Atmospheric reactive nitrogen: sources, sinks, and impacts on air quality

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Reactive nitrogen

N\textsubscript{2}

nitrate

ammonia

NO/NO\textsubscript{2}

ammonium

N\textsubscript{2}O

Biologically, photochemically, or radiatively active

Inert
Global nitrogen cycle

Atmospheric molecular Nitrogen (N₂)

Dinitrification: 300 (200-400)
Biological: 160 (140-177)
Lightning: 4 (3-5)
Cultivation: 60 (50-70)
Denitrification: 109 (101-118)
Industrial: 124 (117-126)
Fossil fuel: 30 (27-33)
Natural biological: 58 (50-100)

Tg (million tons) N year⁻¹

3.9 x 10⁹
2.0 x 10⁹

[IPCC 2013]
The Haber-Bosch process significantly changed the availability of nitrogen.

Agricultural production for food was limited by nitrogen availability. Most of them is in its chemically and biologically unusable gaseous form (N₂).

The Haber-Bosch process by generating NH₃ from N₂ and H₂ in the presence of iron at high pressures and temperatures now feeds 44% of the world’s population.

[Graph showing world population growth and fertilizer input from 1900 to 2000.]

[Erisman et al., 2008]
Environmental consequences of reactive nitrogen

One atom of reactive nitrogen can cause multiple effects in the atmosphere, in ecosystems, and on human health.

- Photochemical smog (O₃)
- Particulate Matter (NH₄⁺, NO₃⁻)
- Greenhouse Effects (N₂O)
- Stratospheric ozone depletion
- Agroecosystem effects
- Reduction in biodiversity
- Eutrophication

[Galloway et al., 2003]
Present global anthropogenic emissions of reactive nitrogen

Bottom-up emissions estimated from energy statistics (2006).

Industrial combustion
Transportation

Agriculture (fertilizer, livestock)

Anthropogenic emission of NO\textsubscript{x}

5.3 Tg N
6.6 Tg N (million tons)
0.4 Tg N

Anthropogenic emission of NH\textsubscript{3}

2.3 Tg N
11 Tg N
0.5 Tg N

[10\textsuperscript{4} kg N m\textsuperscript{-2} a\textsuperscript{-1}]
1996-2012 satellite-derived ground-level NO$_2$ concentrations

[Geddes, Martin, et al., EHP 2016]
Substantial uncertainty in Chinese NH$_3$ emission estimates

<table>
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<tr>
<th>References</th>
<th>Fertilizer</th>
<th>Livestock</th>
<th>Other</th>
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<td>Yan et al.(2003)</td>
<td>4.32</td>
<td>2.48</td>
<td>0.21</td>
<td>7.01</td>
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</table>
Uncertainties in spatial and seasonal variations
The TES satellite instrument estimates atmospheric NH$_3$ concentrations from infrared spectral measurements.

High NH$_3$ levels reflect areas with intensive agricultural activities.
Top-down estimate of NH$_3$ emissions by the adjoint method

$$J(x) = (F(x) - y)^T S_e^{-1} (F(x) - y) + (x - x_a)^T S_a^{-1} (x - x_a)$$

Solving $\nabla J(x) = 0$
NH₃ columns: observations vs. prior and top-down emissions

\[ J(x) = (F(x) - y)^T S_e^{-1} (F(x) - y) + (x - x_a)^T S_a^{-1} (x - x_a) \]

Solving \( \nabla J(x) = 0 \)

- The source inversions largely improve comparisons of model results with TES observations;
- Current Chinese NH₃ emissions tend to underestimate their seasonal variations.

[Zhang et al. to be submitted]
Revisit bottom-up agricultural NH₃ emissions in China

- Better quantify how fertilizers are applied in China over 18 different agricultural crops (more practical fertilizer application timing and magnitude)
- Account for influences of meteorological conditions (near-surface temperature and wind) on the emission factors.

[Collaboration with F. Paulot (GFDL), Y. Song (PKU)]
Fertilizer application rate calculation for early rice

Emission factor $\alpha$: $\alpha_F = e^{f_{PH} + f_{CEC} + f_{type} + f_{crop} + f_{mode} \times f_{met}}$

$f_{met} = e^{0.0223T + 0.0419W}$
NH₃ emissions from fertilizer application and livestock are **4.75** and **5.31 Tg**, respectively, in 2008. **11.4 Tg** in total.

Both bottom-up and top-down show the highest NH₃ emissions in summer.

