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Coarse particulate matter air quality in East Asia: implications for fine particulate nitrate

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Author Contributions: S.Z. and D.J.J. designed the research. S.Z. performed the research. Q.Z. provided the MEIC emission inventory. J.H.W. and Y.K. provided the KORUSv5 emission inventory. H.K., J.E.D., T.L., and J.S.H provided KORUS-AQ data. G.L., F.Y., and K.L. helped with model simulations. V.S., L.H.Y., Y.S., S.W., and H.L. helped with results interpretation. S.Z. and D.J.J wrote the paper with input from all other authors.

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Main Text
Figures 1 to 4
Abstract

Air quality network data in China and South Korea show very high year-round mass concentrations of coarse particulate matter (PM) between 2.5 μm and 10 μm aerodynamic diameter, as inferred by the difference between PM$_{10}$ and PM$_{2.5}$ observations. This coarse PM averages 47 μg m$^{-3}$ in the North China Plain (NCP) region in 2015-2019 and 21 μg m$^{-3}$ in the Seoul Metropolitan Area (SMA). It is dominantly contributed by urban fugitive dust, rather than by natural dust as is often presumed. Concentrations decreased by 21% from 2015 to 2019 and further dropped abruptly in 2020 due to COVID-19 reductions in construction and vehicle traffic. This anthropogenic coarse PM is generally not included in air quality models but acts as a sink of nitric acid (HNO$_3$), thus affecting fine particulate nitrate which is a major air quality concern in China and South Korea. GEOS-Chem model simulation of surface and aircraft observations from the KORUS-AQ campaign over the SMA in May-June 2016 shows that consideration of anthropogenic coarse PM largely resolves the previous model overestimate of PM$_{1}$ nitrate. Anthropogenic coarse PM in the model increases the sensitivity of PM$_{2.5}$ nitrate to ammonia (NH$_3$) uptake, and we find that the decrease of anthropogenic coarse PM over 2015-2019 offset the PM$_{2.5}$ nitrate reductions expected from decreasing NO$_x$ and NH$_3$ emissions.

Significance Statement

Coarse particulate matter (PM) is a serious air pollution problem in East Asia and we show that it is overwhelmingly urban and anthropogenic. Emission controls to reduce fugitive dust have driven steady 2015-2020 coarse PM decreases in both China and South Korea. Coarse PM can affect fine particulate (PM$_{2.5}$) nitrate air pollution by taking up nitric acid (HNO$_3$). We find that in winter, coarse PM increases the effectiveness of ammonia (NH$_3$) emission controls to reduce PM$_{2.5}$ nitrate. In summer, the decrease of coarse PM drives a direct increase in PM$_{2.5}$ nitrate. The continuing decrease of coarse PM from abating fugitive dust pollution will require more stringent NH$_3$ and NO$_x$ emission controls to successfully decrease PM$_{2.5}$ nitrate.

Main Text

Introduction

Coarse particulate matter (coarse PM; particulate matter between 2.5 μm and 10 μm in aerodynamic diameter) poses a severe air pollution problem in East Asia, constituting a particle mass comparable to fine particulate matter (PM$_{2.5}$) and thus about half of PM$_{10}$ (1-4). That coarse PM is mainly fugitive mineral dust, with contributions from both natural desert dust and human activity including on-road traffic, construction, and agriculture (5-8). Atmospheric chemistry models used in air quality applications generally do not include anthropogenic fugitive dust, due to the lack of available emission inventories except for a few urban areas (9-11). Aside from its interest as an air quality issue, coarse PM can also affect PM$_{2.5}$ by heterogeneously taking up acids (HNO$_3$, SO$_2$, and H$_2$SO$_4$). This uptake has been observed for natural dust events (12-16), but the more ubiquitous effect from anthropogenic dust has received little study (17, 18). With increasingly stringent control measures to decrease fugitive dust pollution in East Asia (5, 19-21), it is pressing to better understand its impacts on PM$_{2.5}$ air quality.

