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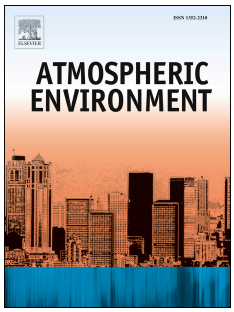

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Linking Improvements in Sulfur Dioxide Emissions to Decreasing Sulfate Wet Deposition by Combining Satellite and Surface Observations with Trajectory Analysis

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Abstract:

Sulfur dioxide (SO_2), a criteria pollutant, and sulfate (SO_4^{2-}) deposition are major environmental concerns in the eastern U.S. and both have been on the decline for two decades. In this study, we use satellite column SO_2 data from the Ozone Monitoring Instrument (OMI), and SO_4^{2-} wet deposition data from the NADP (National Atmospheric Deposition Program) to investigate the temporal and spatial relationship between trends in SO_2 emissions and the downward sulfate wet deposition over the eastern U.S. from 2005 to 2015. To establish the relationship between SO_2 emission sources and receptor sites, we conducted a Potential Source Contribution Function (PSCF) analysis using HYSPLIT back trajectories for five selected Air Quality System (AQS) sites - (Hackney, OH, Akron, OH, South Fayette, PA, Wilmington, DE, and Beltsville, MD) - in close proximity to NADP sites with large downward SO_4^{2-} trends since 2005. Back trajectories were run for three summers (JJA) and three winters (DJF) and used to generate seasonal climatology PSCFs for each site. The OMI SO_2 and interpolated NADP sulfate deposition trends were normalized and overlapped with the PSCF, to identify the areas that had the highest contribution to the observed drop. The results suggest that emission reductions along the Ohio

River Valley have led to decreases in sulfate deposition in eastern OH and western PA (Hackney, Akron and South Fayette). Farther to the east, emission reductions in southeast PA resulted in improvements in sulfate deposition at Wilmington, DE, while for Beltsville, reductions in both the Ohio River Valley and nearby favorably impacted sulfate deposition. For Beltsville, sources closer than 300 km from the site contribute roughly 56% observed deposition trends in winter, and 82% in summer, reflecting seasonal changes in transport pattern as well as faster oxidation and washout of sulfur in summer. This suggests that emissions and wet deposition are linked through not only the location of sources relative to the observing sites, but also to photochemistry and the weather patterns characteristic to the region, as evidenced by a west to east shift in the contribution between winter and summer. The method developed here is applicable to other regions with significant trends such as China and India, and can be used to estimate the potential benefits of emission reduction in those areas.

1 Introduction:

Sulfur dioxide (SO_2) and sulfate (SO_4^{2-}) are major pollutants resulting from coal burning and industrial processes. Sulfate wet deposition negatively affects surface and ground water and certain ecosystems through changing chemical characteristics of soil (U.S. EPA, 2003; Butler et al., 2001; Likens et al., 2002). While posing a major pollution problem in the second half of the 20th century, both species have shown a definite downward trend in the eastern United States. The reason for their decreases is undisputed –initiatives such as the various phases of the Clean Air Act (U.S. EPA, 2015; Butler et al, 2001) and increased monitoring of pollutants and deposition by EPA's Acid Rain Program (U.S. EPA, 2002) have led to drastic reductions in sulfur emissions and the subsequent SO_4^{2-} formation, especially in regional hotspots such as the Ohio River Valley. Sulfate is produced chemically in the atmosphere mainly through the

oxidation of SO_2. Sulfur dioxide's lifetime in the atmosphere strongly depends on the oxidation rate. The lifetime was shown to vary from up 48 hours in winter to around 13 hours in summer based on a study performed with GEOS-Chem model simulations and observations (Lee et al, 2011). The deposition of SO_4^{2-} does not necessarily occur near the emission site or in the same areas with high SO_2 concentrations. The wet deposition process is driven by precipitation and air flow patterns in addition to sulfur chemistry. It is important to quantitatively attribute changes in emissions to those in the deposition trends over downwind areas in order to characterize benefits of regulatory controls.

The advent of satellite remote sensing has greatly aided in quantifying amounts of various pollutants. In particular, remote sensing of SO_2 column amounts is performed using the Aura satellite / Ozone Monitoring Instrument (OMI). This product has proved useful in locating SO_2 sources and observing their changes in emissions (McLinden et al., 2016; Li et al., 2017a). For example, a study using the previous OMI SO_2 product detected a 40% decline in SO_2 near the largest coal power plants between 2005-2007 and 2008-2010, consistent with regulations on emissions (Fioletov et al, 2011). The latest OMI product is based on a new retrieval technique (Li et al., 2013; 2017b) that further reduces retrieval noise and artifacts, allowing for better detection of sources. A study using this new OMI SO_2 products demonstrates good correlation ($r = 0.91$) between reported emission rates and OMI-estimated emissions, and sources with emissions greater than 30 kt/y can be detected (Fioletov et al., 2015), as compared with 70 kt/y from the previous OMI products. Another study (Krotkov et al, 2016) indicates that from 2005-2015, OMI column amounts of SO_2 decreased by up to 80% in the eastern United States due to stricter pollution control measures.

The wet and dry deposition of SO_2 and its secondary SO_4^{2-} aerosol product are a significant environmental issue, especially downwind of the source areas. In particular, acid

deposition is harmful for tree health and soil chemistry by depleting plant nutrient cations and increasing acidity (Driscoll et al, 2001). Furthermore, much of the aerosol formed from gaseous pollutants gets deposited in areas downwind of sources. A number of studies have been published attempting to link the wet deposition with emissions and atmospheric transport processes. Samson et al. (1980) performed a meteorological analysis based on air trajectories and found little relationship between SO_4^{2-} and sulfur emissions. However, a later study by the same group showed that the two could be explicitly linked in several areas while being unrelated in others (Brook et al., 1994). Wet deposition was shown through modeling to have a statistically significant relationship with SO_2 emission reduction due to policy changes in the late 1980s and early 1990s (Shannon, 1999). An earlier study also estimated separation distances and atmospheric transport for atmospheric SO_2 and SO_4^2 (Shannon, 1997). In the late 20th century, locations in upstate New York, despite their relatively low local SO_2 concentrations, experienced acid rain and deposition problems. Emission reductions upwind have been found to have a linear relationship with SO_4^2 aerosol concentrations in several locations in the area (Dutkiwicz et al, 2000). The study used NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Stein et al, 2015) to track air trajectories to identify major source regions of SO_4^{2-} in Ontario and the Ohio River Valley. In particular, lakes in the Adirondack region in upstate New York have shown decreases in SO_4^{2-} concentrations and reasonable correlation (r^2 = 0.58) between SO_2 emission in the eastern United States and wet deposition changes downwind, at Whiteface Mountain and Huntington Forest (Driscoll et al, 2003).

Several more recent works have also focused on how meteorology plays a role in aerosol transport and deposition. One such study incorporated methods such as the Positive Matrix Factorization (PMF), Conditional Probability Function (CPF) and the Potential Source Contribution Function (PSCF) to attribute sources of $PM_{2.5}$ in the Pittsburgh, PA area through

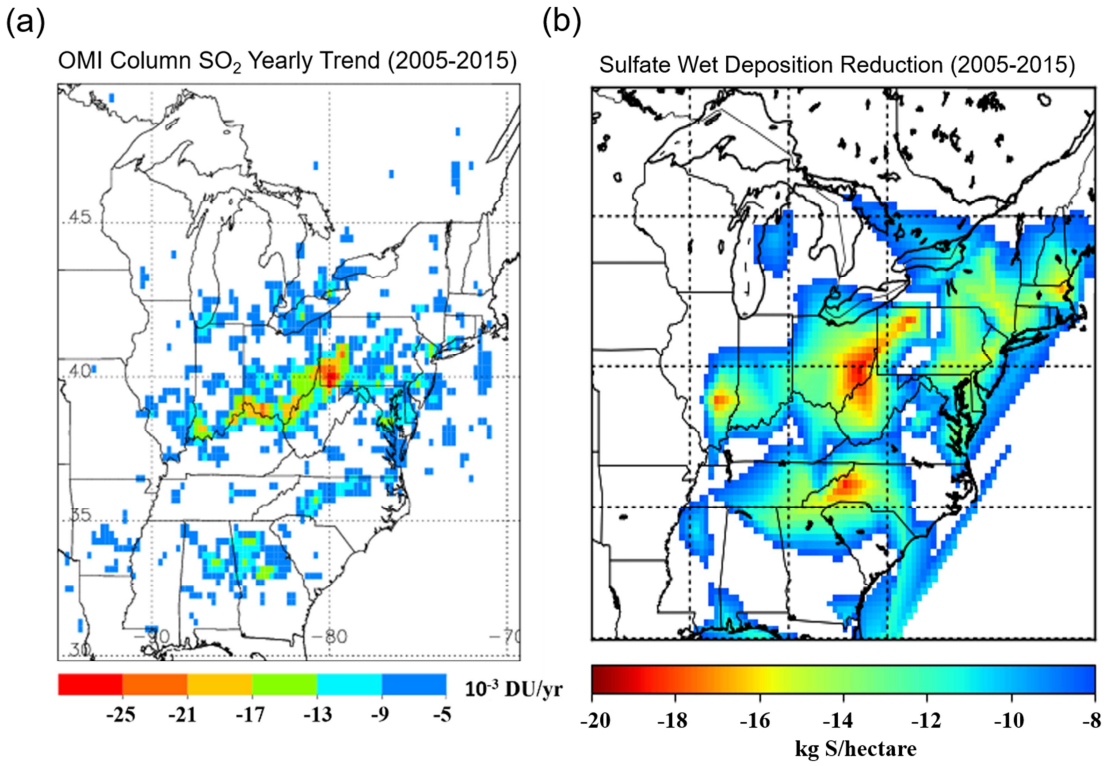
trajectory modeling (Peckney et al, 2017). In another study (Begum et al, 2002), the PSCF method was employed to identify the source location of a Quebec forest fire from $PM_{2.5}$ measurements. An earlier study modeled the transport of sulfur species from source to the receptor sites in Southern California (Gao et al, 1993). Other localized trends in particulate matter have also been addressed, particularly in the I-95 corridor of the Mid-Atlantic region. A study incorporating modeling and observations showed contributions from both regional and local sources within 100 km of the Baltimore-Washington, D.C. corridor and that the local contribution to $PM_{2.5}$mass varies seasonally, from >60% in winter to <30% in the summer (Chen et al., 2002).

