

# The Changing Sensitivity of Wintertime Particulate Nitrate to Precursor Emissions Diagnosed via [GEOS-Chem](#) and Satellite Observations of Ammonia and Nitrogen Dioxide over the Midwestern United States

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**Abstract.** Particulate nitrate (PN) is a critical component of fine particulate matter (PM<sub>2.5</sub>). During wintertime, the contribution of PN to PM<sub>2.5</sub> over the Midwestern United States (MWUS), an agriculturally intensive region, has increased over the past decade and now contributes up to 40% of the particle mass. PN formation is controlled by nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>), ammonia (NH<sub>3</sub>), and volatile organic compounds (VOCs). To best control wintertime PM<sub>2.5</sub> burden, it is critical to determine PN formation sensitivity to precursor gases, but this is not well constrained. Prior efforts to diagnose PN sensitivity have been limited on both spatial and temporal scales. Satellite tropospheric column NH<sub>3</sub>/NO<sub>2</sub> ratios cover large areas and long timeframes, and they have been shown to be effective in diagnosing PN sensitivity over East Asia, Europe, and the Eastern United States. Here, we expand this approach to quantify spatially and temporally resolved multidecadal wintertime PN formation sensitivity to NH<sub>3</sub>, NO<sub>x</sub>, and VOCs in the MWUS from 2007 to 2023 via satellite observations and GEOS-Chem sensitivity simulations. More than half of the total diagnosed pixels are classified as NO<sub>x</sub>-sensitive in 2007, and this increases to 89.0% by 2023. VOCs do not control MWUS PN formation. The shift in PN formation sensitivity is explained by relatively flat trends in satellite NO<sub>2</sub> column densities ( $0.48 \pm 0.60\% \text{ yr}^{-1}$ ) in combination with increases in satellite NH<sub>3</sub> column densities ( $1.3 \pm 0.3\% \text{ yr}^{-1}$ ). Our work indicates that targeting NO<sub>x</sub> emissions is chemically effective for reducing wintertime PN and PM<sub>2.5</sub> burden.

## 1. Introduction

PM<sub>2.5</sub>, particulate matter with an aerodynamic diameter of 2.5 μm or less, is the largest environmental health risk factor in the United States (Di et al., 2017; Pokharel et al., 2023; Shi et al., 2022; Tessum et al., 2019; Wu et al., 2018). PM<sub>2.5</sub> is formed via acid-base reactions between the acidic precursor species, nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>), and the basic gas ammonia (NH<sub>3</sub>) to form ammonium sulfate and ammonium nitrate. Regulations on SO<sub>2</sub> and NO<sub>x</sub> emissions via the Clean Air Act have led to notable decreases in the PM<sub>2.5</sub> burden across the United States over the past few decades, primarily through the reduction in particulate nitrate (PN) and particulate sulfate (PS) (Hand et al., 2012). PS, which has historically dominated the inorganic fraction of PM<sub>2.5</sub>, has decreased more quickly than PN, increasing the relative contribution of PN to total PM<sub>2.5</sub> mass. PN concentrations are highest during wintertime because the gas-to-particle partitioning

of PN is favored at low temperatures (Pitchford et al., 2009). During wintertime over the Midwestern United States (MWUS), a highly agricultural region, the PN/PS ratio has increased, [and PN mass concentrations have started to surpass PS as PS has decreased at a faster rate compared to PN](#) over the past decade (Figure S1). The increase in relative PN abundance may also be influenced by increases in the atmospheric lifetime of total nitrate during wintertime (Zhai et al., 2021). Over the MWUS, wintertime PN now comprises up to 40% of the total PM<sub>2.5</sub> mass on average.

PN is highly hygroscopic, which affects particle properties and enhances the reflectivity of particles (Wang et al., 2018; Wu et al., 2019). PN has been found to drive pollution events over certain regions of the US (Franchin et al., 2018; Womack et al., 2019) and the globe (Qin et al., 2024; Xu et al., 2019). PN has also become the controlling factor behind particle water uptake in some regions, impacting particle chemical processes and visibility (Christiansen et al., 2020; Jefferson et al., 2017). Recent studies have shown that the products from PN photolysis may influence the formation of tropospheric O<sub>3</sub> and thus atmospheric oxidation capacity (Cao et al., 2022; Gen et al., 2022; Sarwar et al., 2024). It is critical to accurately understand PN properties and formation to better understand PN impacts and create effective policy that controls PM<sub>2.5</sub> burden.

NO<sub>x</sub>, NH<sub>3</sub>, and volatile organic compounds (VOCs) are critical to the formation of PN (Wang et al., 2023a). During the daytime, NO<sub>2</sub> is oxidized to HNO<sub>3</sub> via reaction with hydroxyl radical (•OH). HNO<sub>3</sub> then reacts with NH<sub>3</sub> to form ammonium nitrate, which partitions into the particle phase. During nighttime, PN is formed via the heterogenous hydrolysis of N<sub>2</sub>O<sub>5</sub>, which is formed from the oxidation of NO<sub>2</sub> with ozone (O<sub>3</sub>). In these mechanisms, the availability of •OH and O<sub>3</sub> are highly dependent on VOC abundance. Thus, PN formation is sensitive to the precursor gases NO<sub>x</sub>, NH<sub>3</sub>, and VOCs, and its formation is controlled by whichever precursor gas is the limiting reagent. Competing mechanisms with organic molecules also contribute to total PN, but the exact mechanisms and processes behind organo-nitrate formation are not well constrained, and inorganic nitrate is most prominent in particles (Romer Present et al., 2020; Wang et al., 2023a).

Precursor gas emissions have changed drastically over the past few decades, potentially altering PN formation sensitivity and its relative contribution to total PM<sub>2.5</sub> mass. Urban NO<sub>x</sub> emissions dominated by anthropogenic sources have decreased by 40% from 2005 to 2018 across the US (Jiang et al., 2022). Over rural areas, total surface NO<sub>2</sub> trends decreased strongly until 2010, after which they flattened. The decreasing prevalence of urban NO<sub>x</sub> emissions have caused rural total NO<sub>x</sub> trends to be influenced more strongly by relatively constant background emissions (e.g., lightning, soil, etc.), and NO<sub>x</sub> trends over rural areas post-2010 are typically insignificant (Christiansen et al., 2024; Jiang et al., 2022; Silvern et al., 2019). Satellite NO<sub>2</sub> column densities show similar flattening trends after 2010, which is attributed to the increasingly strong relative influence of free tropospheric NO<sub>2</sub> in satellite column trends (Dang et al., 2023a; Fioletov et al., 2022; He et al., 2022; Jiang et al., 2018; Tong et al., 2015; Wang et al., 2021).

In contrast, NH<sub>3</sub> is not regulated as a criterion pollutant, although there exist some regulations on agricultural NH<sub>3</sub> practices, which target livestock emissions (United States Environmental Protection Agency, 2014). Recently, satellite NH<sub>3</sub> column densities have increased strongly over the US ( $2.40 \pm 0.45\% \text{ yr}^{-1}$  from 2002 to 2018), which matches increases in surface NH<sub>3</sub> concentrations (Van Damme et al., 2021; Wang et al., 2023b; Yu et al., 2018). The increase in NH<sub>3</sub> concentrations over the agricultural Central United States is disproportionately higher than over the US as a whole, ranging from 1–7% yr<sup>-1</sup> (Yu et al.,

65 2018). This increase can be explained by increases in emissions from both agriculture (Vo and Christiansen, 2024; Yang et al.,  
2023) and vehicles (Fenn et al., 2018; Sun et al., 2017; Walters et al., 2022), as well as decreases in NO<sub>2</sub> and SO<sub>2</sub> emissions  
that increase unreacted NH<sub>3</sub> abundance (Warner et al., 2017).

