



Chemical feedbacks weaken the wintertime response of particulate sulfate and nitrate to emissions reductions over the eastern United States

Viral Shah^{a,1}, Lyatt Jaeglé^a, Joel A. Thornton^a, Felipe D. Lopez-Hilfiker^{a,2}, Ben H. Lee^a, Jason C. Schroder^{b,c}, Pedro Campuzano-Jost^{b,c}, Jose L. Jimenez^{b,c}, Hongyu Guo^d, Amy P. Sullivan^e, Rodney J. Weber^d, Jaime R. Green^f, Marc N. Fiddler^g, Solomon Bililign^{g,h}, Teresa L. Campos^{i,j}, Meghan Stell^{i,3}, Andrew J. Weinheimerⁱ, Denise D. Montzkaⁱ, and Steven S. Brown^{b,k}

^aDepartment of Atmospheric Sciences, University of Washington, Seattle, WA 98195; ^bDepartment of Chemistry, University of Colorado Boulder, Boulder, CO 80309; ^cCooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado Boulder, Boulder, CO 80309; ^dSchool of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332; ^eDepartment of Atmospheric Science, Colorado State University, Fort Collins, CO 80523; ^fDepartment of Energy and Environmental Systems, North Carolina A&T State University, Greensboro, NC 27411; ^gNational Oceanic and Atmospheric Administration (NOAA) Interdisciplinary Scientific Environmental Technology (ISET) Cooperative Science Center, North Carolina A&T State University, Greensboro, NC 27411; ^hDepartment of Physics, North Carolina A&T State University, Greensboro, NC 27411; ⁱAtmospheric Chemistry Observations and Modeling Laboratory, National Center for Atmospheric Research, Boulder, CO 80305; ^jEarth Observing Laboratory, National Center for Atmospheric Research, Boulder, CO 80305; and ^kChemical Sciences Division, Earth System Research Laboratory, NOAA, Boulder, CO 80305

Edited by Mark H. Thiemens, University of California, San Diego, La Jolla, CA, and approved June 19, 2018 (received for review February 22, 2018)

Sulfate (SO₄²⁻) and nitrate (NO₃) account for half of the fine particulate matter mass over the eastern United States. Their wintertime concentrations have changed little in the past decade despite considerable precursor emissions reductions. The reasons for this have remained unclear because detailed observations to constrain the wintertime gas-particle chemical system have been lacking. We use extensive airborne observations over the eastern United States from the 2015 Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER) campaign; ground-based observations; and the GEOS-Chem chemical transport model to determine the controls on winter SO₄²⁻ and NO₃. GEOS-Chem reproduces observed SO₄²⁻-NO₃-NH₄⁺ particulate concentrations (2.45 μg sm⁻³) and composition (SO₄²⁻: 47%; NO₃: 32%; NH₄⁺: 21%) during WINTER. Only 18% of SO₂ emissions were regionally oxidized to SO₄²⁻ during WINTER, limited by low [H₂O₂] and [OH]. Relatively acidic fine particulates (pH~1.3) allow 45% of nitrate to partition to the particle phase. Using GEOS-Chem, we examine the impact of the 58% decrease in winter SO₂ emissions from 2007 to 2015 and find that the H₂O₂ limitation on SO₂ oxidation weakened, which increased the fraction of SO₂ emissions oxidizing to SO₄²⁻. Simultaneously, NO_x emissions decreased by 35%, but the modeled NO₃ particle fraction increased as fine particle acidity decreased. These feedbacks resulted in a 40% decrease of modeled [SO₄²⁻] and no change in [NO₃], as observed. Wintertime [SO₄²⁻] and [NO₃] are expected to change slowly between 2015 and 2023, unless SO₂ and NO_x emissions decrease faster in the future than in the recent past.

sulfate | nitrate | winter | anthropogenic emissions | PM_{2.5}

The past decade has seen dramatic reductions of sulfur dioxide (SO₂) and nitrogen oxides (NO_x) emissions from power plants and vehicles in the United States (1, 2). Thus, hundreds of thousands of deaths and illnesses from exposure to fine particulate matter of aerodynamic diameter less than 2.5 μm (PM_{2.5}) have been averted (3). Between 2007 and 2015, annual SO₂ and NO_x emissions in the United States have decreased by 68% and 36%, respectively (1). SO₂ and NO_x are precursors of sulfate (SO₄²⁻) and particulate nitrate (NO₃)—two major constituents of PM_{2.5} in the eastern United States (4). Ground-based observations show that in response to these decreases in precursor emissions, annual average PM_{2.5} concentrations in the eastern United States have decreased by a third between 2007 and 2015 (5). However, this decrease in PM_{2.5} has occurred mostly in summer; PM_{2.5} decreased only half as much in winter as in summer (1, 6). A similar seasonal difference in the PM_{2.5} response to emission reductions has occurred in Western Europe too (6, 7). Severe wintertime PM_{2.5} pollution is prevalent in

eastern China and northern India (8, 9) and has led to strong mitigation measures. The design of effective strategies for air-quality improvement in the United States and many other countries critically depends on a process-based understanding of the response of wintertime PM_{2.5} to emission reductions.

A closer examination of the PM_{2.5} composition observed at the US Environmental Protection Agency (EPA) monitoring sites in the eastern United States illustrates the stark seasonal differences in [SO₄²⁻] and [NO₃] changes between 2007 and 2015 (Fig. 1A and *SI Appendix, Fig. S1*). [The eastern United States

Significance

Exposure to fine particulate matter is a leading cause of premature deaths and illnesses globally. In the eastern United States, substantial cuts in sulfur dioxide and nitrogen oxides emissions have considerably lowered particulate sulfate and nitrate concentrations for all seasons except winter. Simulations that reproduce detailed airborne observations of wintertime atmospheric chemistry over the eastern United States indicate that particulate sulfate and nitrate formation is limited by the availability of oxidants and by the acidity of fine particles, respectively. These limitations relax at lower ambient concentrations, forming particulate matter more efficiently, and weaken the effect of emission reductions. These results imply that larger emission reductions, especially during winter, are necessary for substantial improvements in wintertime air quality in the eastern United States.

