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Contrasting seasonal responses of sulfate aerosols to declining SO_2 emissions in the Eastern U.S.: Implications for the efficacy of SO_2 emission controls

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Abstract Stringent controls have reduced U.S. SO_2 emissions by over 60% since the late 1990s. These controls have been more effective at reducing surface $\left[SO_4^{2-}\right]$ in summer (June, July, and August) than in winter (December, January, and February (DJF)), a seasonal contrast that is not robustly captured by Climate Model Intercomparison Project 5 global models. We use the Geophysical Fluid Dynamics Laboratory AM3 chemistry-climate model to show that oxidant limitation during winter causes $\left[SO_4^{2-}\right]$ (DJF) to be sensitive to primary SO_4^{2-} emissions, in-cloud titration of H_2O_2, and in-cloud oxidation by O_3. The observed contrast in the seasonal response of $\left[SO_4^{2-}\right]$ to decreasing SO_2 emissions is best explained by the O_3 reaction, whose rate coefficient has increased over the past decades as a result of increasing NH_3 emissions and decreasing SO_2 emissions, both of which lower cloud water acidity. The fraction of SO_2 oxidized to SO_4^{2-} is projected to keep increasing in future decades, delaying improvements in wintertime air quality.

1. Introduction

Long-term observations in both the U.S. and Europe show that regulations aimed at curbing SO_2 emissions have successfully reduced the surface concentration of sulfate aerosols $\left(\left[SO_4^{2-}\right]\right)$ with major benefits for visibility [*Mueller*, 2003; *Hand et al.*, 2014], air quality [*Hand et al.*, 2012b], and acid rain [*Garmo et al.*, 2014]. These observations also show that $\left[SO_4^{2-}\right]$ has declined less rapidly than SO_2 emissions, especially in winter [*Manktelow et al.*, 2007; *Hand et al.*, 2012a, 2012b; *Tanner et al.*, 2015; *Banzhaf et al.*, 2015]. In this study, we focus on the photochemical processes that induce these observed seasonal differences in the response of $\left[SO_4^{2-}\right]$ to decreasing SO_2 emissions.

SO_2 oxidation can proceed via the gas phase reaction with OH but is thought to be dominated by the in-cloud reaction of H_2O_2 with bisulfide (HSO_3^-) [*Seinfeld and Pandis*, 2006]. This reaction is fast and largely insensitive to cloud acidity, such that the in-cloud oxidation of SO_2 is effectively limited by the availability of H_2O_2 [*Seinfeld and Pandis*, 2006; *Ervens*, 2015]. *Manktelow et al.* [2007] noted that the in-cloud titration of H_2O_2 by SO_2 is consistent with the sublinear response of $\left[SO_4^{2-}\right]$ to changes in SO_2 emissions, especially in winter when H_2O_2 production is lowest in the northern midlatitudes. In-cloud oxidation of SO_2 to SO_4^{2-} may also proceed via the reaction of O_3 with sulfide $\left(SO_3^{2-}\right)$. Unlike the oxidation by H_2O_2, this reaction exhibits a strong pH dependence, with the effective reaction rate coefficient $\left(k_{O_3}^{SO_2}\right)$ increasing as 10^{pH} above $pH = 4.5$ [*Seinfeld and Pandis*, 2006]. The relative contribution of the O_3 pathway to SO_4^{2-} production remains uncertain, with model estimates ranging widely from 1% to 50% [*Barth et al.*, 2000; *Berglen et al.*, 2004; *Alexander et al.*, 2009; *Bellouin et al.*, 2011; *Paulot et al.*, 2016]. In the 1990s, acid rain was prevalent and the oxidation of SO_2 by O_3 was often neglected in models of the sulfur cycle [*Chin et al.*, 1996; *Koch et al.*, 1999], an assumption supported by isotopic measurements [*Alexander et al.*, 2009; *Sofen et al.*, 2011]. In the last 10 years, cloud acidity has declined in the U.S. and Europe [*Garmo et al.*, 2014] as a result of controls on NO_x and SO_2 emissions. *Banzhaf et al.* [2015] recently showed that the associated increase of $k_{O_3}^{SO_2}$ was an important contributor to the sublinear response of $\left[SO_4^{2-}\right]$ to SO_2 emission controls in Europe.

In this study, we first compare the observed change of $\left[SO_4^{2-}\right]$ in winter (December, January, and February (DJF)) and in summer (June, July, and August (JJA)) in the Eastern U.S. over the last 30 years with the SO_2

emission trend and the $[SO_4^{2-}]$ trend simulated by models from the Climate Model Intercomparison Project 5 (CMIP5). Second, we use the atmospheric chemistry-climate model (AM3) from the Geophysical Fluid Dynamics Laboratory (GFDL) to examine the photochemical processes that contribute to the weaker decline of $[SO_4^{2-}]$ in DJF relative to JJA. Finally, we discuss the indirect contribution of anthropogenic NH_3 emissions to challenges in reducing wintertime $[SO_4^{2-}]$.