Similar studies were performed for sites in Wisconsin, where enhanced SO_4^{2-} and nitrate concentration originated from air arriving from potential sources near the Ohio River (Heo et al, 2013). Recent work incorporated observations of satellites such as GOME and SCHIAMACHY along with GEOS-Chem transport model to constrain global reactive nitrogen deposition rates and trends since 1996 (Geddes et al, 2017). While a considerable number of studies have quantified source-receptor relationships in regards to atmospheric deposition for multiple sites, less work has been done with more recent deposition data and satellite data. This study aims to take advantage of the spatial consistency of OMI column SO_2 measurements, ground based SO_2 observations and SO_4^{2-} deposition. Between 2005 and 2015, many sites in the eastern U.S. saw substantial reductions in wet deposition of SO_4^{2-}. But it is not yet clear which sources of atmospheric SO_2 contributed most to these reductions in deposition and whether there is significant difference in between summer and winter. This study aims to shed some light on these important questions. The methodology and analysis presented in this study can be applicable to other areas, especially those experiencing significant pollution and deposition problems.

2 Methods:

2.1 Data

The Ozone Monitoring Instrument (Levelt et al., 2006) has been providing remote sensing products of gaseous pollutants, including sulfur dioxide since 2004. SO_2 column amount is retrieved using an algorithm based on principal component analysis of radiances measured by the satellite (Li et al., 2013) that significantly reduces the retrieval noise and artifacts. The SO_2 data from OMI has been used in a number of previous studies, particularly those on SO_2 emission source regions. For the purposes of this study, Level 3 column SO_2 data (NASA GES-DISC, 2017) was used to derive the trend over the eastern United States for the period of 2005-2015. This data has a spatial resolution of 0.25° latitude by 0.25° longitude, and is limited to scenes with relatively small cloud fraction (< 0.3). To reduce the impacts of extreme values on the average trend, negative outliers ($< -2\sigma$**)** were filtered out in the calculation of the averages, following Zhang et al. (2017). In addition, to remove the effects of extreme values likely caused by transient volcanic plumes, values greater than the 99^{th} percentile of the SO_2 values in the U.S. domain were excluded from the averaging process (McLinden et al., 2016). The OMI column SO_2 ten-year trend (Figure 1a) was obtained by calculating the three year running mean from 2005 to 2015 and deriving to a linear trend with an annual time step. This trend also highlights the areas that have experienced reduced emissions in the last ten years.



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143 Figure 1: (a) Annual trend in OMI Column SO_2 in the eastern United States calculated using
144 yearly averages, from 2005 to 2015 (b) Change in wet SO_4^{2-} deposition between 2005 and 2015
145 over the same domain and time period, based on NADP deposition measurements.

146 Sulfate wet deposition data was obtained from the National Atmospheric Deposition Network
147 (NADP). This network, consisting of over 150 monitoring sites nationally, collects rainwater
148 samples and analyzes them for various chemical species (Lamb et al, 2000). Total SO_4^{2-} wet
149 deposition is estimated annually for each station, as end of year totals with the deposition given
150 in units of kg S/ha. Due to the non-gridded nature of the data, we interpolated the annual
151 deposition to a regular grid, using Inverse Distance Weighting (IDW) and Kriging interpolation
152 methods, shown to be most efficient for calculating special deposition patterns (Qu et al, 2016).
153 A ten-year trend and net reduction (Figure 1b) in SO_4^{2-} over the entire U.S. domain (CONUS)
154 was calculated for each grid box in the same way as for the SO_2, to provide SO_2 and SO_4^{2-} trend

values for each grid square. While the NADP does not have ideal coverage, there are sufficient active sites in the Eastern U.S. to create a gridded field with spatial interpolation (Figure 2a), albeit with some error.

Another dataset employed in this study is from the Environmental Protection Agency (EPA) Air Quality System (AQS). This network provides hourly and daily ground-based measurements of SO_2. For the purposes of this study, AQS data was used in the PSCF analysis, described later in this section. Dry deposition, a variable percentage of total SO_4^{2-} deposition (Vet et al, 2013), is measured by the CASTNET network (U.S. EPA CASTNET, 2017). Our primary focus in this study was on wet deposition, since wet deposition is more dependent on weather and precipitation tracks than is dry deposition. At sites in our domain west of the Appalachians, dry deposition contributed >50 % of the S deposition, but east of the mountains wet deposition dominated (NADP, 2016) for the study period. The deposition trends discussed in the methodology and results will refer to wet deposition unless otherwise stated. Lastly, we used some hourly SO_2 emission data obtained from power plant continuous emission reporting systems (CEMs) through the EPA (U.S. EPA, 2017).

2.2 Trajectory Analysis

A trajectory analysis was used to diagnose the possible origins of the air containing elevated amounts of SO_2 at various sites in the Eastern United States. Airflow patterns revealed by this analysis can help to establish the link between the trends in SO_2 emissions and SO_4^{2-} wet deposition. The sites chosen for the trajectory analyses (Figure 2b) are in the AQS network with available SO_2 in-situ data, as well as a corresponding NADP site nearby with deposition data. The five sites chosen were 1) Hackney, OH [81.670° W, 39.632° N], 2) Beltsville, MD [76.817° W, 39.028° N], 3) Akron, OH [81.469° W, 41.0635° N], 4) South Fayette, PA [80.167° W, 40.3756° N] and 5) Wilmington, DE [75.558° W, 39.7394° N]. All of these sites had a

179 significant downward trend and at least 50% decrease in deposition between 2005 and 2015
180 (Table 1). A site in upstate New York [74.500° W, 43.4336° N], Piesco Lake, was also
181 considered due to a considerable downward 10-year SO_4^{2-} wet deposition trend in the region,
182 however the in-situ SO_2 concentrations were too low to perform a meaningful trajectory analysis.
183 The SO_2 at the this AQS site only exceeded 2.5 ppb 28 days in the winters and not once in the
184 summers over a three year period.

Table 1: The 2005 and 2015 sulfate wet deposition amounts for the six initial case sites. Values were obtained directly from the annual NADP dataset for each site.

Site	SO_4^{2-} Wet Deposition 2005 (kg S /ha)	SO_4^{2-} Wet Deposition 2015 (kg S /ha)	% decrease 2005-2015
Hackney, OH	26.70	8.76	67.2
Akron, OH	22.08	11.08	49.8
Beltsville, MD	18.83	6.93	63.2
Wilmington, DE	19.41	5.57	71.3
South Fayette, PA	25.82	9.82	62.0
Piesco Lake, NY	19.04	7.93	58.3

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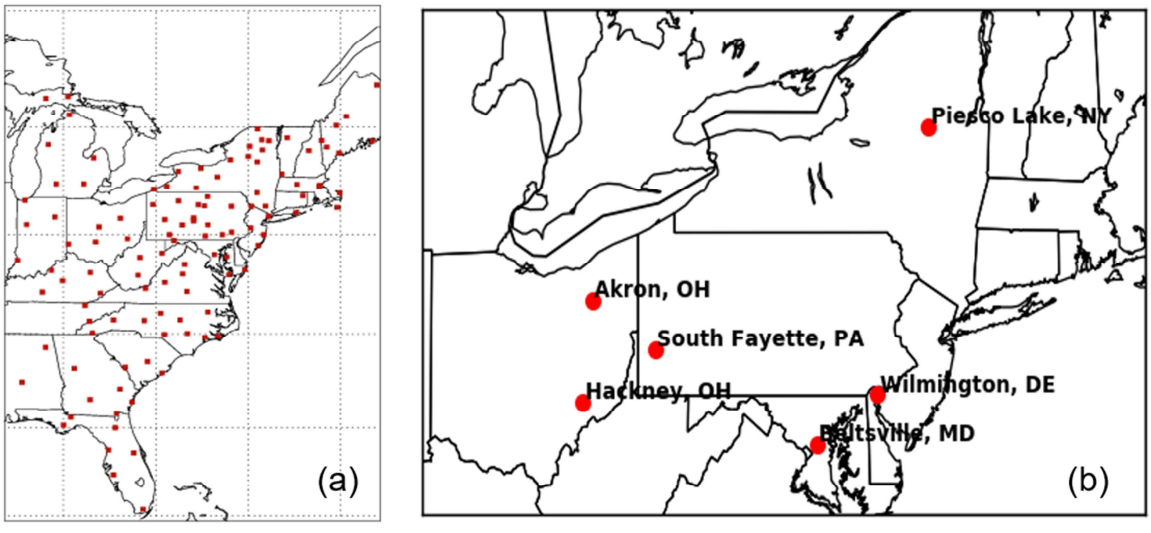

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187 Figure 2: Locations of (a) observing sites in the NADP network, shown by the red squares and
188 (b) AQS sites initially chosen for the main analysis. These sites are in reasonably close proximity

189 to NADP sites. Refer to the text for the exact coordinates. The site in New York was removed
190 from the analysis due to SO_2 concentrations frequently below the detection despite having a
191 considerable sulfate wet deposition trend.

192 The HYSPLIT trajectory model from NOAA (Stein et al, 2015) was used to calculate
193 back trajectories. Three day back trajectories were calculated each day using archived Eta Data
194 Assimilation System (EDAS) meteorological data at 40 km resolution. The HYSPLIT model
195 runs were initialized daily at 18Z near the overpass time of the satellite. The initialized height
196 was kept constant in the model runs at 500 m above ground level. A climatology of back
197 trajectories was obtained for each site by running daily 72-hour back trajectories for three
198 summers (JJA) and three winters (DJF), in the period 2006-2009. This period was selected
199 because larger downward trends in column SO_2 and SO_4^{2-} wet deposition occurred in 2005-2010
200 than in 2010-2015, as shown by trend maps for the two time periods (Figure 3). However,
201 changes in the average seasonal large-scale flow pattern are unlikely to be strongly dependent on
202 the period selected.