Anthropogenic VOC emissions are low during winter, but they have continuously decreased over time. Urban VOC  
emissions over the United States have decreased by -36.4% from 2000 to 2019, which is attributable to decreases in  
70 transportation and industrial solvent emissions (Xiong et al., 2024). Emissions of isoprene, a biogenic VOC, conversely  
showed an increase of 0.14% yr<sup>-1</sup> from 2000 to 2020 in US, which is primarily influenced by meteorological factors and  
changes in vegetation coverage (Wang et al., 2024).

To most effectively reduce PM<sub>2.5</sub> burden, it is critical to understand how these large changes in precursor gas emissions  
have influenced PN formation sensitivity over time. Over past decades, controlling NH<sub>3</sub> emissions has been suggested to be  
75 most effective in reducing wintertime PM<sub>2.5</sub> burden over agricultural regions, but more recent analyses suggest that NO<sub>x</sub>  
controls may now be more effective, although at a higher cost and more technologically complex approach than NH<sub>3</sub> controls  
(Guo et al., 2024; Holt et al., 2015; Pan et al., 2024; Paulot et al., 2014; Pinder et al., 2007; Wiegand et al., 2022). Therefore,  
the most effective strategy to control PN and PM<sub>2.5</sub> in agriculturally impacted areas, such as the MWUS regions, remains an  
open question. Few prior studies have attempted to diagnose PN and PM<sub>2.5</sub> sensitivity to precursor gases in the MWUS. Holt  
80 et al. (2015) diagnosed the wintertime inorganic PM<sub>2.5</sub> sensitivity over the US to NO<sub>x</sub>, NH<sub>3</sub>, and SO<sub>2</sub> emissions between 2005  
and 2012 using only GEOS-Chem simulations and found that NO<sub>x</sub> sensitivity increased over time (Holt et al., 2015). Dang et  
al. (2024) conducted a PN formation sensitivity diagnosis over the US across all seasons in 2017, but this focused mostly on  
the Eastern US and covered very little of agricultural MWUS (Dang et al., 2024). Neither of these studies captured the long-  
term (multidecadal) dynamics of wintertime PN formation sensitivity over highly agricultural areas.

85 Determining PN formation sensitivity has traditionally proven challenging. Methods used in previous studies are subject  
to large uncertainties, especially in the measurement of HNO<sub>3</sub> (Franchin et al., 2018; Petetin et al., 2016), are computationally  
intensive (Paulot et al., 2016; Shimadera et al., 2014; Zhai et al., 2021), and typically have only been applied to short  
timeframes (Nenes et al., 2020; Wen et al., 2018; Zhai et al., 2023). Recently, Dang et al. (2023) introduced an innovative  
approach to overcome these limitations and diagnose PN sensitivity using satellite tropospheric column NH<sub>3</sub>/NO<sub>2</sub> ratios and  
90 chemical transport models without the need for HNO<sub>3</sub> measurements or exceedingly computationally intensive calculations  
(Dang et al., 2023b). Importantly, this method can quickly diagnose PN sensitivity to precursor gases across a broad region  
and a longer timeframe due to the large spatial and temporal coverage of satellite observations. This approach has been applied  
on short timeframes over East Asia, Europe, and the Eastern United States across all seasons with high accuracy when  
compared to previous studies (Dang et al., 2024). Here, we will expand this methodology over the MWUS to track multidecadal  
95 changes in wintertime PN formation sensitivity.

In this work, we evaluate changes in wintertime PN formation sensitivity by quantifying the changes in the sensitivity  
regime of wintertime PN to NH<sub>3</sub>, NO<sub>x</sub>, and VOCs over the MWUS from 2007 to 2023 via satellite observations of NO<sub>2</sub> and  
NH<sub>3</sub> column density and model sensitivity simulations. We also explore whether controlling NO<sub>x</sub> emissions or controlling NH<sub>3</sub>

emissions is the best PN and PM<sub>2.5</sub> mitigation strategy over the MWUS during winter. These methods can be expanded in the  
100 future to investigate PN formation sensitivity in other seasons, as both NO<sub>2</sub> and NH<sub>3</sub> exhibit strong seasonality.

## 2. Methodology:

### 2.1. Satellite observations:

#### 2.1.1. General information:

NO<sub>2</sub> column density was obtained from the Ozone Monitoring Instrument (OMI) using version 4.0 of the NASA  
105 OMI/Aura NO<sub>2</sub> Level 2 product ([https://disc.gsfc.nasa.gov/datasets/OMNO2\\_003/summary](https://disc.gsfc.nasa.gov/datasets/OMNO2_003/summary)). OMI is operated onboard the  
sun-synchronous NASA Earth Observing System (EOS) Aura satellite (Krotkov et al., 2019). NO<sub>2</sub> is detected at visible  
wavelengths (402–465 nm), and the measurements are in swaths of 2,600 km width at 13:45 ± 0:15 local solar time (Lamsal  
et al., 2021).

NH<sub>3</sub> column density was obtained from the Infrared Atmospheric Sounding Interferometer (IASI) onboard the Metop-A  
110 and Metop-B sun-synchronous satellites (Clarisse et al., 2018a, 2018b) ([https://iasi.aeris-  
data.fr/catalog/?currentSelection=871d9366-22d7-4d8d-997e-02e7721f7e94#masthead\\_for\\_Metop-A](https://iasi.aeris-data.fr/catalog/?currentSelection=871d9366-22d7-4d8d-997e-02e7721f7e94#masthead_for_Metop-A); [https://iasi.aeris-  
data.fr/catalog/?currentSelection=44a739bf-8b68-4b64-b594-d7bb3fbe40bf#masthead\\_for\\_Metop-B](https://iasi.aeris-data.fr/catalog/?currentSelection=44a739bf-8b68-4b64-b594-d7bb3fbe40bf#masthead_for_Metop-B)). Here, we use the  
reanalyzed daily IASI/Metop-A (2007–2020) and IASI/Metop-B (2021–2023) dataset (ANNI-NH3-v4R). This satellite  
provides measurements twice daily in the morning (9:30 local solar time) and the evening (21:30 local solar time) (Van Damme  
115 et al., 2014). In this study, we use only morning overpass measurements to minimize time separation from OMI (13:45 ± 0:15  
local solar time). IASI captures backscattered infrared radiation (~645–2760 cm<sup>-1</sup>) of atmospheric trace gases directly  
perpendicular to Earth's surface with a 12-km circular footprint (Clerbaux et al., 2009; Van Damme et al., 2017).

#### 2.1.2. Analyzing satellite observations:

[The methodology of this study is summarized in Figure S2.](#) We obtained NO<sub>2</sub> and NH<sub>3</sub> column density from winter 2007  
120 to winter 2023 over the MWUS (36° to 49° latitude and -104° to -87° longitude) from OMI and IASI. We used measurements  
from November, December, January, and February to represent winter to ensure >60% coverage over the MWUS both spatially  
and temporally due to the limited satellite sensitivity. For NO<sub>2</sub> columns, we filtered out any pixels with solar zenith angle >  
85°, cloud fraction > 0.3, terrain reflectivity > 0.3, NO<sub>2</sub> column density < 0, and any observations impacted by the row  
anomaly, which arose from problems with radiance measurements (Dang et al., 2023b). For NH<sub>3</sub> column density, we then  
125 removed any pixels with cloud fraction > 0.1, NH<sub>3</sub> column density < 0, and pixels with limited sensitivity to NH<sub>3</sub> using the  
post retrieval quality flag (Dang et al., 2023b).

Next, both NO<sub>2</sub> and NH<sub>3</sub> data sets were averaged seasonally to a 0.5° x 0.625° resolution (latitude x longitude) to spatially  
match the GEOS-Chem simulation pixels (see Section 3), and we removed any grid cells with < 20 successful retrievals to

further reduce noise. We computed the median NO<sub>2</sub> and NH<sub>3</sub> column density for each pixel for each winter to visualize the distribution of precursor gases over MWUS from 2007 to 2023.