2. Method

We use surface observations of $[SO_4^{2-}]$ from the Clean Air Status and Trend Network (CASTNET). CASTNET was established under the 1991 Clean Air Act Amendments to monitor changes in air quality associated with emission control programs. Total SO_4^{2-} (TSO4) is collected weekly on filters 10 m above ground at over 100 sites [*Malm et al.*, 2002]. Comparisons against independent measurement techniques suggest that CASTNET TSO4 has no significant bias [*Ames and Malm*, 2001; *Malm et al.*, 2002]. We obtain seasonally averaged TSO4 (DJF) and TSO4 (JJA) from the U.S. Environmental Protection Agency (EPA, https://www.epa.gov/castnet). For a seasonal mean to be valid, the U.S. EPA requires at least 75% of the measurements over this season to pass quality controls. We focus our analysis on the Eastern U.S., where $[SO_4^{2-}]$ has historically been most elevated [*Hand et al.*, 2012b].

We use simulated surface $[SO_4^{2-}]$ from 11 global models that participated in CMIP5 and reported $[SO_4^{2-}]$ [*Taylor et al.*, 2012; *Flato et al.*, 2013; *Collins et al.*, 2013]. These models include a comprehensive representation of SO_2 gas phase and aqueous oxidation [*Flato et al.*, 2013]. We consider the model response of $[SO_4^{2-}]$ (DJF) and $[SO_4^{2-}]$ (JJA) to declining SO_2 emissions over both the historical period (1985–2005) and the RCP4.5 scenario (2005–2050). For models reporting several realizations over both periods, we consider the mean surface $[SO_4^{2-}]$ across these realizations (see Table S1 in the supporting information).

We perform additional simulations with the GFDL-AM3 model [*Donner et al.*, 2011; *Naik et al.*, 2013], the atmospheric chemistry-climate component of the GFDL-CM3 model [*Donner et al.*, 2011; *Griffies et al.*, 2011; *John et al.*, 2012], with revisions to the treatment of SO_4^{2-} chemistry and wet deposition as described in *Paulot et al.* [2016]. Anthropogenic emissions are identical to those used in CMIP5 models [*Lamarque et al.*, 2011; *Meinshausen et al.*, 2011; *Thomson et al.*, 2011; *van Vuuren et al.*, 2011] except for NH_3 to which we apply monthly variations from HTAPv2 [*Janssens-Maenhout et al.*, 2015]. In AM3, SO_4^{2-} is produced through the oxidation of SO_2 in the gas phase by OH, in liquid cloud by H_2O_2 and O_3, in precipitation by H_2O_2, and by heterogeneous reaction on dust particles [*Paulot et al.*, 2016]. Cloud pH is calculated iteratively based on the in-cloud concentrations of gases (NH_3, HNO_3, SO_2, CO_2, HCOOH, and CH_3COOH) and aerosols $(NH_4^+, NO_3^-, and SO_4^{2-})$. Seventy percent of aerosols are assumed to be dissolved in liquid clouds, while the solubility of gases reflects their effective Henry's law constants. To quantify the impact of cloud pH on SO_4^{2-} production, we perform three additional simulations: with prescribed cloud pH = 5 (AM3_pH5), without anthropogenic emissions of NH_3 (AM3_NA), and without seasonality for anthropogenic NH_3 emissions (AM3_NS), similar to the emissions used in CMIP5. A further simulation considers the impact of transition metal chemistry following *Alexander et al.* [2009] (AM3_TM; see supporting information for details). Anthropogenic S is emitted entirely as SO_2, except in AM3_TM where 3% is emitted as SO_4^{2-} [*Chin et al.*, 2000]. Each simulation is performed in two segments. First, from 1985 to 2014, the model horizontal winds are nudged to 6-hourly horizontal winds from the National Centers for Environmental Prediction reanalysis [*Kalnay et al.*, 1996; *Lin et al.*, 2012] and observed sea surface temperature (SST) and sea ice cover (SIC) are used [*Rayner et al.*, 2003]. Second, from 2015 to 2050, no nudging is performed and we use 1980–2000 climatological monthly mean SST and SIC [*Rayner et al.*, 2003]. The contributions of the different oxidation pathways to SO_4^{2-} production for each configuration in 2005 are provided in Table S2. Differences in simulated $[SO_4^{2-}]$ across configurations are dominated by photochemistry especially in the first segment, as nudging results in similar circulation, precipitation, and other climate variables. Nudging also facilitates comparison with observations.

