

1 Wintertime trends of fine particulate matter (PM_{2.5}) in South Korea, 2 2012-2022: response of nitrate and organic components to decreasing 3 NO_x emissions

4 Drew C. Pendergrass¹, Daniel J. Jacob^{1,2}, Yujin J. Oak¹, Ruijun Dang¹, Laura Hyesung Yang¹, Ellie
5 Beaudry¹, Nadia K. Colombi², Shixian Zhai³, Hwajin Kim^{4,5}, Jin-soo Choi⁶, Jin-soo Park⁶, Soontae
6 Kim⁷, Ke Li⁸, and Hong Liao⁸

7 ¹School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.

8 ²Department of Earth and Planetary Science, Harvard University, Cambridge, MA 02138, USA.

9 ³Earth and Environmental Sciences Programme and Graduation Division of Earth and Atmospheric
10 Sciences, Faculty of Science, The Chinese University of Hong Kong, Sha Tin, Hong Kong SAR, China

11 ⁴Department of Environmental Health Sciences, Graduate School of Public Health, Seoul National
12 University, 08826 Seoul, South Korea

13 ⁵Institute of Health and Environment, Graduate School of Public Health, Seoul National University,
14 08826 Seoul, South Korea

15 ⁶Air Quality Research Division, National Institute of Environmental Research, Incheon 22689, South
16 Korea

17 ⁷Department of Environmental and Safety Engineering, Ajou University, Suwon, South Korea.

18 ⁸Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Jiangsu
19 Collaborative Innovation, Center of Atmospheric Environment and Equipment Technology, School of
20 Environmental Science and Engineering, Nanjing University of Information Science and Technology,
21 Nanjing, Jiangsu, China.

22 Correspondence to: Drew C. Pendergrass (pendergrass@g.harvard.edu)

23 **Abstract.** We analyze 2011-2022 trends in wintertime fine particulate matter (PM_{2.5}) and its
24 composition in South Korea. PM_{2.5} concentrations decreased nationwide by 1.2 μg m⁻³ a⁻¹ after
25 correcting for meteorology. However, Seoul PM_{2.5} only declines after 2019 and has shifted toward
26 particulate nitrate (pNO₃⁻) and secondary organic aerosol (SOA) which have been resistant to decrease.
27 Surface nitrogen dioxide (NO₂) and ozone (O₃) trends including weekday versus weekend suggest
28 nighttime formation of the nitrate radical (NO₃) from the NO₂ + O₃ reaction is a key driver of pNO₃⁻ and
29 OA formation. Increasing O₃ as nitrogen oxide (NO_x) emissions decline has increased NO₃ production
30 promoting pNO₃⁻ and SOA formation. As NO_x emissions in South Korea decrease, we see a crossover
31 from NO_x-saturated to NO_x-limited conditions for both NO₃ formation and pNO₃⁻ gas-particle
32 partitioning, explaining the pNO₃⁻ decrease after 2019. Further NO_x and volatile organic compound
33 (VOC) emissions decreases should reduce pNO₃⁻ and SOA.

34

35 **Plain language summary.** Fine particulate matter (PM_{2.5}) is a severe air pollution problem in South
36 Korea and is worst in winter. Strong local emissions controls and emissions reductions upwind have led

37 winter PM_{2.5} to decline throughout South Korea. However, PM_{2.5} around Seoul (where half the
38 population lives) has been resistant to decrease and only declined after 2019. With an ensemble of
39 surface observations augmented by machine learning, we find that PM_{2.5} composition in Seoul has
40 shifted toward two kinds of secondary PM_{2.5}, meaning that they are formed in the atmosphere through
41 chemical reactions rather than emitted directly, and that these species are both resistant to decrease.
42 Both species, particulate nitrate (pNO₃⁻) and secondary organic aerosol (SOA), can be formed by
43 nighttime chemistry. We find that as nitrogen oxide (NO_x) pollution (largely from combustion) has
44 declined due to emissions controls, this nighttime chemistry accelerates and increases the formation of
45 pNO₃⁻ and SOA. However, pNO₃⁻ appears to have begun responding to NO_x controls after 2019 and we
46 propose a physical driver of this decrease. We argue that further decreases in NO_x combined with
47 reductions in emissions of volatile organic compounds should drive faster pNO₃⁻ reductions and also
48 SOA reductions because the nighttime chemistry may decelerate.

49

50 **Key points.**

- 51 • Fine particulate matter (PM_{2.5}) has declined throughout South Korea due to emissions controls
52 but only decreases in Seoul after 2019
- 53 • Nighttime nitrate radical chemistry in Seoul accelerated with nitrogen oxide emissions controls,
54 increasing nitrate and organic PM_{2.5}
- 55 • Nitrate radical and nitrate PM_{2.5} chemistry are increasingly sensitive to nitrogen oxide emissions
56 and its decrease should improve PM_{2.5}

57 **1 Introduction**

58 Fine particulate matter less than 2.5 μm in diameter (PM_{2.5}) is a leading cause of mortality, responsible
59 in South Korea for 34,000 annual deaths (Y.-H. Lim et al., 2020; N. R. Kim & Lee, 2024; Oh et al.,
60 2024). PM_{2.5} concentrations in South Korea have decreased over the past decade (Pendergrass et al.,
61 2022, 2025), driven by domestic pollution controls (Joo, 2018; Ministry of the Environment, 2019) and
62 by reduced transport from China where pollution controls have driven PM_{2.5} declines as well (Zhai et
63 al., 2019). However, wintertime PM_{2.5} in South Korea remains high and particularly in the Seoul
64 Metropolitan Area (SMA), where over half of the population lives. PM_{2.5} is highest in winter and early
65 spring because of suppressed vertical mixing, long-range transport, and local emissions (H. Kim et al.,
66 2017; Lee et al., 2024; E. Kim et al., 2025; Kwon et al., 2025).

67 PM_{2.5} can be emitted directly (primary) or can be formed in the atmosphere following oxidation
68 of precursor gases (secondary). PM_{2.5} mass concentrations have been monitored hourly by the AirKorea
69 surface network beginning in 2015, while oxidants including nitrogen dioxide (NO₂) and ozone (O₃)
70 have been monitored since 2001. PM_{2.5} speciation has also been measured at six supersites since 2015
71 (Kumar et al., 2021; NIER, 2022). The data show rapid decrease of black carbon (BC) and sulfate
72 (SO₄²⁻) PM_{2.5} components, while particulate nitrate (pNO₃⁻) and secondary organic aerosol (SOA)
73 contribute an increasing fraction of PM_{2.5} mass (Y. Kim et al., 2020; Lee et al., 2024). The decreases of
74 BC and SO₄²⁻ are consistent with decreasing primary emission from fuel combustion and decreasing
75 emission of sulfur dioxide (SO₂) (E. Kim et al., 2025). pNO₃⁻ and SOA originate from emissions of

76 nitrogen oxides (NO_x) and volatile organic compounds (VOCs), respectively. NO_x emissions in South
77 Korea (mainly from fuel combustion) decreased by 30% over the 2015-2023 period while VOC
78 emissions have been flat (Oak et al., 2025).

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

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

94 **2 Data and methods**

95 We use hourly 2015-22 $\text{PM}_{2.5}$ and 2012-22 NO_2 and O_3 data from the AirKorea surface network
96 (<https://www.airkorea.or.kr/>). We supplement the national network data with 2012-2014 hourly $\text{PM}_{2.5}$
97 data collected at 25 sites in the city of Seoul by the Seoul Research Institute of Public Health and
98 Environment (NIER, 2022). Outside of Seoul between 2012 and 2014, we use the synthetic $\text{PM}_{2.5}$
99 network produced by Pendergrass et al. (2025) with a random forest (RF) algorithm trained on
100 AirKorea measurements available for related pollutants including PM_{10} . We also use a daily continuous
101 $\text{PM}_{2.5}$ product produced using aerosol optical depth (AOD) data from the GOCI geostationary satellite
102 (Pendergrass et al., 2025).