A specific issue is the effect of anthropogenic dust on PM$_{2.5}$ nitrate. PM$_{2.5}$ in winter is dominated by the nitrate component (22, 23), and both winter and summer haze pollution events are driven by nitrate (24, 25). PM$_{2.5}$ over North China in winter has not been effectively decreasing despite reductions in emissions of the precursor nitrogen oxides (NO$_x ≡$ NO + NO$_2$) (23, 24). Simulation with the GEOS-Chem model of fine particulate nitrate and HNO$_3$ observations from the KORUS-
AQ ground and aircraft campaign over South Korea in May-June 2016 previously showed a factor of two overestimate of observed PM$_2.5$ nitrate (26, 27). At the same time, coarse PM at KORUS-AQ surface sites averaged 21 μg m$^{-3}$ while the GEOS-Chem model simulated only 3.5 μg m$^{-3}$ from natural dust and sea salt sources (26). Ref (27) postulated a five-fold increase in the HNO$_3$ dry deposition to explain the fine particulate nitrate overestimate in KORUS-AQ. Uptake of HNO$_3$ by coarse PM could provide an alternative explanation.

Ammonia (NH$_3$) emissions have previously been found to be the most effective lever for PM$_{2.5}$ nitrate control over North China in winter by altering the gas-particle partitioning of total nitrate (particulate nitrate + HNO$_3$) and affecting the lifetime of total nitrate against deposition (23). NH$_3$ is also important in summer in driving the partitioning of HNO$_3$ to PM$_{2.5}$ nitrate (25). Coarse PM would affect the HNO$_3$-NH$_3$ thermodynamics by providing a sink of HNO$_3$, thus potentially affecting the sensitivity of PM$_{2.5}$ nitrate to NH$_3$ emissions. Better understanding this sensitivity is of crucial importance because of recent efforts by the Chinese government to decrease NH$_3$ emissions (28).

In this work, we show that coarse PM decreased by 21% over the North China Plain (NCP) region and the Seoul Metropolitan Area (SMA) over the 2015-2019 period as a result of measures to control fugitive dust emissions. We also show from the abrupt drop of coarse PM in China observed during the COVID-19 lockdown and the strong daily correlations between coarse PM and carbon monoxide (CO) that coarse PM in urban China and South Korea is mainly anthropogenic. We find that coarse PM largely resolves the previous GEOS-Chem model overestimate of PM$_1$ nitrate in the SMA during the KORUS-AQ campaign. We infer from model simulations that coarse PM has a major and highly seasonal effect on PM$_{2.5}$ nitrate and on the sensitivity of PM$_{2.5}$ nitrate to NH$_3$ emission, with implications for the impact of fugitive dust emission controls on PM$_{2.5}$ nitrate levels.

Results and Discussion

Coarse PM in China and South Korea.

Concentrations of coarse PM are available in China and South Korea from the dense air quality monitoring networks reporting PM$_{2.5}$ and PM$_{10}$ (29, 30). Fig. 1 shows the annual mean concentrations in 2015, 2019, and 2020. Concentrations in each country are highest in the NCP and in the SMA, indicating a dominant urban anthropogenic origin. Concentrations decreased by 21% in both regions from 2015 to 2019, reflecting efforts to control fugitive dust pollution (5, 20, 31, 32). They further decreased sharply in 2020 because of the COVID-19 slowdown that curtailed traffic and construction. Concentrations before and during the sharp COVID-19 lockdown in China starting on January 24, 2020, show a 40-50% drop (SI Appendix, Fig. S1).

