The impact of size-resolved aerosol microphysics on heterogeneous chemistry: Uncertainties associated with aerosol size and composition

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The impact of aerosols on atmospheric chemistry

- changing the photolysis rate
- providing the surface where heterogeneous reactions occur

The dominant heterogeneous reaction in the troposphere is the reactive uptake of $\text{N}_2\text{O}_5$ (Martin et al., 2003)

- producing nitric acid
- removing oxides of nitrogen from the atmosphere

In current GEOS-Chem

- using bulk aerosol to calculate uptake rate

**GEOS-Chem/APM**: size-resolved aerosol microphysics in GEOS-Chem (Yu and Luo, ACP, 2009)

- SP: 40 bins; Sea-salt: 20 bins; Dust: 15 bins
- BC: 15 bins; OC: 15 bins

Coating of SP on primary particles

State-of-the-art new particle formation schemes and aerosol microphysics
Impacts of aerosol microphysics on heterogeneous chemistry: ‘size effect’ and ‘mixing effect’

\[ R_{\text{uptake}} = \frac{S}{4 \gamma \cdot v} \]

Where \( R_{\text{uptake}} \) is uptake rate (s\(^{-1}\)); \( S \) is aerosol surface area; \( \gamma \) is uptake parameter; \( v \) is mean molecular speed

- **‘size effect’**: impact \( R_{\text{uptake}} \) via aerosol surface area
- **‘mixing effect’**: impact \( R_{\text{uptake}} \) via uptake parameter

\[
\gamma_{SP} = \frac{\gamma_{SO4} \cdot (M_{SO4} + M_{MSA} + M_{(NH_4)_2SO_4}) + 0.1 \gamma_{SO4} \cdot (M_{NIT} + M_{NH_4NO_3}) + \gamma_{OC} \cdot M_{SOA}}{M_{SP}}
\]

\[
\gamma_{PP} = \frac{\gamma_{SP} \cdot M_{\text{coatedSP}} + \gamma_{PP} \cdot M_{PP}}{M_{\text{coatedSP}} + M_{PP}}
\]

**SP**: secondary particles

**PP**: primary particles
dust, sea-salt, black carbon,
primary organic carbon

Cases: Old; NewSF; NewAll

Relative changes of [N\(_2\)O\(_5\)] at surface layer
Impacts on $[\text{N}_2\text{O}_5]$ at surface layer

(NewSF-Old)/Old (%): $\gamma_{\text{N}_2\text{O}_5}$ 201212 surface, Mean=2.6%

(NewAll-Old)/Old (%): $\gamma_{\text{N}_2\text{O}_5}$ 201212 surface, Mean=17.9%

(NewSF-Old)/Old (%): $[\text{N}_2\text{O}_5]$ 201212 surface, Mean=87.0%

(NewAll-Old)/Old (%): $[\text{N}_2\text{O}_5]$ 201212 surface, Mean=175.1%

(NewSF-Old) (ppt): $[\text{N}_2\text{O}_5]$ 201212 surface, Mean=10.9ppt

(NewAll-Old) (ppt): $[\text{N}_2\text{O}_5]$ 201212 surface, Mean=28.0ppt
Impacts on $[\text{HNO}_3]$ , and $[\text{NO}_2]$

$\Delta[\text{HNO}_3]$:
USA: -20-40%; Europe: -40-60%; East Asia: -20-60%

$\Delta[\text{NO}_2]$:
USA: 10-30%; Europe: 20-60%; East Asia: 30-60%
Column \( \text{NO}_2 \): GOME-2 vs GEOS-Chem

Column \( \text{NO}_2 \) is enhanced due to the use of aerosol microphysics

<table>
<thead>
<tr>
<th></th>
<th>GOME-2</th>
<th>Old</th>
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<th>NewAll</th>
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<td>10.9</td>
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</tbody>
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Impacts on [NIT], [NH4], and [NH3]
Summary

- With GEOS-Chem/APM, we studied aerosol ‘size effect’ and ‘mixing effect’ on N₂O₅ heterogeneous chemistry and found they are comparable.

- After including aerosol microphysics in heterogeneous chemistry, 2012-12 20ºN-60ºN surface layer:
  - N₂O₅ $\uparrow$ 175%; HNO₃ $\downarrow$ 6%; NO₂ $\uparrow$ 17%
  - At source regions, N₂O₅ $\uparrow$ 500-1000%; HNO₃ $\downarrow$ 60%; NO₂ $\uparrow$ 80%

- Winter time NO₂ simulation has been improved.

- $\Delta$HNO₃ impacts aerosol thermodynamic equilibrium.