103 $\text{PM}_{2.5}$ composition measurements are sparse in South Korea. We obtain SO_4^{2-} , pNO_3^- , NH_4^+ ,
104 organic carbon (OC), and BC data from an ambient ion monitor at the Seoul supersite (37.62°N,
105 126.93°E) managed by the National Institute for Environmental Research (NIER). We obtain inorganic
106 particle-phase (SO_4^{2-} , pNO_3^- , and NH_4^+) and gas-phase (HNO_3 and NH_3) components from the
107 Kanghwa site (37.71°N, 126.27°E) of the Acid Deposition Monitoring Network in East Asia (EANET).
108 Kanghwa is an agricultural island northwest of Seoul. We analyze diurnal variability in PM_1
109 composition data from an aerosol mass spectrometer deployed in 2016-2018 at the Korea Institute of
110 Science and Technology (KIST) in northeast Seoul (37.60°N, 127.05°E) (H. Kim et al., 2017).

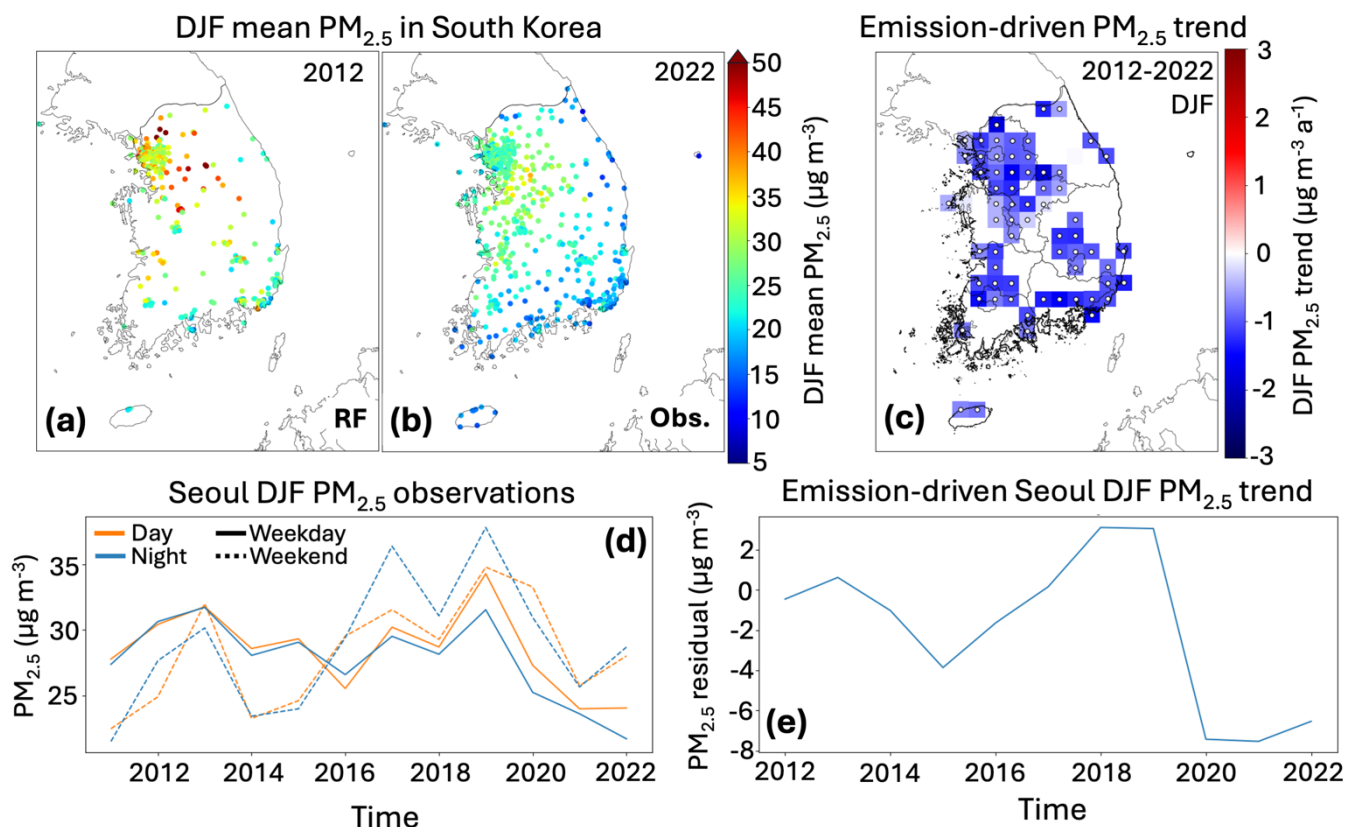
111 Meteorology plays a substantial role in controlling interannual variability in $\text{PM}_{2.5}$ (Koo et al.,
112 2020; Jeong et al., 2024). To remove meteorological influence and thus capture the long-term trend in
113 $\text{PM}_{2.5}$ due to emission changes, we use multi-linear regression (MLR) to relate AirKorea and synthetic
114 $\text{PM}_{2.5}$ network data to meteorological fields from the ECMWF hourly $9 \times 9 \text{ km}^2$ resolution ERA5-Land

115 replay of the ERA5 global reanalysis and hourly $30\times 30\text{ km}^2$ from ERA5 (Hersbach et al., 2020; Muñoz-
116 Sabater et al., 2021). To increase statistical robustness, we only use sites with continuous 2011-22
117 records and average the data on a $0.25^\circ\times 0.3125^\circ$ grid (Shen et al., 2017; Tai et al., 2010; Zhai et al.,
118 2019). Predictor meteorological variables in the MLR include boundary layer height, mean sea-level
119 pressure, precipitation, 2 m temperature, 10 m wind speed, 2 m relative humidity (RH), and 850 hPa
120 meridional wind velocity, which have been identified in previous studies to correlate with $\text{PM}_{2.5}$ in the
121 region (Leung et al., 2018; Pendergrass et al., 2019; Zhai et al., 2019). To construct our MLR model, we
122 follow the methodology of Zhai et al. (2019) by deseasonalizing and detrending input datasets and then
123 fitting the MLR to the $\text{PM}_{2.5}$ observations. We determine the best model for each grid cell by finding the
124 MLR fit with at most three meteorological variables that has the highest Akaike Information Criterion
125 (AIC) value (Akaike, 1974). We then subtract the prediction from the observed $\text{PM}_{2.5}$ and use the
126 residual to obtain emission-driven trends (Zhai et al., 2019). The Pearson's correlation coefficient of the
127 MLR model with 24-h $\text{PM}_{2.5}$ observations in $0.25^\circ\times 0.3125^\circ$ grid cells ranges between 0.41 and 0.72
128 with a median value of 0.60, in line with previous studies (Tai et al., 2010; Zhai et al., 2019).