Author contributions: L.J., J.A.T., J.L.J., R.J.W., and S.S.B. designed research; V.S., L.J., J.A.T., F.D.L.-H., B.H.L., J.C.S., P.C.-J., J.L.J., H.G., A.P.S., R.J.W., J.R.G., M.N.F., S.B., T.L.C., M.S., A.J.W., D.D.M., and S.S.B. performed research; V.S., L.J., J.C.S., P.C.-J., and J.L.J. analyzed data; and V.S., L.J., J.A.T., J.C.S., P.C.-J., J.L.J., A.P.S., R.J.W., and S.S.B. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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Data deposition: The WINTER HR-ToF-AMS measurement data are available at the National Center for Atmospheric Research Earth Observing Laboratory (EOL) data archive (<https://doi.org/10.5065/D6HX19V6>), and the GEOS-Chem simulation results are available at the University of Washington data archive (<http://hdl.handle.net/1773/41973>).

¹To whom correspondence should be addressed. Email: vshah@uw.edu.

²Present address: TOFWERK AG, CH-3600 Thun, Switzerland.

³Present address: Undergraduate Research Opportunities Center, California State University, Monterey Bay, CA 93955.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1803295115/-DCSupplemental.

Published online July 23, 2018.

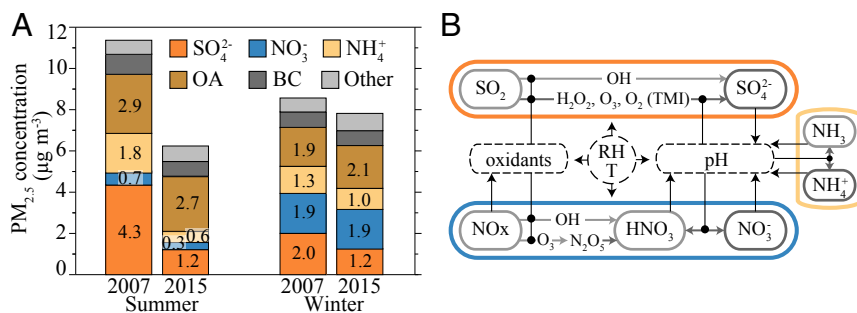


Fig. 1. PM_{2.5} concentration change and SO₄²⁻, NO₃, and NH₄⁺ wintertime chemistry. (A) Population-weighted PM_{2.5} concentration and composition observed over the eastern United States for summer (July, August, and September) and winter (January, February, and March) of 2007 and 2015. The PM_{2.5} composition is separated into sulfate (SO₄²⁻), nitrate (NO₃), ammonium (NH₄⁺), organic aerosol (OA), black carbon (BC), and sea-salt and crustal material (Other). PM_{2.5} observations are from 59 EPA PM_{2.5} monitoring stations (*SI Appendix, Fig. S1*). In 2007–2015, annual SO₂ and NO_x emissions in the United States decreased by 68% and 36%, respectively (1). (B) A representation of the important interactions in the wintertime chemistry of SO₄²⁻, NO₃, NH₄⁺, and their precursors.

is defined here as 31–43°N, 67–86.5°W (*SI Appendix, Fig. S1A*) and [...] denotes atmospheric concentration; that is, amount of the chemical constituent in a unit volume of air.] During this time, average summertime [SO₄²⁻] and [NO₃] decreased by 72% and 50%, respectively, with an associated 67% decrease in ammonium (NH₄⁺) concentrations. In contrast, wintertime [SO₄²⁻] decreased by only 40%, [NH₄⁺] by 23%, and [NO₃] did not change (Fig. 1A). These wintertime trends in SO₄²⁻–NO₃–NH₄⁺ PM_{2.5} have been unfolding since 1990 (10), but a robust explanation for this weak response has been elusive.

During winter, the formation of SO₄²⁻–NO₃–NH₄⁺ PM_{2.5} from emitted precursors is governed by strong feedbacks associated with oxidant availability, cloud water chemistry, and gas–particle partitioning (Fig. 1B). Due to lower concentrations of gas-phase photochemical oxidants during winter, SO₄²⁻ is formed mostly through aqueous-phase oxidation of SO₂ via reactions with hydrogen peroxide (H₂O₂), ozone (O₃), and oxygen (O₂) in clouds. The SO₂–O₂ reaction is catalyzed by transition metal ions (TMI). Particulate NO₃ and particulate NH₄⁺ are in equilibrium with nitric acid (HNO₃) and ammonia (NH₃) gases, respectively. Particulate NO₃ and NH₄⁺ are favored at low temperature and high relative humidity (RH). During winter, HNO₃ formation by hydrolysis of dinitrogen pentoxide (N₂O₅) on aqueous particles becomes more important than by reaction of nitrogen dioxide (NO₂) with hydroxyl radicals (OH). NO_x concentrations themselves, in turn, control oxidant concentrations, which influence SO₂ to SO₄²⁻ oxidation rates. In-cloud SO₂ oxidation by O₃ becomes faster with increasing pH. Similarly, the fraction of HNO₃ forming particulate NO₃ increases with increasing fine-particle pH (11, 12). Most of the NH₃ gas partitions to particulate NH₄⁺ at pH below 3, which is typical for fine particles in the eastern United States. The pH of fine particles and cloud water depends on the overall gas and particle composition (Fig. 1B). In the eastern United States during winter, fine-particle pH increases with increasing [NH₃] and decreases as [SO₄²⁻] increases but is less sensitive to changes in [HNO₃] and [NO₃] (13).