[Zhang et al. to be submitted]
Satellite NH$_3$ measurements from AIRS: variability and trends

[Warner et al., 2017]
Nitrogen: what goes up has to come down

[Galloway et al., Biogeochem. 2004]
Increasing importance of NH$_x$ deposition in the US

3-year average NH$_4^+$ percentage of inorganic nitrogen wet deposition ([NH$_4^+$]/([NH$_4^+$]+[NO$_3^-$])) over the US (1990-1992 vs. 2010-2012 NADP measurements)

Red: < 50%
Blue: > 50%

[Li et al. PNAS 2016]
Increasing nitrogen deposition over China

[Liu et al., Nature 2013]
Nationwide nitrogen deposition monitoring network in China

- 43 monitoring sites (2010-);
- Wet deposition collected by precipitation gauge method;
- Dry deposition estimated using airborne concentrations ($\text{NH}_3$, $\text{NO}_2$, $\text{HNO}_3$, $\text{NH}_4^+$, $\text{NO}_3^-$) and inferential method.

[Xu et al., ACP 2015; Prof. Xuejun Liu at CAU]
Measured and GEOS-Chem simulated surface nitrogen fluxes and concentrations

Annual NH$_4^+$ wet deposition  Annual NO$_3^-$ wet deposition  Surface NH$_3$ concentration

2008-2012 averages

[Zhao, Zhang, et al. 2017]
Atmospheric nitrogen deposition to China: emissions and processes

2008-2012 annual total deposition flux to China 16.4 Tg N: wet (61%), dry (39%)
NH\textsubscript{x} (62%), NO\textsubscript{y} (38%)
Budgets of atmospheric nitrogen deposition to China

- Mean annual deposition flux of 16.4 kg N ha\(^{-1}\) to China, \(\text{NH}_x\) contributing 62%;
- 24% of \(\text{NH}_3\) emissions (13 Tg) and 36% of \(\text{NO}_x\) emissions (9.4 Tg) are exported.

[Zhao, Zhang, AE et al. 2017]
Nitrogen deposition is about half of fertilizer nitrogen input, and is much higher than that from natural biological fixation over China.

About 15% of the land over China experiences eutrophication critical load exceedances.
Atmospheric nitrogen deposition over the US

GEOS-Chem simulation at 1/2x2/3 resolution averaged for 2006-2008

NO$_x$ emissions

NH$_3$ emissions

NO$_3^-$ wet deposition

NH$_4^+$ wet deposition

NO$_y$ dry deposition

NH$_x$ dry deposition

2006-2008 annual total deposition flux to the US 6.5 Tg N: wet (40%), dry (60%)
NH$_x$ (35%), NO$_y$ (65%)
38% NO$_x$, 21% NH$_3$ exported
Response of surface ozone air quality to enhanced nitrogen deposition through land-atmosphere exchanges

[Zhao, Zhang, et al. ACP, 2017]
Global nitrogen deposition fluxes and anthropogenic contributions

**Total nitrogen deposition**

- **NH$_4^+$ wet deposition**
  - $r=0.86$ bias=-5%
- **NO$_3^-$ wet deposition**
  - $r=0.70$ bias=-8%

**Anthropogenic emissions contribution**

- land: 65 Tg N a$^{-1}$
- land: 46 Tg N a$^{-1}$

**Scatter plots**

- North America: $r = 0.81$ b = 4%
- Europe: $r = 0.50$ b = -21%
- Asia: $r = 0.79$ b = -10%

- North America: $r = 0.86$ b = 1%
- Europe: $r = 0.60$ b = 0.3%
- Asia: $r = 0.53$ b = -23%
Impact of anthropogenic nitrogen deposition on land properties

Changes in vegetation LAI and subsequent responses

(1) Changes in biogenic VOC emissions

(2) Changes in ozone dry deposition velocity

(3) Changes in soil NO$_x$ emissions
Changes in summer mean surface ozone driven by anthropogenic nitrogen deposition can be comparable to those due to changes in climate and land use.

Influences of anthropogenic nitrogen deposition may largely offset the surface ozone reduction due to historical land use change.

Large uncertainties still exist associated with parameterizations of surface-atmosphere exchange processes.
Urgent needs to better quantifying sources contributing to PM$_{2.5}$ pollution over North China

Annual surface PM$_{2.5}$ concentration in 2013

Total premature mortalities attributable to PM$_{2.5}$ in 2013.