To reduce potential errors arising from differences in the assumed vertical profiles between OMI and GEOS-Chem, a correction factor was calculated to adjust air mass factors (AMFs). Differences in underlying vertical profile assumptions can lead to inconsistencies between the model and satellite observations. We replaced the *a priori* profile used in the OMI retrieval to match that of GEOS-Chem to minimize those errors (Visser et al., 2019). For NO<sub>2</sub> column density, we applied the method described by Lamsal et al. (2010), Boersma et al. (2016), and Visser et al. (2019) to derive a correction factor, which we applied to the AMF in OMI for each aggregated grid cell (Equation 1) (Boersma et al., 2016; Lamsal et al., 2010; Visser et al., 2019).

$$AMF_{GC} = AMF_{OMI} \times \frac{\sum_{l=1}^L A_{trop} x_{l,GC}}{\sum_{l=1}^L x_{l,GC}} \quad (1)$$

In (1), AMF<sub>OMI</sub> is the air mass factor from OMI, A<sub>trop</sub> is the averaging kernel, and x<sub>l,GC</sub> is NO<sub>2</sub> column density obtained from GEOS-Chem in molecules cm<sup>-2</sup> (Boersma et al., 2016; Lamsal et al., 2010; Visser et al., 2019). The averaging kernel is obtained by taking the ratios of scattering weight and AMF<sub>OMI</sub> at each level (Boersma et al., 2016; Palmer et al., 2001). Then, the newly calculated AMFs (AMF<sub>GC</sub>) were used to correct the NO<sub>2</sub> column density (NO<sub>2,OMI</sub>) from OMI (Equation 2). In (2), NO<sub>2,new</sub> is the corrected OMI NO<sub>2</sub> column, with the underlying *a priori* profile replaced by the profile in GEOS-Chem.

$$NO_{2,new} = NO_{2,OMI} \times \frac{AMF_{GC}}{AMF_{OMI}} \quad (2)$$

Note that correction of satellite column densities by replacing *a priori* vertical profiles with those from GEOS-Chem only applies to NO<sub>2</sub> since there is not enough information from IASI to correct satellite NH<sub>3</sub> column densities. We then calculated the winter average of satellite NO<sub>2</sub> and NH<sub>3</sub> from the median of each grid cell over the MWUS for each year from 2007 to 2023. We then computed the wintertime NH<sub>3</sub>/NO<sub>2</sub> ratios across the MWUS by overlaying spatial and temporal 0.5° x 0.625° composites of NH<sub>3</sub> and NO<sub>2</sub> column density.

## 2.2. GEOS-Chem simulations:

**Table 1: Description of GEOS-Chem simulations of all sensitivity simulations using GEOS-Chem 14.4.2**

Model	GEOS-Chem version 14.4.2
Horizontal resolution (latitude x longitude)	Nested 0.5° x 0.625° resolution with the boundary conditions from a global 4° x 5° resolution simulations <sup>a</sup>
Chemistry	14.4.2 <sup>b</sup>
Meteorology	Modern-Era Retrospective analysis for Research and Applications, version 2 (MERRA-2) <sup>c</sup>

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Anthropogenic emissions	Community Emissions Data System (CEDS) and National Emissions Inventory 2016 (NEI 2016) <sup>d</sup>
Biomass burning emissions	Quick Fire Emissions Dataset, version 2 (QFED2) <sup>e</sup>

150 (a) Y.X. Wang et al., 2004; (b) DOI: 10.5281/zenodo.12807579; (c) Gelaro et al., 2017; (d) Hoesly et al., 2018; (e) Koster et al., 2018.

We used the 3D chemical transport model GEOS-Chem to examine the sensitivity of PN formation to NO<sub>x</sub>, NH<sub>3</sub>, and VOCs. The simulation parameters are summarized in Table 1. In this study, we used GEOS-Chem version 14.4.2, and all the simulations were performed at the nested 0.5° x 0.625° horizontal resolution with boundary conditions from a global 4° x 5° resolution simulation (DOI: 10.5281/zenodo.12807579) (Wang et al., 2004). Next, we assumed that January could represent the entire winter season to reduce computational burden (Dang et al., 2023b). Although GEOS-Chem underestimates observed PN mass concentrations by 38%, trends in wintertime PN simulated by GEOS-Chem and observations from the IMPROVE and CSN networks agree well (R<sup>2</sup> > 0.6 between GEOS-Chem and ground monitoring networks) (Figure S32). [We will evaluate the performance of GEOS-Chem furthermore in Section 2.5.](#)

160 All sensitivity simulations were conducted using 72 vertical pressure levels from 2007 to 2022. GEOS-Chem includes detailed HO<sub>x</sub>-NO<sub>x</sub>-VOC-O<sub>3</sub>-BrO<sub>x</sub>-aerosol tropospheric chemistry with over 200 species. We used the reanalysis product Modern-Era Retrospective analysis for Research and Applications, Version 2 (MERRA-2), developed by the NASA Global Modeling and Assimilation Office (GMAO), for meteorological inputs (Gelaro et al., 2017). Emissions were computed by the Harvard-NASA Emissions Component (HEMCO) (Keller et al., 2014). All global anthropogenic emissions were provided by the Community Emissions Data System inventory (Hoesly et al., 2018). Until winter 2018, these emissions were overwritten over the CONUS by the National Emissions Inventory 2016 (NEI 2016) at 0.1° x 0.1° resolution, which was created by NEI Collaborative for air quality modeling over the United States (National Emissions Inventory Collaborative, 2019). Since NEI emissions in the model were only available through January 2019, we used the CEDS inventory at the ~~0.1° x 0.1°~~ 0.5° x 0.5° resolution after to simulate anthropogenic emissions over the CONUS (Hoesly et al., 2018). Despite some differences in estimates of emissions magnitudes, [which mainly arise from differences in horizontal resolution and the methods used in estimating agricultural emissions](#), the CEDS and NEI2016 inventories show similar trends (Figures S43 and S54), and both predict the same wintertime PN sensitivity at various time slices and locations from 2007 to 2019 (see Section 3.1 and Figure S5), suggesting the sensitivity findings are continuous regardless of inventory ([Hoesly et al., 2018; Inventory Collaborative 2016v1 Emissions Modelling Platform](#)).

175 Aircraft emissions were taken from the Aviation Emissions Inventory Code 2019 (AEIC 2019), which covered up to 2019 (Simone et al., 2013). Emissions after 2019 were kept constant at 2019 values. Offline soil NO<sub>x</sub> emissions were used, [which were provided by Hudman et al. \(2012\)](#), and offline biogenic VOC emissions were provided by the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN) as implemented by Hu et al. (2015) [from 2007 to 2020](#) (Guenther et al., 2012; Hu et al., 2015; Hudman et al., 2012). [Similar to aircraft emissions, emissions after 2020 for soil NO<sub>x</sub> and biogenic VOC emissions were kept constant at 2020 values.](#) Biomass burning emissions were provided by the Quick Fire Emissions

Dataset, version 2 (QFED2) (Koster et al., 2015). Thermodynamic PN formation was calculated with ISORROPIA-II (Fountoukis and Nenes, 2007). We used the Luo et al. (2020) wet deposition scheme to improve the accuracy of modelled PN (Luo et al., 2020). The PN photolysis scheme is described by Shah et al. (2023) (Shah et al., 2023).

