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Key Points:

- Nighttime nitrate radical chemistry in Seoul has accelerated as nitrogen oxide emissions have decreased, increasing nitrate $PM_{2.5}$
- A NO_x emission threshold is now being crossed in Seoul where further emission controls should effectively decrease $PM_{2.5}$
- This emission threshold can be determined in urban areas worldwide using routine ozone and NO_x measurements from air quality networks

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Wintertime Trends of Fine Particulate Matter ($PM_{2.5}$) in South Korea, 2012–2022: Response of Nitrate and Organic Components to Decreasing NO_x Emissions

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Abstract We analyze 2011–2022 trends in wintertime fine particulate matter ($PM_{2.5}$) and its composition in South Korea using surface network data and machine learning. $PM_{2.5}$ decreased nationwide by 1.2 μg m^{-3} per year after correcting for meteorology. However, Seoul $PM_{2.5}$ declined only after 2019 and its composition has shifted toward particulate nitrate (pNO_3^-) and organic aerosol (OA). Trends in pNO_3^-, OA, nitrogen dioxide (NO_2), and ozone (O_3) suggest that nighttime formation of the nitrate radical (NO_3) from the $NO_2 + O_3$ reaction is a key driver of pNO_3^- and secondary OA (SOA) formation. Increasing O_3 as nitrogen oxide (NO_x) emissions decline has increased nighttime NO_3 production over the 2012–2022 period, promoting pNO_3^- and SOA formation. As NO_x emissions in South Korea continue to decline, transition from NO_x-saturated to NO_x-limited conditions for NO_3 formation should lead to rapid decreases in nighttime $PM_{2.5}$ formation.

Plain Language Summary Fine particulate matter ($PM_{2.5}$) is a severe air pollution problem in South Korea and is worst in winter. Domestic and Chinese emission controls have driven winter $PM_{2.5}$ declines throughout South Korea over the 2011–2022 period. However, $PM_{2.5}$ around Seoul (where half the population lives) has been resistant to decrease and only declined after 2019. Using surface network observations augmented by machine learning, including the differences in pollution on weekdays and weekends, we find evidence that $PM_{2.5}$ composition in Seoul has shifted toward the secondary (atmospherically produced) particulate nitrate (pNO_3^-) and organic aerosol (OA) formed by nighttime chemistry. We find that as nitrogen oxide (NO_x) pollution (largely from combustion) has declined due to emissions controls, this nighttime chemistry accelerates which should increase the formation of pNO_3^- and SOA. Below a certain NO_x emission threshold, however, this pathway for pNO_3^- and SOA formation should effectively decrease in response to further emission controls. This threshold is now being crossed in Seoul. We show that this NO_x emission threshold can be determined in urban areas worldwide using routine measurements available from surface air quality networks.

1. Introduction

Fine particulate matter less than 2.5 μm in diameter ($PM_{2.5}$) is a leading cause of mortality, responsible in South Korea for 34,000 annual deaths (N. R. Kim & Lee, 2024; Y.-H. Lim et al., 2020; Oh et al., 2024). $PM_{2.5}$ concentrations in South Korea have decreased over the past decade (Pendergrass et al., 2022, 2025), driven by domestic pollution controls (Joo, 2018; Ministry of the Environment, 2019) and by reduced transport from China where pollution controls have driven $PM_{2.5}$ declines as well (Zhai et al., 2019). However, wintertime $PM_{2.5}$ in South Korea remains high particularly in the Seoul Metropolitan Area (SMA), where over half of the population lives. $PM_{2.5}$ is highest in winter and early spring because of suppressed vertical mixing, long-range transport, and local emissions (H. Kim et al., 2017; E. Kim et al., 2025; Kwon et al., 2025; Lee et al., 2024).

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$PM_{2.5}$ can be emitted directly (primary) or can be formed in the atmosphere following oxidation of precursor gases (secondary). $PM_{2.5}$ mass concentrations have been monitored hourly by the AirKorea surface network beginning in 2015, while oxidants including nitrogen dioxide (NO_2) and ozone (O_3) have been monitored since 2001. $PM_{2.5}$ speciation has also been measured at six supersites since 2015 (Kumar et al., 2021; NIER, 2022). The data show rapid decrease of black carbon (BC) and sulfate (SO_4^{2-}) $PM_{2.5}$ components, while particulate nitrate (pNO_3^-) and organic aerosol (OA) contribute an increasing fraction of $PM_{2.5}$ mass (Y. Kim et al., 2020; Lee et al., 2024). The decreases of BC and SO_4^{2-} are consistent with decreasing primary emission from fuel combustion and decreasing emission of sulfur dioxide (SO_2) (E. Kim et al., 2025). pNO_3^- and secondary OA (SOA) originate from emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs), respectively. NO_x emissions in South Korea (mainly from fuel combustion) decreased by 30% over the 2015–2023 period while VOC emissions have been flat (Oak et al., 2025).

