Evolving understanding of particulate matter (PM) air pollution: lessons from East Asia

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The industrial revolution and air pollution

“Make great efforts to build China into a strong and prosperous industrialized country under the leadership of the Party and chairman Mao!”
London fog

Aerosols a.k.a. particulate matter (PM) from domestic + industrial coal combustion

“Killer fog” of December 1952 resulted in 10,000 excess deaths

Altitude

Temperature

Coal combustion

Sulfur dioxide (SO₂)

particles

{ sulfate, organic carbon, black carbon }

< 1km inversion
AIR POLLUTION TODAY:
Ozone and fine particulate matter (PM$_{2.5}$) are the major pollutants

PM$_{2.5}$ ≡ particulate matter smaller than 2.5 μm in diameter

US population exposed to air pollutants
in excess of national ambient air quality standards (NAAQS), 2020

- Ozone: 79.2M, 70 ppb (8-h average)
- PM$_{2.5}$: 50.5M, 12 µg m$^{-3}$ (annual), 35 µg m$^{-3}$ (24-h)
- PM$_{10}$: 36.1M
- CO: 1.3M
- SO$_2$: 1.2M

Million environmental deaths per year worldwide

2010 data

US EPA [2022], OECD [2012]
PM$_{2.5}$ is a major cause of mortality worldwide
Annual mean PM$_{2.5}$ inferred from satellite observations of aerosol optical depth.

Satellite-Derived PM$_{2.5}$ [μg/m$^3$]

US air quality standard (12 μg m$^{-3}$)

http://www.nasa.gov/topics/earth
Why **fine** particulate matter? Because it penetrates deep in lung.

Typical PM size distribution

Deposition efficiency in upper airways

Condensation from gas phase (secondary particles):

Direct emission (primary particles)

Typical PM size distribution by mass:

PM$_{2.5}$
Sources and life cycle of particulate matter

Atmospheric transport

- 1 nm
- 10 nm
- 100 nm
- 1 μm
- 10 μm

- gas condensation
- coagulation
- cloud cycling

condensation from gases (secondary aerosol)

- molecular clusters (nucleation)
- direct emission (primary aerosol)

condensation from gases (secondary aerosol)

- oxygenated VOCs
- H₂SO₄
- HNO₃
- NH₃
- SO₂
- NOₓ (NO+NO₂)
- VOCs

atmospheric oxidation

organic particles
- black carbon

soil dust
- sea salt

wind

deposition
Mean PM$_{2.5}$ composition in Beijing [Huang et al., 2017]

- **Organic aerosol**: 27%
- **Sulfate**: 16%
- **Nitrate**: 20%
- **Ammonium**: 12%
- **Mineral dust**: 17%
- **Black carbon**: 8%
- **Combustion**: Primary (POA) from combustion, Secondary (SOA) from VOCs emitted by combustion, industry, household products, vegetation
- **SO$_2$ from coal combustion**: Combustion
- **NH$_3$ from agriculture, vehicles**: Construction, roads, soils
- **NO$_x$ from combustion**: Construction, roads, soils
In 2013, the Chinese government initiated the “Clean Air Action”

- Scrubbing of SO$_2$ emissions from coal combustion
- Ban on residential coal combustion
- Closing of polluting industries
- Emission standards for vehicles
- Ban on agricultural fires
- Encouragement of renewable energy sources
Clean Air Action has led to great improvement in PM$_{2.5}$ air quality

Annual mean PM$_{2.5}$ at China Ministry of Ecology and Environment (MEE) sites:
PM$_{2.5}$ decreased by 30-50% across urban China over 2013-2018

Zhai et al., ACP 2019
PM$_{2.5}$ trends have been driven by controls on SO$_2$ and primary emissions

Zhai et al., ACP 2019; Zheng et al., ACP 2018
Evolution of PM$_{2.5}$ composition in Beijing: transition from sulfate-organic dominated to nitrate-organic dominated

- Sulfate and organic components have been most effectively controlled
- Nitrate is of increasing relative importance

H. Li et al., 2019
NO$_x$ emissions have decreased by 30% since 2013 - but PM nitrate has not decreased, and is up in winter haze events

Beijing wintertime data: nitrate is now the most important component of PM$_{2.5}$

Zhai et al., 2021a
Decreasing NO$_x$ emission can increase nitrate production through nighttime chemistry.