The spring maxima in the NCP and SMA are due to natural desert dust events superimposed on a high anthropogenic baseline. It is well known that the influence of natural dust in East Asia peaks in spring (33). Fig. 2 shows the daily correlations of regional mean coarse PM and carbon monoxide (CO, a tracer of incomplete combustion) over the NCP and SMA in 2015 separated by seasons. Correlations are strong except for spring, and then mainly because of high coarse PM outliers attributable to events of long-range transport of natural dust. Taking CO as a tracer of urban air, this further implies that coarse PM is dominantly urban in origin. Similar correlations are found in other years (SI Appendix, Fig. S2). Observed coarse PM decreases from 2015 to 2019 in the NCP are 32% in winter and 40% in summer, and in the SMA are 38% in winter and 40% in summer, when the natural contribution is minimum (SI Appendix, Fig. S3).
Effect of anthropogenic coarse PM on fine particulate nitrate. Coarse PM in East Asia is alkaline (34, 35) and can therefore readily take up HNO₃ to affect PM$_{2.5}$ nitrate. We included anthropogenic coarse PM in the GEOS-Chem model by using the air quality network observations as boundary conditions in the lowest model level (Materials and Methods). The resulting model provides a simulation of coarse PM vertical profiles consistent with KORUS-AQ aircraft observations over the SMA (SI Appendix, Fig. S4). We simulate alkalinity and the uptake of acids (HNO₃, SO₂, and H₂SO₄) by coarse PM on the basis of laboratory data and ambient dust composition observations in East Asia (34-37) as detailed in Materials and Methods. We find that dust uptake of SO₂ and H₂SO₄ does not affect sulfate significantly during KORUS-AQ (SI Appendix, Fig. S5). We therefore focus our analysis on the effect on nitrate.

We start by applying GEOS-Chem to the simulation of observations during the KORUS-AQ campaign over South Korea (May 1 to June 10, 2016), including continuous gas and aerosol concentrations at surface sites and vertical profiles from 20 flights all in daytime (38). Nitrate was measured at the Korea Institute of Science and Technology (KIST) surface site and on the aircraft by Aerosol Mass Spectrometers (AMSs) with size cut of 1 μm diameter (PM$_{1}$ nitrate) (39, 40), and also on the aircraft by the Soluble Acidic Gases and Aerosol (SAGA) instrument with size cut of 4 μm diameter (PM$_{4}$ nitrate) (41, 42). The PM$_{1}$ nitrate measured by the AMS during KORUS-AQ was mainly inorganic (SI Appendix, Fig. S6). Here we take ammonium nitrate in the model for comparison to PM$_{1}$ observations, and ammonium nitrate plus size-resolved dust nitrate for comparison to PM$_{4}$ observations.

Fig. 3 shows SMA observations during KORUS-AQ and their simulation by GEOS-Chem including median PM$_{1}$ nitrate diurnal variations at the KIST surface site and median vertical profiles of PM$_{1}$ nitrate, PM$_{1-4}$ nitrate (between 1 and 4 μm), PM$_{4}$ Ca$^{2+}$ (a tracer of dust), and HNO₃. PM$_{1}$ nitrate at the KIST site increases over the course of the night, which is attributed in the model to reactive uptake of NO$_{2}$ and N₂O₅ by aqueous-phase particles and decreases in the morning due to dilution by mixed layer growth (27). Here we adjusted the diurnal variation of NH$_{3}$ emission in the model to match the NH$_{3}$ observations made at the Olympic Park site, 7 km southeast of KIST (Materials and Methods, SI Appendix, Fig. S7). We find that the standard GEOS-Chem simulation without anthropogenic coarse PM overestimates the observed PM$_{1}$ nitrate and HNO$_{3}$ concentrations by about a factor of two (by about a factor of 3-4 for PM$_{1}$ nitrate during the night), and underestimates PM$_{1-4}$ nitrate and PM$_{4}$ Ca$^{2+}$ by about a factor of two. Adding anthropogenic coarse PM to the model largely corrects model biases for daytime PM$_{1}$ nitrate, PM$_{1-4}$ nitrate, and PM$_{4}$ Ca$^{2+}$ and corrects half of the overestimate of HNO$_{3}$ and nighttime PM$_{1}$ nitrate. One reason for the remaining model overestimate of PM$_{1}$ nitrate at the KIST site could be that a large fraction of ammonium nitrate has diameter larger than 1 μm and is not detected by AMS (40). We find that coarse PM takes up HNO$_{3}$ three times faster than dry deposition and that this uptake is not limited by alkalinity (only 60% of the dust alkalinity in surface air is neutralized on average).