pNO_3^- in South Korea has not responded to the decrease of NO_x emissions and is now a major component of extreme winter haze events in the SMA (Bae et al., 2020; B.-U. Kim et al., 2017; S. Lim et al., 2022; J. Park et al., 2022). Formation of pNO_3^- requires alkalinity (largely from ammonia, NH_3) beyond that needed to neutralize SO_4^{2-}. In the absence of alkalinity, pNO_3^- partitions to the gas phase as nitric acid (HNO_3). NH_3 is mainly emitted by agriculture, with a small urban source from vehicles (T. Park et al., 2023). pNO_3^- formation in South Korea was limited in the past by the supply of NH_3 (Dang et al., 2023, 2024) but is now increasingly limited by the supply of NO_x as NO_x emissions have decreased (Oak et al., 2025). The decrease of NO_x emissions has increased wintertime ozone (Colombi et al., 2023), which would promote nighttime formation of pNO_3^- by way of the nitrate radical (NO_3) (Shah et al., 2020; Zhang et al., 2024). Oxidation of VOCs to form SOA would also be enhanced by the increase of O_3 and NO_3 (Hu et al., 2023; Ng et al., 2017; H. Wang et al., 2023).

Here we analyze 2012–2022 trends in wintertime $PM_{2.5}$ and its composition in South Korea using a combination of data sources from surface networks, supersites, and satellites, augmented by machine learning. We examine trends in oxidants as drivers of pNO_3^- and OA trends and draw implications for future pollution control priorities.

2. Data and Methods

We use hourly 2015-22 $PM_{2.5}$ and 2012–22 NO_2 and O_3 data from the AirKorea surface network (https://www.airkorea.or.kr/). We supplement the national network data with 2012–2014 hourly $PM_{2.5}$ data collected at 25 sites in the city of Seoul by the Seoul Research Institute of Public Health and Environment (NIER, 2022). Outside of Seoul between 2012 and 2014, we use the synthetic $PM_{2.5}$ data at AirKorea sites produced by Pendergrass et al. (2025) with a random forest (RF) algorithm trained on AirKorea measurements available for related pollutants including PM_{10}. We also use a daily continuous $PM_{2.5}$ product produced using aerosol optical depth (AOD) data from the GOCI geostationary satellite (Pendergrass et al., 2025).

$PM_{2.5}$ composition measurements are sparse in South Korea. We obtain SO_4^{2-}, pNO_3^-, NH_4^+, organic carbon (OC), and BC data from an ambient ion monitor at the Seoul supersite (37.62°N, 126.93°E) managed by the National Institute for Environmental Research (NIER). Lee et al. (2024) finds that $PM_{2.5}$ concentrations observed at the supersite show the same trends as AirKorea observations across Seoul. We obtain inorganic particle-phase (SO_4^{2-}, pNO_3^-, and NH_4^+) and gas-phase (HNO_3 and NH_3) components from the Kanghwa site (37.71°N, 126.27°E) of the Acid Deposition Monitoring Network in East Asia (EANET). Kanghwa is an agricultural island northwest of Seoul.

Meteorology plays a significant role in driving interannual variability in $PM_{2.5}$ (Jeong et al., 2024; Koo et al., 2020). To remove meteorological influence and thus capture the long-term trend in $PM_{2.5}$ due to emission changes, we use multi-linear regression (MLR) to relate AirKorea and synthetic $PM_{2.5}$ network data to meteorological fields from the ECMWF hourly 9×9 km^2 resolution ERA5-Land replay of the ERA5 global reanalysis and hourly 30×30 km^2 fields from ERA5 (Hersbach et al., 2020; Muñoz-Sabater et al., 2021). To increase statistical robustness, we only use sites with continuous 2011–22 records and average the data on a $0.25° \times 0.3125°$ grid (Shen et al., 2017; Tai et al., 2010; Zhai et al., 2019). Predictor meteorological variables in the MLR include boundary layer height, mean sea-level pressure, precipitation, 2 m temperature, 10 m wind speed, 2 m relative humidity (RH), and 850 hPa meridional wind velocity, which have been identified in previous studies to correlate with $PM_{2.5}$ in the region (Leung et al., 2018; Pendergrass et al., 2019; Zhai et al., 2019). To construct our MLR model, we follow the methodology of Zhai et al. (2019) by deseasonalizing and detrending