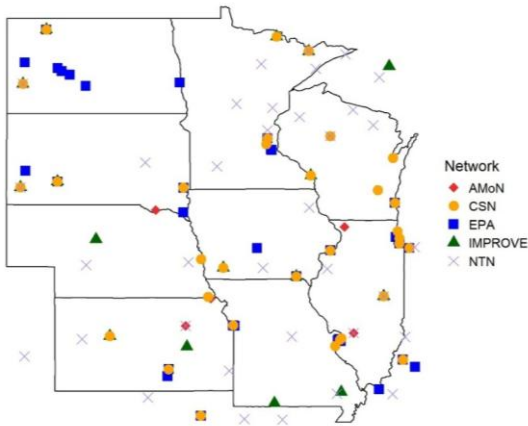
Sensitivity simulations used to quantify formation regime cutoffs are summarized in Table 2. The standard simulation (“Base”) was conducted from 2007 to 2022, where no modifications were applied to any emissions. The sensitivity of PN formation to the precursor gases NO<sub>x</sub>, NH<sub>3</sub>, and VOCs was evaluated with 3 simulations: (1) “Reduced-NO<sub>x</sub>”, where NO<sub>x</sub> emissions were decreased by 20%; (2) “Reduced-NH<sub>3</sub>”, where NH<sub>3</sub> emissions were decreased by 20%; and (3) “Reduced-VOC”, where VOC emissions were decreased by 20%. [The total quantities \(in Tg\) for NO<sub>x</sub>, NH<sub>3</sub>, and VOC emissions for each sensitivity simulation from 2007 to 2022 are shown in Figure S6.](#) In each sensitivity simulation, the decrease of the precursor gas applied to all emissions sources (natural and anthropogenic). Each sensitivity simulation was run with a full-year spin up for boundary conditions (4° x 5°) followed by one-week spin up for nested simulations (0.5° x 0.625°). [Production runs were performed for January of each year.](#) These sensitivity simulations allowed us to examine the influence of each precursor gas on wintertime PN formation, how that sensitivity changed over time, and quantify cutoffs for PN formation regime determination.

**Table 2: Description of all sensitivity simulations using GEOS-Chem 14.4.2**

Simulations	NO <sub>x</sub> emissions	NH <sub>3</sub> emissions	VOC emissions
Base	<a href="#">Normal Base</a>	<a href="#">Normal Base</a>	<a href="#">Normal Base</a>
Reduced-NO <sub>x</sub>	-20%	<a href="#">Normal Base</a>	<a href="#">Normal Base</a>
Reduced-NH <sub>3</sub>	<a href="#">Normal Base</a>	-20%	<a href="#">Normal Base</a>
Reduced-VOC	<a href="#">Normal Base</a>	<a href="#">Normal Base</a>	-20%

2.3. Ground monitoring observations:

Sites Location for Ground Monitoring Networks



200 Figure 1: Site locations for Ammonia Monitoring Network (AMoN), Chemical Speciation Network (CSN), US Environmental Protection Agency (EPA), Interagency Monitoring of PROtected Visual Environments (IMPROVE), and National Trends Network (NTN) ground monitoring networks. Note that some sites are part of multiple networks.

Table 3: Description of ground monitoring networks.

Name	Retrievals	Number of Sites	Descriptions	Citations
United States Environmental Protection Agency (US EPA) <a href="https://aqs.epa.gov/aqsweb/air_data/download_files.html#Daily">https://aqs.epa.gov/aqsweb/air_data/download_files.html#Daily</a>	Surface NO <sub>2</sub> concentrations	33	24-hour average daily surface NO <sub>2</sub> concentrations using chemiluminescent detectors, primarily over urban areas.	Demerjian, 2000; United States Environmental Protection Agency. (US EPA; Demerjian, 2000)
National Trends Network (NTN) <a href="https://nadp.slh.wisc.edu/networks/national-trends-network/">https://nadp.slh.wisc.edu/networks/national-trends-network/</a>	Nitrate wet deposition (NWD)	35	Bi-weekly samples via an automated wet precipitation collector and a rain gauge, mainly located over rural areas.	Lamb and Bowersox, 2000; National Trends Network. (NTN; Lamb and Bowersox, 2000)

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Ammonia Monitoring Network (AMoN) <a href="https://nadp.slh.wisc.edu/networks/ammonia-monitoring-network/">(https://nadp.slh.wisc.edu/networks/ammonia-monitoring-network/)</a>	Surface NH <sub>3</sub> concentrations	9	NH <sub>3</sub> concentrations using Radiello-brand diffusive samplers located mainly over rural areas.	Puchalski et al., 2015; Ammonia Monitoring Network. (AMoN; Puchalski et al., 2015)
Interagency Monitoring of PROtected Visual Environments (IMRPOVE) <a href="https://views.cira.colostate.edu/fed/QueryWizard/">(https://views.cira.colostate.edu/fed/QueryWizard/)</a>	PM <sub>2.5</sub> mass concentrations and chemical speciation (PN, NH <sub>4</sub> <sup>+</sup> , PS, and total organic carbon (OC))	16	24-hour integrated PM <sub>2.5</sub> and chemical speciation mass concentrations every 3 days over rural areas.	Malm et al., 1994; Solomon et al., 2014; Interagency Monitoring of PROtected Visual Environments. (IMPROVE; Malm et al., 1994; Solomon et al., 2014)
Chemical Speciation Network (CSN) <a href="https://aqs.epa.gov/aqsweb/air_data/download_files.html#Daily"> (https://aqs.epa.gov/aqsweb/air_data/download_files.html#Daily)</a>	PM <sub>2.5</sub> mass concentrations and chemical speciation (PN, NH <sub>4</sub> <sup>+</sup> , PS, and total organic carbon (OC))	32	24-hour integrated PM <sub>2.5</sub> and chemical speciation mass concentrations every 3 days over urban areas.	Solomon et al., 2014; United States Environmental Protection Agency. (US EPA; Solomon et al., 2014)

205 The descriptions of all ground monitoring observations and the locations of each site are summarized in Figure 1 and Table 3. We define winter in this analysis to be November, December, January, and February to match satellite retrievals. [In addition, We analyzed trends in gas concentrations, wet deposition, and particle speciation and compared them to satellite NO<sub>2</sub> column densities, NH<sub>3</sub> column densities, and model simulations to place results into context. We assume NWD and surface NH<sub>3</sub> concentrations trends are representative of the entire MWUS. While this introduces uncertainty, the agreement of trends between satellite and ground observations is excellent. This will be further discussed in Section 3.](#)

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#### 2.4. Diagnosing PN formation sensitivity over the MWUS: PN formation sensitivity diagnostic methods:

We calculated the local PN sensitivity to each precursor gas,  $S_i$ , for individual  $0.5^\circ \times 0.625^\circ$  grid cells from GEOS-Chem using Equation 3. Here, we calculated the ratio of the changes in monthly PN concentrations to changes in emissions of species  $i$ ,  $E_i$  between the sensitivity and Base simulations. In Equation 3,  $i$  is NO<sub>x</sub>, NH<sub>3</sub>, or VOCs (Dang et al., 2023b).

$$S_i = \frac{\Delta \log(PN)}{\Delta \log(E_i)} \quad (3)$$

215 To determine the wintertime PN sensitivity regime cutoff, we performed reduced-major-axis linear regression for all the pixels  
with sensitivity ratios of  $0.95 < S_i/S_j < 1.05$  from 2007 to 2022. We then chose all the pixels with sensitivity ratios of  $0.95 <$   
 $S_i/S_j < 1.05$  from 2007 to 2023 (i.e., sites without a distinct dominant regime for PN sensitivity), where  $S_i$  is the dominant  
sensitivity, and  $S_j$  is the one of the other two sensitivities different from  $S_i$  (e.g., if  $S_i$  is  $S_{NO_x}$ , then  $S_j$  is  $S_{NH_3}$  or  $S_{VOC}$ ), to perform  
reduced-major-axis linear regression and deduce the wintertime PN sensitivity regime cutoff (Figure S7) (Dang et al., 2023b).  
220 In this work, we chose to derive the regime cutoffs for the whole timeframe instead of deriving for individual years because  
there was not enough data without a dominant regime in some years to perform the regression. However, it is important to note  
that long-term trends in the formation sensitivity are the same whether using individual year or multi-year regressions (Figure  
S8). We focused on the  $NO_x$ -sensitive and  $NH_3$ -sensitive regime because MWUS PN had limited sensitivity to VOC emissions  
during wintertime (Section 3.1). After diagnosing the PN sensitivity for each pixel for each winter season, we analyzed the  
225 changes in PN sensitivity from 2007 to 2023.

