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

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A scholarly paper in partial fulfillment of the requirements for the degree of

Master of Science

April 2018

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Abstract:

Sulfur dioxide (SO_2), a criteria pollutant, and sulfate (SO_4^{2-}) deposition used to be 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 the downward trends in SO_2 emissions and sulfate 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 deposition trend at each site. The results suggest that emission reductions in the Ohio River Valley have led to decreases in sulfate deposition at Hackney, Akron and South Fayette. Farther to the east, emission reductions in southeast PA have resulted in improvements in sulfate deposition at Wilmington, while for Beltsville, reductions from both the Ohio River Valley and near the Chesapeake Bay have had an impact on sulfate deposition. For Beltsville, sources over 300 km away from the site contribute roughly 44% in winter but only 18% of the observed deposition trends in winter and summer, respectively, reflecting seasonal changes in transport pattern as well as faster oxidation and washout of sulfur in summer. This suggests that pollution and deposition are linked through not only the location

of sources relative to the observing sites, but also the weather patterns characteristic to the region. The methodology developed here is applicable to other regions with significant trends such as China and India, and estimate the potential benefits of emission reduction in those areas.

Acknowledgements:

I would like to thank the NASA Earth Science Division (ESD) Aura Science Team program for funding of the OMI SO_2 product development and analysis (Grant # 80NSSC17K0240). The OMI project is managed by the Royal Meteorological Institute of the Netherlands (KNMI) and the Netherlands Space Agency (NSO). I also acknowledge partial support for this study from NASA's Earth Science New Investigator Program (Grant # NNX14AI02G). I am extremely grateful for my advisors Dr. Can Li and Professor Russell R. Dickerson, for their guidance, patience and valuable feedback in conducting this study and the writing of the manuscript. Additionally I thank Tim Canty, Nick Krotkov and other members of the atmospheric chemistry group for additional feedback and input along the way. Lastly, I thank my close friends, colleagues, and family for their ongoing support and encouragement throughout my first two years of graduate school.

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List of Abbreviations

AQS - Air Quality System

CONUS – Continental United States

DJF - December – January - February

EDAS - Eta Data Assimilation System (EDAS)

EPA - Environmental Protection Agency

HYSPLIT - Hybrid Single Particle Lagrangian Integrated Trajectory

JJA - June-July-August

NADP - National Atmospheric Deposition Program

NASA - National Aeronautics and Space Administration

OMI - Ozone Monitoring Instrument

ppb – parts per billion

PSCF - Potential Source Contribution Function

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). 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 Clean Air Act (U.S. EPA, 2015) and increased monitoring of pollutants and deposition by EPA's Acid Rain Program (U.S. EPA, 2002) have led to drastic reductions in sulfur based emissions and the subsequent sulfate formation, especially in regional hotspots such as the Ohio River Valley. Sulfate is produced chemically in the atmosphere mainly through the oxidation of sulfur dioxide. Sulfur dioxide 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 (Lee et al, 2011). The deposition of sulfate 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. It is important to quantitatively attribute changes in emissions to those in the deposition trends over downwind areas in order to realize benefits of regulatory controls and applications to other regions.

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). The OMI SO_2 product has proved to be 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 smaller sources to be detected. A study using this new OMI SO_2 products demonstrates that there is good correlation ($r = 0.91$) between reported emission rate 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 product. 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 sulfate aerosol product is 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 sulfate 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). Another study by the same author estimated separation distances and atmospheric transport for atmospheric sulfur dioxide and sulfate (Shannon, 1997). In the late 20^{th} century, locations in upstate New York, despite their relatively low local SO_2 concentrations, also experienced acid rain and deposition problems. Indeed, emission reductions upwind have been found to have a linear relationship with sulfate 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 in Ontario and the Ohio River Valley. In particular, lakes in the Adirondack region have shown decreases in SO_4^{2-} concentrations and reasonable correlation ($r^2 = 0.58$) between SO_2 emission and wet deposition changes upwind, 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. Overall, the PSCF method has been used for many years, having been employed in an earlier study modeling 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 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, with >60% in winter to <30% in the summer (Chen et al., 2002).

Similar studies were performed for sites in Wisconsin, where enhanced sulfate 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, 2016). 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 sulfate. 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.

2 Methods:

2.1 Data

The Ozone Monitoring Instrument (OMI) (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 PBL 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.