The state of this chemical system and its feedbacks determine the response of [SO₄²⁻] and [NO₃] to emission reductions. However, reproducing the observed concentrations and trends has been a challenge for current atmospheric chemical transport models. Models are largely unable to reproduce observed wintertime concentrations, particularly of NO₃ (14–16), and fail to capture wintertime trends in [SO₄²⁻] and [NO₃] (6, 17), resulting in unclear policy guidance. Explanations for the weak response of [SO₄²⁻] to emission reductions include higher SO₂ oxidation efficiency because of a weakening H₂O₂ limitation on the SO₂–H₂O₂ reaction (17, 18), rising cloud water pH (17), and higher [OH] and [H₂O₂] with lower NO_x emissions (18, 19). Some modeling studies have suggested that NO₃ formation in the eastern United States is limited by the availability of NH₃, such that [NO₃] is weakly sensitive to [HNO₃] but increases as [SO₄²⁻] is lowered and NH₃ availability increases (18–21).

A lack of detailed observations of SO₄²⁻–NO₃–NH₄⁺ PM_{2.5} and particularly of their precursors during winter has impeded verification of these various hypotheses. The 2015 Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER) aircraft campaign has produced a unique set of comprehensive atmospheric composition observations over the eastern United States. Here, we use the GEOS-Chem chemical transport model, evaluated against airborne WINTER observations and ground-based observations, to show that the formation of SO₄²⁻ and NO₃ PM_{2.5} in winter is controlled by OH- and H₂O₂-mediated SO₂ oxidation and by fine-particle pH, respectively. We demonstrate that the weakening H₂O₂ limitation and increasing fine-particle pH have caused the weak response of [SO₄²⁻] and [NO₃] to emission reductions.

Observations and Simulation Results for Winter 2015

The WINTER campaign consisted of 13 daytime and nighttime flights between February 1 and March 15, 2015 (*SI Appendix, Fig. S2*) on the US National Science Foundation (NSF)/National Center for Atmospheric Research (NCAR) C-130 aircraft equipped with a detailed payload to measure gas and particle concentrations. The majority (71%) of the measurements were made below an altitude of 1 km. Concentrations of nonrefractory SO₄²⁻–NO₃–NH₄⁺ PM₁ (PM with aerodynamic diameter <1 μm) were made with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS; Aerodyne Research Inc.) (22, 23). SO₂ was measured by pulsed UV fluorescence (Thermo Electron Corporation) and HNO₃ with the Iodide-adduct high-resolution time-of-flight chemical ionization mass spectrometer (HRTof-CIMS) (24). Other instruments onboard measured carbon monoxide (CO), O₃, reactive nitrogen (NO_y), and meteorological variables. These measurements were used to fully evaluate the GEOS-Chem model (*SI Appendix, Fig. S3*).

In the following analysis, we assume that the PM₁ mass composition is representative of that of PM_{2.5} for SO₄²⁻–NO₃–NH₄⁺ over land and that the influence of other ions (such as Na⁺, Ca²⁺, or Cl⁻) on the chemistry of SO₄²⁻–NO₃–NH₄⁺ PM_{2.5} is negligible. SO₄²⁻ and NO₃ are present on coarse (diameter >1 μm) sea-salt and dust particles, but sea salt and dust are minor components of the PM_{2.5} over the eastern United States (Fig. 1A) and, when present, are typically externally mixed with SO₄²⁻–NO₃–NH₄⁺ PM₁ (25). Guo et al. (12) showed that during WINTER nearly all SO₄²⁻ and NO₃ over land is present as PM₁ and that excluding the other ions in thermodynamic calculations results in better agreement with the observations. Therefore, hereafter, SO₄²⁻–NO₃–NH₄⁺ refers to those components in PM₁.

The observed horizontal and vertical distributions of SO₄²⁻–NO₃–NH₄⁺ are reproduced by the GEOS-Chem model (Fig. 2). Below 1 km altitude, mean observed SO₄²⁻–NO₃–NH₄⁺ during WINTER was 2.45 μg·sm⁻³ (1 sm³ is 1 m³ at 273.15 K and 1,013.25 hPa), with higher concentrations downwind of the

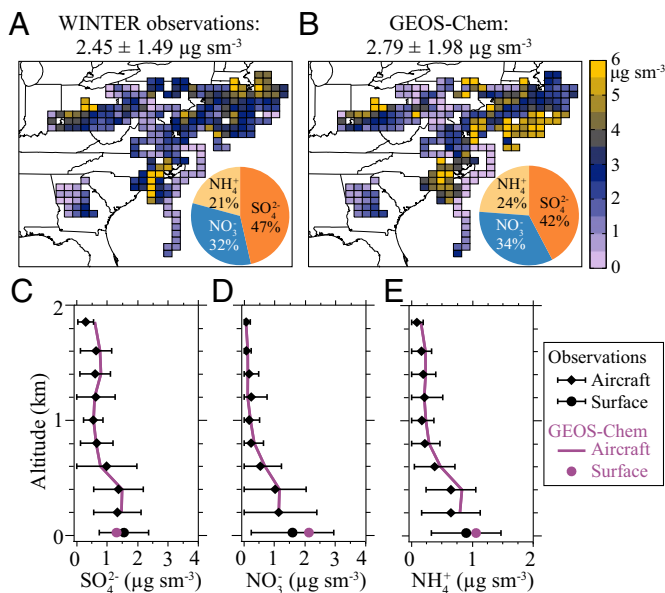


Fig. 2. Spatial distribution of (A) observed and (B) GEOS-Chem concentrations of SO_4^{2-} – NO_3^- – NH_4^+ PM_{10} along the WINTER flight paths (February 1–March 15, 2015) below 1 km altitude (in units of $\mu\text{g}\cdot\text{sm}^{-3}$, where 1 sm^3 equals 1 m^3 at 273.15 K and 1013.25 hPa). The observations are gridded onto the 0.5° latitude by 0.625° longitude GEOS-Chem grid. The number of 1-min average observations in each grid box varies from 1 to 79, with a median of 10 observations. The WINTER campaign means \pm standard deviations (SD) are shown above A and B. The *Inset* pie charts show the corresponding mean composition of PM_{10} . Also shown are the mean vertical profiles of observed (black diamonds and error bars: mean \pm SD for each altitude bin) and GEOS-Chem (purple line) concentrations of (C) SO_4^{2-} , (D) NO_3^- , and (E) NH_4^+ along the WINTER flight tracks. Also shown are the mean observations for the ground-based CSN, IMPROVE, and CASTNET networks (black filled circles with SD) and corresponding model results (purple filled circles) for February 1–March 15, 2015.