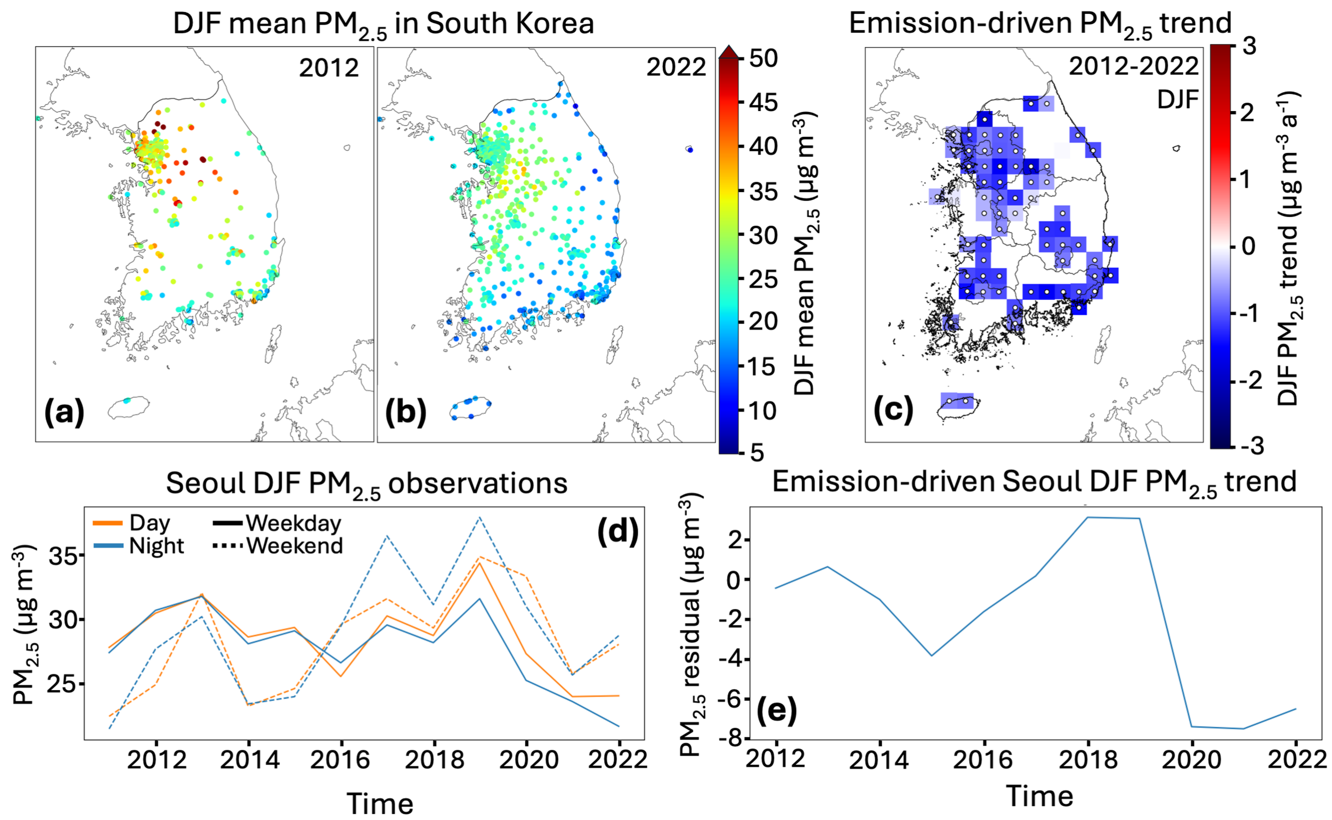

Figure 1. December–February (DJF) $PM_{2.5}$ and trends in South Korea. Panels (a) and (b) show DJF mean $PM_{2.5}$ at AirKorea surface stations in (a) 2012 and (b) 2022. $PM_{2.5}$ monitoring at these stations started in 2015, and data for 2012 are produced using a random forest (RF) algorithm applied to the then-available station data including PM_{10} (Pendergrass et al., 2025). Panel (c) shows the DJF emission-driven trend in $PM_{2.5}$ after removing meteorological influence with a multi-linear regression (MLR) fit. Panel (d) shows observed DJF $PM_{2.5}$ averaged over 25 sites in the city of Seoul, disaggregated into daytime (8–18 LT) and nighttime (22–5 LT) for weekdays and weekends. Panel (e) shows the emission-driven $PM_{2.5}$ timeseries (residual from the meteorological MLR model) for the Seoul 0.25° × 0.3125° grid cell (centered at 37.5°N, 127.0°E) and averaging data from 37 sites.

