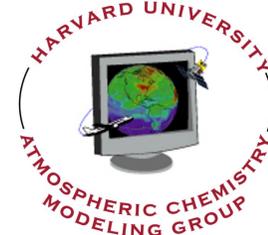
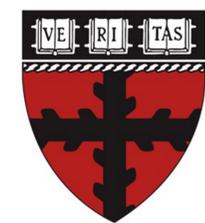


# Wintertime trends of fine particulate matter (PM<sub>2.5</sub>) in South Korea, 2012-2022: response of nitrate and organic components to decreasing NO<sub>x</sub> emissions

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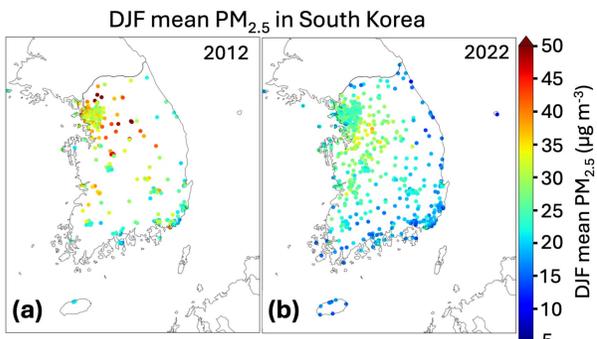
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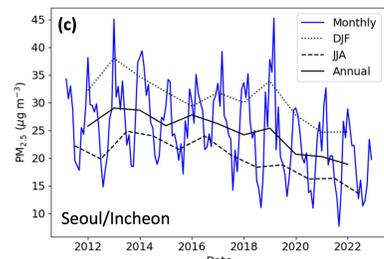
**Abstract.** We analyze 2011-2022 trends in wintertime fine particulate matter (PM<sub>2.5</sub>) and its composition in South Korea using data from the AirKorea and other surface networks complemented by machine learning. PM<sub>2.5</sub> concentrations decreased nationwide by 1.2 μg m<sup>-3</sup> per year during that period after correcting for meteorology. However, Seoul PM<sub>2.5</sub> starts to decline only after 2019 and shows a shift toward particulate nitrate (pNO<sub>3</sub><sup>-</sup>) and secondary organic aerosol (SOA) which have been resistant to decrease. Trends in the concentrations of pNO<sub>3</sub><sup>-</sup>, organic aerosol, nitrogen dioxide (NO<sub>2</sub>) and ozone (O<sub>3</sub>) indicate that nighttime formation of the nitrate radical (NO<sub>3</sub><sup>•</sup>) from the NO<sub>2</sub> + O<sub>3</sub> reaction is a key driver of pNO<sub>3</sub><sup>-</sup> and SOA formation. Increasing O<sub>3</sub> as nitrogen oxide (NO<sub>x</sub>) emissions decline has increased nighttime NO<sub>3</sub><sup>•</sup> production promoting pNO<sub>3</sub><sup>-</sup> and SOA formation. As NO<sub>x</sub> emissions in South Korea decrease, we see a crossover from NO<sub>x</sub>-saturated to NO<sub>x</sub>-limited conditions for both NO<sub>3</sub><sup>•</sup> formation and pNO<sub>3</sub><sup>-</sup> gas-particle partitioning, explaining the pNO<sub>3</sub><sup>-</sup> decrease after 2019. Further NO<sub>x</sub> and volatile organic compound (VOC) emissions decreases should effectively reduce pNO<sub>3</sub><sup>-</sup> and SOA. Our work shows that the transition between NO<sub>x</sub>-saturated and NO<sub>x</sub>-limited conditions for nighttime pNO<sub>3</sub><sup>-</sup> and SOA formation in urban areas can be readily diagnosed using hourly O<sub>3</sub> and NO<sub>2</sub> observations available from surface networks.

## Non-monotonic winter PM<sub>2.5</sub> trends in South Korea over 2012-2022

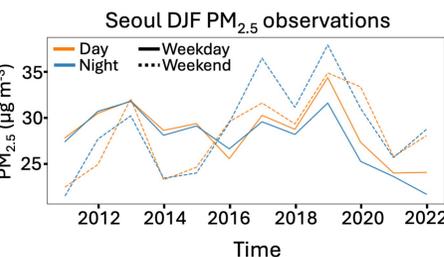
The below figure shows mean December-February (DJF) PM<sub>2.5</sub> in South Korea in 2012 and 2022. Data are from the AirKorea network (2015-22) and from a synthetic PM<sub>2.5</sub> network (2012-2014) described by the "GOCI PM<sub>2.5</sub>" QR code with a random forest trained on AirKorea measurements available for related pollutants including PM<sub>10</sub>.