source regions in the Northeast Urban Corridor and in the Ohio River Valley (Fig. 2A). GEOS-Chem predicts mean concentrations ($2.79\ \mu\text{g}\cdot\text{sm}^{-3}$) and spatial patterns consistent with the observations (Fig. 2B). Furthermore, the observed composition of SO_4^{2-} – NO_3^- – NH_4^+ (47% SO_4^{2-} ; 32% NO_3^- ; 21% NH_4^+) is reproduced by GEOS-Chem (42% SO_4^{2-} ; 34% NO_3^- ; 24% NH_4^+). GEOS-Chem results are also in agreement with the ground-based observations at the Chemical Speciation Network (CSN), the Interagency Monitoring of Protected Visual Environments (IMPROVE) network, and the Clean Air Status and Trends Network (CASTNET) for February 1–March 15, 2015 (SI Appendix, Fig. S4 A and B). The ability of GEOS-Chem to simulate the wintertime SO_4^{2-} – NO_3^- – NH_4^+ over the eastern United States is further demonstrated by the agreement between the simulated and observed vertical profiles of $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{NH}_4^+]$ (Fig. 2 C–E), $[\text{SO}_2]$, and $[\text{HNO}_3]$ (SI Appendix, Fig. S5).

Past studies have found that GEOS-Chem simulations overestimate wintertime $[\text{NO}_3^-]$ over the eastern United States by a factor of 3 (15, 19)—an issue common to many models (14, 16). The WINTER observations have allowed a detailed analysis of nighttime and daytime NO_x chemistry, HNO_3 formation, and HNO_3 dry deposition, leading to improvements in the representation of these processes in GEOS-Chem and a substantial reduction of the $[\text{NO}_3^-]$ overestimate. In particular, we have updated the dry deposition velocities for winter conditions and assume that for HNO_3 the resistance to surface uptake is negligible, resulting in faster deposition of HNO_3 and other gas species (SI Appendix, Section 1.1). We have also updated the calculation of the reactive uptake probability of N_2O_5 on particles based on recent laboratory studies,

resulting in slower conversion of NO_x to HNO_3 (SI Appendix, Section 1.2).

Having evaluated the consistency of the GEOS-Chem results with aircraft and ground-based observations, we now explore how wintertime SO_4^{2-} and NO_3^- are formed.

Processes Controlling the Formation of SO_4^{2-} and NO_3^- in Winter

Gas-phase and in-cloud oxidation of SO_2 to SO_4^{2-} account for 90% of the modeled SO_4^{2-} source below 2 km altitude in the eastern United States during WINTER, with primary anthropogenic emissions of SO_4^{2-} accounting for the remaining 10%. We use GEOS-Chem to determine the SO_2 to SO_4^{2-} oxidation efficiency $[\eta(\text{SO}_4^{2-})]$:

$$\eta(\text{SO}_4^{2-}) = \frac{\text{SO}_2 \text{ mass oxidized below 2 km (kg d}^{-1}\text{)}}{\text{SO}_2 \text{ mass emitted (kg d}^{-1}\text{)}}. \quad [1]$$

We calculate that over the eastern United States during WINTER $\eta(\text{SO}_4^{2-}) = 0.18$. In GEOS-Chem, we find that 46% of SO_2 oxidation is due to reaction with H_2O_2 in cloud water, 35% due to gas-phase reaction with OH , and the rest due to in-cloud SO_2 – O_3 and the TMI-catalyzed pathways. The slow winter photochemistry results in low $[\text{H}_2\text{O}_2]$ (GEOS-Chem winter $[\text{H}_2\text{O}_2]$ is 0.2 ppbv, 10-fold lower than summer) and $[\text{OH}]$. While recent work suggests higher oxidant concentrations in winter than previously expected (26, 27), these oxidant sources are not large enough to shift the relationship between H_2O_2 and SO_2 (SI Appendix, Section 2). SO_2 oxidation during winter is limited by the availability of H_2O_2 , which can be entirely consumed in the SO_2 – H_2O_2 reaction. Fig. 3A illustrates the relationship in GEOS-Chem between the $[\text{H}_2\text{O}_2]/[\text{SO}_2]$ ratio and the oxidation rate of SO_2 to SO_4^{2-} by reaction with H_2O_2 ($R_{\text{SO}_2\text{-H}_2\text{O}_2}$), defined here as:

$$R_{\text{SO}_2\text{-H}_2\text{O}_2} = \frac{\text{SO}_2 \text{ mass oxidized by H}_2\text{O}_2 \text{ below 2 km (kg d}^{-1}\text{)}}{\text{SO}_2 \text{ mass present below 2 km (kg)}}. \quad [2]$$

The winter H_2O_2 limitation is demonstrated by the increase of $R_{\text{SO}_2\text{-H}_2\text{O}_2}$ to around 0.35 d^{-1} as $[\text{H}_2\text{O}_2]/[\text{SO}_2]$ increases to 3, beyond which $R_{\text{SO}_2\text{-H}_2\text{O}_2}$ becomes independent of this ratio and no longer H_2O_2 -limited (Fig. 3A). Part of the variability in $R_{\text{SO}_2\text{-H}_2\text{O}_2}$ is due to local variability in cloud liquid water content. The lower troposphere over land in the eastern United States lies in the H_2O_2 -limited regime (mean $[\text{H}_2\text{O}_2]/[\text{SO}_2] = 0.4$). The modeled $[\text{H}_2\text{O}_2]/[\text{SO}_2]$ ratio increases over the ocean as $[\text{SO}_2]$ decreases away from source regions and $[\text{H}_2\text{O}_2]$ increases southward with stronger photochemical production.