### 2.5. GEOS-Chem evaluation:

We perform a series of simulations in GEOS-Chem to assess the sensitivity of PN to changes in precursor gas emissions  
from 2007 to 2022. First, we establish the reliability of GEOS-Chem for this analysis by evaluating the ability of the GEOS-  
Chem Base simulations to reproduce ground monitoring observations and trends. We compare PN magnitudes and trends  
230 during January and sample GEOS-Chem at the IMPROVE and CSN monitoring locations (Figure S3). On average, GEOS-  
Chem underestimates wintertime PN mass concentrations by -33.6% compared to ground observations (GEOS-Chem:  $1.3 \mu g$   
 $m^{-3}$ , IMPROVE:  $1.6 \mu g m^{-3}$ , CSN:  $2.3 \mu g m^{-3}$ ). The biases in modelled PN may be due to uncertainties in nighttime chemistry,  
especially  $N_2O_5$  uptake and the extent to which residual upper-planetary boundary layer PN sinks to the ground, emissions  
inventories, aerosol liquid water, and wet deposition of  $HNO_3$  (Norman et al., 2025; Travis et al., 2022; Heald et al., 2012;  
235 Curci et al., 2015; Tang et al., 2021). Despite underestimation, GEOS-Chem shows good agreement with ground monitor  
trends, indicating that the sensitivity of PN to changes in emissions is captured. PN mass concentrations from GEOS-Chem  
show a decreasing trend from 2007 to 2013 ( $-10.3 \pm 2.3\% yr^{-1}$ ), which then flattens from 2014 to 2022 ( $-0.14 \pm 1.16\% yr^{-1}$ ).  
This is consistent with the trends from CSN and IMPROVE on average: PN decreases by  $-11.0 \pm 4.5\% yr^{-1}$  from 2007 to 2013,  
and it flattens afterward to  $1.1 \pm 1.9\% yr^{-1}$ . Thus, GEOS-Chem successfully captures the decrease and subsequent flattening  
240 trends of wintertime PN over both rural (IMPROVE) and urban (CSN) areas from 2007 to 2022. Modeled nitrate wet deposition  
is overestimated by 139%, but nitrate wet deposition trends are also captured well by GEOS-Chem (Figure S9) (Luo et al.,  
2020; Christiansen et al., 2024; Silvern et al., 2019).

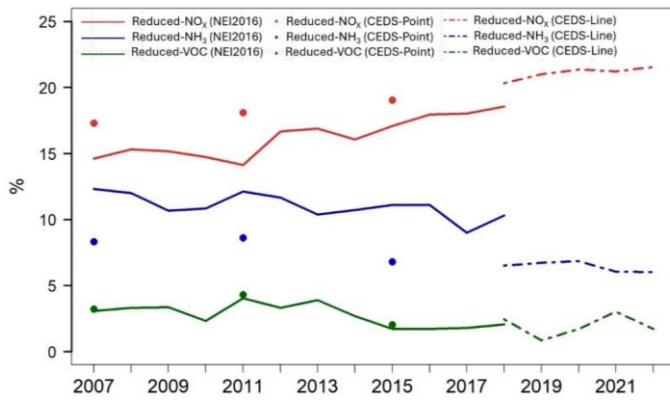
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### 3. Results and Discussions:

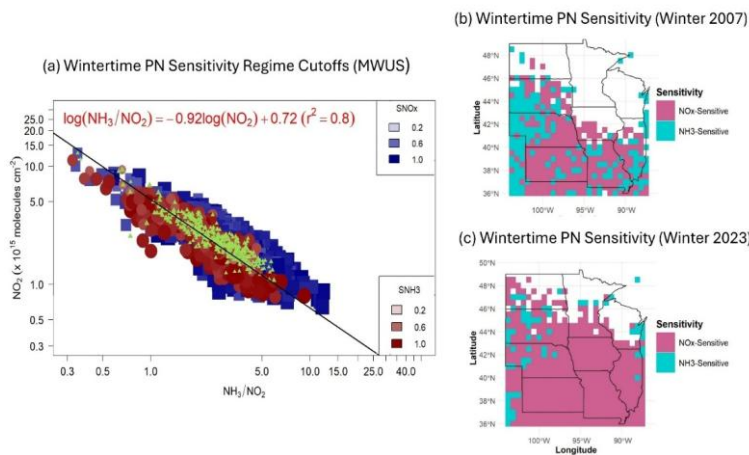
#### 3.1. Diagnosing PN sensitivity regime over the MWUS:

MWUS Wintertime : PN Formation Sensitivity from GEOS – Chem (2007 – 2022)

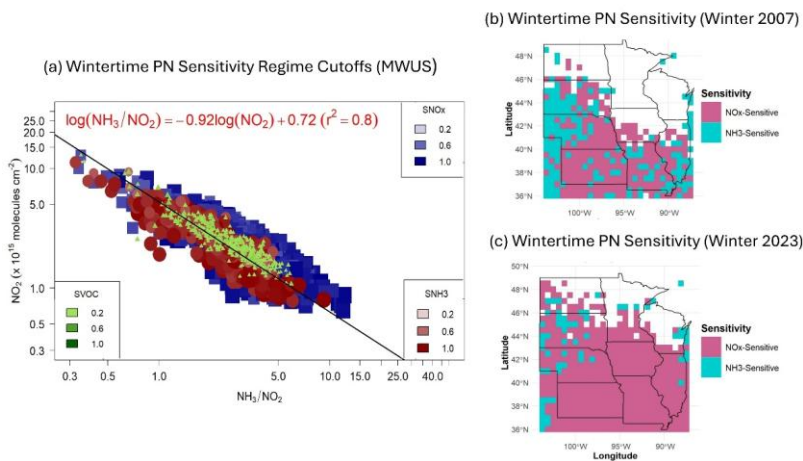


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Figure 2: The percentage difference in PN mass concentrations between the Base simulations and Reduced-NO<sub>x</sub> simulations (red), Base simulations and Reduced-NH<sub>3</sub> simulations (blue), and Base simulations and Reduced-VOC simulations (green). The solid lines indicate sensitivity simulations using the NEI2016 emissions inventory, and the dashed lines and points indicate sensitivity simulations using the CEMS emissions inventory.



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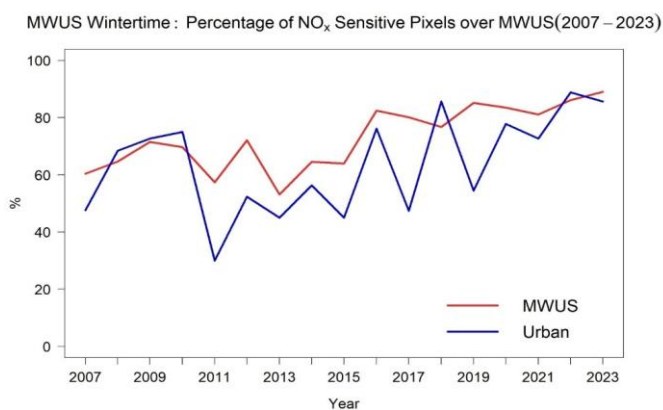
**Figure 3: Wintertime PN formation sensitivity over the MWUS.** Panel (a) shows the wintertime PN diagnostic regime cutoffs using GEOS-Chem and satellite observations. The x-axis is satellite tropospheric  $\text{NH}_3/\text{NO}_2$  ratio, and the y-axis is satellite  $\text{NO}_2$  column densities from OMI. The colors of the data points shown here are GEOS-Chem-calculated local PN sensitivity to each precursor gas ( $S_i$ ). The data points are GEOS-Chem-calculated sensitivity ratios ( $S_i/S_j > 1.1$ ) in independent model grid cells from 2007 to 2023 with sensitivity ratio  $0.95 < S_i/S_j < 1.05$ . Blue squares represent the  $\text{NO}_x$ -sensitive regime, red circles represent the  $\text{NH}_3$ -sensitive regime, and green triangles represent the VOC-sensitive regime. As no pixels are dominated by For the VOC-sensitive regime (i.e., no  $S_{\text{VOC}}/S_i > 1.1$ ), only pixels with sensitivity values  $S_{\text{VOC}} > 0.2$  are shown for illustration but not included in calculations. The regression line is derived via reduced-major-axis linear regression using pixels of all years with sensitivity ratios of  $0.95 < S_i/S_j < 1.05$ . Panel (b) and (c) shows the wintertime PN formation sensitivity over the MWUS in 2007 and in 2023, respectively, after satellite grid cell ratios are placed into sensitivity regimes using Equations (4) and (5). In panel (b) and (c), pink indicates  $\text{NO}_x$ -sensitive regions, and blue indicates  $\text{NH}_3$ -sensitive regions.