input data sets and then fitting the MLR to the $PM_{2.5}$ observations. We determine the best model for each grid cell by finding the MLR fit with at most three meteorological variables that has the highest Akaike Information Criterion (AIC) value (Akaike, 1974). We then subtract the prediction from the observed $PM_{2.5}$ and interpret the residual as the emission-driven trend (Zhai et al., 2019). The Pearson's correlation coefficient of the MLR model with 24-hr $PM_{2.5}$ observations in 0.25° × 0.3125° grid cells ranges between 0.41 and 0.72 with a median value of 0.60, in line with previous studies (Tai et al., 2010; Zhai et al., 2019).

3. Results and Discussion

Figure 1 shows mean December-February (DJF) $PM_{2.5}$ in South Korea in 2012 and 2022, together with emission-driven trends. Emission changes have driven a mean 1.2 μg m^{-3} a^{-1} decrease in DJF $PM_{2.5}$ that is spatially consistent across the country. Although emissions of precursor species SO_2 and NO_x have declined steadily and nationwide throughout the study period (Oak et al., 2025), DJF emission-driven $PM_{2.5}$ trends in Seoul showed an increase in the 2015–2019 period before dropping in 2020 and remaining low afterward (Figure 1e). This 2015-2019 increase is confined to the SMA while the rest of South Korea on average shows a steady decline (Pendergrass et al., 2022, 2025), leading to similar decreases in the 2012–2022 period in both the SMA and the rest of the country (Figure 1c). The 2015–19 SMA increase is most pronounced on weekend nights (Figure 1d). $PM_{2.5}$ decreased sharply in the SMA in 2020 which has been attributed to COVID-19 lockdowns (Ju et al., 2021) but this decrease is sustained past the lockdowns implying a more persistent decrease of emissions (Pendergrass et al., 2025).