Particle-phase NO_3^- is in equilibrium with gas-phase HNO_3 [$\text{HNO}_3(\text{g}) \leftrightarrow \text{H}^+ + \text{NO}_3^-$]. This equilibrium shifts to the particle phase at colder temperatures and at higher particle pH. Fig. 3B shows how the GEOS-Chem nitrate particle fraction ($\epsilon(\text{NO}_3^-) = \frac{[\text{NO}_3^-]}{[\text{HNO}_3] + [\text{NO}_3^-]}$) varies as a function of modeled PM_{10} pH and temperature during WINTER below 1 km altitude. The WINTER campaign observations of $\epsilon(\text{NO}_3^-)$ and PM_{10} pH inferred from thermodynamic analysis of observed PM_{10} composition (shown as gray circles in Fig. 3B) confirm this pattern of increasing $\epsilon(\text{NO}_3^-)$ with increasing PM_{10} pH (12). During WINTER, the GEOS-Chem predicted median PM_{10} pH over land below 1 km altitude was 1.29 and $\epsilon(\text{NO}_3^-)$ was 0.45, in good agreement with those inferred from the measurements (pH = 1.34 and $\epsilon(\text{NO}_3^-) = 0.48$ for $\text{RH} > 40\%$) (12). Local variations in PM_{10} pH and temperature influence the variability in $\epsilon(\text{NO}_3^-)$ in the model, with larger $\epsilon(\text{NO}_3^-)$ (>0.7) simulated over the colder Midwest with high PM_{10} pH (~ 2) owing to higher NH_3 and lower SO_2 emissions and smaller $\epsilon(\text{NO}_3^-)$ (<0.4) simulated off the East Coast over the warmer ocean and with lower PM_{10}

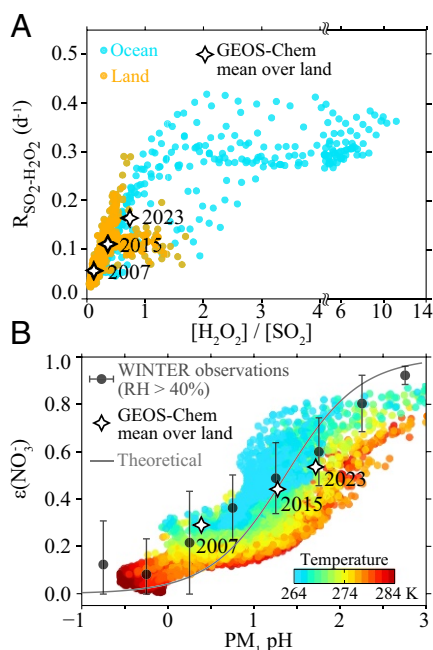


Fig. 3. Factors controlling wintertime SO_4^{2-} and NO_3^- formation. (A) GEOS-Chem simulated relationship between the oxidation rate of SO_2 to SO_4^{2-} by reaction with H_2O_2 ($R_{\text{SO}_2\text{-H}_2\text{O}_2}$) and the $\text{H}_2\text{O}_2/\text{SO}_2$ concentration ratio for February 1–March 15, 2015 in the bottom 2 km over the eastern United States ($31\text{--}43^\circ\text{N}$, 67 to 86.5°W). The stars represent the mean $R_{\text{SO}_2\text{-H}_2\text{O}_2}$ and $\text{H}_2\text{O}_2/\text{SO}_2$ ratio over land in the eastern United States for the 2007, 2015, and 2023 simulations. The 2007–2015 change in wintertime SO_2 and NO_x emissions is -58% and -35% , respectively, and the 2015–2023 change is -47% and -25% . (B) GEOS-Chem simulated fraction of nitrate in the particle phase [$\epsilon(\text{NO}_3^-)$] as a function of PM_{10} pH and temperature in the bottom 1 km over the eastern United States. Dark gray circles and error bars represent the measured $\epsilon(\text{NO}_3^-)$ (means \pm SD) as a function of the measurement-inferred PM_{10} pH for WINTER observations below 1 km altitude (12). Only observations with $\text{RH} > 40\%$ are considered. The stars are the mean $\epsilon(\text{NO}_3^-)$ and PM_{10} pH in the bottom 1 km over land in the eastern United States for the 2007, 2015, and 2023 simulations. The theoretical relationship between $\epsilon(\text{NO}_3^-)$ and PM_{10} pH for the 2015 mean WINTER conditions is shown by the gray curve.

pH. Further away from the coast, sea-salt particles can mix with $\text{SO}_4^{2-}\text{-NO}_3\text{-NH}_4^+$ and influence the pH.

The WINTER observations provide constraints for the simulated values of $\eta(\text{SO}_4^{2-})$, PM_{10} pH, and $\epsilon(\text{NO}_3^-)$ —the parameters controlling the formation of winter SO_4^{2-} and NO_3^- . There were no WINTER measurements of $[\text{OH}]$, $[\text{H}_2\text{O}_2]$, and cloud water pH, adding uncertainty to our calculated contributions of the different SO_2 oxidation pathways to $\eta(\text{SO}_4^{2-})$. However, we find good agreement between GEOS-Chem and the WINTER observations of OH and H_2O_2 precursors (*SI Appendix, Fig. S3*), which provides indirect constraints on the simulated $[\text{OH}]$ and $[\text{H}_2\text{O}_2]$. Moreover, we find that the GEOS-Chem results are weakly sensitive to uncertainties in the simulated $[\text{OH}]$ and $[\text{H}_2\text{O}_2]$ (*SI Appendix, Section 2*). A 50% increase in modeled $[\text{H}_2\text{O}_2]$ increases $R_{\text{SO}_2\text{-H}_2\text{O}_2}$ by 37%, and SO_4^{2-} formation remains H_2O_2 -limited. The resulting increase in $[\text{SO}_4^{2-}]$ is less than 5% because of compensating effects by other oxidation pathways. Our results are somewhat more sensitive to uncertainties in NH_3 emissions (via PM_{10} pH; *SI Appendix, Section 2.3*), which have few observational constraints on their magnitude and seasonality. We estimate an uncertainty in our simulated PM_{10} pH of ~ 0.3 units because of the uncertainty in NH_3 emissions and a similar uncertainty due to neglecting the influence of Na^+ cations (12). A change in PM_{10} pH of 0.3 units changes the simulated $[\text{NO}_3^-]$ for WINTER by $\sim 30\%$ and does not alter the dependence of $\epsilon(\text{NO}_3^-)$ on PM_{10} pH.