129 **3 Results and discussion**

130 Figure 1 shows mean DJF $\text{PM}_{2.5}$ in South Korea in 2012 and 2022, together with emission-driven
131 trends. Emission changes have driven a $1.2\text{ }\mu\text{g m}^{-3}\text{ a}^{-1}$ decrease in DJF $\text{PM}_{2.5}$ that is spatially consistent
132 across the country. Although emissions of precursor species SO_2 and NO_x have declined steadily and
133 nationwide throughout the study period (Oak et al., 2025), DJF emission-driven $\text{PM}_{2.5}$ trends in Seoul
134 showed an increase in the 2015-2019 period before dropping in 2020 and remaining low afterwards
135 (Figure 1e). This 2015-2019 increase is confined to the SMA (Pendergrass et al., 2022) and is most
136 pronounced on weekend nights (Figure 1d). The impact of COVID-19 lockdowns is not manifest in the
137 overall $\text{PM}_{2.5}$ trends (Pendergrass et al., 2025).

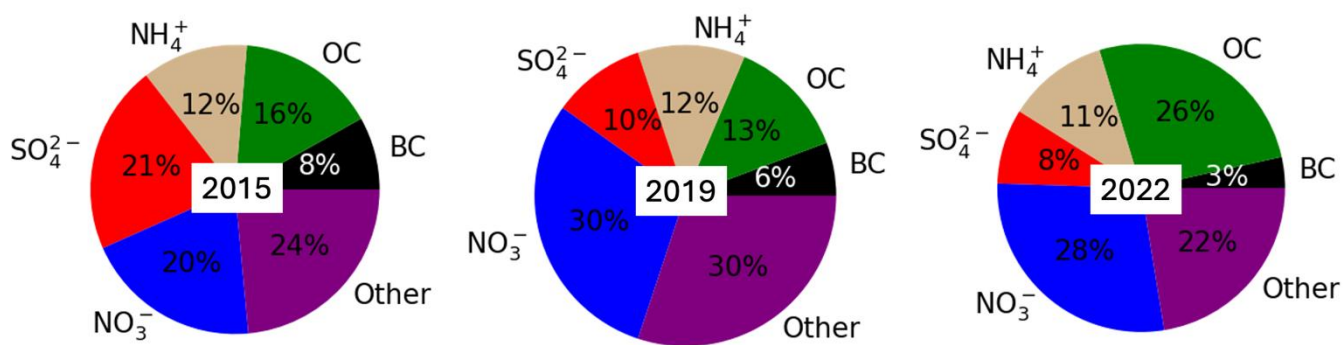
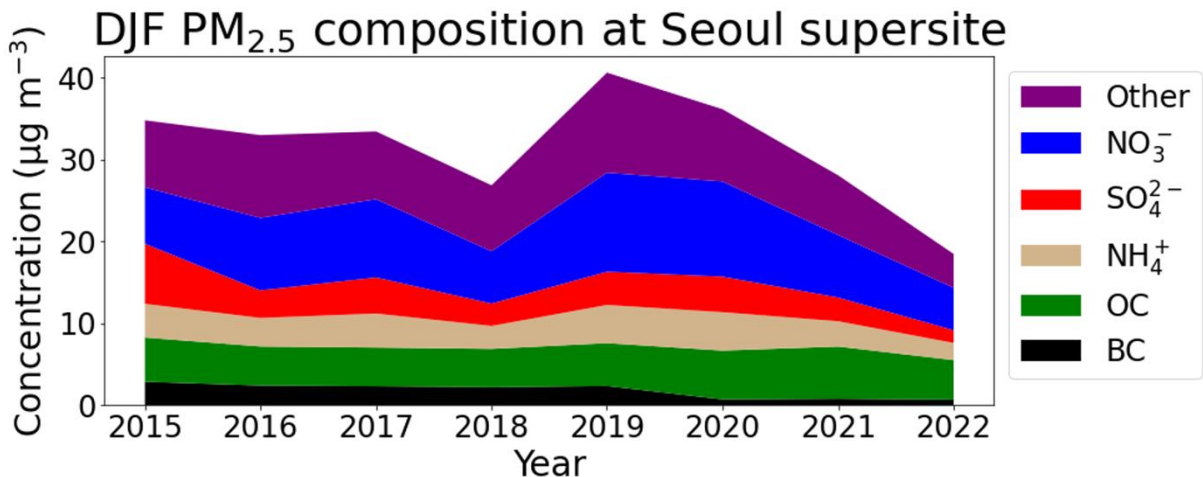
138



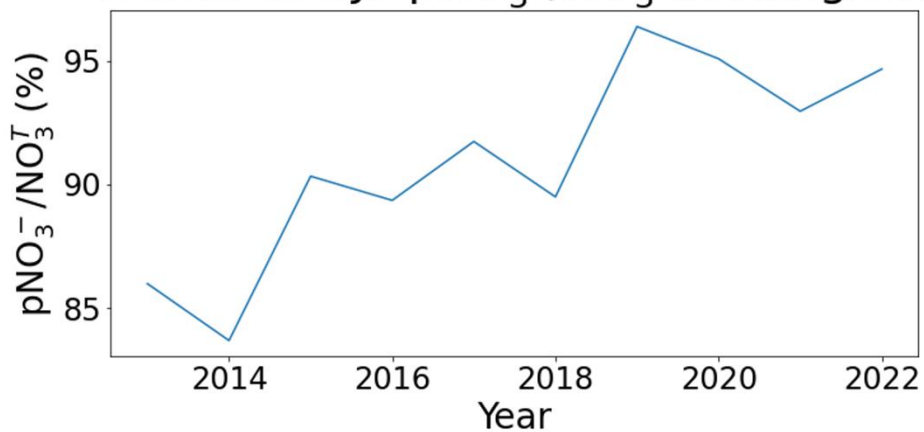
139
 140 Figure 1: DJF PM_{2.5} and trends in South Korea. Panels (a) and (b) show DJF mean PM_{2.5} at AirKorea
 141 surface stations in (a) 2012 and (b) 2022. PM_{2.5} monitoring at these stations started in 2015, and data for
 142 2012 is from a synthetic PM_{2.5} network produced using a random forest (RF) algorithm applied to the
 143 station data including PM₁₀ (Pendergrass et al., 2025). Panel (c) shows the DJF emission-driven trend in
 144 PM_{2.5} after removing meteorological influence with a multi-linear regression (MLR) fit. Panel (d)
 145 shows observed DJF PM_{2.5} averaged over 25 sites in the city of Seoul, disaggregated into daytime (8-18
 146 LT) and nighttime (22-5 LT) for weekdays and weekends. Panel (e) shows the emission-driven PM_{2.5}
 147 timeseries (residual from the meteorological MLR model) for the Seoul 0.25°×0.3125° grid cell
 148 (centered at 37.5°N,127.0°E) and averaging data from 37 sites.

149
 150 In the 2015-2019 period, reductions in SO₄²⁻ in Seoul were more than compensated by
 151 increasing pNO₃⁻ (Figure 2, top panel), but pNO₃⁻ grew faster than simple acid substitution for SO₄²⁻.
 152 The Kangwha data show that the fraction of total nitrate (NO₃^T≡HNO₃+pNO₃⁻) in the particle phase
 153 increased from 85% to 95% between 2013 and 2019 (Figure 2, bottom panel). The pNO₃⁻/NO₃^T fraction
 154 remained above 92% after 2019 when Seoul pNO₃⁻ begins to decline. The NH₃/NO₂ satellite indicator
 155 (Dang et al., 2023, 2024) shows that pNO₃⁻ sensitivity shifted from a NH₃-limited to a NO_x-limited
 156 regime around 2019 (Oak et al., 2025), consistent with a high pNO₃⁻/NO₃^T fraction. OC has both
 157 primary and secondary (SOA) components (Brewer et al., 2023), did not decrease over the 2015-2022
 158 period, and by 2022 comprised a similar fraction of PM_{2.5} as pNO₃⁻ (Figure 2, middle panel), while BC

159 declined substantially. Other contributions to PM_{2.5} mass include sea salt, dust, and metals, which show
 160 a decline in the later phase of the record. Dust emissions from construction and road traffic have been
 161 decreasing rapidly in South Korea (Zhai et al., 2023).
 162



Trends in DJF $\text{pNO}_3^- / \text{NO}_3^T$ at Kanghwa



163

164 Figure 2: Wintertime PM_{2.5} speciation at the Seoul supersite (37.62°N, 126.93°E) and pNO₃⁻/NO₃^T gas-
 165 particle fractionation at the Kanghwa EANET site NW of Seoul (37.71°N, 126.27°E), where
 166 NO₃^T≡HNO₃+pNO₃⁻ is total (gas + particle) nitrate. Contributions to PM_{2.5} mass labeled as “Other”
 167 include sea salt, dust, and metals. Values are DJF seasonal means.