The local model sensitivity of PN,  $S_i$ , is calculated by Equation (3) for each model grid cell to derive the regime cutoffs using reduced-major-axis linear regression. PN is not sensitive to changes in VOC emissions (Reduced-VOC) at any point during the timeframe. In the Reduced-VOC simulation, changes in PN as a result of a 20% decrease in VOC emissions range from 0.84% to 4.0%, which is substantially lower than changes seen in the Reduced- $\text{NO}_x$  and Reduced- $\text{NH}_3$  simulations (range of 6.0% to 21.6%) (Figure 2). Hence,  $S_{\text{VOC}}$  is excluded from the regression, although it is shown in Figure 3a for illustration.

In Figure 3, each point represents a GEOS-Chem grid cell with a dominant wintertime PN sensitivity regime (i.e.,  $S_i/S_j > 1.1$ ) plotted at its corresponding independent satellite  $\text{NO}_2$  column densities and satellite tropospheric  $\text{NH}_3/\text{NO}_2$  ratios. Some overlap of data points in Figure 3a is expected for two reasons: 1) this figure combines all dominant sites from 2007 to 2022, and 2) wintertime  $\text{NO}_x$  and  $\text{NH}_3$  concentrations shift drastically across the timeframe. As noted previously, the trend in the shift of PN formation regimes is the same regardless of whether we determine formation regimes with individual-year or combined-year data (Figure S8). After performing reduced-major-axis linear regression, the diagnostic cutoffs for  $\text{NO}_x$  and  $\text{NH}_3$ -sensitive regimes are expressed by the inequalities (4) and (5).

$$NH_3 - \text{sensitive: } \log\left(\frac{NH_3}{NO_2}\right) < 0.72 - 0.92 \times \log(NO_2) \quad (4)$$

$$NO_x - \text{sensitive: } \log\left(\frac{NH_3}{NO_2}\right) > 0.72 - 0.92 \times \log(NO_2) \quad (5)$$



**Figure 4: The percentage of NO<sub>x</sub>-sensitive pixel counts over the MWUS (red) and over just urban areas (blue) (2007 -2023).**

The percent differences in PN mass concentrations between the Base and Reduced-NO<sub>x</sub> simulations increase from 14.6% in 2007 to 21.6% in 2022. By contrast, the percent differences between the Base and Reduced-NH<sub>3</sub> simulations decrease from 12.3% in 2007 to 6.0% in 2022 (Figure 2). Together, these results suggest that PN is becoming increasingly sensitive to NO<sub>x</sub> emissions and less sensitive to NH<sub>3</sub> emissions. [Our satellite-based results are consistent with an independent analysis of chemical mechanics \(Text S1\) and PN thermodynamic sensitivity \(Text S2\). This is covered in more detail in the supplemental, but briefly, we use the thermodynamic equilibrium model ISORROPIA-II to investigate the thermodynamic sensitivity of PN and the roles of other potential drivers of trends \(Fountoukis and Nenes, 2007\). Our results suggest that the thermodynamics of wintertime PN formation over the MWUS is shifting away from NH<sub>3</sub>-sensitivity \(Figure S10 and Text S2\), consistent with our satellite-based diagnostic, and that PN trends cannot be explained by changes in aerosol liquid water, meteorological variability, or N<sub>2</sub>O<sub>5</sub> uptake \(Text S1\).](#)

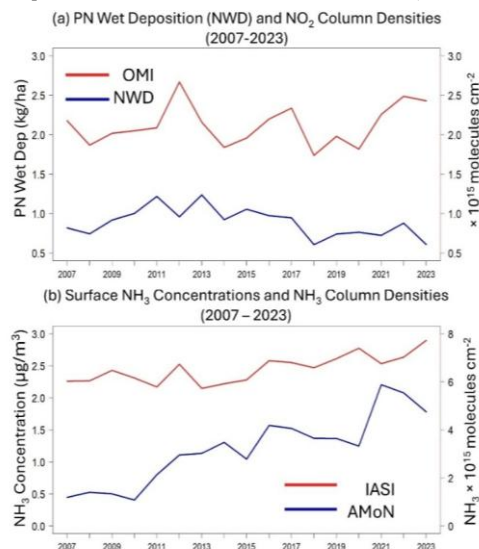
Quantitatively, the NO<sub>x</sub>-sensitive regime is the dominant regime in the MWUS, as the distribution of NO<sub>x</sub>-sensitive grid cells is always > 50% (Figure 4), and this is especially prevalent over the Central MWUS ([Figure S5 Movie S1](#)). In 2007, 60.4% of the diagnosed pixels are NO<sub>x</sub>-sensitive, but this increases to 89.0% in 2023 (Figures 3 and 4). The largest shift in PN sensitivity over the MWUS occurs after 2013, where 76.9% of the total diagnosed pixels are classified as NO<sub>x</sub>-sensitive on average from 2014 to 2023, compared to 66.0% on average from 2007 to 2013 (Figure 4). [Satellite NO<sub>2</sub> and NH<sub>3</sub> column uncertainties may propagate to errors in classification. We find that accounting for the extreme ends of the uncertainty may](#)

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295 [cause a change in diagnosed sensitivity regime in ~30% of the classified grid cells, but wintertime PN formation shows a](#)  
[consistent shift toward a predominant NO<sub>x</sub>-sensitive regime after 2013 in all cases \(Figure S11\).](#) PN sensitivity over urban  
 areas also follows the shifts in regime found for the rural MWUS (Figure 4). Our findings are consistent with previous studies  
 which diagnosed PN sensitivity over agricultural areas. Holt et al. (2015) found that the wintertime sensitivity of inorganic  
 PM<sub>2.5</sub> over Northern Midwest has become more sensitive to NO<sub>x</sub> emissions in 2012 compared to 2005 (Holt et al., 2015).  
 300 Wintertime PN formation is also NO<sub>x</sub>-sensitive over South Korea, where 76% of anthropogenic NH<sub>3</sub> emissions originate from  
 livestock (Oak et al., 2025). In addition, Guo et al. (2018) found that PN formation is more sensitive to NO<sub>x</sub> than NH<sub>3</sub> during  
 wintertime over an agricultural area in the Netherlands (Guo et al., 2018). Overall, our findings suggest that MWUS PN  
 formation was sensitive to both changes in NO<sub>x</sub> and NH<sub>3</sub> emissions from 2007 to 2013, but this has shifted to a predominantly  
 NO<sub>x</sub>-sensitive regime afterward.

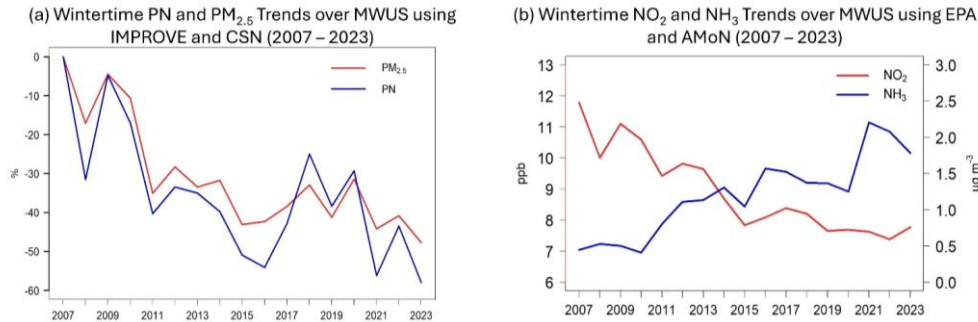
305 The distribution of PN sensitivity regimes from 2007 to 2023 over the MWUS is shown in [Movie S1 Figure S5](#). Spatially,  
 much of the shift in PN formation sensitivity is driven by changes in emissions over the eastern portion of the MWUS, which  
 is more densely populated. In 2007, MWUS PN formation was highly sensitive to NH<sub>3</sub> emissions over the eastern part of  
 MWUS (Figure 3b,c), which shifted strongly toward NO<sub>x</sub> sensitivity by 2023. The shift in formation regime is consistent with  
 the spatial trends of NO<sub>2</sub> and NH<sub>3</sub> column densities ([Movie S2 – Movie S4, Figure S12 Figure S6–S9](#)).