Implications for the trends of fine particulate nitrate and the response to emission controls. PM$_{2.5}$ nitrate observations in the North China Plain in winter show either no or marginal decreases since 2015 (24, 43). No observations are available outside of winter. The Multi-resolution Emission Inventory for China (MEIC) reports that NCP emissions of NOx decreased by 16% from 2015 to 2019, while SO$_{2}$ emissions decreased by 58% (44). Efforts to control agricultural NH$_{3}$ emissions in China began in 2015 (28). The MEIC reports a 15% decrease in NH$_{3}$ emission over China from 2015 to 2019 (22% for the NCP), while the PKU-NH$_{3}$ emission inventory reports a 6% decrease from 2015 to 2018 (28). Emissions of primary PM$_{2.5}$ from combustion also decreased by 35% in winter and by 20% in summer from 2015 to 2019. As previously mentioned, coarse PM decreased by 32% in winter and 40% in summer.
Here we use the GEOS-Chem model driven by the MEIC emission inventory and observed coarse PM to investigate the factors controlling the PM$_{2.5}$ nitrate trend in the NCP over 2015-2019. The model simulates a 27% decrease of January-February-March mean fine particulate nitrate in downtown Beijing from 2015 to 2019, comparable to the 22% decrease in concurrent observations (43). By contrast, the mean 2015-2019 January-February-March PM$_{2.5}$ nitrate over the NCP in GEOS-Chem increased by 5%, with changes in meteorology as an important driver (SI Appendix, Fig. S8).

Fig. 4 attributes the anthropogenic changes of PM$_{2.5}$ nitrate between 2015 and 2019 over the NCP in winter and summer as simulated by the model, and the contributions from changes in individual emissions as obtained in model sensitivity simulations (SI Appendix, Table S1). The weak trend in winter reflects the effect of decreasing SO$_2$ emissions offsetting the benefits of decreasing NO$_x$ and NH$_3$ emissions. The 16% reduction of NO$_x$ emission decreases PM$_{2.5}$ nitrate only by 3%, consistent with our previous finding (23). The 22% reduction of NH$_3$ emission decreases PM$_{2.5}$ nitrate by 6% if not accounting for coarse PM, again consistent with our previous finding. Accounting for coarse PM, the 22% reduction of NH$_3$ emission decreases PM$_{2.5}$ nitrate by 9%. The 35% decrease of primary PM$_{2.5}$ from combustion decreases PM$_{2.5}$ nitrate by 6.6%, mainly due to less NO$_2$ hydrolysis on aerosol surfaces. Coarse PM has little direct effect on PM$_{2.5}$ nitrate because the thermodynamics of ammonium nitrate formation drives HNO$_3$ into fine particles in winter (SI Appendix, Fig. S9), but it increases the sensitivity of PM$_{2.5}$ nitrate to NH$_3$ and SO$_2$ emissions because it accelerates the loss rate of HNO$_3$ and thus amplifies the effect of NH$_3$ on total nitrate lifetime (23).

In summer, we find in the model that the 40% decrease of coarse PM over 2015-2019 increases summertime PM$_{2.5}$ nitrate by 20%, offsetting the effectiveness of NO$_x$ and NH$_3$ emission controls. This is because a large fraction of total nitrate in summer remains in the gas phase as HNO$_3$ under the warm temperatures, and with the decrease of coarse PM, HNO$_3$ scavenged by coarse PM is reduced (SI Appendix, Fig. S9). The 58% decrease in SO$_2$ emission reduces PM$_{2.5}$ nitrate by 12% because less sulfate makes HNO$_3$ less likely to partition to the aerosol phase (45).