3. Results and Discussion

3.1. Relative Trends of $[SO_4^{2-}]$ in Winter and Summer From Observations and CMIP5 Model Simulations

Figure 1 shows observed and simulated $[SO_4^{2-}]$ in JJA and DJF at Shenandoah National Park (38.5°N,−78.4°E) from 1990 to 2014. The average model bias is +20% in winter and −20% in summer, but seasonal biases can exceed 100% for individual models, which could reflect errors in SO_2 and SO_4^{2-} deposition, SO_2 photochemistry, and SO_2 emissions [*Ervens*, 2015]. For instance, we recently showed that the large positive bias in summer
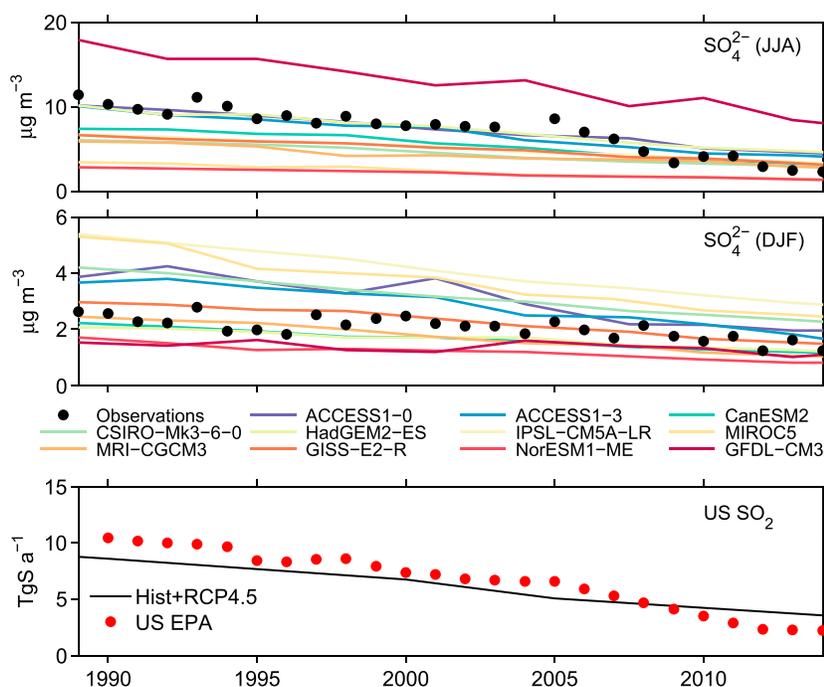
Figure 1. Observed and simulated changes in $\left[SO_4^{2-}\right]$ at Shenandoah National Park in summer (top) and winter (middle). Anthropogenic U.S. SO_2 emissions from the U.S. EPA National Emission Inventory [*EPA*, 2016] and the CMIP5 inventory are shown in the bottom panel. For readability, the model outputs are binned over 3 consecutive years.

(+80%) and negative bias in winter (−30%) in GFDL-CM3 stemmed from a poor representation of wet deposition [*Paulot et al.*, 2016]. Observations show that $\left[SO_4^{2-}\right]$ has decreased by 10% a^{-1}, similar to the trend in U.S. SO_2 emissions [*U.S. Environmental Protection Agency* (*U.S. EPA*), 2016], while $\left[SO_4^{2-}\right]$ in DJF has declined by only 5% a^{-1}. Over the same period, simulated $\left[SO_4^{2-}\right]$ (JJA) and $\left[SO_4^{2-}\right]$ (DJF) have decreased by $3.4 \pm 0.4\%$ a^{-1} and $2.8 \pm 0.7\%$ a^{-1}, respectively, underestimating the observed trend and failing to capture its large seasonality. The underestimate of the $\left[SO_4^{2-}\right]$ decline is consistent with the weaker decline of SO_2 emissions in the RCP4.5 scenario over the 2000–2014 period relative to the U.S. EPA National Emission Inventory (Figure 1, bottom). In subsequent analysis, we focus on change in the ratio of winter to summer $\left[SO_4^{2-}\right]$ $\left(R_{ws}\right)$, as this metric allows us to better isolate changes in SO_2 photochemistry from biases in wet deposition or SO_2 emissions, whose seasonalities are unlikely to have changed significantly.

Figure 2 shows that R_{ws} increases at all CASTNET stations over the 1985–2015 period, similar to Shenandoah. The value of R_{ws} varies spatially. It is highest in the Midwest (where it exceeds 1 in Wisconsin) and lowest near large sources of SO_2 (e.g., Ohio Valley).