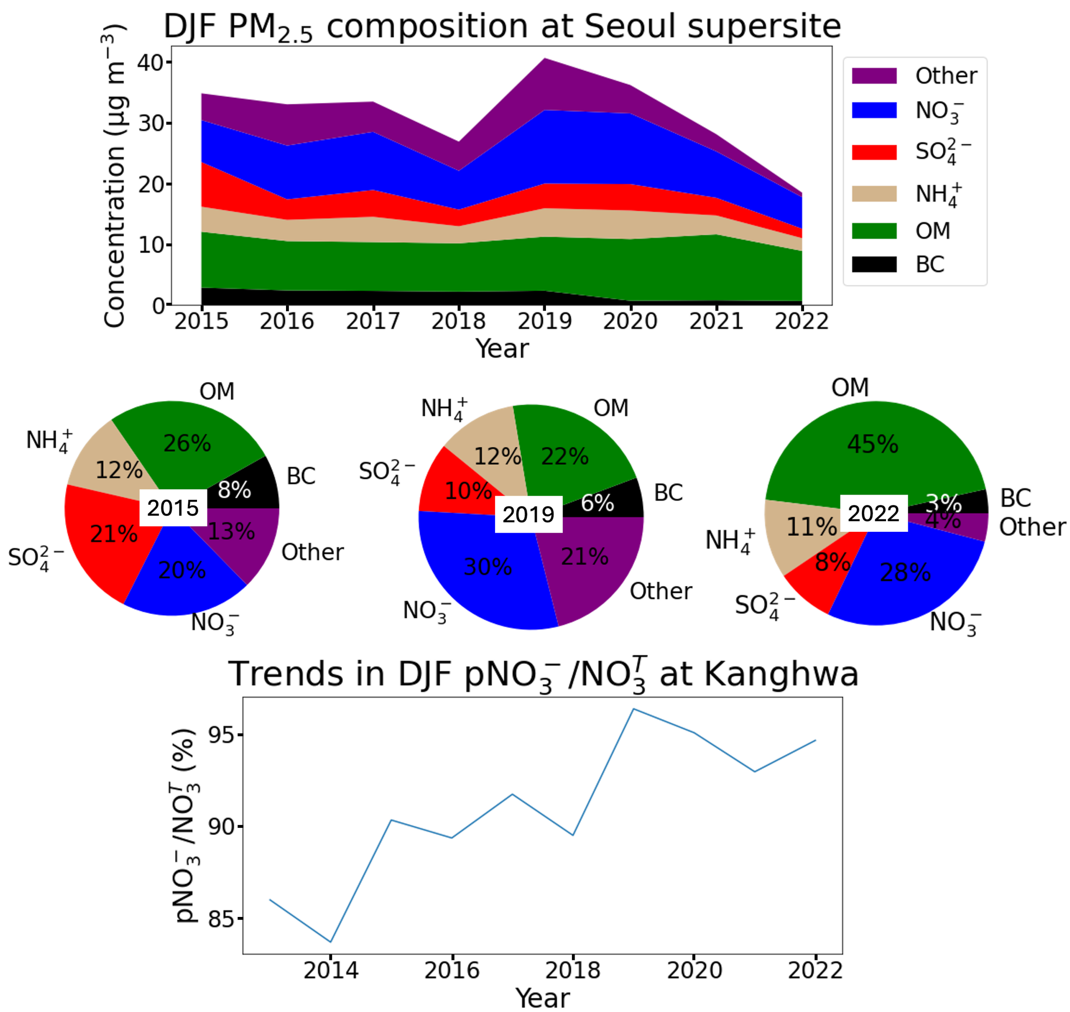

Figure 2. Wintertime $PM_{2.5}$ speciation trend at the Seoul supersite (37.62°N, 126.93°E) and pNO_3^-/NO_3^T gas-particle fractionation at the Kanghwa EANET site NW of Seoul (37.71°N, 126.27°E), where $NO_3^T \equiv HNO_3 + pNO_3^-$ is total (gas + particle) nitrate. Contributions to $PM_{2.5}$ mass labeled as "Other" include sea salt, dust, and metals. Values are DJF seasonal means.

In the 2015–2019 period, reductions in SO_4^{2-} in Seoul were more than compensated by increasing pNO_3^- (Figure 2, top panel), but pNO_3^- grew faster than simple acid substitution for SO_4^{2-}. The Kangwha data show that the fraction of total nitrate ($NO_3^T \equiv HNO_3 + pNO_3^-$) in the particle phase increased from 85% to 95% between 2013 and 2019 (Figure 2, bottom panel). The pNO_3^-/NO_3^T fraction remained above 92% after 2019 when Seoul pNO_3^- begins to decline. The NH_3/NO_2 satellite indicator (Dang et al., 2023, 2024) shows that pNO_3^- sensitivity shifted from a NH_3-limited to a NO_x-limited regime around 2019 (Oak et al., 2025), consistent with a high pNO_3^-/NO_3^T fraction. Organic matter (OM) has both primary and secondary (SOA) components (Brewer et al., 2023), did not decrease over the 2015–2022 period, and by 2022 comprised a similar fraction of $PM_{2.5}$ as pNO_3^- (Figure 2, middle panel), while BC declined substantially. We compute OM from observed OC using an OM/OC mass ratio of 1.7 based on prior winter observations in Seoul which find a range of 1.5–1.9 (H. Kim et al., 2018; S.-M. Park et al., 2018; Seo et al., 2017). Other contributions to $PM_{2.5}$ mass include sea salt, dust, and metals, which show a decline in the later phase of the record. Dust emissions from construction and road traffic have been decreasing rapidly in South Korea (Zhai et al., 2023).

The increase of wintertime pNO_3^- over the 2015–2019 period despite reductions in NO_x emissions can be explained in part by an increase in nighttime oxidants, which could also explain why OM has been resistant to decrease. At night, pNO_3^- mainly forms through N_2O_5 heterogeneous chemistry, as described in the mechanism