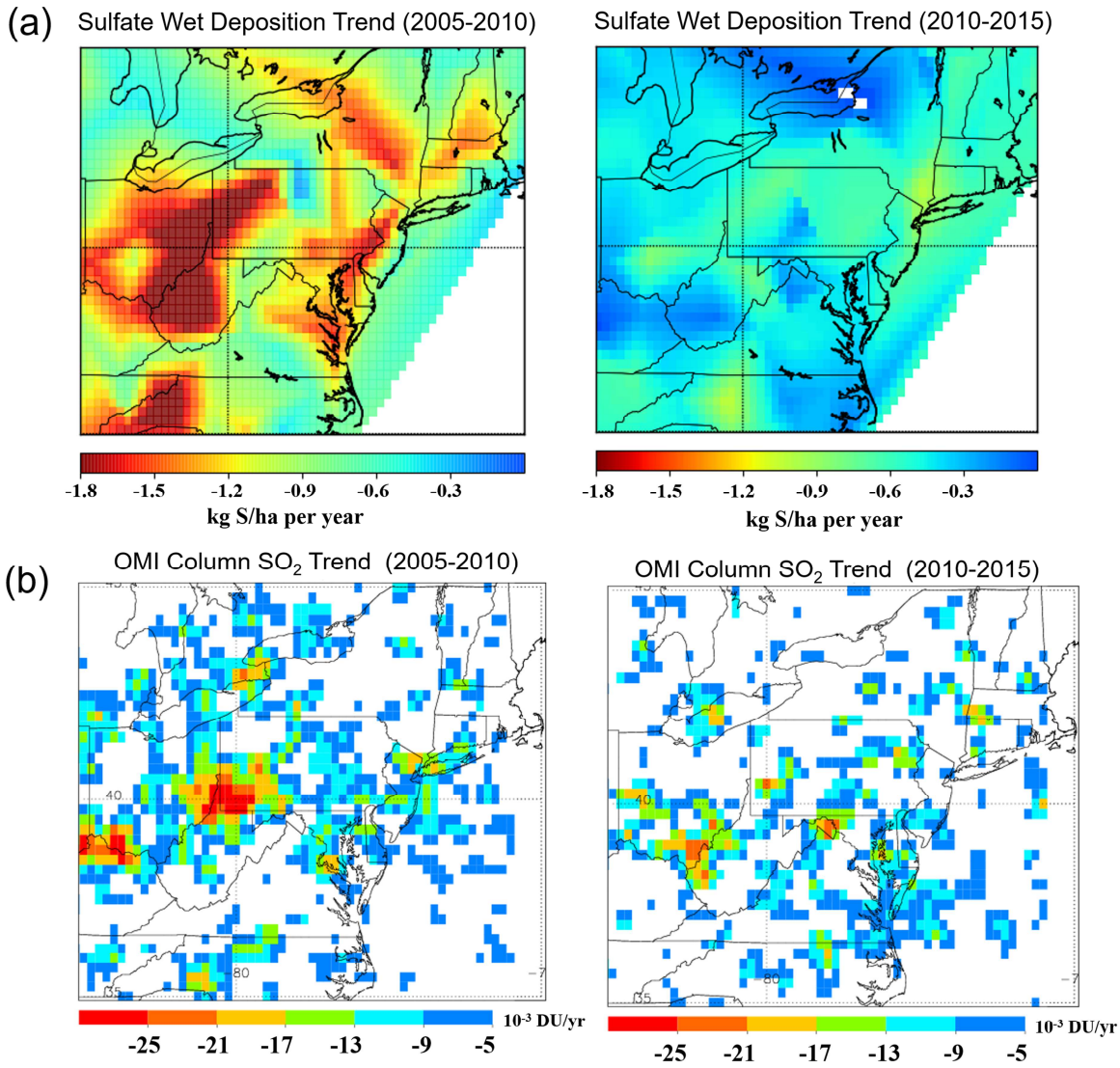


Figure 3: Annual trend for a) NADP sulfate wet deposition and b) OMI Column SO_2 for 2005-2010 (left) and 2010-2015 (right). The improvements in column SO_2 occurred at sites closer to the sources than did the improvements in deposition, but the trends are consistent.

2.3 Potential Source Contribution Analysis

The need for a trajectory and PSCF analysis stems from the fact that the spatial correlation between wet SO_4^{2-} deposition and OMI column SO_2 trends is overall fairly weak across the entire domain. The low R^2 coefficient (0.036) showed poor correlation between the two

211 normalized trends (Figure A.1). The method used to normalize the trends will be discussed
212 further in section 2.4.To link the trends, characteristic air patterns for a given location are needed
213 to understand the trends occurring in those locations. The calculated trajectories were obtained
214 for the purpose of calculating the probability of high concentrations of SO_2 coming from a given
215 grid box in the domain.

216 The Potential Source Contribution Function (PSCF) is defined as the number of trajectories
217 passing through a grid box carrying an amount of SO_2 exceeding a set threshold (m) divided by
218 the number of total trajectories going through that same grid box (n). Thus each grid box would
219 have its own PSCF value, between 0 and 1. The function is expressed as:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (1)$$

222 The subscript *ij* denotes a single grid box on the grid domain. The domain over which the
223 function was calculated was ±5 degrees latitude and ±7.5 degrees longitude from each site. The
224 domain size and location were chosen based on the typical distance covered by trajectories
225 within 72 hr. Based on the arithmetic mean and median concentrations of SO_2 recorded at each
226 of the sites over the three year period (Table 2), we chose a value of 5 ppb as the SO_2 threshold
227 for all of the base cases except for the winter South Fayette, for which the threshold was set at
228 7.5 ppb. These thresholds were kept constant throughout the entire analysis. A simple weighting
229 scheme was assigned for the calculation to remove the influence of low sample size (Pollisar et
230 al, 1999). The weighting was performed in order to eliminate the sample size issues, or
231 occurrences of low values of n_{ij}. For grid boxes with $n < 8$ trajectories, the PSCF value is
232 multiplied by a weighting factor of 0.07. Similarly, for grid boxes with 8-16 and 16-24
233 trajectories, we use a weighing factor of 0.45 and 0.7, respectively. These new values are the
234 weighted potential source contribution functions (WPSCF) and were calculated for each of the

five sites for JJA and DJF. The weighted scheme is arbitrary and varies across literature, however the one used here is very similar to a study to identify potential source regions of $PM_{2.5}$ in Beijing using the same type of back-trajectory analysis (Zhang et al, 2015). Aside from using HYSPLIT to acquire trajectories and graphics generating scripts, we used a GIS-based software called Trajstat to analyze the trajectories and PSCFs. This software was originally produced for statistical analysis of air pollution data and includes basic geographic map layers and trajectory file conversion capabilities (Wang et al, 2009).

Table 2: Mean and median winter SO_2 concentration as measured by the five AQS sites over the 2006-2009 period. These metrics were used to choose a threshold value for the PSCF analysis.

Site	Mean(ppb)	Median (ppb)
Akron, OH	5.15	4.3
Hackney, OH	6.62	4.9
S. Fayette, PA	7.62	6.9
Beltsville, MD	4.35	6.3
Wilmington, DE	5.14	4.8

2.4 Normalized Trends

To factor in the effect of the PSCF on the trends, we transformed both trends to the same, normalized scale. The SO_4^{2-} wet deposition trends were normalized to a scale of 0 to 1 with the grid box having the highest downward trend assigned a value of 1 and the a grid box with the highest positive trend assigned a value of 0 (eq. 2). The cases of an upward 10-year trend in the deposition were very few in the eastern domain and thus did not influence the outcome. The column SO_2 trend over the entire domain was also normalized the same way (eq. 2):

$$x_{ij,norm} = \frac{X_{ij} - \min(X)}{\max(X) - \min(X)}, \quad (2)$$

Where x is the normalized trend value for a given grid box, X_{ij} is the raw trend for the same grid box and X is the set of gridded trend values for the entire domain. Multiplying the normalized trends result by the PSCF produces a relative product value that describes the relative contribution of the air coming in that grid box to the trend. A grid box with both a high PSCF and large downward wet deposition trend would indicate that air arriving from there has seen significant reductions in sulfur over the years, thus contributing to the decrease in wet deposition at the receptor locations. To relate the NADP trend to OMI observations, the normalized 10 year trend in column SO_2 was added into the calculation.

$$z_{ij} = \text{norm}\ (SO_2\ \text{Trend}) \times \left[\ \text{WPSCF} \times \text{norm}\left(SO_4^{2-}\ \text{Trend}\right)\ \right] \quad (3)$$

This product value helps to identity, for a given receptor site, upwind source locations that not only frequently influence the site through transport and also have large decreases in SO2 emissions between 2005 and 2015 according to OMI. All three terms are necessary since the deposition trend, emissions and transport are accounted for. Using only the normalized SO_2 trend would only indicate contributions to decreasing SO_2 at the site, rather than deposition. Likewise using only the normalized SO_4^{2-} wet deposition trend, the influence of emission reductions is removed from the contribution. A percent contribution was then calculated for each grid box through the summation of individual grid box values and dividing each individual value by the total.

$$\%\ \text{contribution} = \frac{z_{ij}}{\text{sum}(z_{ij})} \times 100\% \quad (4)$$

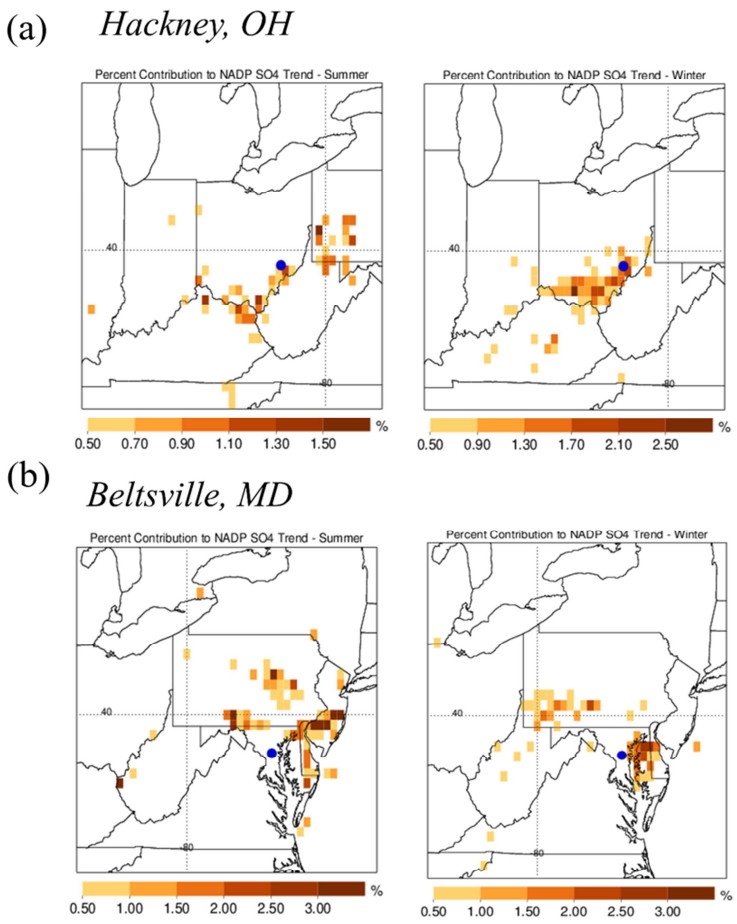
Thus this new value expresses the normalized contribution of a particular grid box

271 to the SO_4^{2-} wet deposition trend at the AQS or NADP site, relative to the domain. This provides
272 a quantitative assessment of the trend data relationship.