1.37 million mortalities in China

[Liu et al., STOTEN 2016]
Sulfate-Nitrate-Ammonium (SNA) aerosols are important components of PM$_{2.5}$

[Image of map showing distribution of SNA aerosols in different cities with pie charts indicating composition of particulate matter]

[Chemical reactions showing formation of (NH$_4$)$_2$SO$_4$ from SO$_2$ and NH$_3$, and formation of NH$_4$NO$_3$ from NO$_x$ and NH$_3$]

[Yang et al., ACP, 2011]
The role of ammonia (NH$_3$) on air pollution

As the main alkaline gas in the atmosphere, neutralizing H$_2$SO$_4$ and HNO$_3$ to form secondary inorganic aerosols;

Neutralizing aerosol surface pH that can enhance formation of sulfate formation?
Adjoint approach to track PM$_{2.5}$ pollution

Mathematically, an operator $A$ and its adjoint $A^*$ satisfy:
inner products $<Ax, y> = <x, A^*y>$
for any scalars $x$ and $y$.
Sources contributing to wintertime PM$_{2.5}$ in Beijing at multiple dimensions

Contributions from different emission sectors

<table>
<thead>
<tr>
<th>Source</th>
<th>Residential (50%)</th>
<th>Industrial (27%)</th>
<th>Power (6%)</th>
<th>Transport (6%)</th>
<th>Agricultural (12%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>0.3%</td>
<td>0.8%</td>
<td>0.0%</td>
<td>0.3%</td>
<td>11.8%</td>
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<tr>
<td>SO$_2$</td>
<td>4.9%</td>
<td>7.0%</td>
<td>2.2%</td>
<td>0.2%</td>
<td>0.0%</td>
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<tr>
<td>NO$_x$</td>
<td>0.8%</td>
<td>2.8%</td>
<td>2.6%</td>
<td>2.2%</td>
<td>0.0%</td>
</tr>
<tr>
<td>BC</td>
<td>6.8%</td>
<td>1.6%</td>
<td>0.0%</td>
<td>1.2%</td>
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<tr>
<td>OC</td>
<td>23.7%</td>
<td>2.8%</td>
<td>0.0%</td>
<td>0.8%</td>
<td>0.0%</td>
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<tr>
<td>Anthro. Dust</td>
<td>13.4%</td>
<td>11.5%</td>
<td>1.2%</td>
<td>1.1%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

Contributions from different chemical species

[Zhang et al., ERL, 2015] Impacts of NH$_3$ emissions on PM$_{2.5}$ resulting from formation of ammonium and nitrate.
Strong regional transport influences of PM$_{2.5}$ pollution

[Zhang et al., ERL, 2015]
A 4D-Var data assimilation system to improve model simulation

The CNEMC Monitoring Sites

Satellite observations

Optimized Simulation

Improved Source Attribution

The GEOS-Chem Model and its Adjoint

Data Assimilation

Emissions

Prior Simulation

Forward Model

Optimized Model

Adjoint Sensitivity

[Zhang et al., ES&T 2016]
Contribution of meteorological variation to “APEC Blue”

Beijing PM$_{2.5}$ concentrations during Oct 15-Nov 15, 2014

Observations
Model results with fixed emissions
Optimized model results

56% of the PM$_{2.5}$ reduction during APEC is attributed to meteorology, and 44% to emission reductions

Surface pressure and 800 hPa winds

More Active cold-surge activities during the APEC

[Zhang et al., ES&T 2016]
A case of PM$_{2.5}$ accumulation and ventilation over North China

Simulated surface PM$_{2.5}$ concentrations over North China
(2014.10.24-10.29)
A case of PM$_{2.5}$ accumulation and ventilation over North China

Simulated surface PM$_{2.5}$ concentrations over North China
(2014.10.24-10.29)
Sources contributing to high PM$_{2.5}$ events at Beijing in October-November 2014

Beijing PM$_{2.5}$ concentrations during Oct 15-Nov 15, 2014

- Oct. 18: (128 ug/m$^3$)
- Oct. 25: (248 ug/m$^3$)

<table>
<thead>
<tr>
<th>Date</th>
<th>Concentration (ug/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct. 18</td>
<td>128</td>
</tr>
<tr>
<td>Oct. 25</td>
<td>248</td>
</tr>
</tbody>
</table>

**Observations**

- Dust (71.9%)
- OC (25%)
- BC
- NO$_x$ (15%)
- SO$_2$ (12%)
- NH$_3$ (17.5%)

**Optimized model results**

[Dust, OC, BC, NO$_x$, SO$_2$, NH$_3$] [Zhang et al., ES&T 2016]
Summary

- **Ammonia sources:**
  
  2008 Chinese anthropogenic NH\textsubscript{3} emissions of 11.4 Tg: 4.75 Tg from fertilizer application, 5.31 Tg from livestock waste;

  Both bottom-up and top-down estimates now show a strong seasonality.