Figure 3 shows the evolution of the observed ratio of R_{ws} as a function of $\left[SO_4^{2-}\right]$ (JJA) at nine stations located from the Midwest to the Atlantic Coast (red stars in Figure 2) with at least 15 years of both winter and summer TSO4 observations. At all sites, we find a significant negative correlation ($p < 0.01$) between $\left[SO_4^{2-}\right]$ (JJA) and R_{ws}, indicating that R_{ws} increases while $\left[SO_4^{2-}\right]$ (JJA) declines. Over the same period, four models CanESM2 ([*Lohmann et al.*, 1999; *von Salzen et al.*, 2000; *Salzen et al.*, 2013], HadGEM2-ES [*Collins et al.*, 2011], IPSL-CM5A-LR [*Dufresne et al.*, 2013], and GFDL-CM3 [*Donner et al.*, 2011]) also show a significant negative correlation between $[SO_4^{2-}]$ (JJA) and R_{ws} at all sites (Table S3). GISS-E2-R [*Schmidt et al.*, 2006; *Shindell et al.*, 2013] also qualitatively captures the relationship between R_{ws} and $\left[SO_4^{2-}\right]$ (JJA) when considering the extended 1985–2050 period. The other six models ACCESS1−0 [*Dix et al.*, 2013], ACESS1−3 [*Dix et al.*, 2013], CSIRO−Mk3−6−0 [*Rotstayn and Lohmann*, 2002; *Rotstayn et al.*, 2012], MIROC5 [*Takemura et al.*, 2005; *Watanabe et al.*, 2010], MRI-CGCM3 [*Yukimoto et al.*, 2012], and NorESM1−ME [*Kirkevåg et al.*, 2013; *Bentsen et al.*, 2013] show no significant change or an increase of R_{ws} at some sites as $\left[SO_4^{2-}\right]$ (JJA) declines (Table S3). Interestingly, there is no clear link between the ability of models to qualitatively capture the relationship between R_{ws} and $\left[SO_4^{2-}\right]$ (JJA) and the model bias for $\left[SO_4^{2-}\right]$(DJF) and $\left[SO_4^{2-}\right]$(JJA) individually.
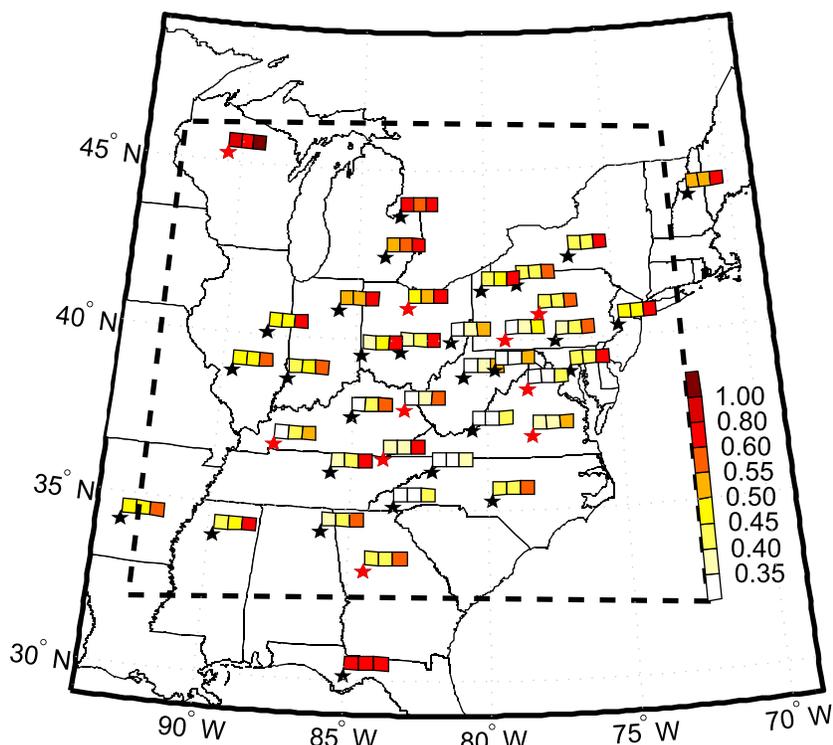
Figure 2. Observed ratio (R_{ws}) of [SO_4^{2-}] in DJF to [SO_4^{2-}] in JJA at CASTNET sites. For each site (star), the three squares denote the mean R_{ws} from 1985 to 1994 (left square), 1995 to 2004 (middle square), and 2006 to 2014 (right square). Red stars highlight the locations of the sites shown in Figures 3 and 4.

3.2. Impact of Cloud pH on [SO_4^{2-}] (DJF)

Figure 4 shows the simulated relationship between [SO_4^{2-}] (JJA) and R_{ws} in the different AM3 configurations described earlier. From 1985 to 2015, AM3_BASE simulates a significant negative correlation between [SO_4^{2-}] (JJA) and R_{ws} at all sites, while AM3_pH5 exhibits no significant change in R_{ws} at seven sites. However, AM3_pH5 shows a lower bias in R_{ws} than in AM3_BASE. These two configurations of AM3 qualitatively capture the range of relationships between [SO_4^{2-}] (JJA) and R_{ws} across CMIP5 models, suggesting that differences in the representation of cloud pH contribute to model diversity.

Figure 5 shows the winter and summer conversion efficiency (η) of SO_2 to SO_4^{2-} in the Eastern U.S. (Figure 2) as a function of the total source of SO_2 over the 1985–2050 period. We define η as follows:

$$\eta = \frac{P(SO_4^{2-})}{S(SO_2)} \quad (1)$$

where $P(SO_4^{2-})$ is the photochemical production of SO_4^{2-} and $S(SO_2)$ is the total source of SO_2 (i.e., emissions, photochemical production, and import). Note that emissions of primary SO_4^{2-} (in AM3_TM) are included in both $P(SO_4^{2-})$ and $S(SO_2)$. In summer, $P(SO_4^{2-})$ is dominated by the oxidation of SO_2 by H_2O_2 and OH. η_{JJA} is comparable across experiments and increases little as $S(SO_2)$ decreases by more than an order of magnitude. In contrast, η_{DJF} increases from 5% to 50% in AM3_BASE and from 20 to 35% in AM3_pH5. As the lifetime of SO_4^{2-} changes little over the 1985–2050 period, the increase of R_{ws} with decreasing [SO_4^{2-}] (JJA) in our model reflects the increase of η_{DJF} with decreasing $S(SO_2)$.