273 **3. Results and Discussion**

274 **3.1 Percent contributions**

275 This section describes the qualitative and some quantitative aspects of the grid boxes that
276 contribute to wet deposition trends at five different sites. Figures 3 and 4 show grid cells in the
277 domain with a color representing the final percent contribution value calculated with equation 4.
278 We aim to show the specific grid boxes which had the most contribution in the domain to the wet
279 deposition trend at the receptor site, as well as the cumulative contribution at various distances
280 from the site through summations of the percent contribution values.



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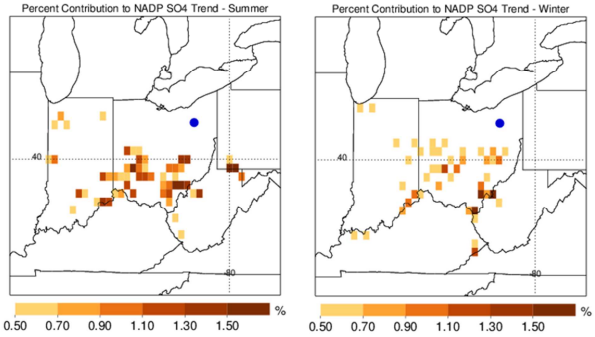
282 Figure 4: Percent contribution for each grid box in the domain with only values above 0.5%.

283 Shown for (a) Hackney, OH and (b) Beltsville, MD sites in JJA (left) and DJF (right). The

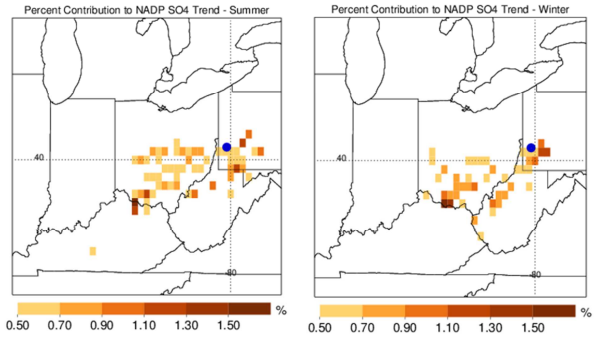
284 observation sites are marked with a blue dot.

285

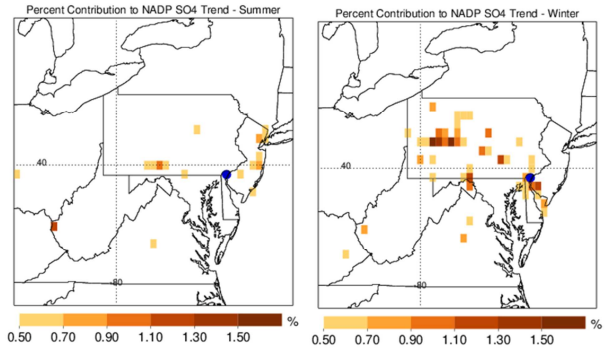
(a) *Akron, OH*



(b) *South Fayette, PA*



(c) *Wilmington, DE*



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287 Figure 5: Percent contribution for each grid box in the domain with only values above 0.5%.
288 Shown for (a) Akron, Ohio, (b) South Fayette, PA and (c) Wilmington, DE AQS sites in JJA
289 (left) and DJF (right). The observation sites are marked with a blue dot. Note that only values
290 greater than 0.5% are colored.

291

Hackney, OH

Due to its proximity to numerous sulfur emitting coal-fired power plants, the Hackney, OH AQS site shows high concentrations of SO_2 with average daily value of around 7 ppb and often exceeding 20 ppb in winter. The corresponding NADP site for this area is in Caldwell, OH (Site ID OH49), ~18 km away. We would expect similar characteristic deposition and trajectory patterns for the two locations given the flat terrain and proximity to the same SO_2 sources. In wintertime (DJF), wet deposition trend at the Caldwell NADP site is driven by the dominant southwesterly flow and high outputs of emissions upwind near the Ohio River (Figure 4a). The observed annual wet deposition at the Caldwell site decreased from 23.35 kg S/ha in 2005 to 8.76 kg S/ha in 2015 according to the NADP dataset. The wet deposition has significant year-to-year variability (Figure 6), however, the overall 10-year trend from 2005 to 2015 was downward.

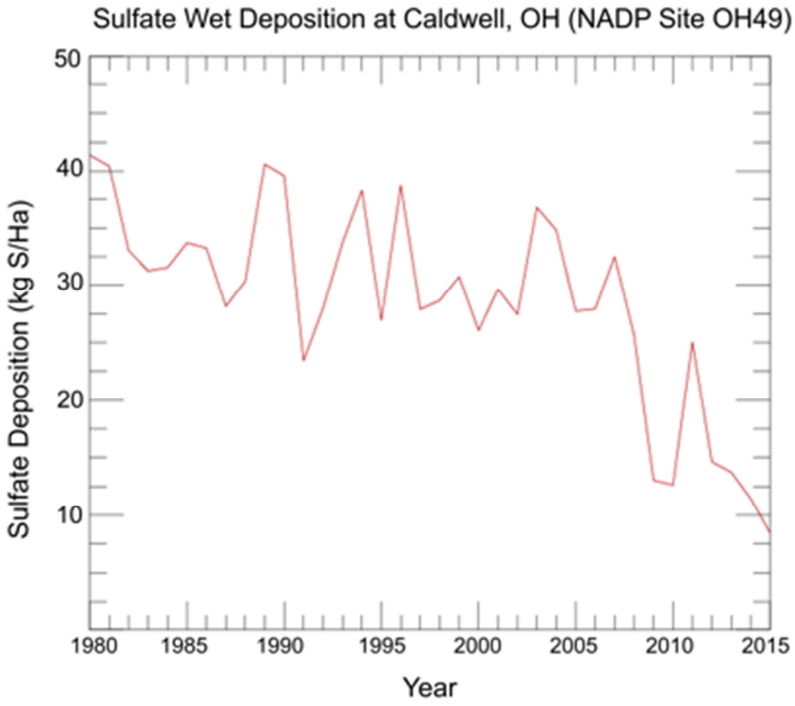
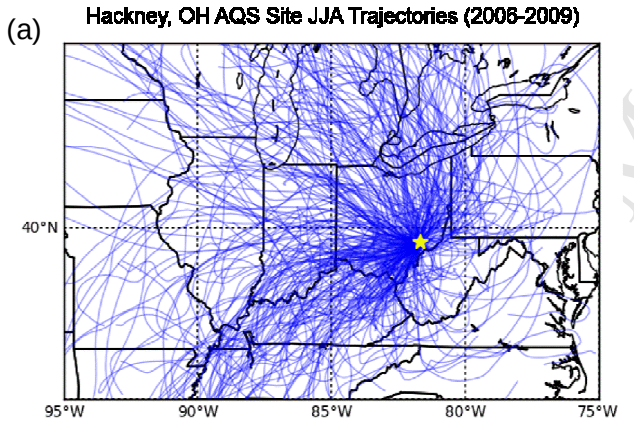


Figure 6: Sulfate Wet Deposition amounts at Caldwell, OH NADP site, shown as a time series from 1980 to 2015. The plotted data is from the NADP network at the OH49 site [39.7928 N, 83.5311 W]

Qualitatively, the area with the colored grid boxes in southern Ohio largely contributed to the decreasing deposition (Figure 4a). In summer (JJA), major areas in southwestern PA with large SO_2 columns somewhat contribute to the observed trend at the Hackney site, however less so than the sources along the Ohio River. The trajectory climatology for this site (Figure 7) shows a clear seasonal change in direction trajectories indicating that emission reduction in the west have likely contributed to the majority of the observed trend at the site.



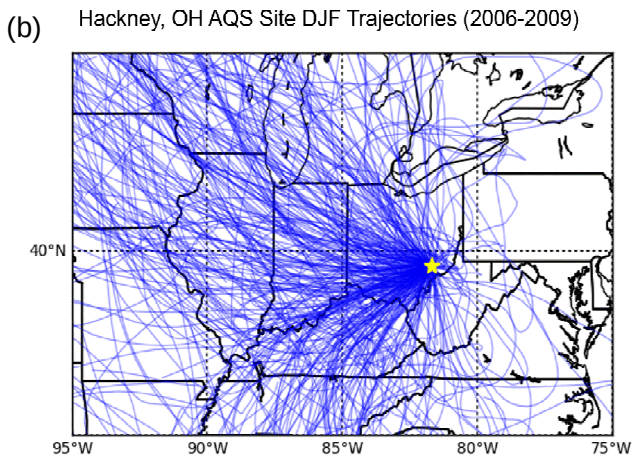


Figure 7: Map of (a) summer (JJA) and (b) winter (DJF) trajectory climatology for 2006-2009 at Hackney, OH. The yellow star shows the location of the site and the blue lines are the individual 72 hour back trajectory for each day, initialized at 18Z using the HYSPLIT model.

Beltsville MD

The Beltsville, MD site experienced a downward SO_4^{2-} wet deposition trend, especially in the years 2008-2012, and has two primary regions that contributed to the 10-year decrease. The Southwest PA region shows the greatest cumulative percent contribution which implies that wet deposition has dropped due to the decrease in sulfur emissions in Pennsylvania. However, we also see a signal to the east of the site in the PSCF and contribution map (Figure 4b). While the dominant trajectory is from the northwest in winter, air can occasionally arrive from the east in both seasons. In summer, wind direction is more variable compared to winter, as indicated by the trajectories from HYSPLIT (Figure 8). Just before the turn of the decade in 2010, Maryland's Healthy Air Act led to cuts of sulfur emissions of 80-85% from levels in the early 2000s (He et al., 2016). While most of the contribution is due to decreased emissions to the west, it is probable that local emission controls have also played a role in decreasing SO_4^{2-} deposition in the general vicinity. The case for this site will be further investigated in section 3.3.