In summary, we find that coarse PM (PM$_{10}$ - PM$_{2.5}$) in urban areas of China and South Korea is very high year-round and is dominantly anthropogenic fugitive dust except in spring, with important implications for both PM$_{10}$ and PM$_{2.5}$ air quality. Control measures reduced annual mean coarse PM by 21% from 2015 to 2019 in the North China Plain (NCP) and the Seoul Metropolitan Area (SMA), with steeper decreases in 2020 because of COVID-19 lockdowns. The 2015-2019 seasonal decreases were 32% in winter and 40% in summer when natural dust influence is minimum. Anthropogenic dust can take up HNO$_3$ effectively and thus affect PM$_{2.5}$ nitrate. Comparison of GEOS-Chem model simulations to PM$_1$ nitrate, PM$_{1-4}$ nitrate, PM$_2$ Ca$^{2+}$, and HNO$_3$ observations from the KORUS-AQ campaign over South Korea in May-June 2016 shows that anthropogenic coarse PM largely resolves the previous large model overestimates of PM$_1$ nitrate. We find in the model that the summertime decrease of coarse PM in the NCP from 2015 to 2019 increased fine particulate nitrate by 20%, offsetting the effectiveness of NO$_x$ and NH$_3$ emission reductions. In winter, the decrease of coarse PM has little direct effect on fine particulate nitrate trends but increases the effectiveness of NH$_3$ emission reductions. As coarse PM continues to decrease in response to fugitive dust pollution control, there is a greater need to reduce NH$_3$ and NO$_x$ emissions in order to decrease fine particulate nitrate air pollution in East Asia.

Materials and Methods

**GEOS-Chem model description.** We use the GEOS-Chem global atmospheric chemistry model version 13.0.2 (https://zenodo.org/record/4681204) in a nested-grid simulation over East Asia.
(100 - 150° E, 20 - 50° N) with a horizontal resolution of 0.5°× 0.625°. The GEOS-Chem model simulates detailed oxidant-aerosol chemistry (46-50) and is driven by meteorological data from the NASA Modern-Era Retrospective Analysis for Research and Applications, Version 2 (MERRA-2). Dry deposition of gases and particles follows a standard resistance-in-series scheme (51). Wet deposition of gases and particles includes contributions from rainout, washout, and scavenging in convective updrafts (52-55), with recent updates featuring faster below-cloud scavenging of HNO$_3$ (56). We conducted a number of sensitivity simulations as listed in SI Appendix, Table S1 to investigate the model sensitivity of 2015-2019 PM$_{2.5}$ nitrate trends to decreases in individual emissions of NO$_x$, SO$_2$, NH$_3$, primary PM$_{2.5}$, and coarse PM. PM$_1$ nitrate is diagnosed in the model by the ammonium nitrate component, while PM$_{2.5}$ nitrate is diagnosed as the sum of the ammonium nitrate and fine (PM$_{2.5}$) dust nitrate components.

**Coarse PM simulation.** We simulate coarse PM in GEOS-Chem by using 24-hour average coarse PM observations from the national networks in China and South Korea as boundary conditions at the lowest model level. For this purpose, we linearly interpolate the daily network data to the GEOS-Chem model grid and apply them to the coarse dust GEOS-Chem model component (57) at an effective diameter of 4.8 μm. Dust alkalinity is included in these boundary conditions with 7.1% Ca$^{2+}$ and 1.1% Mg$^{2+}$ as carbonates by dry mass (34, 35, 58). We include reactive uptake of HNO$_3$ and SO$_2$ on dust limited by dust alkalinity and mass transfer, and uptake of H$_2$SO$_4$ limited by competition with other aerosol surfaces (59). The relative humidity (RH)-dependent reactive uptake coefficients (γ) of HNO$_3$ and SO$_2$ are based on laboratory studies (36, 37) and constrained by observations of coarse and fine particulate nitrate and sulfate observations during natural dust events in Beijing (12, 60). γ(HNO$_3$) increases from 0.06 to 0.21 as RH increases from 40% to 80%, and γ(SO$_2$) increases from 7.0×10$^{-5}$ to 4×10$^{-4}$.