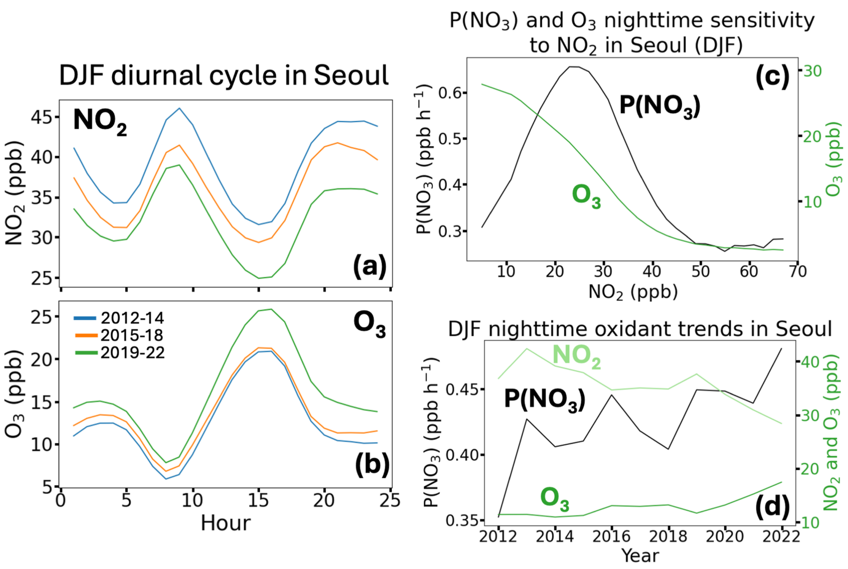

Figure 3. Mean diurnal and nighttime (22–05 LT) trends of oxidants in Seoul in winter (DJF). Values are averages for the 25 AirKorea surface sites in Seoul with continuous 2012–2022 records. Left panels show the average diurnal cycles of (a) NO_2 and (b) O_3 concentrations aggregated for the 2012–2014, 2015–2018, and 2019–2022 periods. Panel (c) shows mean nighttime O_3 concentrations and production rates of the nitrate radical $P(NO_3)$ binned as a function of NO_2 concentrations sorted in 2 ppb bins. $P(NO_3)$ is calculated from Equation 1. Panel (d) shows 2012–2022 trends of nighttime NO_2 concentrations, O_3 concentrations, and $P(NO_3)$.

below. NO_x emission is mainly as NO, which is oxidized to NO_2 by (R1). Subsequent oxidation of NO_2 by O_3 produces the NO_3 radical, which can either react with NO_2 to form pNO_3^- via N_2O_5 or with VOCs to form SOA:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R1)}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R2)}$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \quad \text{(R3)}$$

$$NO_3 + VOC \rightarrow SOA \quad \text{(R4)}$$

$$N_2O_5 + H_2O \xrightarrow{\text{aerosol}} 2pNO_3^- \quad \text{(R5)}$$

The mechanism operates only at night because NO_3 photolyzes on a time scale of a minute in the daytime, suppressing Reactions R3 and R4 which are much slower. The nighttime nitrate production rate $P(NO_3)$ can be calculated from the hourly observed NO_2 and O_3 concentrations at the AirKorea sites:

$$P(NO_3) = k[O_3][NO_2]; \qquad k = 1.4 \times 10^{-13} \exp(-2470/T) \quad (1)$$

where the rate constant k as a function of temperature T is from Atkinson et al. (2004).

Figures 3a and 3b shows 2012–2022 observed trends and diurnal variations of hourly NO_2 and O_3 concentrations in the AirKorea Seoul data. Figure 3c shows the observed nighttime dependences of the O_3 concentration and $P(NO_3)$ on the hourly NO_2 concentration, as obtained by averaging the hourly AirKorea data into 2 ppb NO_2 bins. Decrease in NO_x emissions drives a decrease in nighttime NO_2 concentrations over the 2012–2022 period but an increase in nighttime O_3 concentrations. When NO_2 is observed to be in excess of 50 ppb, O_3 is titrated by Reaction R1 (Figure 3c) and NO_3 production by Reaction R2 cannot take place. As NO_2 drops to lower concentrations, O_3 increases rapidly which stimulates NO_3 production. This results in a sharp maximum of $P(NO_3)$ for 25 ppb NO_2 (Figure 3c). At lower NO_2 concentrations $P(NO_3)$ is limited by the supply of NO_x, while at higher NO_2 concentrations it is limited by the supply of O_3.