168

169

170 The increase of wintertime pNO₃⁻ over the 2015-2019 period despite reductions in NO_x
 171 emissions can be explained in part by an increase in nighttime oxidants, which would also explain an
 172 increase in SOA. At night, pNO₃⁻ mainly forms through N₂O₅ heterogeneous chemistry, as described in
 173 the mechanism below. NO_x emission is mainly as NO, which is oxidized to NO₂ by (R1). Subsequent
 174 oxidation of NO₂ by O₃ produces the NO₃ radical, which can either react with NO₂ to form pNO₃⁻ via
 175 N₂O₅ or with VOCs to form SOA:

176



177 The mechanism operates only at night because NO₃ photolyzes on a time scale of a minute in the
 178 daytime.

179 Figure 3ab shows 2012-2022 trends and diurnal variations of NO₂ and O₃ concentrations in
 180 Seoul. Decrease in NO_x emissions drives a decrease in nighttime NO₂ concentrations over the 2012-
 181 2022 period but an increase in nighttime O₃ concentrations. When NO₂ is observed to be in excess of 50
 182 ppb, O₃ is titrated by reaction (R1) (Figure 3c) and NO₃ production by reaction (R2) cannot take place.
 183 As NO₂ drops to lower concentrations, O₃ increases rapidly which stimulates NO₃ production. We
 184 calculate the NO₃ production rate P(NO₃) from the rate of reaction (R2) (Atkinson et al., 2004; H. Wang
 185 et al., 2021, 2023; Y. Wang et al., 2023):

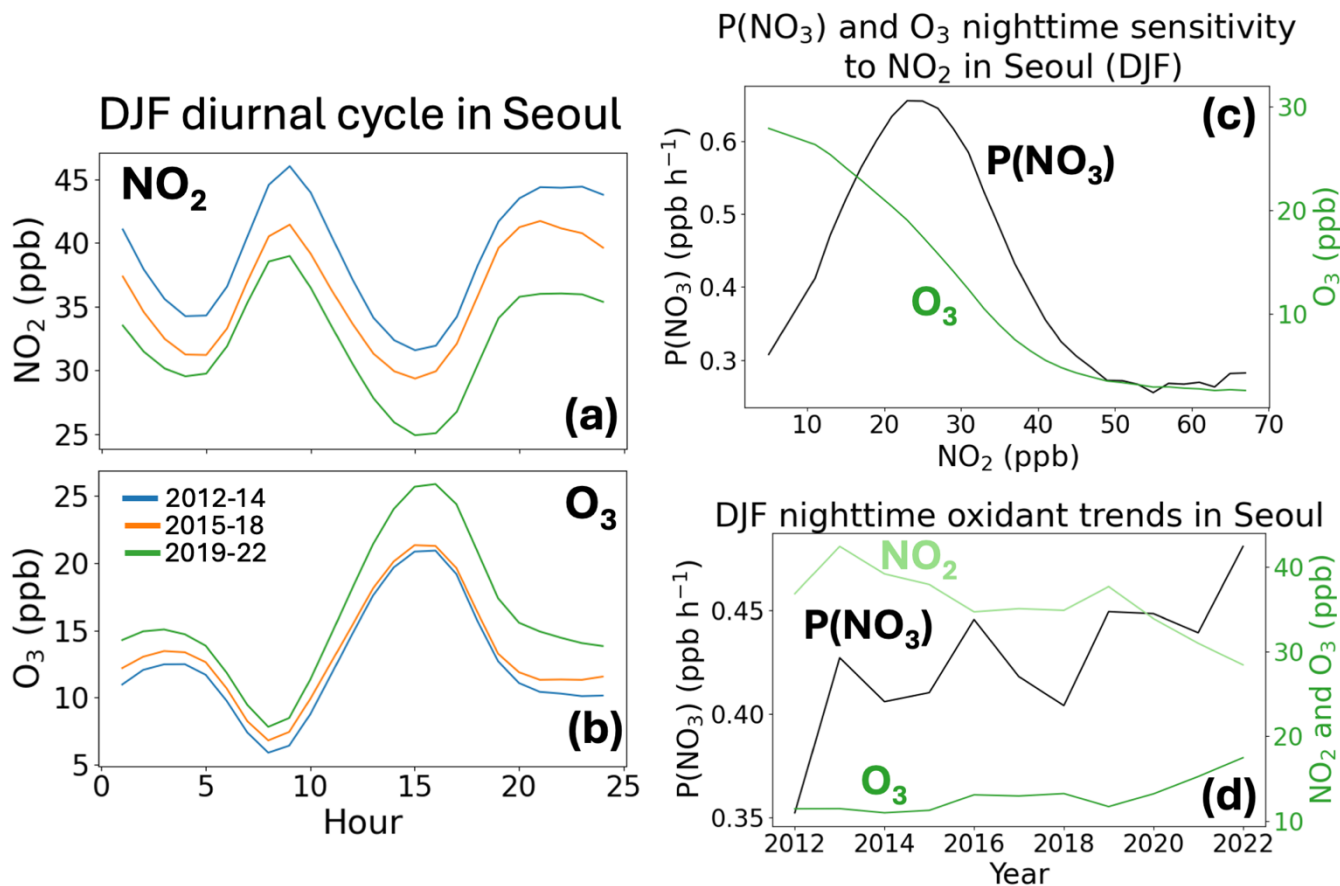
186

$$P(\text{NO}_3) = k[\text{O}_3][\text{NO}_2]; \quad k = 1.4 \times 10^{-13} \exp(-2470/T) \quad (\text{1})$$

187

188 Plotting P(NO₃) versus the NO₂ concentrations indicates a sharp maximum for 25 ppb NO₂ (Figure 3c).
 189 At lower NO₂ concentrations P(NO₃) is limited by the supply of NO_x, while at higher NO₂
 190 concentrations it is limited by the supply of O₃.