Response of Winter $[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$ to Emissions Reductions

We now turn to explaining the weak response of wintertime $[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$ to decreases in SO_2 and NO_x emissions between 2007 and 2015 and examining the future response of $[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$ under the 2023 EPA emissions projections (28). To address these issues, we have performed additional GEOS-Chem simulations for February 1–March 15 with varying US SO_2 and NO_x anthropogenic emissions: (i) a simulation with 2007 emissions of SO_2 ($15.8 \text{ GgS}\cdot\text{d}^{-1}$) and NO_x ($11.8 \text{ GgN}\cdot\text{d}^{-1}$) (29), and (ii) a simulation with 2023 EPA projected emissions of SO_2 ($3.5 \text{ GgS}\cdot\text{d}^{-1}$) and NO_x ($5.8 \text{ GgN}\cdot\text{d}^{-1}$) (29). Anthropogenic US emissions of SO_2 and NO_x in 2015 were $6.6 \text{ GgS}\cdot\text{d}^{-1}$ and $7.7 \text{ GgN}\cdot\text{d}^{-1}$, respectively (*SI Appendix, Table S1*). Meteorology can affect the interannual variability of $\text{PM}_{2.5}$ (30); therefore, to isolate the effect of SO_2 and NO_x emissions reductions, we have used the same meteorological fields as for our 2015 simulation. Furthermore, our simulations do not include the EPA estimated 2007–2015 emission changes for other species, including NH_3 (-2%), CO (-30%), and volatile organic compounds (-14%) (29). Despite these simplifying assumptions, the 2007 simulation is consistent with ground-based $\text{PM}_{2.5}$ observations for February 1–March 15, 2007 (*SI Appendix, Fig. S4 C and D*).

Simulated surface $[\text{SO}_4^{2-}]$ for February 1–March 15, 2015 is higher near SO_2 source regions in the Ohio River Valley (*SI Appendix, Fig. S6*) but display little spatial variation elsewhere (Fig. 4A). The regional extent of SO_4^{2-} pollution reflects the slow oxidation of SO_2 as it is transported downwind of its sources. Between 2007 and 2015, simulated $[\text{SO}_4^{2-}]$ decreased everywhere in response to lower SO_2 emissions and continues to decrease between 2015 and 2023 (Fig. 4A and *SI Appendix, Fig. S7 A–C*). The 2007–2015 $[\text{SO}_4^{2-}]$ decrease observed at surface sites ($-0.83 \mu\text{g}\cdot\text{sm}^{-3}$; -31%) is reproduced by GEOS-Chem ($-1.06 \mu\text{g}\cdot\text{sm}^{-3}$; -40%). Between 2015 and 2023, the mean modeled $[\text{SO}_4^{2-}]$ at surface sites is projected to decrease by another $0.38 \mu\text{g}\cdot\text{sm}^{-3}$ (-24%) (Fig. 5A).

The decrease in modeled $[\text{SO}_4^{2-}]$ (2007–2015: -40% ; 2015–2023: -24%) is significantly lower than the decrease in US SO_2 emissions (2007–2015: -58% ; 2015–2023: -47%). This subdued response to emissions reductions is caused by a corresponding increase in $\eta(\text{SO}_4^{2-})$, from 0.11 (2007) to 0.18 (2015) and 0.26 (2023) (Fig. 5B), which counteracts the effect of reduced SO_2 emissions by allowing a larger fraction of the emissions to be oxidized to SO_4^{2-} on regional and local scales. In the model, the increase in $\eta(\text{SO}_4^{2-})$ is driven by the $\text{SO}_2\text{-H}_2\text{O}_2$ pathway (Fig. 5B): Reduced SO_2 concentrations lead to a factor of 2.7 increase in the $[\text{H}_2\text{O}_2]/[\text{SO}_2]$ ratio between 2007 and 2015 and another factor of 2 increase between 2015 and 2023, thereby lowering the degree of H_2O_2 limitation (Fig. 3A). The $[\text{H}_2\text{O}_2]/[\text{SO}_2]$ ratio increases mostly because of the decrease in SO_2 concentrations

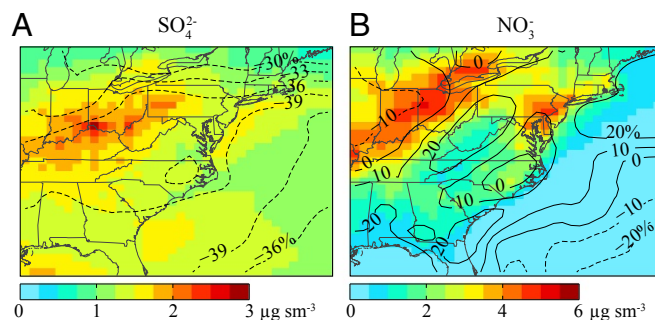


Fig. 4. GEOS-Chem surface concentrations of (A) SO_4^{2-} and (B) NO_3^- PM_{10} for February 1–March 15, 2015. The contour lines show the percent change relative to February 1–March 15, 2007 concentrations $100 \times \left(\frac{[\text{2015}] - [\text{2007}]}{[\text{2007}]} \right)$.