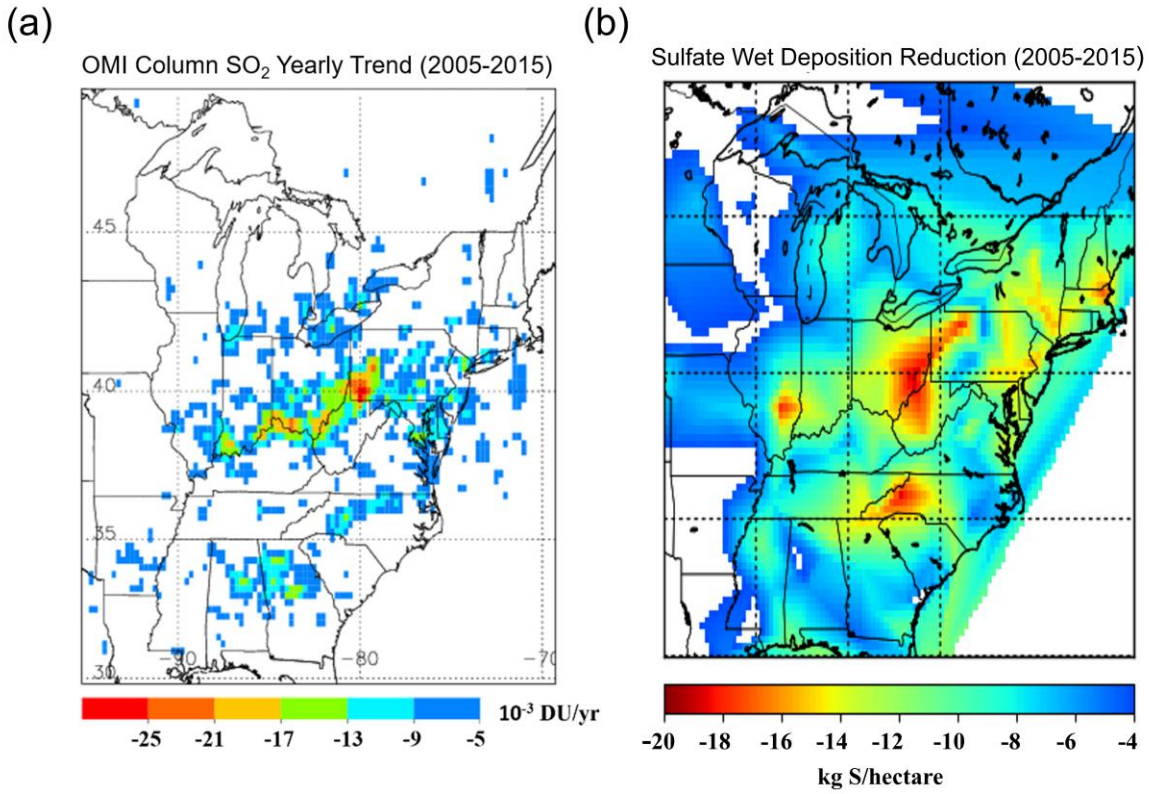


Figure 1: (a) Annual trend in OMI Column SO_2 in the eastern United States calculated using yearly averages, from 2005 to 2015 (b) Change in wet sulfate deposition between 2005 and 2015 over the same domain and time period, based on NADP deposition measurements.

Sulfate (SO_4^{2-}) wet deposition data was obtained from the National Atmospheric Deposition Network (NADP). This network, consisting of over 150 monitoring sites nationally, collects rainwater samples and analyzes them for various chemical species (Lamb et al, 1999). Total sulfate wet deposition is estimated annually for each station, as end of year totals with the deposition given in units of kg S/ha. Due to the non-gridded nature of the data, we interpolated the annual deposition to a regular grid, using Inverse Distance Weighting (IDW) and Kriging interpolation methods, shown to be most efficient for calculating special deposition patterns (Qu et al, 2016). A ten-year trend and net reduction (Figure 1b) in sulfate over the entire U.S.

domain (CONUS) 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.

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 sulfate 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 to 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. 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 sulfate deposition. The sites chosen for the trajectory analyses 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]. A site in upstate New York [74.500° W, 43.4336° N], Piesco Lake, was also considered due to a noticeable downward 10-year deposition trend in the region, however the in-situ SO_2 data was too low to perform a meaningful trajectory analysis.

The HYSPLIT trajectory model from NOAA (Stein et al, 2015) was used to calculate back trajectories. Three day back trajectories were calculated each day using archived Eta Data Assimilation System (EDAS) meteorological data at 40 km resolution. The HYSPLIT model runs were initialized daily at 18Z near the overpass time of the satellite. The initialized height was kept constant in the model runs at 500 m above ground level. A climatology of back trajectories was obtained for each site by running daily 72-hour back trajectories for three summers (JJA) and three winters (DJF), in the period 2006-2009. This period was selected because larger downward trends in column SO_2 and sulfate wet deposition occurred in 2005-2010 than in 2010-2015. In addition, changes in the average seasonal large-scale flow pattern are unlikely to be strongly dependent on the periods selected.

2.3 Potential Source Contribution Analysis

The need for a trajectory and PSCF analysis stems from the fact that the spatial correlation between wet sulfate deposition and OMI column SO_2 observations is overall fairly weak across the entire domain (Figure 2). To link the trends, characteristic air patterns for a given location are needed to understand the trends occurring in those locations. The calculated trajectories were obtained for the purpose of calculating the probability of high concentrations of SO_2 coming from a given grid box in the domain.