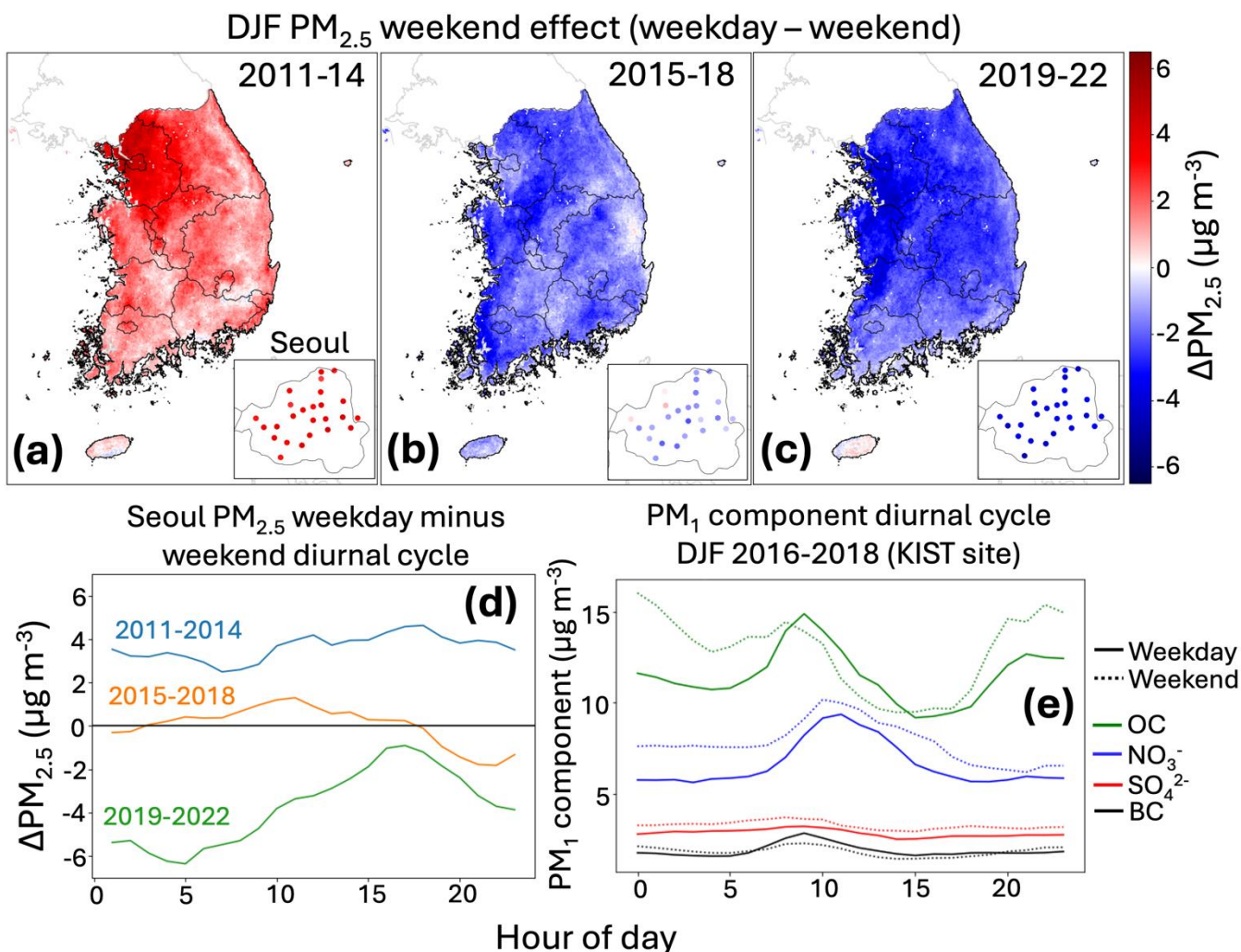
191



192
 193 Figure 3: Mean diurnal and nighttime (22-05 LT) trends of oxidants in Seoul in winter (DJF). Values
 194 are averages for the 25 AirKorea surface sites in Seoul with continuous 2012-2022 records. Left panels
 195 show the average diurnal cycles of (a) NO₂ and (b) O₃ concentrations aggregated for the 2012-2014,
 196 2015-2018, and 2019-2022 periods. Panel (c) shows mean nighttime O₃ concentrations and production
 197 rates of the nitrate radical P(NO₃) binned as a function of NO₂ concentrations (2 ppb bins). P(NO₃) is
 198 calculated from equation (1). Panel (d) shows 2012-2022 trends of nighttime NO₂ and O₃,
 199 concentrations, and P(NO₃)

200 Declining NO_x emissions has led to decreases in NO₂ with nighttime mean values in Seoul
 201 dropping just below 30 ppb by 2022 (Figure 3d). This remains in the regime where decreasing NO₂
 202 continues to increase P(NO₃), and indeed P(NO₃) has steadily grown over the 2012-2022 period (Figure
 203 3d). Such growth in P(NO₃) increases the nighttime production of pNO₃⁻, SOA, and organonitrates
 204 that may hydrolyze to pNO₃⁻ (Farmer et al., 2010; Fisher et al., 2016; Kiendler-Scharr et al., 2016; Ng et al.,
 205 2017; H. Wang et al., 2021, 2023; Y. Wang et al., 2023). As NO₂ declines, growing P(NO₃) makes
 206 more NO₃ available to react with VOCs and form SOA (R4), which may explain why OC is not
 207 decreasing while pNO₃⁻ is. NO₂ concentrations in the SMA decline in sync with NO_x emissions (Oak et
 208 al., 2025), and if NO_x emissions decrease by another 20% they will clear the 25 ppb threshold below
 209 which P(NO₃) should decline rapidly to decrease both pNO₃⁻ and SOA.

210 Further evidence of this oxidant limitation is apparent in the difference between weekdays and
211 weekends. O_3 is higher on the weekends than on weekdays over the study period, a result of titration by
212 vehicle NO emissions and VOC-saturated conditions. The $PM_{2.5}$ data show a weekend effect consistent
213 with the oxidants. Figure 4 shows the DJF 2012-2022 trend in the difference between weekday and
214 weekend $PM_{2.5}$ concentrations in South Korea for an AOD-inferred $PM_{2.5}$ product (Pendergrass et al.
215 2025) and for direct measurements of $PM_{2.5}$ within Seoul. Use of the AOD-inferred $PM_{2.5}$ product
216 allows us to go back to before 2015 outside of Seoul. Previous work has observed a weekend effect in
217 Seoul and in some Chinese cities where $PM_{2.5}$ levels are higher on weekends than weekdays as would
218 be driven by higher oxidant levels (Choi et al., 2022; Y. Wang et al., 2019; Zhao et al., 2018). But we
219 find that the opposite in South Korea for the period prior to 2015, with weekdays more polluted by
220 weekends, and with our AOD-inferred $PM_{2.5}$ product we also find that the weekend effect transition in
221 2015 occurred everywhere in South Korea. Early air pollution controls targeting primary $PM_{2.5}$
222 emissions from vehicles (OC and BC) would have more effect on weekdays than weekends, and indeed
223 the BC fraction of $PM_{2.5}$ in Seoul declined from 14% in 2003 to less than 3% by 2017 (Y. Kim et al.,
224 2020).



225
 226 Figure 4: Wintertime (DJF) PM_{2.5} weekend effect in South Korea. $\Delta PM_{2.5}$ denotes the difference
 227 between mean weekday and weekend PM_{2.5} concentrations. Panels (a) through (c) show maps of
 228 $\Delta PM_{2.5}$ for (a) 2011-2014, (b) 2015-2018, and (c) 2019-2022, where red (positive $\Delta PM_{2.5}$) indicates that
 229 weekdays are more polluted than weekends. PM_{2.5} concentrations are inferred using machine learning
 230 from geostationary satellite AOD data (Pendergrass et al., 2025), except for Seoul (inset) where direct
 231 continuous measurements are available from sites through the 2011-2022 period. Panel (d) shows the
 232 diurnal variation of $\Delta PM_{2.5}$ in Seoul for 2011-2014, 2015-2018, and 2019-2022. Panel (e) shows the
 233 diurnal cycle of PM₁ composition observed at the KIST site in Seoul for 2016-2018 (H. Kim et al.,
 234 2017).