The simulated evolution of η_{DJF} with diminishing $S(SO_2)$ in AM3_BASE exhibits two distinct regimes. First, in the 1990s, during which SO_2 oxidation is dominated by H_2O_2, the increase of η_{DJF} reflects the reduced titration of H_2O_2 in clouds (regime 1). Second, from 2000 onward, η_{DJF} increases more rapidly, driven by greater oxidation of SO_2 by O_3 (regime 2). This increase is driven by diminishing cloud acidity (reflected by increasing rain pH, e.g., http://nadp.sws.uiuc.edu), which increases $k_{O_3}^{SO_2}$ and allows faster oxidation of SO_2 by O_3. By 2020, the oxidation of SO_2 by O_3 is projected to be the largest source of SO_4^{2-} in winter.
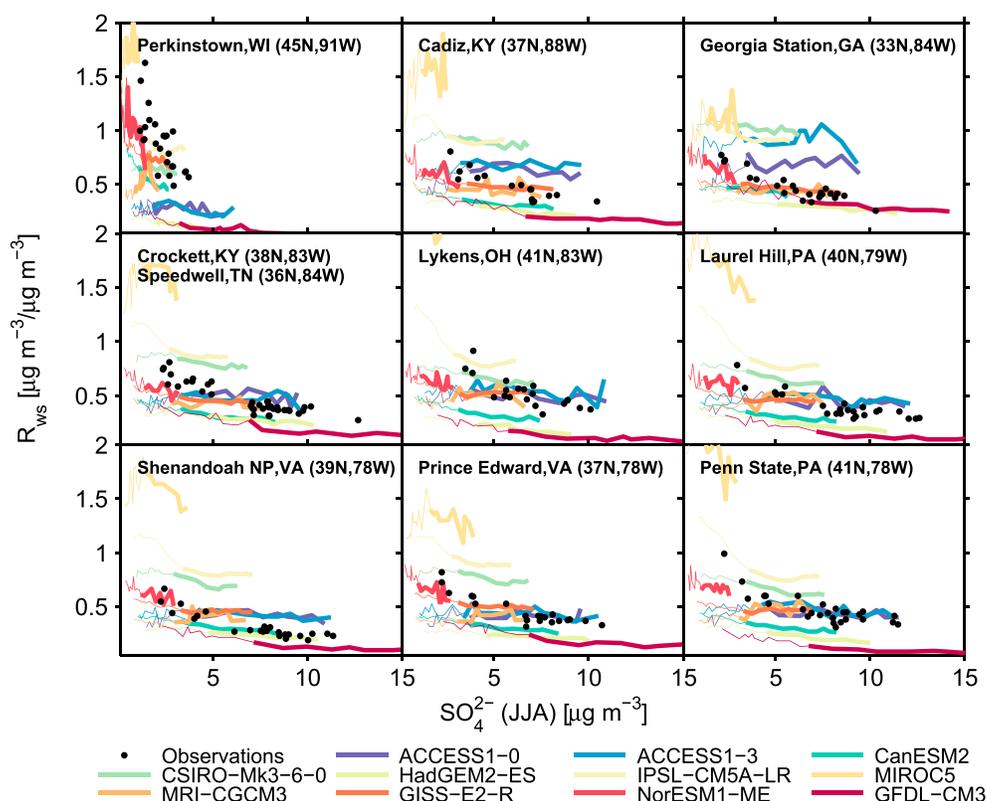
Figure 3. Observed (black) and simulated relationship between $[SO_4^{2-}]$ (JJA) and the ratio of $[SO_4^{2-}]$ (DJF) to $[SO_4^{2-}]$ (JJA) (R_{ws}). Observations are from the U.S. EPA CASTNET network from 1985 to 2014 (see red stars in Figure 2 for the locations of the stations). Simulated surface $[SO_4^{2-}]$ from the different CMIP5 models is sampled at the location of the CASTNET sites from 1985 to 2050. For readability, the model outputs are binned over 3 consecutive $[SO_4^{2-}]$ (JJA). Thick lines denote the CMIP5 model results over the 1985–2015 period.

The existence of two photochemical regimes for winter SO_4^{2-} production helps explain the steeper increase of R_{ws} with decreasing $[SO_4^{2-}]$ (JJA) at Perkinstown (WI) than at other stations (Figure 3). Perkinstown (WI) is located in the U.S. Midwest, where cloud acidity is lower than in the Eastern U.S. due to large agricultural sources of NH_3 and low combustion sources (see http://nadp.sws.uiuc.edu for rain pH). The larger derivative of R_{ws} with respect to $[SO_4^{2-}]$ (JJA) at this site suggests that O_3 makes an important contribution to SO_2 oxidation in this region (regime 2). Indeed, we find that AM3_BASE captures this geographical contrast well, while AM3_pH5, where $k_{O_3}^{SO_2}$ is constant by design, shows similar changes in R_{ws} at all sites.