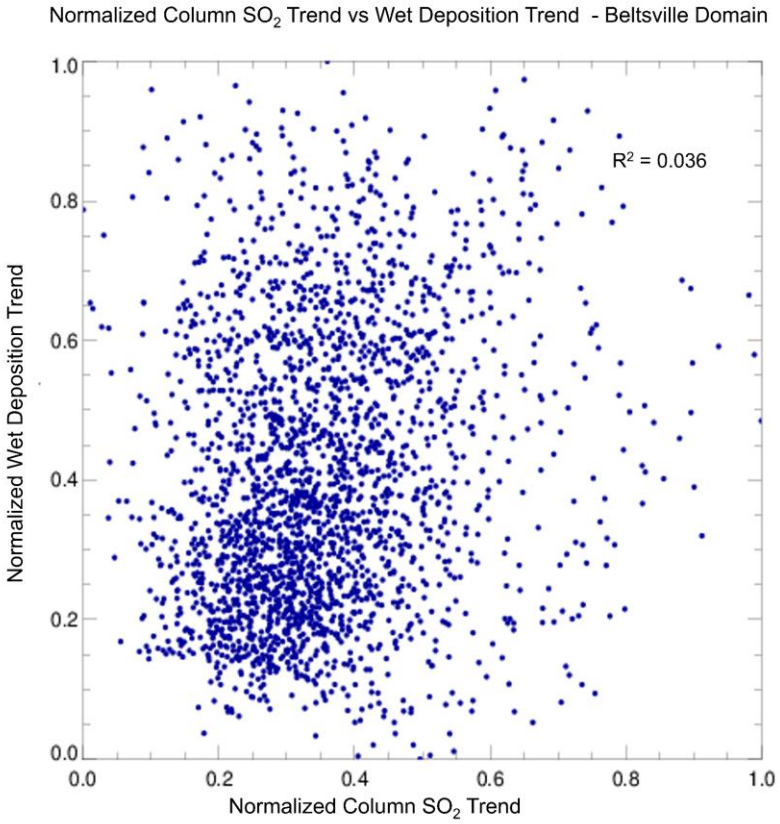


Figure 2: A scatter plot of the normalized trends for the Beltsville, MD site domain. Each point represents a grid box in the domain with a unique normalized SO_2 and deposition trend value. The bounds for the domain are [88.875, 73.875 W] and [35.125, 45.125 N].

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

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

The subscript *ij* denotes a single grid box on the grid domain. The domain over which the function was calculated was ±5 degrees latitude and ±7.5 degrees longitude from each site. The

domain size and location were chosen based on the typical distance covered by trajectories within 72 hr. Based on the concentrations recorded at each of the sites, we chose a value of 5 ppb as the SO_2 threshold for all of the base cases except for the winter South Fayette, for which the threshold was 7.5 ppb. A simple weighting scheme was assigned for the calculation to remove low sample size error. The weighting was performed in order to eliminate the sample size issues, or occurrences of low values of n. Thus for threshold total numbers of trajectories (n) in a single grid box of 24, 16 and 8 the resulting PSCF value was multiplied by 0.7, 0.45 and 0.07 respectively. These new values are the weighted potential source contribution functions (WPSCF) and were calculated for each of the five sites for JJA and DJF. The weighted scheme is mostly arbitrary but is similar to one used in 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).

2.4 Normalized Trends

To factor in the effect of the PSCF on the trends, we transform both trends to the same, normalized scale. The wet sulfate deposition trends were normalized to a scale of 0 to 1 with the grid box having the highest downward trend being 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 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 deposition trend would indicate that air arriving from there has seen significant reductions in sulfur over the years, thus contributing to the decrease in 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.

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

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 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-} 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.

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

Thus this new value expresses the percentage of the total PSCF that the particular grid box contributes to the sulfate deposition trend at the AQS or NADP site and provides a quantitative assessment of the trend data relationship.

3. Results and Discussion

3.1 Percent contributions

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

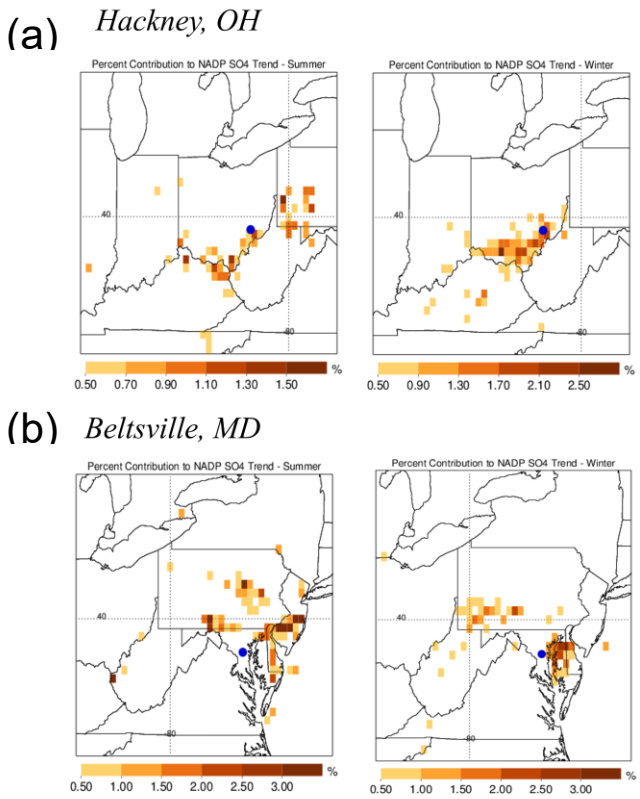
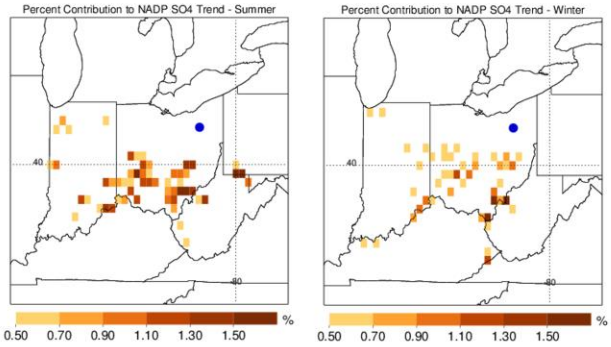
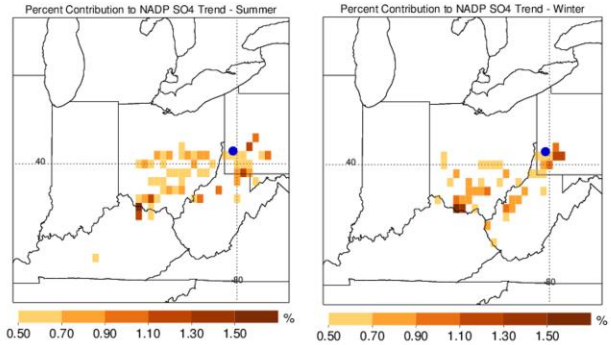