310 **Figure 5: Wintertime NO<sub>2</sub> and NH<sub>3</sub> column density trends over the MWUS (2007 – 2023).** Panel (a) shows the trends between nitrate wet deposition (NWD) (blue) from NADP and NO<sub>2</sub> column density over the MWUS (red) from OMI. Panel (b) shows the trends between surface NH<sub>3</sub> concentrations (blue) from AMoN and NH<sub>3</sub> column density (red) from IASI (2007-2023).

315 The shift in PN sensitivity regime over the MWUS is consistent with the trends in wintertime NO<sub>2</sub> and NH<sub>3</sub> satellite  
column densities and ground observations. We find that these trends cannot be explained by meteorological variability, and  
instead rely on aerosol chemistry and thermodynamic processes (Figure S13 and Text S2). The trends of satellite NO<sub>2</sub> and NH<sub>3</sub>  
column densities from 2007 to 2023 with uncertainties are shown in Figure S14. Trends in NO<sub>2</sub> column densities stayed  
320 relatively flat from 2007 to 2023 ( $0.48 \pm 0.60\% \text{ yr}^{-1}$ ) (Figure 5a). The relatively flat trends in satellite NO<sub>2</sub> are consistent with  
prior analyses of satellite trends over rural areas and nitrate wet deposition (NWD), a good proxy for regional NO<sub>2</sub>. Prior  
decreases in rural NO<sub>2</sub> have flattened out over time due to the increasing relative importance of static background NO<sub>2</sub> sources,  
such as soils, lightning, and biomass burning, as anthropogenic NO<sub>x</sub> emissions decrease (Figure S44) (Christiansen et al.,  
2024; Jiang et al., 2018; Silvern et al., 2019). This is consistent with the flattening trends in NWD, a proxy for regional NO<sub>x</sub>  
trends (Figure S15). When we compare satellite NO<sub>2</sub> to EPA monitors over urban areas, which are dominated by anthropogenic  
325 NO<sub>x</sub> emissions, by matching grid cells exactly, we find that NO<sub>2</sub> concentrations and NO<sub>2</sub> column density exhibit decreasing  
trends, which are  $-2.5 \pm 0.5\% \text{ yr}^{-1}$  and  $-1.2 \pm 0.8\% \text{ yr}^{-1}$ , respectively. In contrast, wintertime NH<sub>3</sub> column densities have  
increased from 2007 to 2023 by  $1.3 \pm 0.3\% \text{ yr}^{-1}$  (Figure 5b). The increase in NH<sub>3</sub> columns agree with increases in surface NH<sub>3</sub>  
concentrations reported by AMoN ( $8.2 \pm 1.0\% \text{ yr}^{-1}$ ) (Figure 5b) and prior studies (Wang et al., 2023b). Interestingly, NH<sub>3</sub>  
column densities significantly increase by  $2.2 \pm 0.5\% \text{ yr}^{-1}$  from 2014 to 2023, a stronger rate compared to the relatively flat  
330 trends from 2007 to 2013 ( $-0.1 \pm 1.2\% \text{ yr}^{-1}$ ). This acceleration in NH<sub>3</sub> column density over the MWUS ~~has been~~ may be  
attributed to wintertime agricultural ~~emissions, which contributes a majority of total NH<sub>3</sub> emissions~~ (Vo and  
Christiansen, 2024; Wang et al., 2023b; Yu et al., 2018). Over the MWUS, fertilizer application contributes ~62% of total  
agricultural NH<sub>3</sub> emissions, and livestock waste contributes ~38% in 2020 (US EPA, 2023). The observed trends from both  
satellites and at the surface are consistent with PN sensitivity shifts toward the NO<sub>x</sub>-sensitive regime. This suggests that  
335 controlling wintertime NO<sub>x</sub> emissions over the MWUS is a critical mitigation strategy for reducing wintertime PN and PM<sub>2.5</sub>  
burden.

### 3.2. Implications for particulate matter:



340 **Figure 6:** Panel (a) shows the relative changes of PM<sub>2.5</sub> (red) and PN (blue) since 2007 over the MWUS using IMPROVE and CSN ground monitoring observations. Panel (b) shows the wintertime trends in NO<sub>2</sub> (red) and NH<sub>3</sub> (blue) concentrations over the MWUS using AMoN and EPA ground monitoring observations.

Throughout the region, PN is the dominant wintertime component of the particle matrix. The average contributions of particle chemical components are 25.7% for PN, ~~11.2% for NH<sub>4</sub><sup>+</sup>~~, 10.3% for SO<sub>4</sub><sup>2-</sup>, and 19.5% for OC over urban areas. The contribution of PN, ~~NH<sub>4</sub><sup>+</sup>~~-SO<sub>4</sub><sup>2-</sup> and OC to total PM<sub>2.5</sub> mass concentrations over rural areas are 32.3%, ~~12.3%~~ 18.7%, and 25.3%, respectively (Figure S1644). Trends in observed PM<sub>2.5</sub> and PN also align with our findings regarding formation sensitivity. Observations from the IMPROVE network and CSN show decreases in wintertime PM<sub>2.5</sub> mass concentrations of  $-3.3 \pm 0.6\% \text{ yr}^{-1}$  from 2007 to 2023 over the MWUS (Figure 6a). Prior to 2013, the decrease in PM<sub>2.5</sub> was stronger compared to the trends after 2013, during which time the trends in PM<sub>2.5</sub> started to level off ( $-7.1 \pm 1.9\% \text{ yr}^{-1}$  from 2007 to 2013,  $-1.0 \pm 1.0\% \text{ yr}^{-1}$  from 2014 to 2023). This similarity persists in PN mass concentrations. Overall, PN shows a decreasing trend of  $-3.4 \pm 0.9\% \text{ yr}^{-1}$ . Prior to 2013, PN decreases by  $-6.3 \pm 2.9\% \text{ yr}^{-1}$ , while the decreases after 2013 slow to  $-1.0 \pm 2.3\% \text{ yr}^{-1}$ . These results suggest that PN and PM<sub>2.5</sub> trends are mostly driven by changes in NO<sub>2</sub>, especially after 2013, when NH<sub>3</sub> concentrations increase strongly and NO<sub>2</sub> remains relatively constant (Figure 6b). These trends are consistent across urban and rural sites (Figure S13). Our model simulations also suggest that overall PM<sub>2.5</sub> formation sensitivity is becoming more sensitive to NO<sub>x</sub> emissions (Figure 7), similar to our findings for PN (Figure 2).