  Factors driving the trend of NH\textsubscript{3} concentrations over China are still unknown.

- **Nitrogen deposition:**
  
  Atmospheric nitrogen deposition contribute 16.4 Tg N over China; a factor of 2 higher than natural biological fixation, and about half of nitrogen from fertilizer use.

  Anthropogenic nitrogen deposition generally enhanced surface ozone concentrations through surface-atmosphere exchange processes.

- **PM\textsubscript{2.5} pollution over North China**
  
  Importance of residential, industrial, and agricultural emissions on PM\textsubscript{2.5} as shown from the adjoint sensitivities;

  Impacts of trends of NH\textsubscript{3}, SO\textsubscript{2}, and NO\textsubscript{x} emissions on PM\textsubscript{2.5} pollution (ongoing)
Thank you for your attention!
Atmospheric Pollution: Sources, Sinks, and Impacts

**Pollution Sources**
- Industry
- Transport
- Residential
- Agriculture
- Natural
- Fires

**Chemical and Physical Transformation**
- CO, SO₂, NOₓ, VOCs
- PM
- SO₂, NOₓ, VOCs
- PM
- CO, SO₂, NOₓ, VOCs
- PM
- NH₃
- VOCs
- NOₓ, VOCs
- PM

**Environmental Consequences**
- Deposition
- Bioproductivity
- Eutrophication

**Air Pollution**
- Inorganic Aerosols
- SOA
- H₂SO₄
- H₂O₂
- NH₄⁺
- NH₃
- HNO₃
- NO₃⁻

**Eutrophication**

**Bioproductivity**

**Deposition**
Observed and simulated PM2.5 and its composition for January 2013

- **a)** Standard GEOS-Chem (8.2 ug m\(^{-3}\))
- **b)** Aqueous-phase oxidation of S(IV) by NO\(_2\) (13.8 ug m\(^{-3}\))
- **c)** Further with H\(_2\)O\(_2\)/O\(_3\) oxidation on deliquescent aerosols (16.8 ug m\(^{-3}\))

[Zhang, L. et al., ERL, 2015]
Evaluation with independent surface measurements

NH$_4^+$ wet deposition flux

Spring

Summer

Fall

Winter

Observations [kg ha$^{-1}$]

GEOS-Chem [kg ha$^{-1}$]

- Measurements
- Improved
- Prior
- Optimized

$1.1\pm0.5$
$1.3\pm0.8$ (0.67)
$1.1\pm0.5$ (0.54)
$1.2\pm0.8$ (0.67)

$2.8\pm1.6$
$2.3\pm1.0$ (0.62)
$2.9\pm1.5$ (0.70)
$3.1\pm1.2$ (0.51)

$1.0\pm0.4$
$1.4\pm0.8$ (0.36)
$1.0\pm0.5$ (0.41)

$0.4\pm0.3$
$0.5\pm0.5$ (0.61)
$0.3\pm0.3$ (0.52)
Emission control measures and air quality improvement during the APEC 2014 period

- The Asia-Pacific Economic Cooperation Summit (November 5-11, 2014)
- Strict emission controls were applied at Beijing, including the suspension of production by factories, cutting the number of on-road vehicles by half, assigning holidays for public-sector employees, etc.

Tropospheric NO$_2$ columns (OMI vs. GEOS-Chem)

<table>
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<tr>
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<th>Nov 5-11</th>
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<td>GEOS-Chem model</td>
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<td>Difference</td>
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</table>

[10$^{15}$ molec. cm$^{-2}$]
Optimized emissions before and during “APEC Blue”

- Assimilation of hourly surface PM$_{2.5}$ measurements into the model captures the emission reduction.
Nitrogen deposition to Chinese seas: seasonal variations and main sources

2008-2010 annual and monthly mean nitrogen deposition fluxes

Excessive nitrogen deposition → eutrophication problems

Yellow Sea: 11.9 kg N ha⁻¹
South CH Sea: 5.6 kg N ha⁻¹

[Zhao, Zhang*, et al. ACP 2015]
Measurements provide important information, while lack details in the processes

**Beijing (January 2013) 158.5 ug m\(^{-3}\)**

**Composition:** OM 40.7%; Second inorganic aerosols 37.8%

**Attribution:** Coal burning 26.1%; Secondary 51.1%

[Huang et al., Nature 2014]