Figure 3: Percent contribution for each grid box in the domain with only values above 0.5%. Shown for (a) Hackney, OH and (b) Beltsville, MD sites in JJA (left) and DJF (right). The observation sites are marked with a blue dot.

(a) *Akron, OH*



(b) *South Fayette, PA*



(c) *Wilmington, DE*

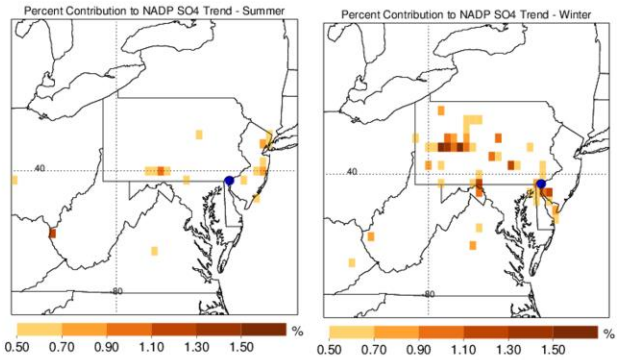


Figure 4: Percent contribution for each grid box in the domain with only values above 0.5%. Shown for (a) Akron, Ohio, (b) South Fayette, PA and (c) Wilmington, DE AQS sites in JJA (left) and DJF (right). The observation sites are marked with a blue dot.

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 on 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 between 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. The observed yearly total 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 5), however, the overall 10-year trend from 2005 to 2015 was downward

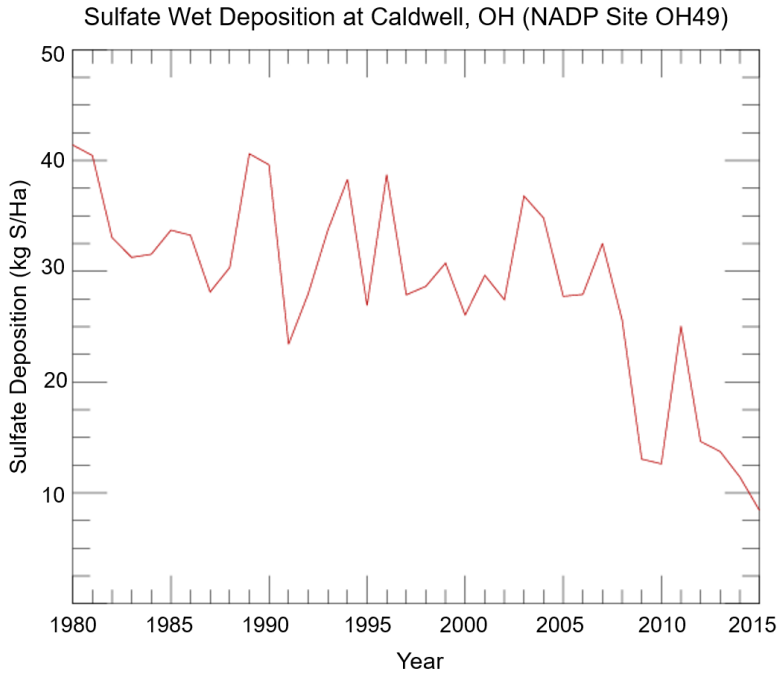


Figure 5: Sulfate Wet Deposition amounts at Caldwell, OH NADP site, shown as a time series from 1980 to 2015. The plotted data is from the NADP network at the OH49 site [39.7928 N, 83.5311 W]

Qualitatively, the area with the colored grid boxes in southern Ohio largely contributed to the decreasing deposition (Figure 3a). In summer (JJA), major areas in southwestern PA with large SO_2 columns contribute remarkably little to the observed trend at the Hackney site. The trajectory climatology for this site (Figure 6) 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.