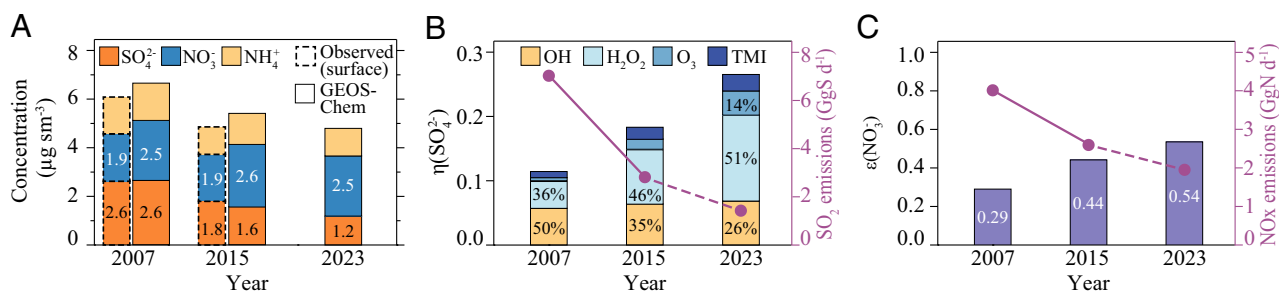


Fig. 5. Past and future changes in wintertime SO_4^{2-} - NO_3 - NH_4^+ concentration and formation efficiency. (A) Average surface concentrations of SO_4^{2-} - NO_3 - NH_4^+ $\text{PM}_{2.5}$ for the eastern United States for February 1–March 15, 2007, 2015, and 2023 simulated by GEOS-Chem and observed at the ground-based sites (2007 and 2015, bars with dashed lines). (B) SO_2 to SO_4^{2-} oxidation efficiency $\eta(\text{SO}_4^{2-})$ over land partitioned by pathway: gas-phase oxidation with OH, aqueous oxidation with H_2O_2 , O_3 , and O_2 catalyzed by TMI. SO_2 emissions over the eastern United States are shown (in purple) for the three simulations. (C) Fraction of nitrate in the particle phase ($\epsilon(\text{NO}_3)$) and NOx emissions (in purple) over land in the eastern United States for the three simulations.

and, to a small extent, because of higher $[\text{H}_2\text{O}_2]$ at lower NOx emissions. A small increase in $\eta(\text{SO}_4^{2-})$ is also caused by a faster rate of the SO_2 - O_3 aqueous reaction with increasing cloud water pH at lower SO_2 emissions (Fig. 5B). In our simulations, mean cloud water pH over the eastern United States rises from 4.2 (2007) to 4.6 (2023). Our results suggest that beyond 2023, $\eta(\text{SO}_4^{2-})$ will continue to increase with continued relaxation of the H_2O_2 limitation and rise in cloud water pH, further weakening the response of $[\text{SO}_4^{2-}]$ to emission reductions. Beyond 2023, rising cloud water pH could become a more important factor in the continued increase in $\eta(\text{SO}_4^{2-})$ and drive wintertime $\eta(\text{SO}_4^{2-})$ to above 0.5 by 2050 (17).

The model reproduces the observed lack of change in $[\text{NO}_3]$ over the region between 2007 and 2015, despite a 35% reduction in NOx emissions (Figs. 4B and 5A and SI Appendix, Fig. S7D and E). We calculate that the additional 25% decrease in NOx emissions expected by 2023 will not produce much change in $[\text{NO}_3]$ (Fig. 5A and SI Appendix, Fig. S6F). We find that the production of total (gas + particle) nitrate in the model decreases linearly with decreasing NOx emissions. But this decrease in nitrate formation is counteracted by an increase in $\epsilon(\text{NO}_3)$, buffering the response of $[\text{NO}_3]$ (Fig. 5C). In addition, the shift of nitrate to the particle phase increases its lifetime [as NO_3 deposits at a slower rate than HNO_3 (31)] and further offsets the decrease in total nitrate production. Between 2007 and 2023, modeled $\epsilon(\text{NO}_3)$ nearly doubles (0.29 to 0.54), canceling the expected effect of NOx emissions reduction. The increase in $\epsilon(\text{NO}_3)$ is caused by an increase in $\text{PM}_{1.0}$ pH from 0.39 to 1.7 (2007–2023) (Fig. 3B) mainly because of decreasing $[\text{SO}_4^{2-}]$ and, to a smaller extent, $[\text{HNO}_3]$ but also because of the positive feedback between $\epsilon(\text{NO}_3)$ and $\text{PM}_{1.0}$ pH due to the hygroscopicity of NO_3 (32). There are local differences in the balance between increasing $\text{PM}_{1.0}$ pH and decreasing NOx emissions. For example, $[\text{NO}_3]$ increases downwind of the Ohio River Valley, where the increase in $\text{PM}_{1.0}$ pH outpaces the decrease in NOx emissions (Fig. 4B and SI Appendix, Fig. S7D–F).

It is important to note that if the 2007–2015 decrease in SO_2 emissions had not been accompanied by a decrease in NOx emissions, the result would have been a 30% increase in $[\text{NO}_3]$ over the eastern United States, in response to decreasing $[\text{SO}_4^{2-}]$ and hence rising $\text{PM}_{1.0}$ pH and $\epsilon(\text{NO}_3)$. It was purely coincidental that the increase in $\epsilon(\text{NO}_3)$, driven largely by the decrease in SO_2 emissions, was closely matched by the decrease in NOx emissions, preventing such a regional increase in $[\text{NO}_3]$. A similar trend is expected to continue until 2023 (Fig. 5A and C). At some point beyond 2023, as $\text{PM}_{1.0}$ pH increases, $\epsilon(\text{NO}_3)$ will approach 1, and $[\text{NO}_3]$ will start responding more linearly to NOx emission reductions. Our simulations suggest that winter $[\text{NO}_3]$ will not decrease much in response to future NOx emissions reductions, unless the rate of winter NOx emission reductions exceeds the rate of increase in $\epsilon(\text{NO}_3)$.

The effectiveness of NOx emissions reductions will be further diminished if emissions of NH_3 were to increase. The EPA projects almost no change in US NH_3 emissions by 2023 (28), but these predictions are uncertain because of weak regulatory oversight on NH_3 . $\text{PM}_{1.0}$ pH is sensitive to NH_3 under present winter conditions over the eastern United States (SI Appendix, Section 2.3). If NH_3 emissions were to increase in the future, $\text{PM}_{1.0}$ pH would increase, causing an increase in the conversion of NOx to $[\text{NO}_3]$ (due to $\epsilon(\text{NO}_3)$ increasing with pH). This response of $\text{PM}_{1.0}$ pH to NH_3 emissions is not necessarily true in other seasons and locations where both the $\text{PM}_{1.0}$ pH and the dependence of $\epsilon(\text{NO}_3)$ on pH may differ (11, 32).