235
 236 Figure 4d shows that the post-2015 weekend effect is most pronounced at night (i.e. weekends
 237 are most polluted than weekdays particularly at night) especially after 2019. This means that nighttime
 238 production of PM_{2.5} has become faster on weekends, consistent with an increase in the secondary

239 component (pNO_3^- , SOA) driven by the faster production of NO_3 radicals at night. Figure 4e shows the
240 diurnal cycle of PM_{10} observations available for DJF 2016-2018 in Seoul (H. Kim et al., 2017),
241 indicating that organic aerosols and pNO_3^- account for the weekend effect and its diurnal cycle.

242 In summary, we analyzed 2012-2022 trends in wintertime (DJF) $\text{PM}_{2.5}$ and its composition in
243 South Korea using surface observations interpreted with statistical methods and machine learning.
244 Declining anthropogenic emissions have led DJF mean $\text{PM}_{2.5}$ to decrease at a rate of $1.2 \mu\text{g m}^{-3} \text{a}^{-1}$ in
245 South Korea but with significant variability including a 2015-2019 increase in Seoul driven by
246 particulate nitrate (pNO_3^-) even as NO_x emissions decreased. pNO_3^- and organic aerosol now contribute
247 over half of total $\text{PM}_{2.5}$. pNO_3^- would not respond to NO_x emission controls if its formation was limited
248 by the supply of NH_3 , but EANET observations of total (gas + particulate) nitrate indicates a switch to
249 NO_x -limited conditions during the 2010s. A major factor driving increased pNO_3^- and secondary
250 organic aerosol (SOA) formation as NO_x emissions decrease is the nighttime formation of the nitrate
251 radical (NO_3), which increases due to weaker titration of O_3 . Using AirKorea hourly network
252 observations of NO_2 and O_3 , we show that the nighttime NO_3 production rate $P(\text{NO}_3)$ in Seoul increased
253 rapidly over the 2012-2022 period. We see evidence for a resulting nighttime increase in pNO_3^- and
254 SOA formation by comparing weekend versus weekday concentrations and their trends. We infer from
255 the AirKorea observations a 25 ppb NO_2 threshold below which $P(\text{NO}_3)$ should begin to decrease
256 rapidly as NO_x emissions decrease. NO_2 concentrations in Seoul in 2019-2022 were approaching that
257 threshold, implying that further NO_x emission reductions should accrue immediate benefits for reducing
258 pNO_3^- and SOA and therefore total $\text{PM}_{2.5}$.

259 Acknowledgements

260 This work was funded by the Harvard-NUIST Joint Laboratory for Air Quality and Climate (JLAQC)
261 and the Samsung $\text{PM}_{2.5}$ Strategic Research Program. DCP was funded in part by a US National Science
262 Foundation Graduate Fellowship.

263 References

- 264
265 Akaike, H. (1974). A new look at the statistical model identification. *IEEE Transactions on Automatic*
266 *Control*, 19(6), 716–723. <https://doi.org/10.1109/TAC.1974.1100705>
- 267 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E.,
268 Rossi, M. J., & Troe, J. (2004). Evaluated kinetic and photochemical data for atmospheric
269 chemistry: Volume I - gas phase reactions of O_x , HO_x , NO_x and SO_x species. *Atmospheric*
270 *Chemistry and Physics*, 4(6), 1461–1738. <https://doi.org/10.5194/acp-4-1461-2004>
- 271 Bae, C., Kim, B.-U., Kim, H. C., Yoo, C., & Kim, S. (2020). Long-Range Transport Influence on Key
272 Chemical Components of $\text{PM}_{2.5}$ in the Seoul Metropolitan Area, South Korea, during the Years
273 2012–2016. *Atmosphere*, 11(1), Article 1. <https://doi.org/10.3390/atmos11010048>
- 274 Brewer, J. F., Jacob, D. J., Jathar, S. H., He, Y., Akherati, A., Zhai, S., Jo, D. S., Hodzic, A., Nault, B.
275 A., Campuzano-Jost, P., Jimenez, J. L., Park, R. J., Oak, Y. J., & Liao, H. (2023). A Scheme for

- 276 Representing Aromatic Secondary Organic Aerosols in Chemical Transport Models: Application
277 to Source Attribution of Organic Aerosols Over South Korea During the KORUS-AQ
278 Campaign. *Journal of Geophysical Research: Atmospheres*, 128(8), e2022JD037257.
279 <https://doi.org/10.1029/2022JD037257>
- 280 Choi, W., Ho, C.-H., Heo, J.-W., Kim, K.-Y., Kim, S.-W., & Kim, J. (2022). Recent Air Quality
281 Deterioration on Weekends in Seoul, South Korea: A Focus on External Contribution. *Asia-
282 Pacific Journal of Atmospheric Sciences*. <https://doi.org/10.1007/s13143-022-00287-0>
- 283 Colombi, N. K., Jacob, D. J., Yang, L. H., Zhai, S., Shah, V., Grange, S. K., Yantosca, R. M., Kim, S.,
284 & Liao, H. (2023). Why is ozone in South Korea and the Seoul metropolitan area so high and
285 increasing? *Atmospheric Chemistry and Physics*, 23(7), 4031–4044. [https://doi.org/10.5194/acp-
23-4031-2023](https://doi.org/10.5194/acp-
286 23-4031-2023)
- 287 Dang, R., Jacob, D. J., Zhai, S., Coheur, P., Clarisse, L., Van Damme, M., Pendergrass, D. C., Choi, J.,
288 Park, J., Liu, Z., & Liao, H. (2023). Diagnosing the Sensitivity of Particulate Nitrate to
289 Precursor Emissions Using Satellite Observations of Ammonia and Nitrogen Dioxide.
290 *Geophysical Research Letters*, 50(24), e2023GL105761. <https://doi.org/10.1029/2023GL105761>
- 291 Dang, R., Jacob, D. J., Zhai, S., Yang, L. H., Pendergrass, D. C., Coheur, P., Clarisse, L., Van Damme,
292 M., Choi, J., Park, J., Liu, Z., Xie, P., & Liao, H. (2024). A Satellite-Based Indicator for
293 Diagnosing Particulate Nitrate Sensitivity to Precursor Emissions: Application to East Asia,
294 Europe, and North America. *Environmental Science & Technology*.
295 <https://doi.org/10.1021/acs.est.4c08082>
- 296 Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., & Jimenez,
297 J. L. (2010). Response of an aerosol mass spectrometer to organonitrates and organosulfates and
298 implications for atmospheric chemistry. *Proceedings of the National Academy of Sciences*,
299 107(15), 6670–6675. <https://doi.org/10.1073/pnas.0912340107>
- 300 Fisher, J. A., Jacob, D. J., Travis, K. R., Kim, P. S., Marais, E. A., Chan Miller, C., Yu, K., Zhu, L.,
301 Yantosca, R. M., Sulprizio, M. P., Mao, J., Wennberg, P. O., Crouse, J. D., Teng, A. P.,
302 Nguyen, T. B., St. Clair, J. M., Cohen, R. C., Romer, P., Nault, B. A., ... Mikoviny, T. (2016).
303 Organic nitrate chemistry and its implications for nitrogen budgets in an isoprene- and
304 monoterpene-rich atmosphere: Constraints from aircraft (SEAC⁴RS) and ground-based (SOAS)
305 observations in the Southeast US. *Atmospheric Chemistry and Physics*, 16(9), 5969–5991.
306 <https://doi.org/10.5194/acp-16-5969-2016>
- 307 Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horányi, A., Muñoz-Sabater, J., Nicolas, J., Peubey,
308 C., Radu, R., Schepers, D., Simmons, A., Soci, C., Abdalla, S., Abellan, X., Balsamo, G.,
309 Bechtold, P., Biavati, G., Bidlot, J., Bonavita, M., ... Thépaut, J.-N. (2020). The ERA5 global
310 reanalysis. *Quarterly Journal of the Royal Meteorological Society*, 146(730), 1999–2049.
311 <https://doi.org/10.1002/qj.3803>
- 312 Hu, H., Wang, H., Lu, K., Wang, J., Zheng, Z., Xu, X., Zhai, T., Chen, X., Lu, X., Fu, W., Li, X., Zeng,
313 L., Hu, M., Zhang, Y., & Fan, S. (2023). Variation and trend of nitrate radical reactivity towards
314 volatile organic compounds in Beijing, China. *Atmospheric Chemistry and Physics*, 23(14),
315 8211–8223. <https://doi.org/10.5194/acp-23-8211-2023>
- 316 Jeong, J. I., Park, R. J., Song, C.-K., Yeh, S.-W., & Woo, J.-H. (2024). Quantitative analysis of winter
317 PM_{2.5} reduction in South Korea, 2019/20 to 2021/22: Contributions of meteorology and