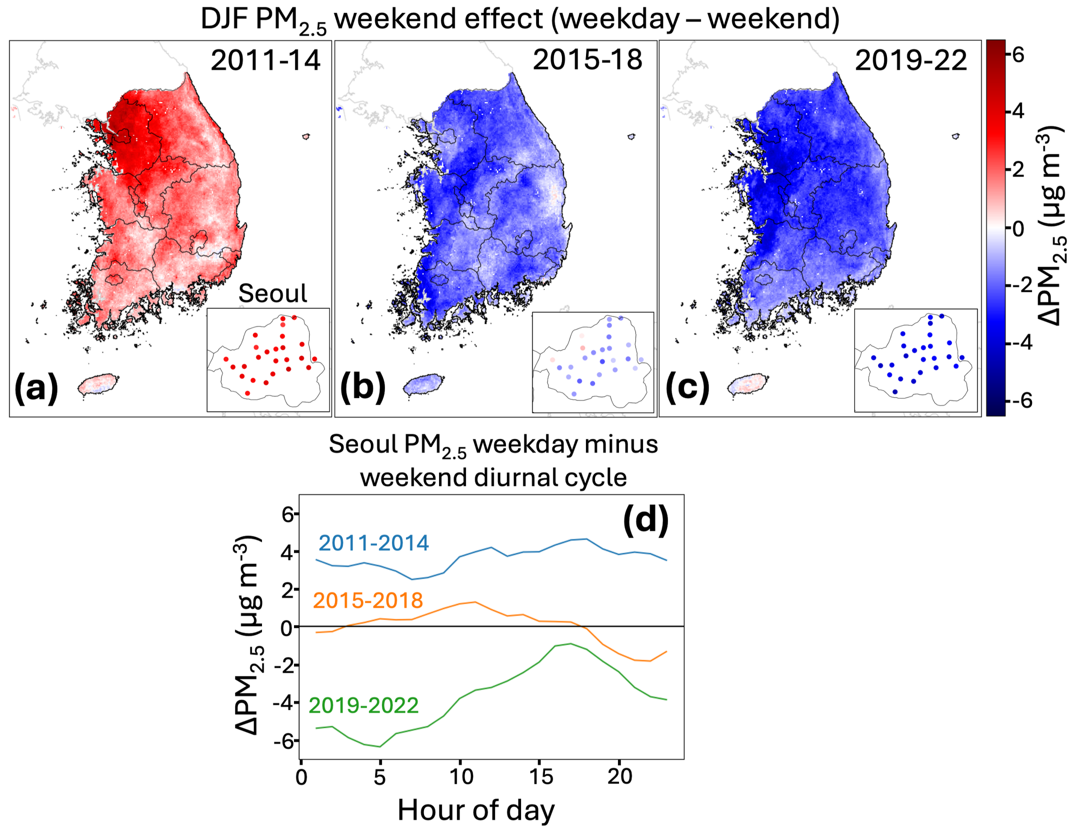

Figure 4. Wintertime (DJF) $PM_{2.5}$ weekend effect in South Korea. $\Delta PM_{2.5}$ denotes the difference between mean weekday and weekend $PM_{2.5}$ concentrations. Panels (a) through (c) show maps of $\Delta PM_{2.5}$ for (a) 2011–2014, (b) 2015–2018, and (c) 2019–2022, where red (positive $\Delta PM_{2.5}$) indicates that weekdays are more polluted than weekends. $PM_{2.5}$ concentrations are inferred using machine learning from geostationary satellite AOD data (Pendergrass et al., 2025), except for Seoul (inset) where direct continuous measurements are available from sites through the 2011–2022 period. Panel (d) shows the diurnal variation of $\Delta PM_{2.5}$ in Seoul for 2011–2014, 2015–2018, and 2019–2022.

Declining NO_x emissions has led to decreases in NO_2 concentrations with nighttime mean values in Seoul dropping just below 30 ppb by 2022 (Figure 3d). This remains in the regime where decreasing NO_2 continues to increase P(NO_3), and indeed P(NO_3) has steadily grown over the 2012–2022 period (Figure 3d). Such growth in P(NO_3) increases the nighttime production of pNO_3^-, SOA, and organonitrates that may hydrolyze to pNO_3^- (Farmer et al., 2010; Fisher et al., 2016; Kiendler-Scharr et al., 2016; Ng et al., 2017; H. Wang et al., 2021, 2023; Y. Wang et al., 2023). As NO_2 declines, growing P(NO_3) makes more NO_3 available to react with VOCs and form SOA (Reaction R4), which may explain why the organic $PM_{2.5}$ fraction is not decreasing while pNO_3^- is. NO_2 concentrations in the SMA decline in sync with NO_x emissions (Oak et al., 2025). If NO_x emissions decrease by another 20% they will clear the 25 ppb threshold below which P(NO_3) should decline rapidly, and with it the nighttime pathway for pNO_3^- and SOA formation.