Conclusions

Wintertime $[\text{SO}_4^{2-}]$ and $[\text{NO}_3]$ in the eastern United States have responded weakly to SO_2 and NOx emissions reductions. While previous modeling studies have examined the sensitivity of wintertime $[\text{SO}_4^{2-}]$ and $[\text{NO}_3]$ to emission reductions, the fidelity of these models could not be verified without the constraints of detailed in situ observations. In this study, we have presented aircraft observations of SO_4^{2-} - NO_3 - NH_4^+ PM_1 concentrations and precursor gases that serve as crucial benchmarks for models. We have shown that the GEOS-Chem model simulation of SO_4^{2-} - NO_3 - NH_4^+ PM_1 concentration and composition is in good agreement with the WINTER campaign observations. GEOS-Chem results for the WINTER campaign showed that 18% of the SO_2 is regionally oxidized to SO_4^{2-} in winter over the eastern United States, compared with about 35% during summer. In GEOS-Chem, SO_2 oxidation happens mostly by H_2O_2 (46%) and OH (35%) and is limited by low wintertime $[\text{H}_2\text{O}_2]$ and $[\text{OH}]$. The observations and model show that about 45% of the total nitrate (gas + particle) was in the particle phase during the WINTER campaign period because of low $\text{PM}_{1.0}$ pH (~ 1.3).

GEOS-Chem is able to reproduce the weak decrease in winter $[\text{SO}_4^{2-}]$ and $[\text{NO}_3]$ between 2007 and 2015 observed at ground-based sites. With our simulations, we find that as SO_2 and NOx emissions decrease, the resulting increase in $[\text{H}_2\text{O}_2]/[\text{SO}_2]$ and $\text{PM}_{1.0}$ pH leads to more efficient regional formation of SO_4^{2-} and NO_3 per unit mass of precursor pollutant emitted during winter. We project that these chemical feedbacks will persist into the near future. Between 2015 and 2023, we predict a 24% decrease in winter $[\text{SO}_4^{2-}]$ and little to no change in winter $[\text{NO}_3]$ despite an expected 47% decrease in SO_2 emissions and 25% decrease in NOx emissions. We also find that without concurrent decreases in NOx emissions, the 2007–2015 SO_2 emissions decrease would have resulted in a 30% increase in regional $[\text{NO}_3]$ due to $\text{PM}_{1.0}$ pH increase and its control on the fraction of nitrate in the particle phase. Similarly, for the future, if only SO_2 emissions were to decrease by 2023 and NOx emissions remained at 2015 levels, regional $[\text{NO}_3]$ would increase by 12%. These counteracting chemical feedbacks necessitate stronger reductions of both

SO₂ and NO_x emissions during winter for faster improvements in wintertime air quality.

Materials and Methods

PM₁ [SO₄²⁻], [NO₃], and [NH₄⁺] were measured by the HR-ToF-AMS (22, 23, 33–35). Air was sampled through a forward-facing inlet mounted under the aircraft. It passes through a pressure-controlled inlet, an aerodynamic focusing lens, and a high-vacuum region to the detection chamber, where nonrefractory species are flash vaporized at 600 °C and ionized with 70 eV electron impact ionization. The ions are orthogonally extracted and analyzed by ToF mass spectrometry. The data were corrected for relative ionization and collection efficiencies (23). One-minute measurements are used here. Detection limits were 57 ng·sm⁻³ (SO₄²⁻), 30 ng·sm⁻³ (NO₃), and 5 ng·sm⁻³ (NH₄⁺), and accuracy was 35% (23).

CSN, IMPROVE, and CASTNET are ground-based PM_{2.5} monitoring networks (36, 37). CSN and IMPROVE report 24-h mean concentrations every third or sixth day. We include only sites that report every third day. CASTNET measurements are weekly averages. We exclude sites with less than 70% temporal coverage for February 1–March 15, 2015. The eastern United States had 26 such CSN sites in 2015 (21 in 2007), 27 IMPROVE sites in 2015 (26 in 2007), and 26 CASTNET sites in 2015 (33 in 2007). When calculating

the 2007–2015 change in PM_{2.5} concentrations, we include only those sites that were operational in both years (CSN: 16; IMPROVE: 23; CASTNET: 23).

GEOS-Chem is driven by assimilated meteorological fields from NASA GMAO's GEOS-5 FP system (38). We use GEOS-Chem v10-01 in a nested-grid configuration: 0.5° latitude × 0.625° longitude resolution over North America and 4° × 5° elsewhere. Simulations were performed for February 1–March 15, 2015. The model is described in *SI Appendix*. Anthropogenic emissions over the United States are from the EPA's 2011v6.1 (for 2011) and 2011v6.3 (for 2023) modeling platforms for the 2011 National Emissions Inventory (28, 39). The 2011 US emissions were scaled to 2015 levels (scaling factors SO₂: 0.72; NO_x: 0.80; NH₃: 1.0) based on the EPA emissions trend report (29) and the Air Markets Program Data (40). Livestock NH₃ emissions were recalculated for 2015 meteorology. The 2007 and 2023 SO₂ and NO_x emissions were based on EPA estimates (28, 29).

ACKNOWLEDGMENTS. We thank all members of the WINTER team for their contributions during the field campaign and the agencies operating the CSN, IMPROVE, and CASTNET networks. We are grateful to the entire GEOS-Chem user community and the NSF/NCAR Research Aircraft Facility pilots and crew. The WINTER campaign was supported by NSF Grant AGS-1360745. J.C.S., P.C.-J., and J.L.J. were supported by NSF Grant AGS-1360834 and NASA Grant NNX15AT96G and H.G. and R.J.W. by NSF Grant AGS-1360730.

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