**Emissions.** Monthly anthropogenic emissions for China are from the Multi-resolution Emission Inventory for China (MEIC) (44, 61, 62), and emissions for other Asian countries including South Korea are from the KORUSv5 inventory (63). We adjusted the diurnal scaling factors of the NH$_3$ emissions in both inventories based on our simulation of the Olympic Park NH$_3$ observations during KORUS-AQ (SI Appendix, Fig. S7). MEIC and KORUSv5 including primary anthropogenic PM$_{2.5}$ emissions but solely from combustion. According to MEIC, NO$_x$ emissions in the North China Plain decreased by 16% from 2015 to 2019, SO$_2$ emission decreased by 58%, NH$_3$ emission decreased by 22%, and primary PM$_{2.5}$ emission from combustion decreased by 35% in winter and by 20% in summer (44). To this we add here a 32% decrease in coarse PM in winter and 40% decrease in summer in the North China Plain region.

**Data Availability.** Hourly PM$_{2.5}$, PM$_{10}$, ad CO observations in China are from the Ministry of Ecology and Environment (MEE) monitoring network in China (http://www.quotsoft.net/air/) and the AirKorea network in South Korea (https://www.airkorea.or.kr/web/last_amb_hour_data?pMENU_NO=123). KORUS-AQ aircraft and surface data are available at: https://doi.org/10.5067/Suborbital/KORUSAQ/DATA01. The MEIC anthropogenic emission inventory for China is at http://www.meicmodel.org/. The KORUSv5 emission inventory is developed by Konkuk University, available at http://aisl.konkuk.ac.kr/#/emission_data/korus-aq_emissions.

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and John D. Crounse from the California Institute of Technology for their contributions to HNO₃ measurements during KORUS-AQ.

References


3. H. Qiu et al., Coarse particulate matter associated with increased risk of emergency hospital admissions for pneumonia in Hong Kong. *Thorax* 69, 1027 (2014).


13. E. W. Heim et al., Asian dust observed during KORUS-AQ facilitates the uptake and incorporation of soluble pollutants during transport to South Korea. *Atmos. Environ.* 224, 117305 (2020).


23. S. Zhai et al., Control of particulate nitrate air pollution in China. *Nat. Geosci.*


Fig. 1. Distributions and trends of coarse PM over China and South Korea during 2015-2020. Annual mean concentrations in 2015, 2019, and 2020 over [A-C] China and [D-F] South Korea. [G] Annual trends relative to 2015 in the North China Plain (NCP; 197 sites) and the Seoul Metropolitan Area (SMA; 33 sites) averaged over sites with at least 70% data coverage each year from 2015 to 2020. [H] Mean 2015-2019 seasonality over the NCP and SMA. The rectangles in [A] and [D] delineate the NCP (113 - 122.5° E, 34.5 - 41.5° N) and SMA (126.7 - 127.3° E, 37.3 - 37.8° N). Here and elsewhere, coarse PM concentrations are obtained by subtracting PM$_{2.5}$ from PM$_{10}$ in the air quality network data.
Fig. 2. Daily correlations of coarse PM and CO over the [A] North China Plain (NCP) and [B] Seoul Metropolitan Area (SMA) in 2015. Coarse PM and CO concentrations are 24-h averages of air quality network observations averaged over the two regions. Also shown are the correlation coefficients and reduced-major-axis regression lines for significant correlations (p-value < 0.05). The correlation coefficients in spring are not shown because they are insignificant. Here spring is defined as February-March-April-May, summer as June-July-August, Autumn as September-October-November, and winter as December and January. We include February in spring to cover the season of natural dust events (34).
Fig. 3. PM nitrate, PM Ca$^{2+}$, and HNO$_3$ concentrations over the Seoul Metropolitan Area (SMA) during KORUS-AQ. GEOS-Chem model results without and with anthropogenic coarse PM are compared to surface and aircraft observations. [A] Median diurnal variations of PM$_1$ nitrate at the Korea Institute of Science and Technology (KIST) site. [B-E] Median vertical profiles of PM$_1$ nitrate, PM$_{1-4}$ nitrate, PM$_4$ Ca$^{2+}$, and HNO$_3$. Horizontal bars for the observations indicate 25th-75th percentiles. We have excluded observations from two process-directed flights (RF7 and RF8) and the Daesan power plant plume following ref. (30). PM$_1$ nitrate refers to particles smaller than 1 μm as measured by the Aerosol Mass Spectrometer (AMS), and PM$_{1-4}$ nitrate refers to particles between 1 and 4 μm diameter as measured by the difference between the Soluble Acidic Gases and Aerosol (SAGA) instrument and the AMS. GEOS-Chem simulates PM$_1$ nitrate by ammonium-associated nitrate, PM$_{1-4}$ nitrate by dust-associated nitrate with a diameter less than 4 μm, and PM$_4$ Ca$^{2+}$ by 7.1% mass of dust with a diameter less than 4 μm.
Fig. 4. Anthropogenic drivers of seasonal mean PM$_{2.5}$ nitrate trends over the North China Plain (NCP) from 2015 to 2019. Results are from GEOS-Chem sensitivity simulations including individual emission trends over the period (SI Appendix, Table S1) and are shown as seasonal means for winter and summer. Results from simulations not accounting for the effect of HNO$_3$ uptake by anthropogenic coarse PM are shown as “+” symbols.
Supplementary Information for
Coarse particulate matter air quality in East Asia: implications for fine particulate nitrate