Further evidence of this oxidant limitation is apparent in the difference between weekdays and weekends. Observed O_3 is higher on the weekends than on weekdays over the study period, which can be explained by lower NO emissions resulting in less O_3 titration; NO_3 concentrations would correspondingly be higher on weekends (Kenagy et al., 2018). The $PM_{2.5}$ data show a weekend effect consistent with the oxidants. Figure 4 shows the DJF 2012–2022 trend in the difference between weekday and weekend $PM_{2.5}$ concentrations in South Korea. Previous work has observed a weekend effect in Seoul and in some Chinese cities where $PM_{2.5}$ levels are higher on weekends than weekdays as would be driven by higher oxidant levels (Choi et al., 2022; Y. Wang et al., 2019; Zhao et al., 2018). But we find the opposite in South Korea for the period prior to 2015, with weekdays more polluted by weekends, and with our AOD-inferred $PM_{2.5}$ product we also find that the weekend effect transition in 2015 occurred everywhere in South Korea (Figures 4a–4c). Our AOD-inferred product is trained to predict 24-hr mean $PM_{2.5}$ even though AOD is retrieved only during daytime, and consistency with observed Seoul $PM_{2.5}$ is shown in the inset (Figures 4a–4c) and discussed in Pendergrass et al. (2025). Early air pollution controls targeting primary $PM_{2.5}$ emissions from vehicles (OC and BC) would have more effect on weekdays than weekends, and indeed the BC fraction of $PM_{2.5}$ in Seoul declined from 14% in 2003 to less than 3% by 2017 (Y. Kim et al., 2020. Figure 2). Figure 4d shows that the post-2015 weekend effect is most pronounced at night (i.e., weekends are more polluted than weekdays particularly at night) especially after 2019. This means that nighttime production of $PM_{2.5}$ has become faster on weekends, consistent with an increase in the secondary component (pNO_3^-, SOA) driven by the faster production of NO_3 radicals at night.

In summary, we demonstrated the critical role of nighttime nitrate radical (NO_3) formation in driving 2012–2022 trends in wintertime (DJF) $PM_{2.5}$ and its composition in South Korea. Declining anthropogenic emissions have led DJF mean $PM_{2.5}$ to decrease at a rate of 1.2 μg m^{-3} a^{-1} in South Korea but with significant variability including a 2015–2019 increase in Seoul driven by particulate nitrate (pNO_3^-) even as NO_x emissions decreased. pNO_3^- and organic aerosol now contribute over half of total $PM_{2.5}$. pNO_3^- would not respond to NO_x emission controls if its formation was limited by the supply of NH_3, but EANET observations of total (gas + particulate) nitrate indicates a switch to NO_x-limited conditions during the 2010s. An important factor driving the $PM_{2.5}$ shift to pNO_3^- and organic aerosol (OA) as NO_x emissions decrease is the increasing nighttime formation of NO_3 due to weaker titration of O_3. Using AirKorea hourly network observations of NO_2 and O_3, we show that the nighttime NO_3 production rate P(NO_3) in Seoul increased rapidly over the 2012–2022 period. We see evidence for a resulting nighttime increase in pNO_3^- and SOA formation by comparing weekend versus weekday $PM_{2.5}$ concentrations and their trends, with reduced NO_x on weekends leading to increased NO_3 production driving a growing nighttime $PM_{2.5}$ weekend effect. The same pattern of enhanced nighttime nitrogen chemistry as NO_x emissions decline was observed in China during COVID-19 lockdowns (Yan et al., 2023). We infer from the AirKorea observations a 25 ppb NO_2 threshold below which P(NO_3) should begin to decrease rapidly as NO_x emissions decrease. NO_2 concentrations in Seoul in 2019–2022 were approaching that threshold, implying that further NO_x emission reductions should accrue immediate benefits for reducing pNO_3^- and SOA and therefore total $PM_{2.5}$. A similar threshold should apply to urban areas worldwide and can be readily diagnosed from routine hourly surface observations of O_3 and NO_2 concentrations.

Data Availability Statement

Hourly 2015–22 $PM_{2.5}$ and 2012–22 NO_2 and O_3 data are available from the AirKorea surface network (https://www.airkorea.or.kr/). Seoul-specific bulk $PM_{2.5}$ data from before 2015 with corresponding NO_2 and O_3 from AirKorea available from Pendergrass (2025). The synthetic $PM_{2.5}$ surface network for Korea prior to 2015 described in Pendergrass et al. (2025) is also hosted at Pendergrass (2025). The gap-free GOCI $PM_{2.5}$ product described in Pendergrass et al. (2025) is available from Pendergrass et al. (2024). PM composition data measurements used in this study are available from Pendergrass (2025). Data for Kanghwa site are archived by EANET (EANET, 2025).

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