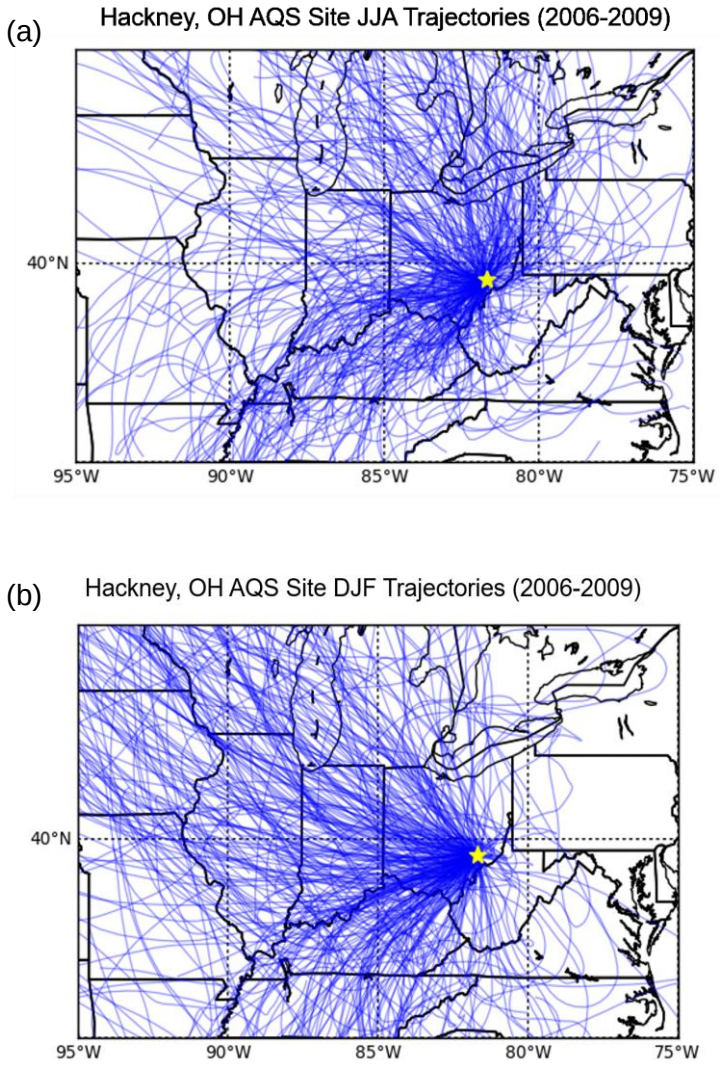


Figure 6: Map of (a) summer (JJA) and (b) winter (DJF) trajectory climatology for 2006-2009 at Hackney, OH. The yellow star shows the location of the site and the blue lines are the individual 72 hour back trajectory for each day, initialized at 18Z using the HYSPLIT model.

Beltsville MD

The Beltsville, MD site which has experienced a downward sulfate wet deposition trend, especially in the years 2008-2012, has two primary regions that have contributed to the 10-year decrease. The Southwest PA region shows the greatest cumulative percent contribution which

implies that 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 3b). While the dominant trajectory is from the northwest in winter, air can occasionally arrive from the east in both seasons. Maryland has cut sulfur emissions with the Healthy Air Act by 80-85% from levels in the early 2000s (He et al., 2016) just before the turn of the decade in 2010. While most of the contribution is due to decreased emissions to the west, it is possible that local emission controls have also played a role in decreasing sulfate deposition in the general vicinity. The case for this site will be further investigated in section 3.3.

Akron, OH

Sources to the south and southwest dominate the deposition trend for the Akron, OH (Figure 4a). Most of the grid cells with a non-negligible percent contribution (greater than 0.5 %) are located near major SO_2 sources, approximately 100-300 km away from Akron in both winter and summer. The percent contributions show less 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). 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 more contribution from the east, indicating a shift from a predominantly

western zonal flow that occurs during winter. The highest percent contributions in both seasons are from southern Ohio and just to the east of the site (Figure 4b), 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

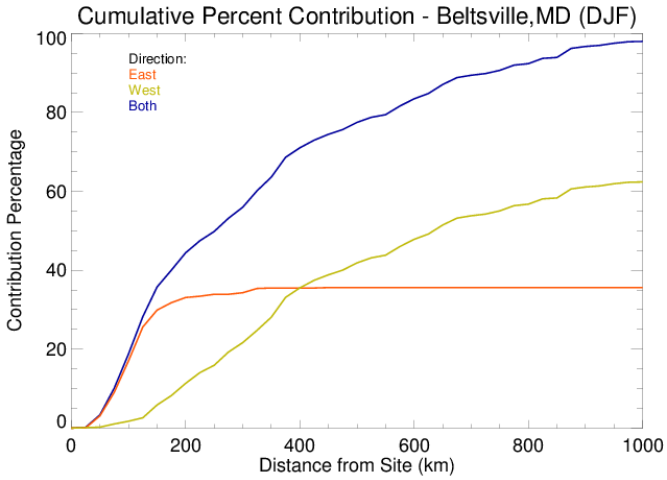
For the Wilmington, DE site (Figure 4c), the most contributing region to the deposition trend is from upwind in Pennsylvania, which is home to several large power plants. As shown by OMI, the region had a strong decrease in column SO_2. Given the winter trajectory pattern, it follows that any reductions 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 sulfate deposition were due to large decreasing trend in winter SO_2 concentrations over upwind areas to the west.

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 would lead to cumulative distributions of total contribution moving away from the site. This would help in diagnosing if the 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 7) and Hackney (Figure 8), for summer and winter seasons.