- NO$_x$ is mainly emitted as NO.
- NO and ozone titrate each other at night.
- In ozone titration regime, decreasing NO emission allows more ozone to react with NO$_2$ and produce nitrate.

\[
\begin{align*}
\text{Combustion:} & \\
O_2 \xrightarrow{\text{heat}} & O + O \\
O + N_2 & \rightarrow NO + N \\
N + O_2 & \rightarrow NO + O \\
\text{net:} N_2 + O_2 & \rightarrow 2NO
\end{align*}
\]
Decreasing NO\textsubscript{x} emission can increase nitrate lifetime by shifting fast-depositing nitric acid to slow-depositing PM\textsubscript{2.5} nitrate.

- Decreasing source of total nitrate shifts partitioning from HNO\textsubscript{3} to PM\textsubscript{2.5} nitrate, slowing down deposition.
- Decreasing ammonia emissions is the most effective strategy for decreasing PM\textsubscript{2.5} nitrate.

Zhai et al. [2021a]
Mapping of PM$_{2.5}$ over East Asia with GOCI geostationary satellite data (2010-)

hourly 6x6 km$^2$ GOCI AOD product from 0.5x0.5 km$^2$ native data

gap-filling random forest algorithm trained with surface network data

hourly 6x6 km$^2$ PM$_{2.5}$ with complete coverage, 2011-2019

Pendergrass et al. [2022]
Application to $\text{PM}_{2.5}$ distribution and long-term trends

GOCI provides
- observations in hotspots missing from AirKorea regulatory network;
- complete coverage of trends and population exposure

Pendergrass et al. [2022]
What is happening in Seoul?

No PM$_{2.5}$ trend over 2015-2019...while the rest of South Korea has decreased

Meteorologically corrected trend for AirKorea sites shows 3% increase driven by winter:

Could winter increase be driven by nitrate? We have seen that previously in Beijing

Pendergrass et al. [2022]; Nadia Colombi, in prep.
PM composition over Korea during KORUS-AQ campaign (May-June 2016)

Median observed PM$_{2.5}$ composition ($\mu$g m$^{-3}$)

- BC 1.2
- Sulfate 6.0
- Organic 8.3
- Nitrate 3.0
- Ammonium 3.2

Surface site data (circles)
GEOS-Chem model (background)

GEOS-Chem model overestimates nitrate (mainly from nighttime) and does not account for coarse PM $\equiv$ PM$_{10}$ – PM$_{2.5}$

Zhai et al. [2021b]
Coarse PM is generally assumed to be mainly from natural desert dust, but we find over East Asia that it is mainly of urban origin.

Gobi desert dust events (spring)

Air quality network data show strong correlation with CO:

- Vehicles
- Construction

Shixian Zhai, in prep.
Coarse PM trends from air quality networks, 2015-2020

- Decreased emissions from construction sites and road dust
- COVID-19 shutdown led to abrupt decrease

Shixian Zhai, in prep.
Coarse anthropogenic dust suppresses PM$_{2.5}$ nitrate formation

- Emitted dust particles are alkaline, take up HNO$_3$ efficiently
- The resulting coarse NO$_3^-$ is eventually deposited

We find in GEOS-Chem model that
- Dust emission controls drive an increase in PM$_{2.5}$ nitrate
- HNO$_3$ uptake by dust particles doubles sensitivity of PM$_{2.5}$ nitrate to NH$_3$ emission

Shixian Zhai, in prep.
Sources of organic aerosol over Korea

- Primary (POA) from combustion, secondary (SOA) from oxidation of VOCs
- New SOM-VBS mechanism in GEOS-Chem including improved aromatic SOA yields

Organic aerosol over S. Korea is mainly from fuel combustion

- 40% is oxidized primary organic aerosol (POA), 25% is aromatic secondary organic aerosol (SOA)
Van Krevelen diagram to interpret chemical evolution of organic aerosol

- Measured H:C and O:C molar ratios gives insight into functionalization
- Observations in the US usually suggest carboxylic acid functionalization
Van Krevelen diagram for Beijing haze organic aerosol

- Both H:C and O:C ratios increase during rapid aging observed at high relative humidity.
- But how do you get an increase in the H:C ratio?