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MWUS Wintertime : PM<sub>2.5</sub> Formation Sensitivity from GEOS – Chem (2007 – 2022)

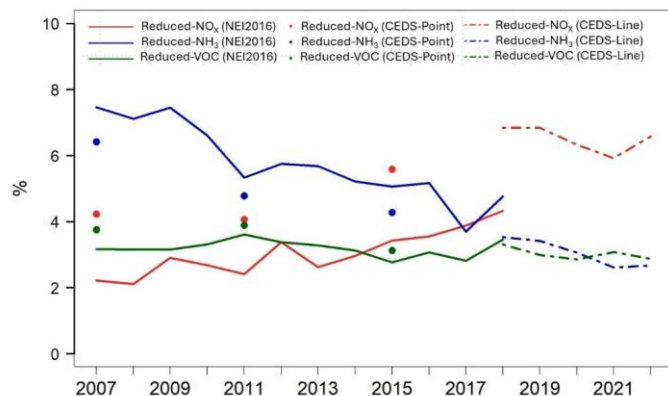


Figure 7: The percentage difference in PM<sub>2.5</sub> mass concentrations between the Base simulations and Reduced-NO<sub>x</sub> simulations (red), Base simulations and Reduced-NH<sub>3</sub> simulations (blue), and Base simulations and Reduced-VOC simulations (green). The solid lines represent sensitivity simulations using the NEI2016 emissions inventory. The dashed lines and points represent sensitivity simulations using the CEDS emissions inventory.

The prominence of PN in the particle matrix, the similarity of PN and PM<sub>2.5</sub> trends, and the increasing sensitivity of both PN and PM<sub>2.5</sub> to NO<sub>x</sub> emissions all suggest that PN may be critical for determining wintertime PM<sub>2.5</sub> burden and trends over the MWUS (Figure S17+2). Hence, reducing PN would be most effective for reducing PM<sub>2.5</sub> burden over the MWUS during winter. The most impactful timeframe for controlling wintertime PM<sub>2.5</sub> via NH<sub>3</sub> reduction in the MWUS may have already passed. Prior to the mid-2010s, regulating NH<sub>3</sub> emissions during wintertime would have decreased PM<sub>2.5</sub> mass concentrations more effectively over the MWUS compared to reducing NO<sub>x</sub> emissions, as reported in many studies starting in the mid-2000s (Gu et al., 2021; Makar et al., 2009; Pinder et al., 2007; Yang et al., 2022). This is consistent with our findings prior to 2010, in which the changes in PM<sub>2.5</sub> burden are more sensitive to changes in NH<sub>3</sub> emissions in almost half the region. However, during this time period, regulations focused on NO<sub>x</sub> and SO<sub>2</sub> emissions, increasing formation sensitivity to NO<sub>x</sub> as emissions continued to decrease. After the late 2000s, reducing NH<sub>3</sub> emissions has become increasingly less effective in controlling wintertime PN and thus PM<sub>2.5</sub> burden. The percentage difference in wintertime PM<sub>2.5</sub> mass concentrations between the Base and Reduced-NO<sub>x</sub> simulations gradually increases by 0.31% yr<sup>-1</sup> from 2007 to 2022 (2.2% in 2007, 6.6% in 2022), while it decreases by -0.33% yr<sup>-1</sup> in the Reduced-NH<sub>3</sub> simulation (7.5% in 2007, 2.7% in 2022). This is consistent with the shifts in wintertime PN sensitivity. These trends are captured using both NEI2016 and CEDS emissions inventories (Figure 7). Our findings are also consistent with more recent studies. In 2015, it was estimated that effective mitigation of PM<sub>2.5</sub> in the MWUS may require anthropogenic NH<sub>3</sub> emissions cuts of 60–90%. (Guo et al., 2024). This requirement will have only become harder to achieve since then. Similarly, Pan et al. (2024) suggested that regulating NH<sub>3</sub> is becoming less effective as secondary

inorganic aerosols have become less sensitive to  $\text{NH}_4^+$ , and reductions in  $\text{NH}_4^+$  concentrations of 40–70% would be needed to  
380 reduce annual secondary inorganic aerosols over the rural United States (Pan et al., 2024). Holt et al. (2015) found that the  
sensitivity of wintertime inorganic  $\text{PM}_{2.5}$  shifted toward  $\text{NO}_x$  emissions from 2005 to 2012, especially over the northern  
Midwest (Holt et al., 2015). Currently and in the future,  $\text{NO}_x$  emissions reductions are likely the most effective way to control  
wintertime PN formation and  $\text{PM}_{2.5}$  burden in the MWUS.

It should be noted that, while PN is most sensitive to  $\text{NO}_x$  in the winter, reducing  $\text{NH}_3$  emissions can still decrease  $\text{PM}_{2.5}$   
385 burden with significant benefits ~~during other seasons within this season~~. Over the MWUS, ~~despite having the lowest~~  
~~agricultural  $\text{NH}_3$  emissions compared to other seasons~~, a reduction of 0.01 Tg  $\text{NH}_3$  could decrease  $\text{PM}_{2.5}$  burden ~~by up to 3.7%~~  
~~during wintertime on an annual basis~~, suggesting that reducing agricultural  $\text{NH}_3$  emissions may still have significant impacts  
over agricultural regions (Vo and Christiansen, 2024). ~~Additionally], as e~~Controlling  $\text{NO}_x$  emissions will become increasingly  
costly, ~~but~~ agricultural  $\text{NH}_3$  emissions may be able to be targeted at a lower cost (Gu et al., 2021; Makar et al., 2009; Muller  
390 and Mendelsohn, 2007; Pinder et al., 2007). ~~In addition, controlling local  $\text{NO}_x$  production may become less effective for~~  
~~mitigating air quality concerns as regional sources (e.g., lightning, soils) become dominant contributors to  $\text{NO}_x$  emissions and~~  
~~trends~~. Careful consideration of technological advancements and economic concerns will be needed for new regulations aimed  
at reducing  $\text{PM}_{2.5}$  burden over agricultural regions. This study was only focused on wintertime PN and  $\text{PM}_{2.5}$  burden, and  
sensitivity conditions in other seasons may differ, as both  $\text{NO}_x$  and  $\text{NH}_3$  emissions show distinct seasonal patterns. This is an  
395 area for future investigation.

#### 4. Conclusion:

Our study shows that wintertime PN formation is becoming more sensitive to  $\text{NO}_x$  emissions over the MWUS from 2007  
to 2023. This is consistent with the relatively flat trends in satellite  $\text{NO}_2$  column densities ( $0.48 \pm 0.60\% \text{ yr}^{-1}$ ) and the continuous  
increases in satellite  $\text{NH}_3$  column densities ( $1.3 \pm 0.3\% \text{ yr}^{-1}$ ) from 2007 to 2023 over MWUS. VOCs do not influence the  
400 formation of PN over the MWUS. Our results indicate that it is most chemically effective to control  $\text{NO}_x$  emissions to reduce  
wintertime PN and  $\text{PM}_{2.5}$  burden. The MWUS might have missed the most impactful window to control wintertime  $\text{PM}_{2.5}$  by  
reducing  $\text{NH}_3$  emissions. Future work to diagnose PN formation sensitivity over the MWUS across other seasons is needed to  
understand whether controlling  $\text{NO}_x$  emissions is effective year-round. This work provides a chemical perspective for  
policymakers interested in effective emissions controls to improve air quality and human health over agriculturally intensive  
405 regions.

#### Code, data, or code and data availability (~~Zenodo link—code, data, ...~~)

Data and R code used in this publication are available at <https://doi.org/10.5281/zenodo.18021326>.

### **Supplement link**

The link to the supplement will be included by Copernicus, if applicable.

### 410 **Author contributions**

AC designed and directed the projects. TV performed the research, compiled and analyzed the data, conducted model simulations, and prepared the manuscript.

### **Competing interests**

The authors declare that they have no conflict of interest.

### 415 **Disclaimer**

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425 for providing open-access data for gaseous NH<sub>3</sub> concentrations and nitrate wet deposition over the United States. We also acknowledge the United States Environmental Agency for publicly available surface NO<sub>2</sub> concentrations, PM<sub>2.5</sub> mass concentrations and particle chemical speciation data over urban areas. We also acknowledge the Interagency Monitoring of PROtected Visual Environments (IMRPOVE) for the public availability of PM<sub>2.5</sub> mass concentrations and particle chemical speciation data over rural areas. Lastly, we thank Daniel Jacob for the development and public availability of GEOS-Chem.

### 430 **Review statement**

The review statement will be added by Copernicus Publications listing the handling editor as well as all contributing referees according to their status anonymous or identified.

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