(a)



(b)

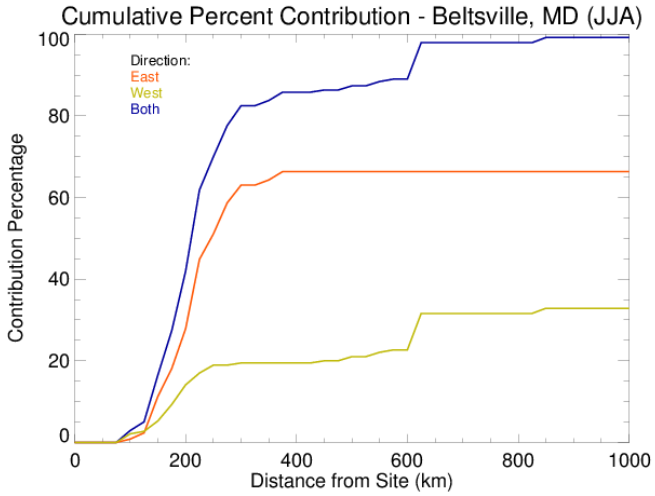


Figure 7: The cumulative percentage of contribution to the wet sulfate deposition trend at the Beltsville AQS site, from areas within a given radius from the site (x-axis) for (a) winter and (b) summer. The orange, green and blue lines represent contributions from locations with a longitude east of the site, west of the site and all locations within the radius respectively.

(a) (b)

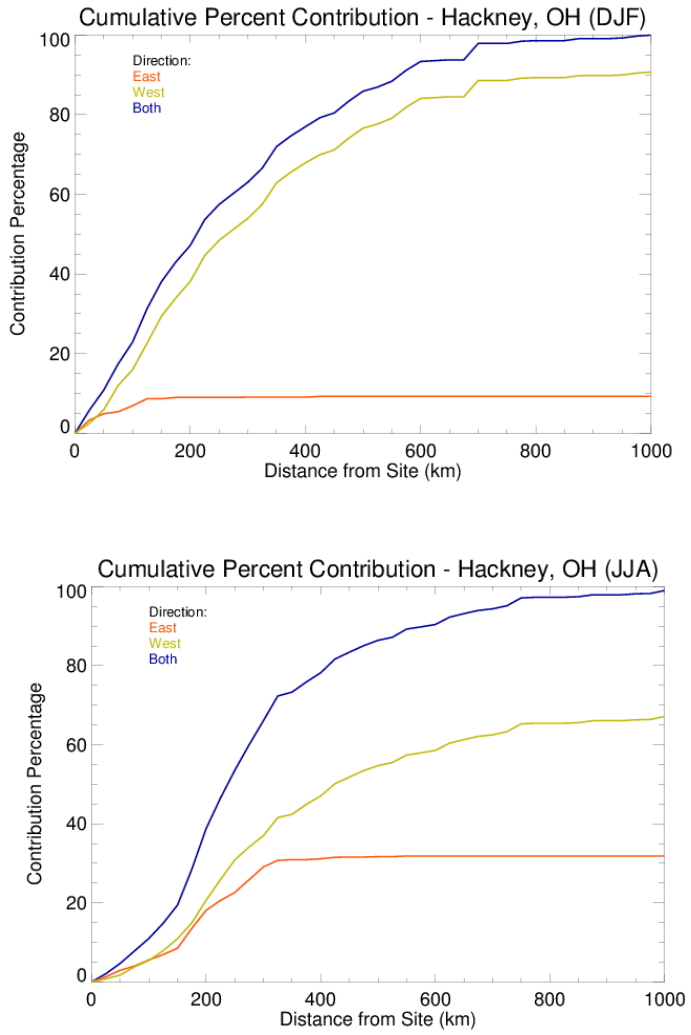


Figure 8: Same as Figure 7 but for the Hackney AQS site.

Beltsville, MD

For the Beltsville site, roughly 41% of the sulfur contributing to the ten-year deposition trend is linked to SO_2 observed within a 300 km radius in winter and within 200 km in summer (Table 1). In addition, 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 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 sulfate. 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

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. While more of the contribution is from the west, the eastern component indicates that some of the sulfate originates from areas to the northeast of the site in PA in addition to areas to the southwest of the site. In DJF, while the total contribution from within 300 km (63%) is similar to JJA for this site, 54% of it is from the west. Areas within 100-200 km from the site, contributed to about 24% and 27% of the sulfate 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.

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 9).