The first five years of AirKorea PM<sub>2.5</sub> records (2015-19) showed an increase in winter PM<sub>2.5</sub> in the Seoul metropolitan area (SMA) despite local emissions controls as well as controls upwind in China, and no decrease in the annual trend. In the longer record, winter and annual PM<sub>2.5</sub> generally decreases in South Korea.



The 2015-19 SMA increase is most pronounced on weekend nights, as shown below. This data is from a Seoul-specific PM<sub>2.5</sub> network (national PM observations are not available prior to 2015). PM<sub>2.5</sub> decreased sharply in the SMA in 2020 which has been attributed to COVID-19 lockdowns, but this decrease is sustained past the lockdowns implying a more persistent decrease of emissions.



This paper investigates chemical mechanisms that could be responsible.

## Nighttime nitrate radical chemistry in Seoul has accelerated with NO<sub>x</sub> emissions controls, increasing nitrate and organic PM<sub>2.5</sub>

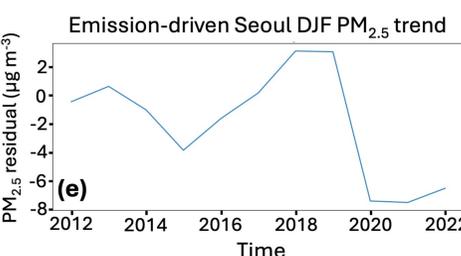
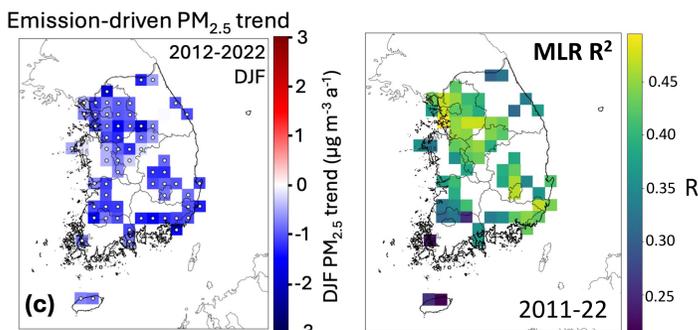
A NO<sub>x</sub> emission threshold is now being crossed in Seoul where further emission controls should effectively decrease PM<sub>2.5</sub>.

This emission threshold can be determined in urban areas worldwide using routine O<sub>3</sub> and NO<sub>x</sub> measurements from air quality networks.

Scan for more about the PM<sub>2.5</sub> product supporting this work (left), and to read our preprint (right)

## Met.-corrected PM<sub>2.5</sub> trends (continued)

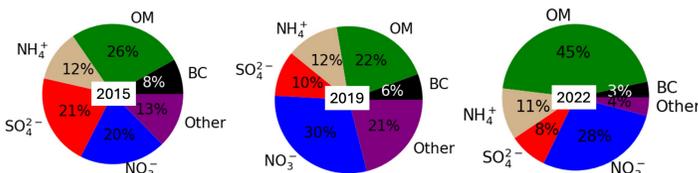
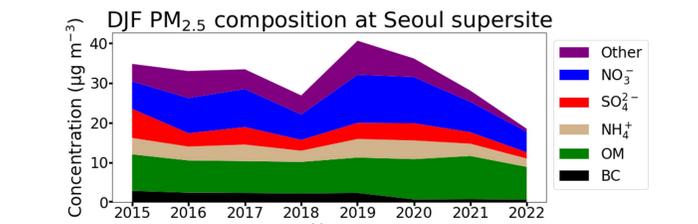
We then subtract the prediction from the observed PM<sub>2.5</sub> and interpret the residual as the emission-driven trend. Winter trends are plotted below along with the MLR R<sup>2</sup>.



Emission changes have driven a mean 1.2 μg m<sup>-3</sup> a<sup>-1</sup> decrease in DJF PM<sub>2.5</sub> that is spatially consistent across the country. However, DJF emission-driven PM<sub>2.5</sub> trends in Seoul showed an increase in 2015-2019 period before dropping in 2020 and remaining low afterwards (below). This 2015-2019 increase is confined to the SMA.