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This PDF file includes:
Supplementary Figs. S1 to S9 and Table. S1.
Fig. S1. Response of coarse PM to the national COVID-19 lockdown in China. [A] Coarse PM averaged for three weeks before the China national lockdown (January 1-23, 2020). [B] Coarse PM averaged during the three-week lockdown (January 24 - February 15, 2020). [C] Percent changes of coarse PM between lockdown and pre-lockdown periods. Here and elsewhere, coarse PM concentrations are obtained by subtracting PM$_{2.5}$ from PM$_{10}$ in the air quality network data. The rectangle in [A] delineates the North China Plain (NCP) region (113 - 122.5° E, 34.5 - 41.5° N).
Fig. S2. Same as Fig. 2 in the main text but for the years 2016, 2017, 2018, and 2019.
Fig. S3. Monthly anomalies of coarse PM in each season averaged over the North China Plain region (NCP) and the Seoul Metropolitan Area (SMA) during 2015-2019. Black dashed lines are linear regression lines for significant trends during 2015-2019. The large monthly variation in March-April-May is influenced by natural dust events while the insignificant trend in September-October-November could be due to that agriculture activities are important sources of coarse dust in this season and are not effectively controlled for its fugitive dust emission.
Fig. S4. Same as the aircraft vertical profiles in Fig. 3 in the main text except that this is for coarse PM up to 8 km altitude. Aircraft observations of coarse PM are derived from the size distribution measurements by in-situ Aerosol Particles from the DMT CPSPD Probe.
Fig. S5. Correlations of PM$_{1-4}$ sulfate with Ca$^{2+}$ (left; a tracer of dust) and PM$_{1-4}$ ammonium (right) during KORUS-AQ over the SMA. The weak correlation between PM$_{1-4}$ sulfate and Ca$^{2+}$ and the significant correlation between PM$_{1-4}$ sulfate and PM$_{1-4}$ ammonium suggest that most PM$_{1-4}$ sulfate is associated with PM$_{1-4}$ ammonium rather than with dust. Size distribution measurements of aerosol species show that a large part of ammonium sulfate is in the coarse mode during KORUS-AQ.
Fig. S6. Ionic charge balance of aerosols during KORUS-AQ over SMA as represented by scatterplots of $2[SO_4^{2-}] + [NO_3^-]$ and $[NH_4^+]$ molar concentrations at the surface KIST site (left) and on the DC-8 aircraft (right). Here $2[SO_4^{2-}] + [NO_3^-]$ and $[NH_4^+]$ are in charge balance, suggesting that AMS measured nitrate is mainly inorganic nitrate that is associated with ammonium.
Fig. S7. Same as Fig. 4 in the main text but with the diurnal profiles of NH₃ at the Olympic Park site in SMA, diurnal scaling factors of NH₃ emission, and GEOS-Chem model results with default and adjusted NH₃ emissions added. NH₃ was measured by ion chromatography at the Olympic Park site in SMA, ~7 km to the southeast of KIST. The default diurnal scaling factors of NH₃ emission is provided by the Multi-resolution Emission Inventory for China (MEIC) agriculture emission sector.
Fig. S8. 2015-2019 changes of January-February-March mean surface relative humidity (RH) and temperature. RH and temperature are from the MERRA-2 reanalysis data from the NASA Goddard Earth Sciences (GES) Data and Information Services Center (https://gmao.gsfc.nasa.gov/reanalysis/MERRA-2/data_access/). The black rectangle delineates the North China Plain region and the blue filled circle is the location of the PM$_{2.5}$ composition observation site in Beijing.
Fig. S9. GEOS-Chem simulation of winter and summer mean particulate nitrate and HNO₃ averaged over the NCP. Particulate nitrate is partitioned to nitrate that is respectively associated with ammonium, fine dust (PM₂.₅), and coarse dust.
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</tr>
<tr>
<td>3 Run_NO\textsubscript{x}</td>
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<tr>
<td>4 Run_NO\textsubscript{x} SO\textsubscript{2}</td>
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<td>2019</td>
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<td>2015\textsuperscript{b}</td>
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</tr>
<tr>
<td>5 Run_NO\textsubscript{x} SO\textsubscript{2} NH\textsubscript{3}</td>
<td>2019</td>
<td>2019</td>
<td>2019</td>
<td>2019</td>
<td>2015\textsuperscript{b}</td>
<td>2015</td>
</tr>
<tr>
<td>6 Run_NO\textsubscript{x} SO\textsubscript{2} NH\textsubscript{3} PMC</td>
<td>2019</td>
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<td>7 Run_2019</td>
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<td>8 Run_NatDst_Met</td>
<td>2019</td>
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<tr>
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<tr>
<td>10 Run_NatDst_NO\textsubscript{x} SO\textsubscript{2}</td>
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<td>NaN\textsuperscript{c}</td>
<td>2015</td>
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<tr>
<td>11 Run_NatDst_NO\textsubscript{x} SO\textsubscript{2} NH\textsubscript{3} PMC</td>
<td>2019</td>
<td>2019</td>
<td>2019</td>
<td>2019</td>
<td>NaN\textsuperscript{c}</td>
<td>2015</td>
</tr>
</tbody>
</table>