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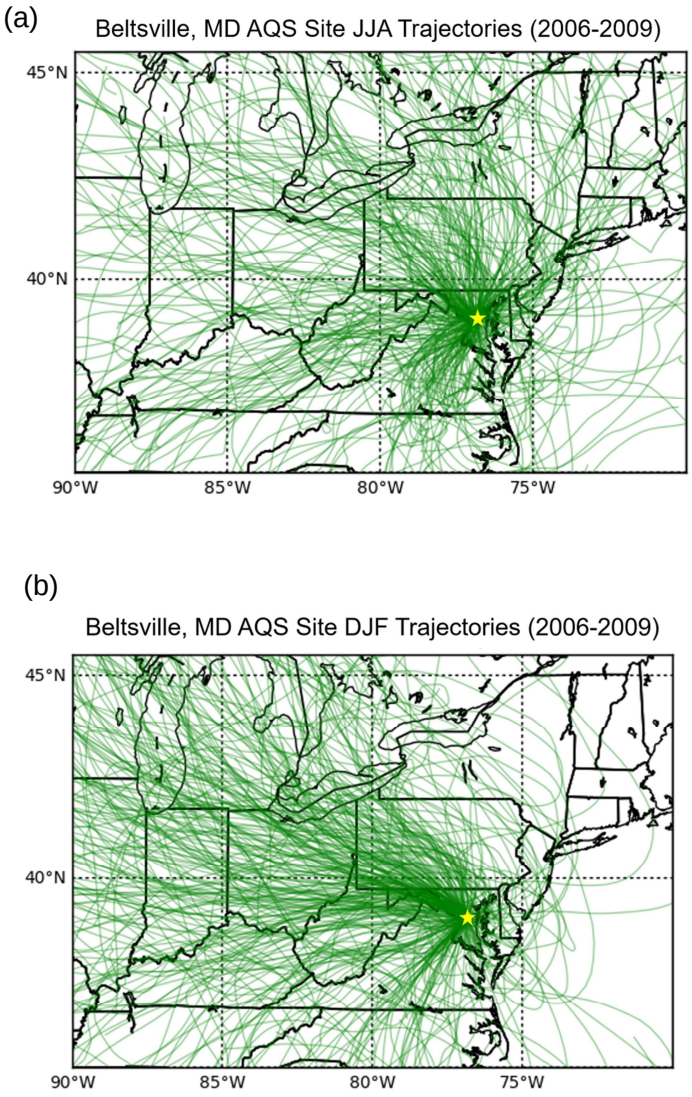


338

339

340 Figure 8: Same as Figure 7 but for Beltsville, MD AQS site. The trajectories are denoted by

341 green lines in this figure

342 *Akron, OH*

343 Sources to the south and southwest dominate the wet deposition trend for the Akron, OH (Figure

344 5a). Most of the grid cells with a non-negligible percent contribution (greater than 0.5 %) are

345 located near major SO_2 sources, approximately 100-300 km away from Akron in both winter and

summer. The percent contributions show fewer grid boxes with contributions over 1.5% in winter as the contribution is spread out over larger number of grid boxes, especially those further away. This is reflected by higher emissions, generally higher wind speed and longer trajectory distance within the 72 hours in wintertime. In summer months there is also signal from southwest PA with over 1.5% contribution for two grid cells in that region.

South Fayette, PA

The AQS site in South Fayette, PA had the highest median in-situ SO_2 amounts of the five sites reported in the 2006-2009 period for both winter (~7.0 ppb) and summer (~3.5 ppb), whereas in Hackney those median amounts were 5.4 and 2.7 ppb respectively. Sulfate deposition is affected by local sources, but the PSCF analysis also shows elevated SO_2 concentrations arriving from the east and southwest, near the sources along the Ohio River. During summer, there is slightly more contribution from the east, indicating a shift from a predominantly western zonal flow that occurs during winter. However, the seasonal difference in the contribution appears to be smaller than at other sites. The highest percent contributions in both seasons are from southern Ohio and just to the east of the site (Figure 5b), which indicates the presence of sulfur emission sources. In this sense, the site is quite similar to the patterns in Hackney, OH, except it is more affected by the local power plants to the east in PA.

Wilmington, DE

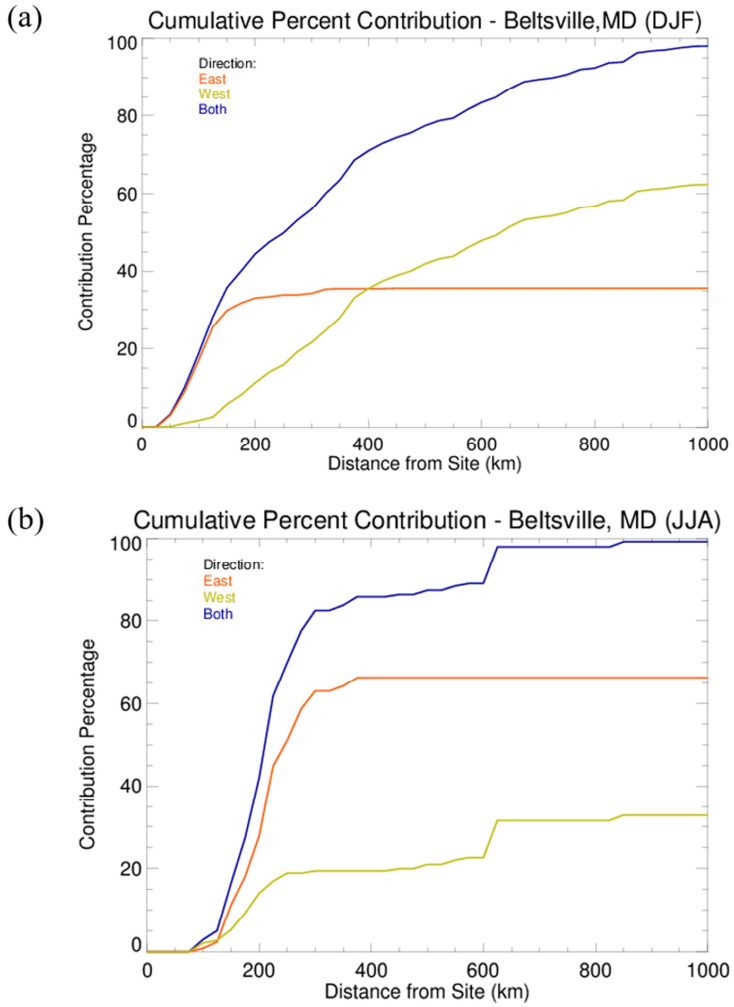
For the Wilmington, DE site (Figure 5c), the region contributing the most in winter to the deposition trend is from upwind in Pennsylvania, which is home to several large power plants. As shown by OMI, the region had a strong decrease in column SO_2. Given the winter trajectory pattern, it follows that any reductions in Pennsylvania benefitted the Wilmington area in terms of deposition amounts. In summer, there is not much signal from any particular area, with isolated

grid boxes in the New York area and in southern PA. It is reasonable to assume that most of the decrease in annual SO_4^{2-} wet deposition were due to large decreasing trend in winter SO_2 concentrations over upwind areas to the west. While there may have been some minor summer contributions as well, their magnitude were not as great as in winter. This shows an absence of SO_2 source near the site and that a stronger wintertime flow pattern is needed to have impacts on the deposition trends.

3.2 Contribution Distributions by Distance

We extend the analysis above by calculating the total percentage contribution to trend observed at a receptor site from all grid boxes within a certain distance from the site. Distances of 50, 100, 200, 300,400, 500 and 1000 km were used in the analysis. The calculation was performed by creating a circle with a radius of the distance from the site and summing up the contribution of all grid boxes that fall within the circle. This process leads to cumulative distributions of total contribution moving away from the site. This would help in diagnosing if the wet deposition at the site is primarily driven by local or upwind sources and the direction from which the sulfur is arriving at the site.

We calculated a cumulative contribution for two sites with significant climatological and geographical differences, Beltsville (Figure 9) and Hackney (Figure 10), for summer and winter seasons.



391

392 Figure 9: The cumulative percentage of contribution to the SO_4^{2-} wet deposition trend at the
393 Beltsville NADP site, from areas within a given radius from the site (x-axis) for (a) winter and
394 (b) summer. The orange, green and blue lines represent contributions from locations with a
395 longitude east of the site, west of the site and all locations within the radius respectively.

396

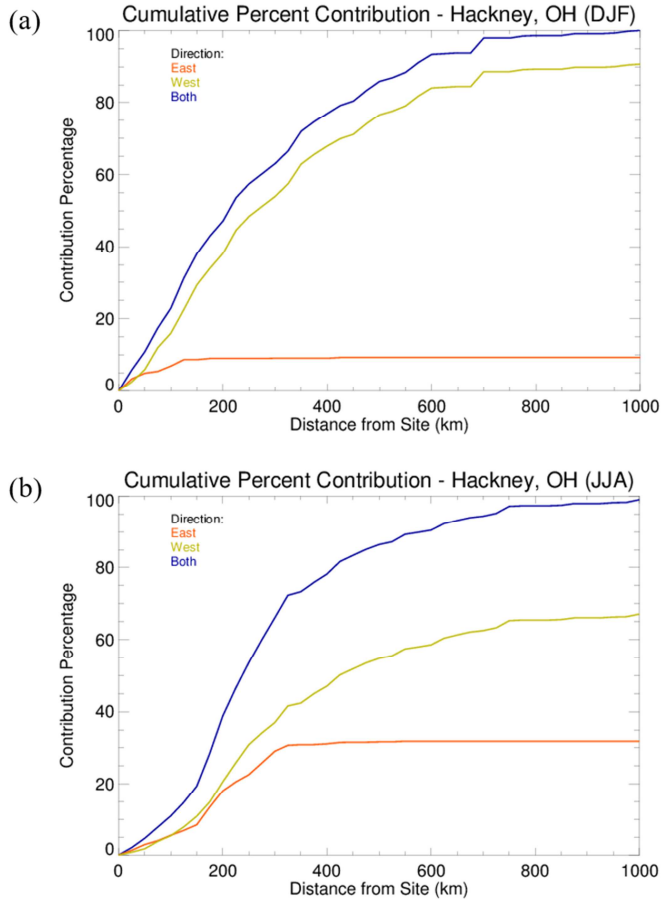


Figure 10: Same as Figure 9 but for the Hackney AQS site.