The increase of η_{DJF} has important implications for the future seasonality of $[SO_4^{2-}]$. In AM3_pH5, η_{DJF} is lower than η_{JJA} over the 1985–2050 period and the seasonality of $[SO_4^{2-}]$ is projected to remain similar to present day, with lower $[SO_4^{2-}]$ in DJF than in JJA. In contrast, η_{DJF} in AM3_BASE is actually simulated to exceed η_{JJA} by 2050, following the increase of $k_{O_3}^{SO_2}$ together with the slower removal of SO_2 by deposition in winter than summer. The increase of η_{DJF} contributes to the simulated shift in the seasonality of $[SO_4^{2-}]$, resulting in higher $[SO_4^{2-}]$ in winter than in summer ($R_{ws} > 1$) in 2050 at all stations (Figure 4). Figure 5 also shows that $[SO_4^{2-}]$ (DJF) is projected to remain stable in the coming decades in AM3_BASE, as the increase in the oxidation of SO_2 by O_3 cancels out much of the expected decrease from SO_2 emissions. In contrast, changes in $[SO_4^{2-}]$ (JJA) reflect more directly the changes in SO_2 emissions, as the increase in the oxidation of SO_2 by H_2O_2 and O_3 is compensated by a decrease of the oxidation of SO_2 by OH (Figure 5).

3.3. Influence of Transition Metals and NH_3 on $[SO_4^{2-}]$ (DJF)

The analysis of η in the previous section suggests that AM3 low bias in R_{ws} at high $S(SO_2)$ is associated with a missing oxidation pathway in winter. Several studies have shown that SO_2 can be oxidized by O_2, either in cloud in the presence of transition metals (TM) [*Hoffmann and Jacob*, 1984; *Martin and Good*, 1991] or on aerosol surfaces [*Turšič et al.*, 2003, 2004; *Hung and Hoffmann*, 2015]. Both of these pathways can operate under acidic conditions and do not exhibit the same titration as H_2O_2 under high SO_2.
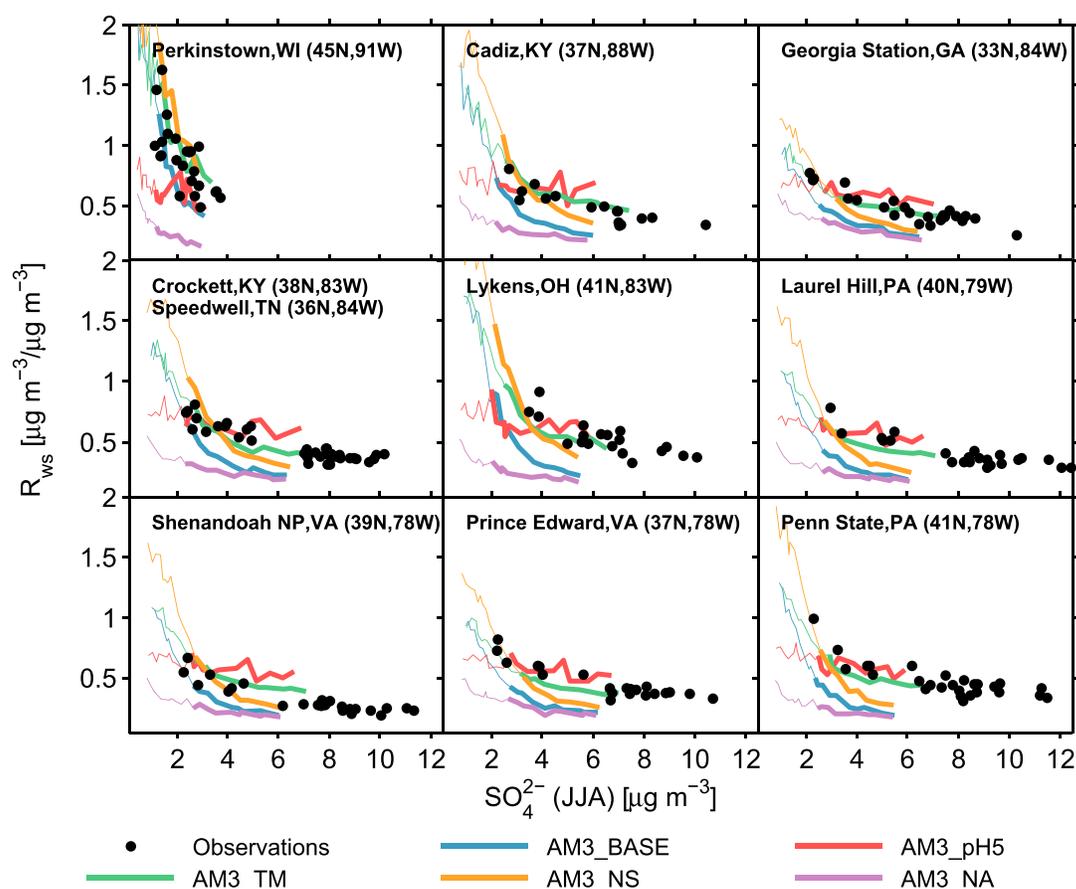
Figure 4. Same as Figure 3 but with different configurations of AM3.