318 emissions. *Science of The Total Environment*, 907, 168179.
319 <https://doi.org/10.1016/j.scitotenv.2023.168179>

320 Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prevot, A. S. H., Äijälä, M.,
321 Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall'Osto, M., Day, D. A.,
322 De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., ... Wu, H.-C. (2016).
323 Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol.
324 *Geophysical Research Letters*, 43(14), 7735–7744. <https://doi.org/10.1002/2016GL069239>

325 Kim, B.-U., Bae, C., Kim, H. C., Kim, E., & Kim, S. (2017). Spatially and chemically resolved source
326 apportionment analysis: Case study of high particulate matter event. *Atmospheric Environment*,
327 162, 55–70. <https://doi.org/10.1016/j.atmosenv.2017.05.006>

328 Kim, E., Jeong, S., Kang, Y.-H., Myung, M., & Kim, S. (2025). Influence of top-down adjusted upwind
329 emissions on PM_{2.5} concentrations: The case of long-range transport in South Korea.
330 *Environmental Pollution*, 368, 125799. <https://doi.org/10.1016/j.envpol.2025.125799>

331 Kim, H., Zhang, Q., Bae, G.-N., Kim, J. Y., & Lee, S. B. (2017). Sources and atmospheric processing of
332 winter aerosols in Seoul, Korea: Insights from real-time measurements using a high-resolution
333 aerosol mass spectrometer. *Atmospheric Chemistry and Physics*, 17(3), 2009–2033.
334 <https://doi.org/10.5194/acp-17-2009-2017>

335 Kim, N. R., & Lee, H. J. (2024). Ambient PM_{2.5} exposure and rapid population aging: A double threat
336 to public health in the Republic of Korea. *Environmental Research*, 252, 119032.
337 <https://doi.org/10.1016/j.envres.2024.119032>

338 Kim, Y., Yi, S.-M., & Heo, J. (2020). Fifteen-year trends in carbon species and PM_{2.5} in Seoul, South
339 Korea (2003–2017). *Chemosphere*, 261, 127750.
340 <https://doi.org/10.1016/j.chemosphere.2020.127750>

341 Koo, J.-H., Kim, J., Lee, Y. G., Park, S. S., Lee, S., Chong, H., Cho, Y., Kim, J., Choi, K., & Lee, T.
342 (2020). The implication of the air quality pattern in South Korea after the COVID-19 outbreak.
343 *Scientific Reports*, 10(1), 22462. <https://doi.org/10.1038/s41598-020-80429-4>

344 Kumar, N., Park, R. J., Jeong, J. I., Woo, J.-H., Kim, Y., Johnson, J., Yarwood, G., Kang, S., Chun, S.,
345 & Knipping, E. (2021). Contributions of international sources to PM_{2.5} in South Korea.
346 *Atmospheric Environment*, 261, 118542. <https://doi.org/10.1016/j.atmosenv.2021.118542>

347 Kwon, S., Hu, Q., Seo, J., Park, S., Moon, J., Kim, J., Park, S., Park, Y., & Kim, H. (2025).
348 Characterization of particulate matter at Mt. Gwanak (at 632 m) and vertical mixing impacts on
349 haze in Seoul during winter. *Science of The Total Environment*, 958, 178106.
350 <https://doi.org/10.1016/j.scitotenv.2024.178106>

351 Lee, H.-M., Kim, N. K., Ahn, J., Park, S.-M., Lee, J. Y., & Kim, Y. P. (2024). When and why PM_{2.5} is
352 high in Seoul, South Korea: Interpreting long-term (2015–2021) ground observations using
353 machine learning and a chemical transport model. *Science of The Total Environment*, 920,
354 170822. <https://doi.org/10.1016/j.scitotenv.2024.170822>

355 Leung, D. M., Tai, A. P. K., Mickley, L. J., Moch, J. M., van Donkelaar, A., Shen, L., & Martin, R. V.
356 (2018). Synoptic meteorological modes of variability for fine particulate matter (PM_{2.5}) air
357 quality in major metropolitan regions of China. *Atmos. Chem. Phys.*, 18(9), 6733–6748.
358 <https://doi.org/10.5194/acp-18-6733-2018>

- 359 Lim, S., Lee, M., Savarino, J., & Laj, P. (2022). Oxidation pathways and emission sources of
360 atmospheric particulate nitrate in Seoul: Based on $\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$ measurements. *Atmospheric*
361 *Chemistry and Physics*, 22(8), 5099–5115. <https://doi.org/10.5194/acp-22-5099-2022>
- 362 Lim, Y.-H., Oh, J., Han, C., Bae, H.-J., Kim, S., Jang, Y., Ha, E., & Hong, Y.-C. (2020). Long-term
363 exposure to moderate fine particulate matter concentrations and cause-specific mortality in an
364 ageing society. *International Journal of Epidemiology*, 49(6), 1792–1801.
365 <https://doi.org/10.1093/ije/dyaa146>
- 366 Muñoz-Sabater, J., Dutra, E., Agustí-Panareda, A., Albergel, C., Arduini, G., Balsamo, G., Boussetta,
367 S., Choulga, M., Harrigan, S., Hersbach, H., Martens, B., Miralles, D. G., Piles, M., Rodríguez-
368 Fernández, N. J., Zsoter, E., Buontempo, C., & Thépaut, J.-N. (2021). ERA5-Land: A state-of-
369 the-art global reanalysis dataset for land applications. *Earth System Science Data*, 13(9), 4349–
370 4383. <https://doi.org/10.5194/essd-13-4349-2021>
- 371 Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue,
372 N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y.,
373 Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., ... Zaveri, R. A. (2017). Nitrate
374 radicals and biogenic volatile organic compounds: Oxidation, mechanisms, and organic aerosol.
375 *Atmospheric Chemistry and Physics*, 17(3), 2103–2162. [https://doi.org/10.5194/acp-17-2103-](https://doi.org/10.5194/acp-17-2103-2017)
376 2017
- 377 NIER. (2022). *Annual report of air quality in Korea 2022*.
378 https://www.airkorea.or.kr/web/detailViewDown?pMENU_NO=125
- 379 Oak, Y. J., Jacob, D. J., Pendergrass, D. C., Dang, R., Colombi, N. K., Chong, H., Lee, S., Kuk, S. K.,
380 & Kim, J. (2024). Air quality trends and regimes in South Korea inferred from
381 2015–2023 surface and satellite observations. *EGU sphere*, 1–35.
382 <https://doi.org/10.5194/egusphere-2024-3485>
- 383 Oak, Y. J., Jacob, D. J., Pendergrass, D. C., Dang, R., Colombi, N. K., Chong, H., Lee, S., Kuk, S. K.,
384 & Kim, J. (2025). Air quality trends and regimes in South Korea inferred from 2015–2023
385 surface and satellite observations. *Atmospheric Chemistry and Physics*, 25(5), 3233–3252.
386 <https://doi.org/10.5194/acp-25-3233-2025>
- 387 Oh, J., Lim, Y.-H., Han, C., Lee, D.-W., Myung, J., Hong, Y.-C., Kim, S., & Bae, H.-J. (2024).
388 Mortality Burden Due to Short-term Exposure to Fine Particulate Matter in Korea. *Journal of*
389 *Preventive Medicine and Public Health*, 57(2), 185–196. <https://doi.org/10.3961/jpmph.23.514>
- 390 Park, J., Kim, H., Kim, Y., Heo, J., Kim, S.-W., Jeon, K., Yi, S.-M., & Hopke, P. K. (2022). Source
391 apportionment of PM_{2.5} in Seoul, South Korea and Beijing, China using dispersion normalized
392 PMF. *Science of The Total Environment*, 833, 155056.
393 <https://doi.org/10.1016/j.scitotenv.2022.155056>
- 394 Park, T., Singh, R., Ban, J., Kim, K., Park, G., Kang, S., Choi, S., Song, J., Yu, D.-G., Bae, M.-S., Ahn,
395 J., Jung, H.-J., Lim, Y.-J., Kim, H. W., Hwang, T. K., Choi, Y. J., Kim, S.-Y., Kim, H. S.,
396 Chang, Y. W., ... Lee, T. (2023). Seasonal and regional variations of atmospheric ammonia
397 across the South Korean Peninsula. *Asian Journal of Atmospheric Environment*, 17(1), 1–11.
398 <https://doi.org/10.1007/s44273-023-00008-7>
- 399 Pendergrass, D. C., Jacob, D. J., Oak, Y. J., Lee, J., Kim, M., Kim, J., Lee, S., Zhai, S., Irie, H., & Liao,
400 H. (2025). A continuous 2011–2022 record of fine particulate matter (PM_{2.5}) in East Asia at