Beltsville, MD

For the Beltsville site, half (50%) of the sulfur contributing to the ten-year wet deposition trend is linked to SO_2 observed within a 300 km radius in both winter (Table A.1) and summer (Table A.2). However, more contribution comes from locations over 300 km away in winter (44%) than in summer (17.5 %), showing that the lifetime and transport distances are generally greater in winter. The lower in-situ SO_2 amounts in summer than in winter are consistent with the fact that the largest SO_2 emitting power plants in the domain are more than 300 km away. Higher contribution values come from several grid boxes closer to the site in the Beltsville, MD case (within 100 km), yet the accumulated contribution in the southwest PA region has arguably more

effect on the deposition trend. This is evidenced by sources more than 300 km to west of Beltsville, MD that contribute more than 50% of the SO_4^{2-}. The result shows the benefit in reducing emissions upwind in western PA and eastern Ohio, as the decrease has led to a downward deposition trend in addition to improved SO_2 levels in the second part of the study period. In summer, 83% of the contribution comes from within 300 km, with roughly 63% of this coming from the east of the site. This indicates that summer transport distance is short and pollutants are less likely to reach from beyond 500 km away as they do in winter.

Hackney, OH

In winter, while the total contribution from within 300 km (63%) is similar to summer for this site, 54% of it is from the west (Table A.3). For summer, roughly 66% of the contribution is from within 300 km of the site, with 29% of it from the east and 37% from the west (Table A.4). While more of the contribution is from the west, the eastern component indicates that some of the SO_4^{2-} originates from areas to the northeast of the site in PA in addition to areas to the southwest of the site. Areas within 100-200 km from the site, contributed to about 24% and 27% of the SO_4^{2-} wet deposition trend in winter and summer respectively, meaning the emission source within that radius are more or less contributing the same in both seasons relative to the rest of the domain. This is a different characteristic from Beltsville, MD since for Beltsville more contribution came from further distances in winter and was not as greatly affected by SO_2 sources within 200 km of the site. Due to proximity of this site to some of the sources, it is possible that the SO_2 from these sources was not resolved in the trajectory analysis with only 40 km resolution of the meteorology data. Over all distances, the western component dominates in both winter and summer with roughly two thirds coming from the west in winter and 90% in summer. This indicates the dominance of the climatological westerlies over source proximity and deposition processes.

3.3 Case study on the impact of the Maryland Healthy Air Act on deposition at Beltsville

Evidence exists that in the present day, much of Maryland's sulfur pollution problem has previously originated upwind in Pennsylvania and Ohio River valley. However, it is interesting to assess the impact of local statewide regulations. The Brandon Shores power plant is one of the biggest emitters of sulfur dioxide in Maryland, especially before the enactment of the Healthy Air Act of 2010. The plotted average monthly emissions show that the facility cut its SO_2 emissions by over 80% post 2009 (Figure 11).

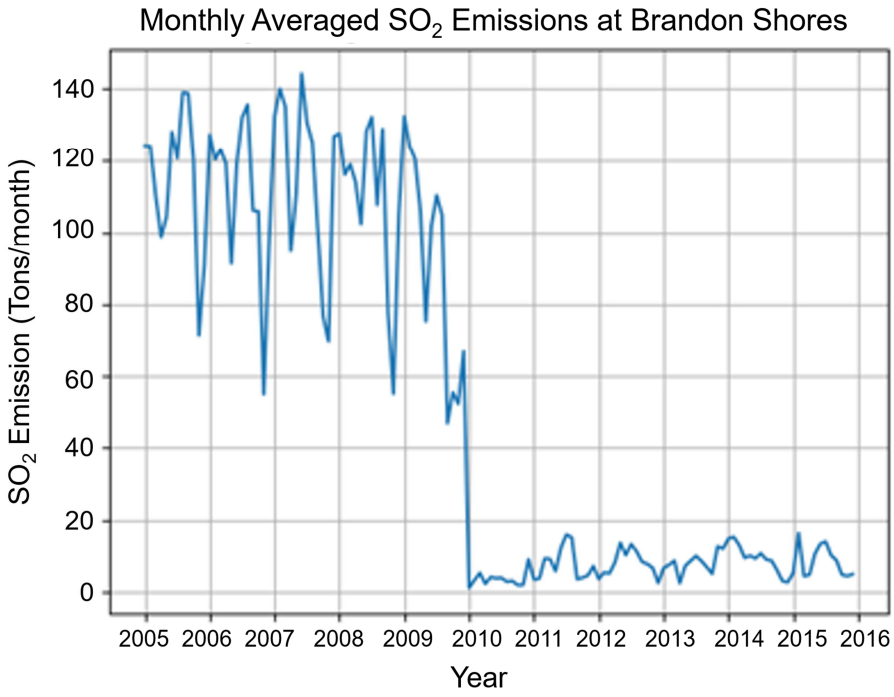


Figure 11: Monthly averages of hourly SO_2 emissions from the Brandon Shores power generating facility, located just to the south of Baltimore, MD. The data were obtained from Continuous Emission Monitoring Systems (CEMs) and are distributed by EPA's Air Markets Program database.

Maryland state emission inventories (Figure 12a) also show roughly 80% drops in SO_2 emissions between 2005 and 2015 in the fuel combustion sector, which includes power plant emissions.

There is a 78% drop in 2007-2012 and 45% drop for 2005-2009, indicating that Maryland cut more of its emissions in 2008-2012. At the same time, emissions have been decreasing consistently in Ohio and Pennsylvania, as well as nationally (Figure 12b). The trends for SO_4^{2-} and SO_2 are also of greater magnitude in 2005-2010 than in 2010-2015 (Figure 3), which aligns with emission trends and the enactment of the Healthy Air Act.

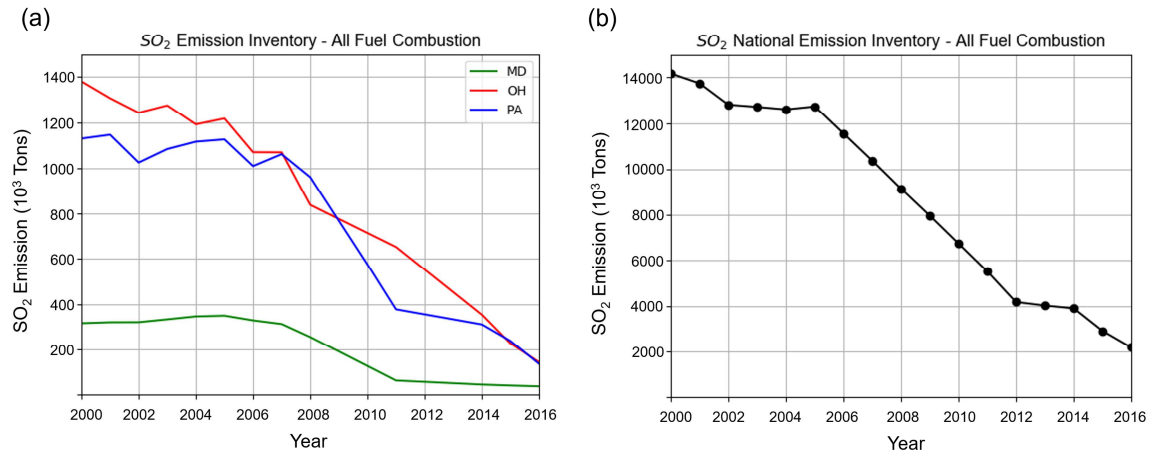
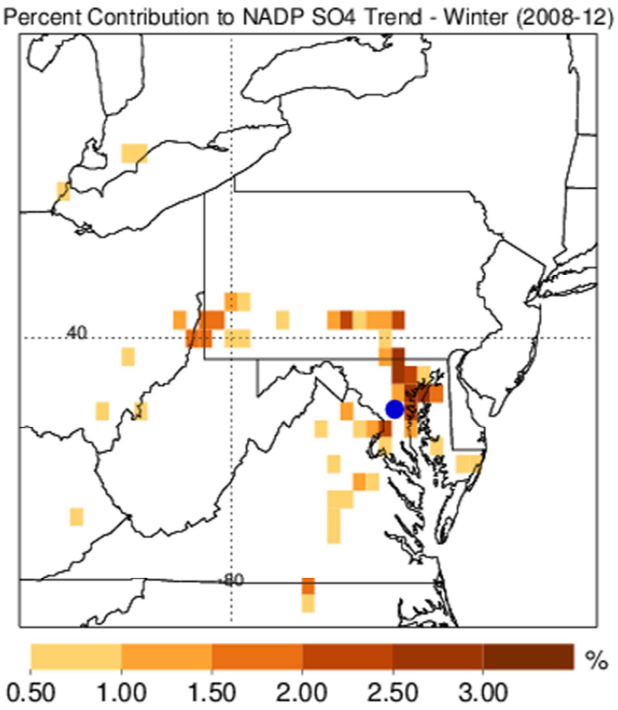


Figure 12: The SO_2 emission inventory for (a) three states: MD, PA and OH and (b) the entire United States. Only the total values for the fuel combustion sector, which includes primary power plant emissions, are included. This sector is the dominant portion of the inventory and accounts for over 80% of the total. Emission inventory data can be found on the EPA Emission Inventory site: https://www.epa.gov/air-emissions-inventories/air-pollutant-emissions-trends-data

Using the same PSCF analysis method as above, we were able to identify contributions to the SO_4^{2-}sulfate wet deposition trend for 2008-2012 by using the trend and PSCF corresponding to this time period only. As seen in Figure 13, there is noticeably larger total contribution from areas close to the site than farther away. There is also a difference between the original 10-year case and this four-year time period in that the grid boxes directly to the northwest (Baltimore

463 area), contribute slightly higher from 1-1.5% in the 10-year case to 2-3% for 2008-12. The
464 results here show that the state legislation may have had a positive impact in reducing sulfate
465 SO_4^{2-} deposition at Beltsville.