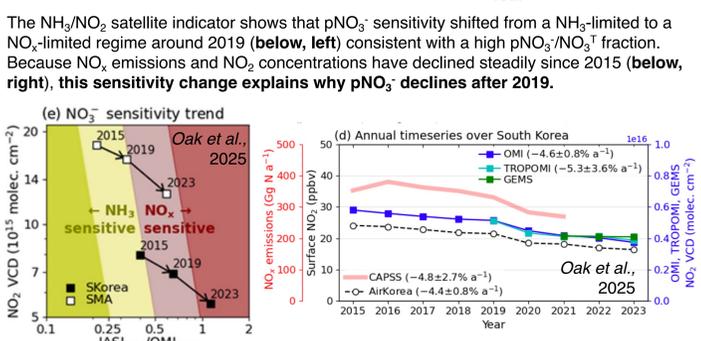
## Trends in observed PM<sub>2.5</sub> composition

We obtain SO<sub>4</sub><sup>2-</sup>, pNO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, organic carbon (OC), and BC data from an ambient ion monitor at the Seoul supersite (37.62°N, 126.93°E). In the 2015-2019 period, reductions in SO<sub>4</sub><sup>2-</sup> in Seoul were more than compensated by increasing pNO<sub>3</sub><sup>-</sup>.



## PM<sub>2.5</sub> nitrate (pNO<sub>3</sub><sup>-</sup>) declines after 2019

We obtain inorganic particle-phase HNO<sub>3</sub> and gas-phase HNO<sub>3</sub> from the Kanghwa site northwest of Seoul. The Kanghwa data show that the fraction of total nitrate (NO<sub>3</sub><sup>-</sup> ≡ HNO<sub>3</sub> + pNO<sub>3</sub><sup>-</sup>) in the particle phase increased from 85% to 95% between 2013 and 2019 (right panel) and remained above 92% after 2019 when Seoul pNO<sub>3</sub><sup>-</sup> begins to decline.



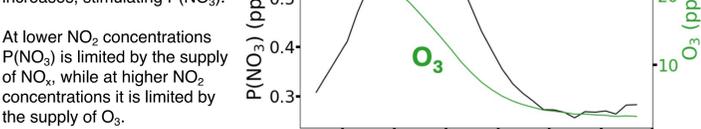
## Nighttime nitrate radical chemistry

The increase of wintertime pNO<sub>3</sub><sup>-</sup> over the 2015-2019 period despite reductions in NO<sub>x</sub> emissions can be explained by increasing in nighttime oxidants, also consistent with SOA resistance to decrease.

At night, pNO<sub>3</sub><sup>-</sup> forms through N<sub>2</sub>O<sub>5</sub> heterogeneous chemistry, shown at left. NO<sub>x</sub> emission is mainly as NO, which is oxidized to NO<sub>2</sub> by O<sub>3</sub>. Subsequent oxidation of NO<sub>2</sub> by NO<sub>3</sub><sup>•</sup> produces the NO<sub>3</sub><sup>•</sup> radical, which can either react with NO<sub>2</sub> to form pNO<sub>3</sub><sup>-</sup> via N<sub>2</sub>O<sub>5</sub> or with VOCs to form SOA. The production rate of the NO<sub>3</sub><sup>•</sup> radical (P(NO<sub>3</sub><sup>•</sup>)) is given below:

$$P(\text{NO}_3) = k[\text{O}_3][\text{NO}_2]; \quad k = 1.4 \times 10^{-13} \exp(-2470/T)$$

At right we show the observed dependence of P(NO<sub>3</sub><sup>•</sup>) on NO<sub>2</sub>.

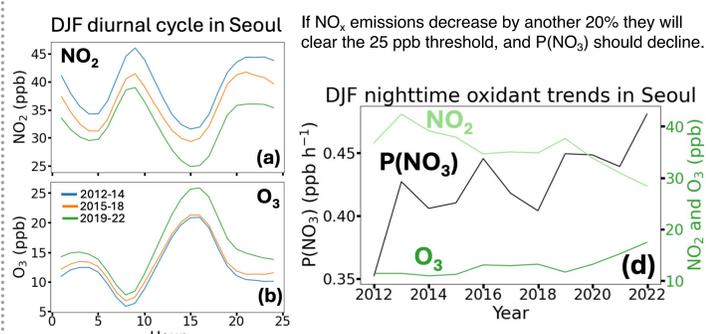


The empirical P(NO<sub>3</sub><sup>•</sup>) maximum is at 25 ppb NO<sub>2</sub>.

## Trends in nitrate radical production

NO<sub>2</sub> has declined over the study period, with nighttime means dropping just below 30 ppb by 2022 (below). This remains in the regime where decreasing NO<sub>2</sub> continues to increase P(NO<sub>3</sub><sup>•</sup>), and indeed P(NO<sub>3</sub><sup>•</sup>) has steadily grown over the 2012-2022 period (below right).

