry deposition to ground and canopy surfaces can be a sink for species sampled at a low elevation in a montane region or in a clearing within a forested area and can deplete airborne concentrations substantially relative to those at higher elevations or at tree tops above a forest. Since regionally representative airborne concentrations are sought, this would likely contribute low biases to concentrations monitored at some locations.

Reply to specific comment 3): We attempt to note the range of uncertainties associated with airborne species concentration, their estimated deposition velocities, dry and wet deposition values both in our Section 2 and in SS07a. Although sampling or other biases may be changing over time, we have very little information to provide quantitative guidance on this issue and as a result assume constant temporal bias.

Reply to specific comment 4): The changes in S and N wet deposition cannot be compared directly with those of Lehmann et al. (2005, Environmental Pollution) or Lehmann and Gay (2011, PPChem) for several reasons. First, the time periods are not the same (e.g., 1985 to 2002 and 1984-1986 to 2008-2010); whereas, our P1-to-P4 covers 1990-1994 to 2005-2009. In addition, they focus on ion concentrations at sites across the continental US, and our work focuses on wet deposition at a sub-set of eastern US sites. Nevertheless, since the data underlying all of the above analyses come from the same source (NADP/NTN), findings are expected to be generally consistent.

Reply to specific comment 5): Volatilization loss of aerosol NH4NO3 may release HNO3 from the Teflon filter to the nylon filter of the CASTNET sampler, and this would likely act to bias reported HNO3 concentration high and reported aerosol NO3 concentration low. However, as noted above and in SS07a, if larger particles containing NaCl and/or soil/mineral dust are collected on the Teflon filter, they could retain sampled HNO3, resulting in biases in the opposite direction. The text will be revised to note potential biases to metrics involving HNO3 and aerosol NO3.

Reply to specific comment 6): The lack of NH3 concentration measurements in the CASTNET data set is noted at least four times our manuscript. As mentioned on page 36, line 19 – 23, it is hoped that future data analyses will include NH3 measurements. The lack of NH3 concentration data does not bias reported metrics as they are defined in our manuscript; however, many of the metrics would change substantially if NH3 were available and our metrics were redefined to include it. Estimation of the contribution NH3 to Total N deposition is very complex and currently a topic of active measurement and modeling research in our laboratory. Sources of NH3 (e.g., feedlots, animal husbandry, agriculture/fertilizer, urban) are widespread, causing concentrations to vary considerably across the landscape. For example, site-specific 2004 – 2010 mean NH3 concentrations from the 8-site SEARCH network range between 0.2 and 1.9 μg m-3 (Blanchard et al., 2013, JAWMA). In addition, NH3 displays bi-directional flux characteristics with variable compensation points, making its deposition velocity highly variable and very site specific. Although bi-directional flux issues are not mentioned, Zhang et al. (2009, JGR) estimated NH3 deposition velocities ranging between 0.12 and 0.63 cm s-1 for 14 short campaigns at 8 rural sites in Canada. Using the

above ranges of NH3 concentrations and deposition velocities along with our P4 Total N results, dry NH3 deposition could contribute from ≈1% to >30% of Total N deposition. Nevertheless, I am reluctant to include this discussion in any revision, due to the large uncertainties associated with these estimates.

Reply to specific comment 7): If the only source of aerosol NO3 bias were the possible loss of aerosol NH4NO3 during sampling (by volatilization and/or by reaction with strong acids), this would contribute a low bias to RNO3; however, the possibility of over-sampling the fine tail of larger aerosols provides opportunities for high biases to RNO3. Previous discussion, has suggested that these two sources of bias will have a minimal impact during cool season sampling. As a result, use of RNO3 as a rough metric to indicate NH3-limited conditions for aerosol formation in the east will be limited to wintertime samples, with an appropriate cautionary note about potential sampling biases included in the text. As an aside, the CASTNET P4 RNO3 value for the south region (0.32) is consistent with the range of values averaged across seasons for 2004-2007 from all 8 SEARCH sites (0.27-0.46) and the mean (0.30) for their two non-urban inland sites (Blanchard et al., 2013, JAWMA).

Reply to specific comment 8): The calculation of the neutralization index (NI) assumes that aerosol NO3 is present as NH4NO3 and neglects other forms of aerosol NO3 (e.g., from sea salt or from soil/mineral dust). Their possible presence from over-sampling the fine tail of larger aerosols will make reported NI results lower bound estimates of NI. The text will be revised accordingly.

Reply to minor comments: (1) The eastern states are defined on page 4, lines 20 – 22. (2) The factors that influenced selection of 5-year periods are listed accurately on page 9, lines 8 – 10. The pattern of emissions shown in Fig. 1 heavily influenced the selection of P1 and P2 and the remaining periods were selected to maintain consistency for continuing data analysis. (3) The manuscript will be revised accordingly.

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