Here we examine the impact of TM chemistry, which is expected to be most important in wintertime in polluted midlatitudes [*McCabe et al.*, 2006; *Alexander et al.*, 2009]. We find that AM3_TM greatly reduces the bias in R_{ws} at high $S(SO_2)$ (Figure 4). However, over much of the historical period, TM–catalyzed chemistry itself only contributes one third of the additional production of SO_4^{2-} in winter (Figure 5) relative to AM3_BASE. The remaining is from direct emissions of SO_4^{2-} (taken as 3% of anthropogenic SO_2 emissions in our AM3_TM simulation). This suggests that the large uncertainty in the fraction of anthropogenic S emitted as SO_4^{2-} [*Textor et al.*, 2006; *Dominguez et al.*, 2008] may also contribute to biases in R_{ws} at high $S(SO_2)$. The contribution of TM chemistry increases as $S(SO_2)$ decreases, which can be attributed to the greater effective solubility of SO_2 at higher pH. In 2050 about 8% of SO_2 is converted to SO_4^{2-} via TM chemistry. However, TM chemistry does not significantly increase the overall conversion of SO_2 into SO_4^{2-} under these conditions ($\eta_{DJF}(AM3\_BASE) \simeq \eta_{DJF}(AM3\_TM)$ at low $S(SO_2)$).

Our analysis of η shows that changes in cloud pH are essential to understanding the rapid increase of R_{ws} in recent years and its future sensitivity to the continued decline of SO_2 sources. NH_3 plays an important role in setting cloud pH, thereby modulating SO_4^{2-} production by the pH sensitive O_3 pathway [*Wells et al.*, 1997; *Redington et al.*, 2009; *Kokkola et al.*, 2003; *Wang et al.*, 2011; *Banzhaf et al.*, 2012; *Megaritis et al.*, 2013]. Unlike SO_2 (and NO_x), whose emissions from fossil fuel combustion are rapidly declining, anthropogenic emissions of NH_3 (primarily from agriculture) have varied little over the last 30 years [*EPA*, 2016] and are expected to increase globally as food demand rises. U.S. NH_3 emissions are not regulated, and significant uncertainties remain in their magnitude, spatial distribution, and seasonality [*Paulot et al.*, 2014]. The temporal variations of anthropogenic NH_3 emissions reflect both the seasonality of agricultural activities (e.g., peak in spring from fertilizer application) and the increase of NH_3 volatility with temperature (peak in summer) [*Pinder et al.*, 2006; *Skjøth et al.*, 2011; *Paulot et al.*, 2014]. No seasonality of NH_3 emissions is included in the inventories used by CMIP5 models [*Lamarque et al.*, 2010], leading to an overestimate of wintertime NH_3 emissions (increasing wintertime cloud pH). Figure 5 shows that this neglect of seasonality results in greater oxidation of SO_2 by O_3 in
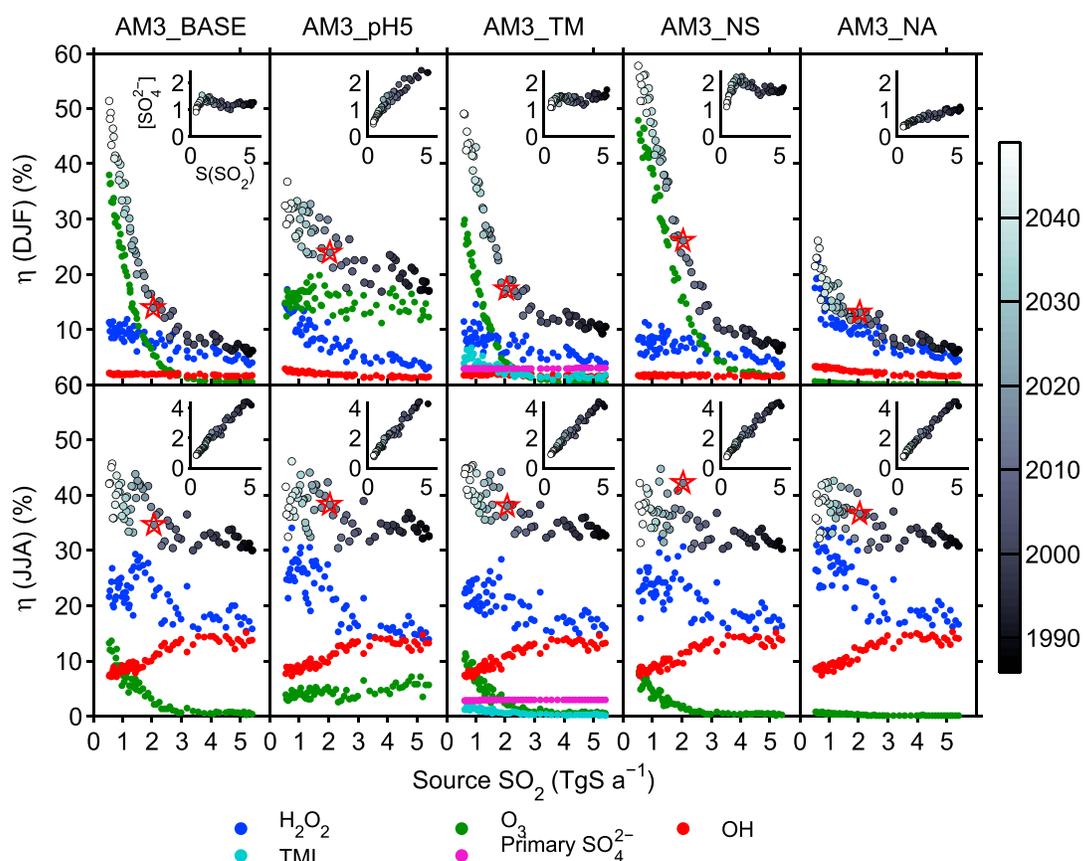
Figure 5. Simulated conversion efficiency (η) of SO_2 to SO_4^{2-} in the Eastern U.S. (dashed region in Figure 2) from 1985 to 2050. Circles are shaded by the simulation year. Year 2015 is indicated by a red star. The simulated change in $[SO_4^{2-}]$ (µg m^{-3}) with decreasing SO_2 emissions ($S(SO_2)$) in the Eastern U.S. is shown in the insets. Colors indicate the contribution of the different pathways to SO_4^{2-} production.