466

467 Figure 13: Percent contribution to the Beltsville, MD winter wet deposition trend for 2008-2012.
468 The same procedure was used as in the other maps, except with a 2008-2012 winter trajectory
469 climatology and PSCF

470 This result can also be related to the specific dry and wet deposition amounts occurring in
471 Beltsville over the years. The data in Table 3 indicates that dry SO_2 and SO_4^{2-} deposition have
472 decreased overall from 2005 to 2015. The decrease is better seen in the SO_2 than SO_4^{2-} between
473 the first and second 5 years. The effect of cutting emissions at Brandon Shores has clearly
474 decreased local dry deposition of SO_2. The result is less obvious in the dry SO_4^{2-}, although by
475 2015, the deposition has dropped by almost 50%, from 1.12 to 0.59 kg S/ha. The fraction of total
476 S deposition due to dry deposition of SO_2 has fallen by roughly a factor of two over this decade,

consistent with greater partition into sulfate (Shah et al., 2018). According to Figure 14, the steepest trend in wet deposition occurred from 2008-2012. The wet deposition end-of-year total for 2012 decreased to 8 kg S/ha from around 20 kg S/ha, reported at the end of 2009 (Figure 14).

Table 3: Flux of dry SO_2 and SO_4^{2-} at the Beltsville, MD site in the CASTNET network with the annual NADP wet deposition totals. The flux value can be seen as dry and wet deposition of SO_4^{2-} at the site. Several years of dry flux data were missing in the dataset.

Year	Dry SO_2 Flux (kg S/ha)	Dry SO_4 Flux (kg S/ha)	Wet SO_4 Flux (kg S /ha)
2005	7.547	1.857	17.42
2007	4.296	1.777	15.49
2008	4.268	1.426	15.72
2009	3.112	1.005	19.36
2010	2.227	1.126	9.34
2011	1.361	1.048	12.04
2013	1.009	0.785	5.95
2014	1.410	0.706	7.14
2015	1.071	0.588	6.46

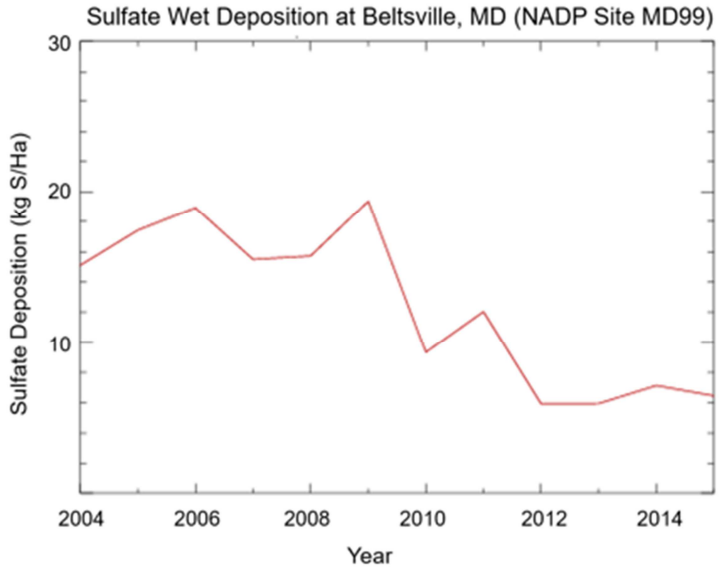


Figure 14: Sulfate Wet Deposition amounts at Beltsville, MD, shown as a time series from 2004 to 2015. The plotted data is from the NADP network at the MD99 site.

However, wet deposition is largely driven by the precipitation patterns and consequently by air trajectory climatology. Given that only less than 25% of back trajectories arrive from east of the site in winter, it is difficult to conclude that the drop in local emissions was the dominant factor in the overall decreasing trend. Yet the effect is non-negligible and may have certainly played a role as the steepest slope indeed occurred between 2009 and 2010. Thus we can speculate that the signal associated with the contribution values to the east and northeast of the site as well as the increase in percent contribution for the 2008-2012 four year period, are not anomalies or artifacts of the method, but significant characteristics of the contribution to the wet deposition trend in Beltsville between 2008 and 2012. The local and statewide emissions likely only affected the short-term trends in deposition given the drastic changes in emissions, rather than the long term deposition changes over a 10 year period. The latter is likely driven by a systematic drop of emissions on a larger regional scale and consistent trajectories from the northwest. Lastly we roughly estimate the SO_2 lifetime qualitatively from the contribution maps. In general, there is indication that lifetime is less than 1 day in the summer, while in winter the SO_2 gets carried 100-200 km more especially for the eastern sites. The latter indicates a longer SO_2 lifetime in excess of 1-1.5 days in winter. This is consistent with the SO_2 lifetimes of 13 h and 48 h for summer and winter respectively found by Lee et al., and may be due to seasonal differences in oxidation rates; Shah et al. (2018) reported only 18% of SO_2 was regionally (over the eastern US) oxidized to SO_4^{2-} in winter, but 35% of summer. As shown previously, SO_2 and SO_4^{2-} deposition trends can appear in geographically different areas. Locations that have drastically reduced their sulfur emissions can still have SO_4^{2-} deposition problems due to upwind

sources and likewise can benefit from the reduction of emissions from those areas. Thus, both local and regional pollution controls are not only important for air quality but for the environment since air trajectory patterns control the transport and deposition of chemical species.

3.4 Method Limitations and Uncertainties

Although the methodology presented in this study was used consistently for all sites, it did not come without limitations or systematic errors. In this section we discuss potential sources of error and uncertainty stemming from the methods and factors that were difficult to constrain in this study.

Quantitative Error Estimates

From the trend calculations, error statistics showed around ±0.1 kg S/ha /yr on average for the SO_4^{2-} wet deposition trend for grid cells with relatively high trend magnitudes. The actual error across the domain varied based on the magnitude of the NADP site distribution. Likewise, the OMI SO_2 trend calculation carried a ±0.001 to ±0.0025 DU/yr uncertainty, with greater uncertainties for grid boxes with low SO_2 amounts or low trends. Interpolation of irregular spaced data such as the case of NADP sites (Figure 2a), inherently carries uncertainty due to varying site coverage and the interpolation method itself. The uncertainty was in the 10-20% error range for more than half the grid boxes in the domain, while areas with less observing sites contained higher percent error. The error analysis was performed through validation of annual wet deposition output from the Community Multi-scale Air Quality (CMAQ) model. These interpolation errors, while having potential impacts on the results, could not be avoided due to limitation of the NADP observing network.

The error in the percent contributions results directly from the uncertainties in the normalized trends and the PSCF, as those are the two components used in the calculation (Eq. 3).

529 Uncertainties in the PSCF can originate from trajectory calculations and from different
530 possibilities of choosing the threshold. Changing the threshold by ±1 ppb resulted in only 25-30
531 of the 2400 grid boxes in the domain having a PSCF change of greater than 0.1, as determined by
532 a sensitivity test. Therefore, the overall result across the domain is not significantly affected by
533 this parameter. The calculations of the trajectories inherently contained errors as a result of
534 limited temporal and spatial resolutions of the model reanalysis meteorological data. However,
535 given the spatial resolution of the OMI instrument, the resolution of the meteorological data was
536 appropriate. We can still estimate roughly 20% relative uncertainty, which is proportional to
537 trajectory distance (Stohl, 1998). In regards to the normalized trends, the grid cells with high
538 trends were estimated through sensitivity tests to have an uncertainty on the order of 20-30%,
539 accounting for OMI and NADP data uncertainty in addition to the normalized trend calculations.
540 In grid boxes with smaller trends, the uncertainty is higher because their weight is closer to 0.
541 However, the areas with low SO_2 and SO_4^{2-} trends generally do not strongly impact the results
542 presented. The total uncertainties in the percent contribution can be estimated to have an upper
543 limit 30-40% in most grid cells of the domain, as an upper limit. This result was obtained by
544 combining the square error of the PSCF and the two normalized trends.

545 *Other Limitations and Uncertainties*

546 One big limitation in this study is the characteristics of wet deposition. Whether the SO_4^{2-} is
547 being deposited or carried further downwind is dependent on nature of the trajectory and if
548 precipitation occurred. Given the uncertainties in diagnosing rain or cloud formation events
549 along the trajectory, we primarily focus on determining where deposition is highly decreasing
550 along with an active flow pattern from trajectory analysis showing possible origins of SO_4^{2-} from
551 nearby sulfur in the atmosphere. The trajectories are utilized as rough interpretations of air flow
552 and to contribute to a seasonal climatology as shown in Section 2. Furthermore, HYSPLIT model

553 parameters were rather simple in the sense that the model was not run at multiple times during
554 the day or from different heights. We kept the constant initialization height of 500 m (above
555 ground) which is a reasonable representation of mid boundary layer height. The back trajectories
556 were only run once a day to match the temporal resolution of OMI and around the time the
557 instrument would pass over the Eastern U.S to make measurements. Due to keeping the
558 initialization time constant at 18Z and the height at 500 meters, there could have been error
559 associated with analyzing the trajectories with respect to high SO_2 amounts since these can
560 change due to weather patterns and within hours. Another limitation was the difficulty in
561 distinguishing between sulfate coming from rainout or washout. With the nature of the data,
562 relative simplicity of HYSPLIT and lack of a chemistry model, there was not much information
563 that could be gathered regarding the exact origin of the sulfate. However, we would expect a lot
564 of the sulfur from power plants to be found closer to the surface than aloft, consistent with the
565 500m trajectory initial height. Overall, chemistry related factors such as how much of the SO_2 is
566 converted to SO_4^{2-} on a daily basis, how much is exported or removed through other pathways,
567 and cloud processes could not be adequately captured by the method, therefore producing
568 additional uncertainty in the results. Lastly, in many cases, the trajectories and the sulfur residing
569 in the atmosphere can be influenced by local and smaller scale meteorology, in addition to the
570 synoptic airflow. This can complicate the deposition and sulfur dioxide transport and can lead to
571 a loss of important information regarding the connection between the two trends. These
572 uncertainties are difficult to quantify but likely do not strongly impact the conclusions of the
573 study, because the lifetime of SO_2 is relatively short and wet deposition is a main sink.
574 Addressing complexities in the future, as opposed to this simplified approach, might gain
575 additional insight on the link between the two trends.