- 401 daily 2-km resolution from geostationary satellite observations: Population exposure and long-
402 term trends. *Atmospheric Environment*, 121068. <https://doi.org/10.1016/j.atmosenv.2025.121068>
- 403 Pendergrass, D. C., Shen, L., Jacob, D. J., & Mickley, L. J. (2019). Predicting the Impact of Climate
404 Change on Severe Wintertime Particulate Pollution Events in Beijing Using Extreme Value
405 Theory. *Geophysical Research Letters*, 46(3), 1824–1830.
406 <https://doi.org/10.1029/2018GL080102>
- 407 Pendergrass, D. C., Zhai, S., Kim, J., Koo, J.-H., Lee, S., Bae, M., Kim, S., Liao, H., & Jacob, D. J.
408 (2022). Continuous mapping of fine particulate matter (PM_{2.5}) air quality in East Asia at daily
409 6 × 6 km² resolution by application of a random forest algorithm to
410 2011–2019 GOCI geostationary satellite data. *Atmospheric Measurement Techniques*, 15(4),
411 1075–1091. <https://doi.org/10.5194/amt-15-1075-2022>
- 412 Shah, V., Jacob, D. J., Li, K., Silvern, R. F., Zhai, S., Liu, M., Lin, J., & Zhang, Q. (2020). Effect of
413 changing NO_x lifetime on the seasonality and long-term trends of satellite-observed tropospheric
414 NO₂ columns over China. *Atmospheric Chemistry and Physics*, 20(3), 1483–1495.
415 <https://doi.org/10.5194/acp-20-1483-2020>
- 416 Shen, L., Mickley, L. J., & Murray, L. T. (2017). Influence of 2000–2050 climate change on particulate
417 matter in the United States: Results from a new statistical model. *Atmospheric Chemistry and
418 Physics*, 17(6), 4355–4367. <https://doi.org/10.5194/acp-17-4355-2017>
- 419 Tai, A. P. K., Mickley, L. J., & Jacob, D. J. (2010). Correlations between fine particulate matter
420 (PM_{2.5}) and meteorological variables in the United States: Implications for the sensitivity of
421 PM_{2.5} to climate change. *Atmospheric Environment*, 44(32), 3976–3984.
422 <https://doi.org/10.1016/j.atmosenv.2010.06.060>
- 423 Wang, H., Lu, K., Chen, S., Li, X., Zeng, L., Hu, M., & Zhang, Y. (2021). Characterizing nitrate radical
424 budget trends in Beijing during 2013–2019. *Science of The Total Environment*, 795, 148869.
425 <https://doi.org/10.1016/j.scitotenv.2021.148869>
- 426 Wang, H., Wang, H., Lu, X., Lu, K., Zhang, L., Tham, Y. J., Shi, Z., Aikin, K., Fan, S., Brown, S. S., &
427 Zhang, Y. (2023). Increased night-time oxidation over China despite widespread decrease across
428 the globe. *Nature Geoscience*, 16(3), 217–223. <https://doi.org/10.1038/s41561-022-01122-x>
- 429 Wang, Y., Duan, X., & Wang, L. (2019). Spatial-Temporal Evolution of PM_{2.5} Concentration and its
430 Socioeconomic Influence Factors in Chinese Cities in 2014–2017. *International Journal of
431 Environmental Research and Public Health*, 16(6), Article 6.
432 <https://doi.org/10.3390/ijerph16060985>
- 433 Wang, Y., Xi, S., Zhao, F., Huey, L. G., & Zhu, T. (2023). Decreasing Production and Potential Urban
434 Explosion of Nighttime Nitrate Radicals amid Emission Reduction Efforts. *Environmental
435 Science & Technology*, 57(50), 21306–21312. <https://doi.org/10.1021/acs.est.3c09259>
- 436 Zhai, S., Jacob, D. J., Pendergrass, D. C., Colombi, N. K., Shah, V., Yang, L. H., Zhang, Q., Wang, S.,
437 Kim, H., Sun, Y., Choi, J.-S., Park, J.-S., Luo, G., Yu, F., Woo, J.-H., Kim, Y., Dibb, J. E., Lee,
438 T., Han, J.-S., ... Liao, H. (2023). Coarse particulate matter air quality in East Asia: Implications
439 for fine particulate nitrate. *Atmospheric Chemistry and Physics*, 23(7), 4271–4281.
440 <https://doi.org/10.5194/acp-23-4271-2023>
- 441 Zhai, S., Jacob, D. J., Wang, X., Shen, L., Li, K., Zhang, Y., Gui, K., Zhao, T., & Liao, H. (2019). Fine
442 particulate matter (PM_{2.5}) trends in China, 2013–2018: Separating contributions from

443 anthropogenic emissions and meteorology. *Atmospheric Chemistry and Physics*, 19(16), 11031–
444 11041. <https://doi.org/10.5194/acp-19-11031-2019>
445 Zhang, Z., Lu, B., Liu, C., Meng, X., Jiang, J., Herrmann, H., Chen, J., & Li, X. (2024). Nitrate
446 pollution deterioration in winter driven by surface ozone increase. *Npj Climate and Atmospheric*
447 *Science*, 7(1), 1–9. <https://doi.org/10.1038/s41612-024-00667-5>
448 Zhao, D., Chen, H., Sun, X., & Shi, Z. (2018). Spatio-temporal Variation of PM2.5 Pollution and its
449 Relationship with Meteorology among Five Megacities in China. *Aerosol and Air Quality*
450 *Research*, 18(9), 2318–2331. <https://doi.org/10.4209/aaqr.2017.09.0351>
451