winter at a given $S(SO_2)$ in AM3_NS than in AM3_BASE, such that simulated $[SO_4^{2-}]$ (DJF) over the Eastern U.S. in AM3_NS in 2045 is similar to that of AM3_BASE in 2015. Conversely, when anthropogenic emissions of NH_3 are neglected entirely, clouds remain too acidic for the oxidation of SO_2 by O_3 to be important even in 2050 (Figure 5). Similar to AM3_pH5, the change in η_{DJF} (and thus R_{ws}) is then almost solely driven by diminishing titration of H_2O_2, resulting in a lower sensitivity of R_{ws} to $S(SO_2)$. By 2050, simulated R_{ws} can be as much as a factor of 4 lower in AM3_NA than in AM3_BASE in 2050. This shows that agricultural NH_3 emissions modulate the atmospheric S budget and delay the response of $[SO_4^{2-}]$ (DJF) to SO_2 emissions controls.

4. Conclusions

Observations indicate a marked seasonal contrast in the response of $[SO_4^{2-}]$ to declining SO_2 emissions with $[SO_4^{2-}]$ declining more rapidly in summer than in winter. The lack of consistency in simulating this seasonal response by CMIP5 models highlights important uncertainties in the representation of the atmospheric S budget. However, the sources of model biases (e.g., emissions, deposition, and chemistry) are challenging to disentangle. Our study suggests that long-term observations of the relative change of winter to summer $[SO_4^{2-}]$ in response to SO_2 emission controls can provide a test of the representation of SO_2 chemistry in global models.

Our analysis suggests that the slower decline of $[SO_4^{2-}]$ in DJF than in JJA is primarily driven by an increase of the photochemical conversion efficiency of SO_2 to SO_4^{2-} in winter. This increase reflects diminishing in-cloud titration of H_2O_2 by SO_2 in the 1990s and faster oxidation of SO_2 by O_3, promoted by decreasing cloud acidity, from the early 2000s onward. Our model suggests that the winter conversion efficiency of SO_2 to SO_4^{2-} will continue to increase as SO_2 emissions decline, such that SO_4^{2-} (DJF) will decrease much less than SO_2

emissions in the coming decades. These contrasting trends are also projected to reverse the current seasonality of $[SO_4^{2-}]$, with concentrations becoming higher in winter than in summer. Isotopic measurements [*McCabe et al.*, 2006; *Alexander et al.*, 2009; *Harris et al.*, 2013]) would be especially useful to test whether SO_2 oxidation by O_3 is increasing as suggested by AM3.

We showed that $[SO_4^{2-}]$ (DJF) declines more sharply in response to SO_2 emission reductions in the absence of NH_3 emissions, as cloud pH would remain too low to allow significant oxidation of SO_2 by O_3. Thus, anthropogenic NH_3 emissions, which are expected to continue to increase in the future, contribute not only directly (via NH_4NO_3) [*Pinder et al.*, 2007; *Heald et al.*, 2012; *Paulot and Jacob*, 2014] but also indirectly (via increased SO_4^{2-} production) to challenges in improving U.S. winter air quality [*Hand et al.*, 2012a].

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