There is also possibility of biases in precipitation collection based on the collector instrument used (Wetherbee et al, 2009). Likewise, the OMI retrieval of SO_2 while much improved over the years, still has substantial noise and errors and could also have had a minor effect on the calculated trends. Another source of error in the method itself could be the low detection rates of SO_2 exceeding a threshold at a site. This happens during summer when the exceedance rate was low compared to winter, resulting in a more scattered PSCF and contribution maps. The resulting PSCF calculation (Eq. 1) would be fairly sporadic as m would be low compared to the total number of trajectories (n). Since calculating percent contribution was heavily based on PSCF (Eq. 3), some grid boxes may not be represented as accurately, especially in JJA and at low SO_2 sites (Wilmington and Beltsville). It is important to note that these methods are mostly probabilistic, meaning we cannot discern concrete locations and say with complete certainty that a specific source contributed to the deposition changes.

4. Summary and Conclusions

In summary, the origin of pollutants in acidic wet deposition can be determined with a combination of in situ and satellite observations coupled to trajectory analysis. In this study we quantified the possible origin of SO_4^{2-} wet deposition for five sites in the eastern United States over 2005-2015. Each site showed characteristic source regions, generally consistent with seasonal wind patterns and observed SO_2 from OMI. Dominant sources depend on prevailing westerly winds, faster summer rates of SO_2 oxidation, and the synoptic conditions associated with precipitation. We also find that contribution changes pattern in direction and range with the season.

Reported emissions, observed concentrations, and monitored deposition all tell a consistent story – efficient scrubbing SO_2 in the eastern US has led to dramatic improvements in SO_4^{2-} wet deposition in the same region and benefits are generally seen within 500 km of the

source. At the Beltsville, MD site in winter, about 2/3 of the SO_4^{2-} wet deposition originates from the west and 1/3 from the east, in keeping with the dominance of westerly winds. In summer, when SO_2 has a shorter lifetime with respect to oxidation to SO_4^{2-}, closer emitters generally have a greater influence – the bulk of the deposition (80%) is due to sources < 300 km away; in winter this range is expanded to over 500 km. Nearby sources to the east do however have a substantive impact in colder months. The winter season is associated with a higher frequency of strong mid-latitude extratropical weather systems, which will produce periods of northeasterly winds off the Atlantic Ocean and larger amounts of moisture and precipitation. Likewise, wind direction becomes more variable and, on average, weaker during the summer months. The region also experiences less precipitation during the summer, with the exception of heavy localized precipitation in convective storms. Nonetheless, 2/3 of the contribution (Table 4) is from east of the site, indicating the importance of source proximity and summer weather patterns. Both statewide emission controls and those upwind, out-of-state appear to have contributed to the decreasing SO_4^{2-} deposition trend. While higher contribution values come from several grid boxes within 100 km of the Beltsville site for the 2008-2012 period, the accumulated contribution in the southwest PA region has arguably more effect on the full ten year deposition trend overall. At the Hackney, OH site, the summer-winter difference is weaker, with 80% of the deposition from within ~400 km in both seasons, reflecting sources located closer to the site. Despite major SO_2 sources to the east, transport of sulfur from the west dominates, accounting for 2/3 of the deposition in the summer, and 9/10 in the winter. At this site, the prevailing wind pattern rather than proximity to emitters is the governing factor for this distribution.

Without the implementation of the appropriate methodology, such as the trajectory analysis used in this work, the regional SO_2 concentrations and deposition could not be adequately linked given their geographic displacement. The satellite data provide a consistent

context for interpreting in-situ measurements and trajectory-based PCSF analyses, allowing us to identify major source areas that contribute to the observed decreases in SO_4^{2-} wet deposition. Future work will incorporate further modeling in addition to the statistical method used in this study. Additional meteorological analyses can also be useful in determining the role of seasonal precipitation patterns and climatology on wet deposition rates. Lastly, a larger sample size of sites and extension of the trajectory climatology to more years in the model and statistical method may increase the robustness and accuracy of the results. Although other locations worldwide are characteristically different from the eastern United States, the methods presented here may prove useful in areas currently planning new emission and pollution reductions such as East and South Asia, and could help guide the selection of key targets for pollution control. Sources from the direction associated with precipitation during the season with greater oxidant (OH and H_2O_2) concentrations may play an outsized role in acid precipitation. The method can be particularly useful for in situ data-poor areas, given that satellite data will help to capture the fast-paced changes in emissions and provide more frequent updates than conventional bottom-up emission inventories.

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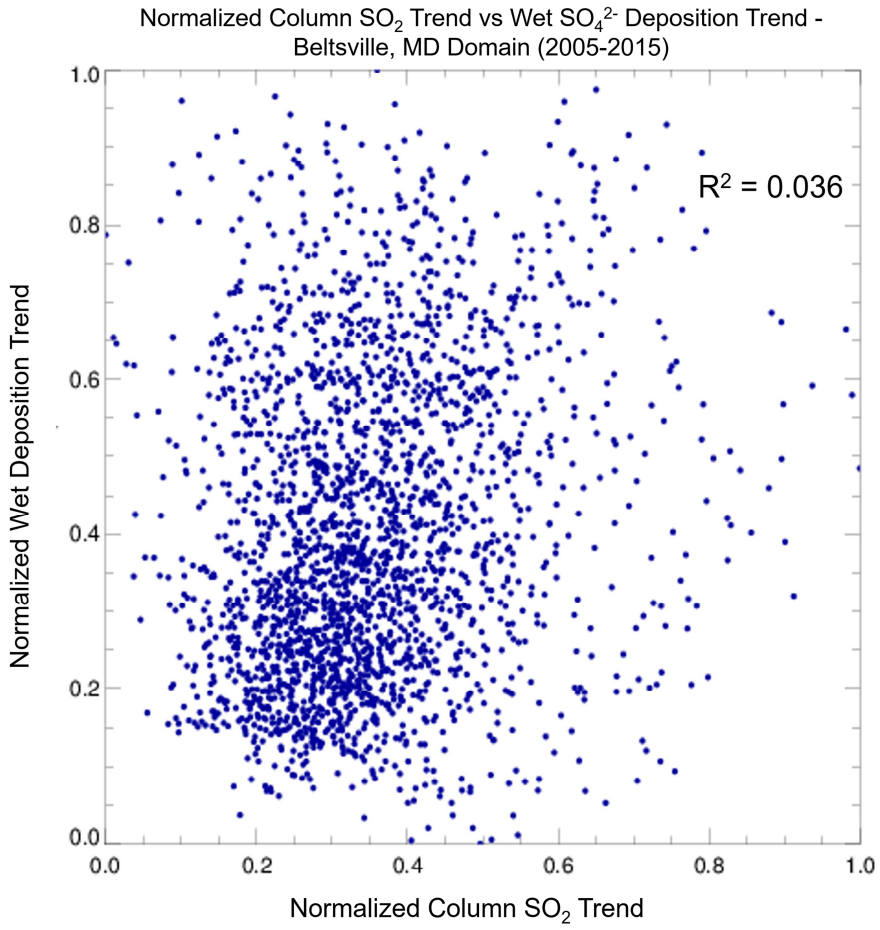
773 **Appendix A:**



774

775 Figure A.1: A scatter plot of the normalized trends for the Beltsville, MD site domain. Each
776 point represents a grid box in the domain with a unique normalized SO_2 and SO_4^{2-} wet deposition
777 trend value. The bounds for the domain are [88.875°, 73.875° W] and [35.125°, 45.125° N].

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Table A.1: Cumulative distribution of winter (DJF) percent contribution to SO_4^{2-} deposition trend at the Beltsville, MD site within given ranges from the site. The totals are summed through each distance range and are broken up by direction with respect to the longitude of the site. The first column is the distance range from the site over which the contribution of grid boxes is summed. The last column is the percent contribution for only the single distance range, not the cumulative amount.

Distance from Site (km)	East	West	Total	Incremental difference (between two radii)
0-50	3.11	0.24	3.35	3.35
50-100	17.04	1.74	18.78	15.43
100-200	33.1	11.34	44.44	25.66
200-300	34.31	21.67	55.98	11.54
300-400	35.51	35.54	71.05	15.07
400-500	35.62	41.88	77.5	6.45
500-1000	35.62	62.41	98.03	20.53

782

Table A.2: Same as Table A.1 but for summer (JJA)

Distance from Site (km)	East	West	Total	Incremental difference (between two radii)
0-50	0.00	0.00	0.00	0.00
50-100	0.81	2.09	2.90	2.90
100-200	27.86	14.11	41.97	39.07
200-300	63.05	19.47	82.52	40.55
300-400	66.36	19.47	85.83	3.31
400-500	65.34	21.02	86.36	0.53
500-1000	66.37	32.87	99.24	12.88

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Table A.3: Cumulative distribution of winter (DJF) percent contribution to SO_4^{2-} wet deposition trend at the Hackney, OH site within given ranges from the site. The totals are summed through each distance range and are broken up by direction with respect to the longitude of the site. The first column is the distance range from the site over which the contribution of grid boxes is

summed. The last column is the percent contribution for only the single distance range, not the cumulative amount.

Distance from Site (km)	East	West	Total	Incremental difference (between two radii)
0-50	4.93	5.94	10.87	8.71
50-100	6.91	16	22.91	12.04
100-200	9.01	38.16	47.17	24.26
200-300	9.09	53.96	63.05	15.88
300-400	9.09	67.9	76.99	13.94
400-500	9.28	76.62	85.9	8.91
500-1000	9.28	90.72	100	14.1

785

Table A.4: Same as Table A.3 but for summer (JJA)

Distance from Site (km)	East (%)	West (%)	Total (%)	Incremental difference (between two radii)
0-50	2.95	1.75	4.70	4.703
50-100	5.56	5.438	11.00	6.297
100-200	18.14	20.67	38.81	27.81
200-300	29.10	37.01	66.11	27.3
300-400	31.16	47.06	78.22	12.11
400-500	31.70	54.73	86.43	8.205
500-1000	31.87	67.15	99.02	12.595

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Highlights:

- Sulfate deposition trends attributed to reduction of emissions from specific areas.
- Trajectory and contribution analysis used to find potential source regions
- Reductions in large SO_2 sources dominate deposition trends near Ohio River Valley
- Key differences between winter and summer contribution to deposition
- Deposition in Maryland decreased due to emission control both in and out of state.