\textsuperscript{a} From 2015 to 2019 over the North China Plain (NCP) region, NO\textsubscript{x} emission decreased by 16%, SO\textsubscript{2} emission decreased by 58%, and NH\textsubscript{3} emission decreased by 22%, according to the Multi-resolution Emission Inventory for China (MEIC).

\textsuperscript{b} Coarse PM scaled to 2015 levels from observations in the year 2019 according to their seasonal linear regression trends over 2015-2019. This is to account for the daily variations of coarse PM.

\textsuperscript{c} When observed coarse PM is not included in GEOS-Chem.

\textsuperscript{d} From 2015 to 2019 over the NCP, primary PM\textsubscript{2.5} emission from combustion decreased by 35% in winter and by 20% in summer.

Coarse PM scaled to 2015 levels from observations in the year 2019 according to their seasonal linear regression trends over 2015-2019. This is to account for the daily variations of coarse PM.

Over the NCP, coarse PM decreased by 32% in winter and by 40% in summer. Over the Seoul Metropolitan Area (SMA), coarse PM decreased by 38% in winter and by 40% in summer.

When observed coarse PM is not included in GEOS-Chem.

From 2015 to 2019 over the NCP, primary PM\textsubscript{2.5} emission from combustion decreased by 35% in winter and by 20% in summer.