Both high RH and rapid aging are observed during the 16-22 December 2016 haze event.

Polycyclic aromatic hydrocarbons (PAHs) are consistent with an increase in the H:C ratio.

Fresh fossil fuel POA transforms into oxidized POA through oxidation, ring opening, hydration, and functionalization.

Oxidized POA is consistent with a PAH source.

Wang et al. [2021]
Some take-aways

- Nitrate is an increasingly important component of PM$_{2.5}$ in East Asia (and elsewhere) as sulfate rapidly decreases
  - Formation of nitrate from NO$_x$ emissions is highly non-linear, and NO$_x$ emission decreases can actually cause nitrate increases
  - Decreasing NH$_3$ emissions from agriculture is more effective for controlling nitrate than decreasing NO$_x$ emissions

- Coarse PM in East Asia is very high and mainly of urban dust origin
  - Emission controls targeting urban dust may be causing increase in PM$_{2.5}$ nitrate and increased sensitivity to NH$_3$ emissions

- Organic aerosol over East Asia is mostly anthropogenic with a large contribution from oxidized primary organic aerosol (POA) and aromatic VOCs
  - Observed aging of POA is consistent with a combustion source from polycyclic aromatic hydrocarbons (PAHs)
  - Observation of high O:C ratios in organic aerosol does not necessarily imply a secondary origin
Van Krevelen diagram: application to organic aerosol

-1 slope suggests that aging is by adding of carboxylic functionalities, consistent with aqueous mechanism
Los Angeles smog
Respiratory problems, vegetation damage due to high surface ozone

Nitrogen oxides ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$)

Volatile organic compounds (VOCs)

Sunlight

Ozone ($\text{O}_3$)

PM

vehicles, industry, vegetation
Coarse PM as ‘forgotten’ component of PM air pollution

Annual mean PM$_{10}$ and PM$_{2.5}$ at AirKorea sites (https://www.airkorea.or.kr)

- PM$_{10}$ has been steadily decreasing since 1995, is close to NAAQS of 50 μg m$^{-3}$
- Coarse PM is about 50% of PM$_{10}$
Background contributions to organic aerosol in Korea from GEOS-Chem simulations for KORUS-AQ period (May-June 2016)

South Korean background $\equiv$ simulation with zero domestic anthropogenic emissions

- 1/3 of OA over South Korea in May-June is from external anthropogenic sources,
- 1/3 is from domestic anthropogenic sources, 1/3 is from biogenic sources
- About half of domestic anthropogenic OA is from aromatics

Brewer et al., submitted.
Ability of random-forest algorithm to infer PM$_{2.5}$ from GOCI satellite data

Statistics over East Asia for independent (withheld) surface network sites:

- **24-h**:
  - RMSE: 8.8 μg m$^{-3}$
  - RRMSE: 37%
  - $R^2$: 0.89
  - MB: 0.23 μg m$^{-3}$

- **Annual**:
  - RMSE: 3.3 μg m$^{-3}$
  - RRMSE: 14%
  - $R^2$: 0.96
  - MB: 0.22 μg m$^{-3}$

Precision of 37% or 8.8 μg m$^{-3}$ (24-h), 14% or 3.3 μg m$^{-3}$ (annual), negligible bias

*Pendergrass et al. [2022]*
Application to tracking of PM$_{2.5}$ pollution episodes

Seoul-Incheon pollution episode
May 24-29, 2016

GOCI PM$_{2.5}$ (background), AirKorea network (circles)

Spatial $R^2 = 0.74$ on 6x6 km$^2$ grid scale

Complete mapping serves need for air quality warnings, public health assessments

Pendergrass et al. [2022]