Such growth in P(NO<sub>3</sub><sup>•</sup>) increases the nighttime production of pNO<sub>3</sub><sup>-</sup>, SOA. As NO<sub>2</sub> declines, growing P(NO<sub>3</sub><sup>•</sup>) makes more NO<sub>3</sub><sup>•</sup> available to react with VOCs and form SOA, which may explain why OM is not decreasing while pNO<sub>3</sub><sup>-</sup> is.

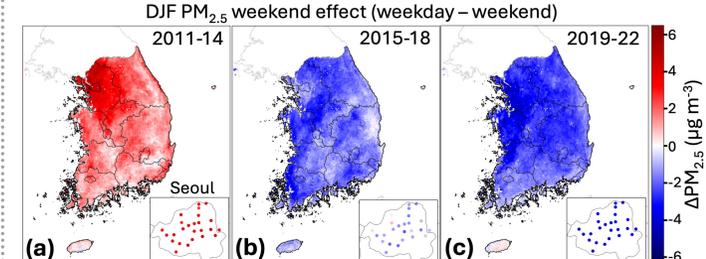


## Nitrate radical influence on PM<sub>2.5</sub> weekend effect and diurnal cycle

Observed O<sub>3</sub> is higher on the weekends than on weekdays over the study period, as would NO<sub>3</sub><sup>•</sup> production. The observed PM<sub>2.5</sub> weekend effect is consistent with the oxidants.

Below we show the difference between weekday and weekend PM<sub>2.5</sub> concentrations in South Korea. We find that after 2015 weekends are more polluted than weekdays in South Korea, with the opposite pattern occurring before 2015. With our AOD-inferred PM<sub>2.5</sub> product we find the weekend transition in 2015 occurred everywhere in South Korea.

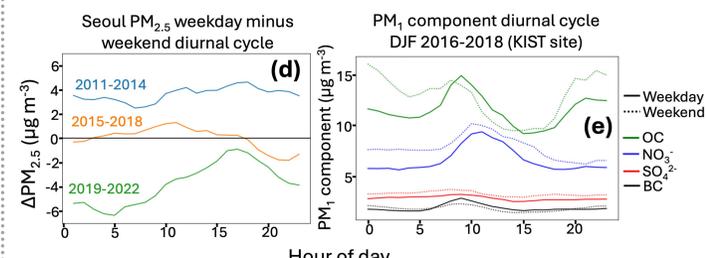
Early air pollution controls targeting primary PM<sub>2.5</sub> emissions from vehicles (OC and BC) would have more effect on weekdays than weekends.



The post-2015 weekend effect is most pronounced at night (i.e., weekends are most polluted than weekdays particularly at night) especially after 2019 (below left). Nighttime production of PM<sub>2.5</sub> has become faster on weekends, consistent with an increase in the secondary component (pNO<sub>3</sub><sup>-</sup>, SOA) driven by the faster production of NO<sub>3</sub><sup>•</sup> radicals at night.

The below right panel shows the diurnal cycle of PM<sub>1</sub> observations in Seoul, indicating that organic aerosols and pNO<sub>3</sub><sup>-</sup> account for the weekend effect and its diurnal cycle.

Nighttime P(NO<sub>3</sub><sup>•</sup>) leading to pNO<sub>3</sub><sup>-</sup> and SOA formation is higher in the residual PBL aloft than the surface because of the lack of O<sub>3</sub> titration; the morning maxima for pNO<sub>3</sub><sup>-</sup> and SOA can be explained by entrainment of this residual PBL air into the growing mixed layer.



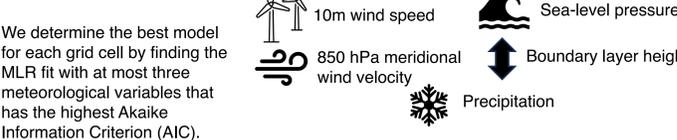
## Acknowledgements and contact

Use the GOCI PM<sub>2.5</sub> data. Acknowledgments. This work was funded by the Samsung PM<sub>2.5</sub> Strategic Research Program and the Harvard-NUIST Joint Laboratory for Air Quality and Climate (JLAQC). DCP was funded in part by a US NSF Graduate Fellowship. Contact: Andrew.Pendergrass@duke.edu. Read the preprint.

## Meteorologically-corrected PM<sub>2.5</sub> trends

To remove meteorological influence and thus capture the long-term trend in PM<sub>2.5</sub> due to emission changes, we use multi-linear regression (MLR) to relate PM<sub>2.5</sub> network data to meteorological fields from ERA5-Land and ERA5, averaging PM<sub>2.5</sub> data on a 0.25°×0.3125° grid. Predictor meteorological variables in the MLR are below.

To construct our MLR model, we deseasonalize and detrend input datasets and then fit the MLR to the PM<sub>2.5</sub> 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).