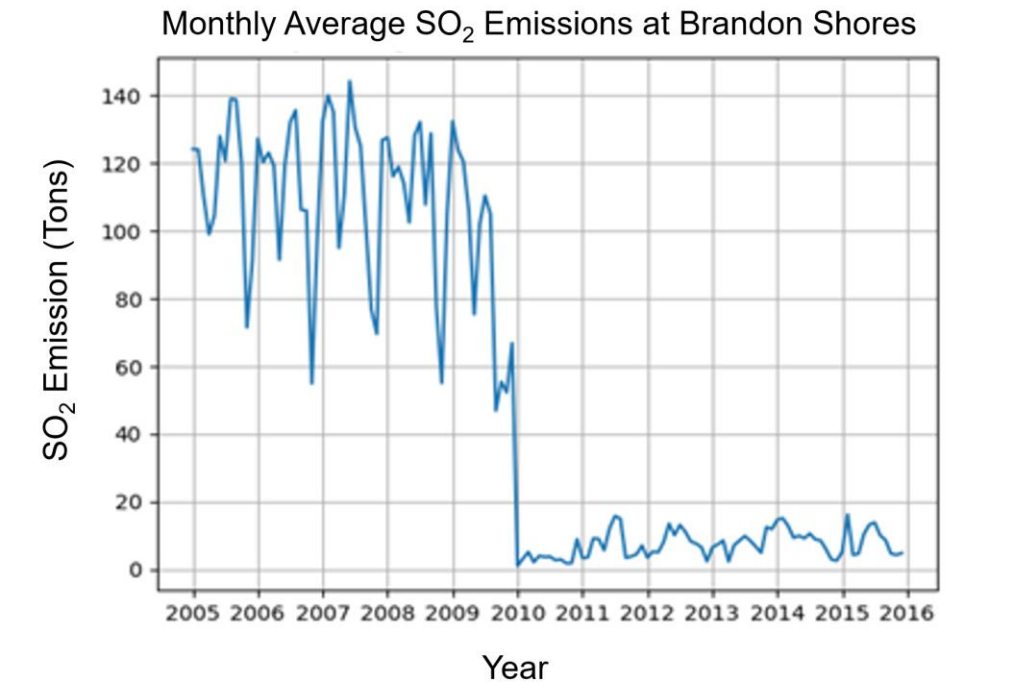


Figure 9: Monthly averages of hourly SO_2 emissions from the Brandon Shores power generating facility, located just to the south of Baltimore, MD. The data were obtained from Continuous Emission Monitoring Systems (CEMs) and are distributed by EPA's Air Markets Program database.

Using the same PSCF analysis method as above, we were able to identify contributions to the sulfate deposition trend for 2008-2012 by using the trend and PSCF corresponding to this time period only. As seen in Figure 10, 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 area), contribute slightly higher from 1-1.5% in the 10-year case to 2-3% for 2008-12. The results here show that the state legislation may have had a positive impact on sulfate deposition at Beltsville.

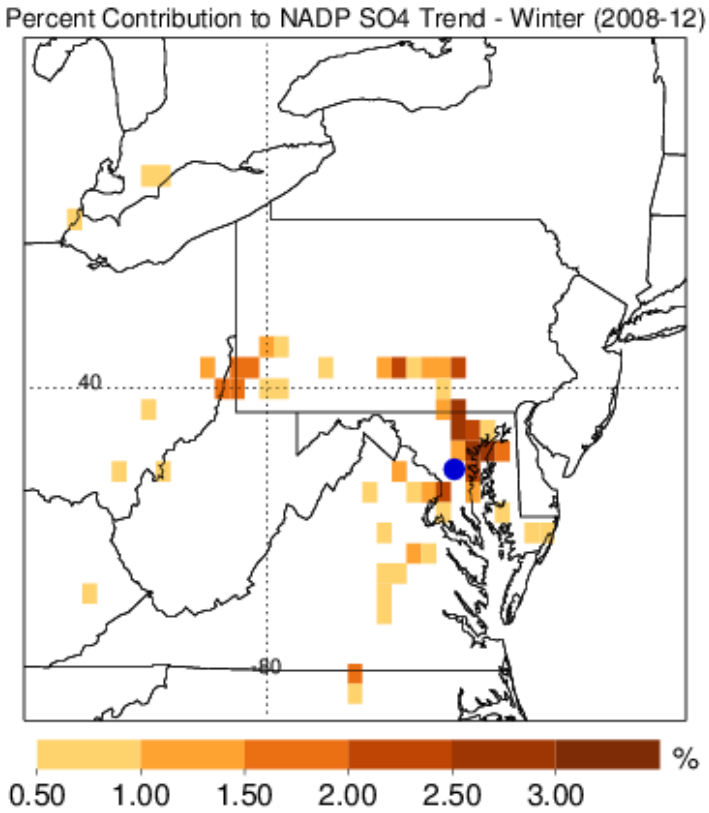


Figure 10: Percent contribution to the Beltsville, MD winter deposition trend for 2008-2012. The same procedure was used as in the other maps, except with a 2008-2012 winter trajectory climatology and PSCF

This result can also be related to the specific dry and wet deposition amounts occurring in Beltsville over the years. The data in Table 5 indicates that dry SO_2 and sulfate deposition have decreased overall from 2005 to 2015. The decrease is better seen in the sulfur dioxide than sulfate between the first and second 5 years. The effect of cutting emissions at Brandon Shores has clearly decreased local dry deposition of SO_2. The result is less obvious in the sulfate,

although by 2015, the deposition has dropped by almost 50%, from 1.12 to 0.59 kg S/ha. According to Figure 11, 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 11).

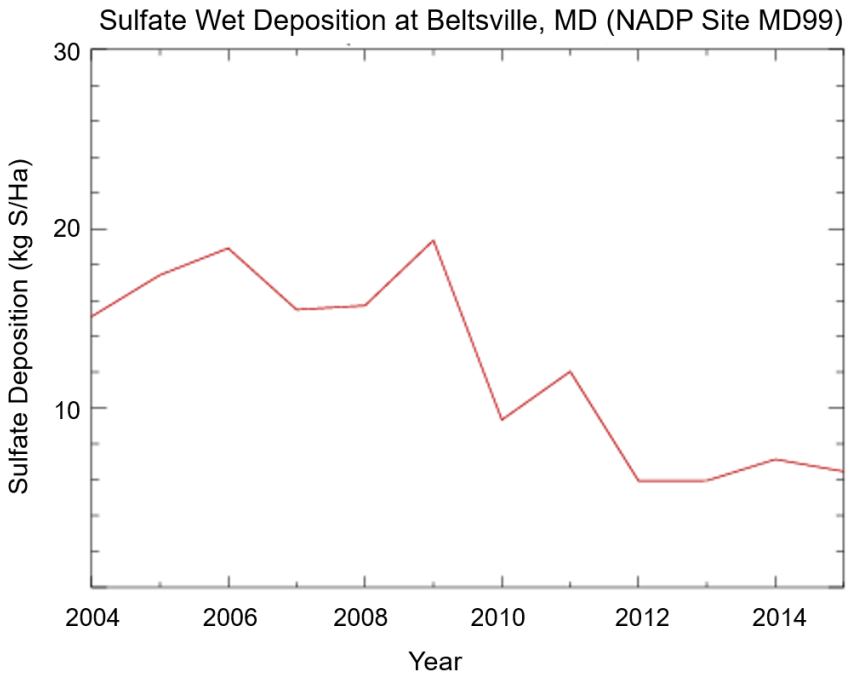


Figure 11: Sulfate Wet Deposition amounts at Beltsville, MD, shown as a time series from 2004 to 2015. The plotted data is from the NADP network at the MD99 site.

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 were 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 fairly consistent with the SO_2 lifetimes of 13 h and 48 h for summer and winter respectively found by Lee et al. As shown, SO_2 and SO_4^{2-} trends do not have direct spatial correspondence. Locations that have drastically reduced their sulfur emissions can still have 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.

Table 5: Flux of dry sulfur dioxide and sulfate 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 sulfate at the site. Several years of dry flux data were missing in the dataset.

Year	Dry SO_2 Flux (kg SO_2/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

3.4 Method Limitations

Although the methodology presented in this study was used consistently for all sites, it did not come without limitations or systematic errors. One big limitation in this study is the characteristics of wet deposition. Whether the sulfate is being deposited or carried further downwind is dependent on nature of the trajectory and if precipitation occurred. Given the uncertainties in diagnosing rain or cloud formation events along the trajectory, we primarily focus on determining where deposition is highly decreasing along with an active flow pattern from trajectory analysis showing possible origins of sulfate from nearby sulfur in the atmosphere. Furthermore, HYSPLIT initialization settings were rather simple in the sense that the model was not run at multiple times during the day or from different heights. We kept the constant initialization height of 500 m (above ground) which is a reasonable representation of

mid boundary layer height around the afternoon OMI overpass. The back trajectories were only run once a day to match the temporal resolution of OMI and around the time the instrument would pass over the Eastern U.S to make measurements. Due to keeping the initialization time constant at 18Z and the height at 500 meters, there could have been error associated with analyzing the trajectories with respect to high SO_2 amounts since these can change due to weather patterns and sometimes within hours. The calculations of the trajectories inherently contained errors, as a result of limited temporal and spatial resolutions of the model reanalysis meteorological data. However, given the spatial resolution of the OMI instrument, the resolution of the meteorological data was appropriate. There is also possibility of biases in precipitation collection based on the collector instrument used (Wetherbee et al, 2009). Another source of error in the method could be the low detection rates of SO_2 exceeding a threshold at a site. This is seen during summer when the exceedance rate was low compared to winter, resulting in a rather scattered PSCF. The resulting PSCF calculation 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, some grid boxes may not be represented as accurately, especially in JJA and at low SO_2 sites (Wilmington and Beltsville). 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 results. Lastly, 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 quantified with a combination of in situ and satellite observations coupled with trajectory analysis. In this study we quantified the possible origin of sulfate 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 winds, but also on the rate of 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 sulfate acid deposition in the same region and benefits are generally seen within 500 km of the source. At the Beltsville, MD site, about 2/3 of the sulfate deposition originates from the west and 1/3 from the east, in keeping with the dominance of westerly winds in winter. In summer, when SO_2 has a shorter lifetime with respect to oxidation to sulfate, closer emitters generally have a greater influence – the bulk of the deposition (80%) is due to sources < 300 km away. In winter, that range is expanded to over 500 km. Nearby sources to the east, however, can make a substantial contribution in winter when winds off the Atlantic Ocean bring moisture and heavy precipitation in systems such as nor'easters. Statewide emission controls may have partially caused the decreasing sulfate trend, in addition to the emission reductions upwind, the more obvious component. 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 cannot be adequately linked given their geographic displacement. The satellite data provides 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 sulfate 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. The method can be particularly useful for these 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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Supplementary Tables:

Table 1: Cumulative distribution of winter (DJF) percent contribution to sulfate 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

Table 2: Cumulative distribution of summer (JJA) percent contribution to sulfate 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	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

Table 3: Cumulative distribution of winter (DJF) percent contribution to sulfate 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

Table 4: Cumulative distribution of summer (JJA) percent contribution to sulfate 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	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