Investigating the role of different nocturnal heterogeneous chemistry schemes on daytime air quality

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Heterogeneous chemistry and air quality

Nitrogen oxides ($NO_x \equiv NO + NO_2$) have a major effect on air quality in the United States. They have direct human health impacts, play a central role in the production of secondary pollutants like ozone and particle pollution, and cause environmental damage. **Nighttime heterogeneous NOx chemistry – chemistry between particles and gases – regulates the reservoirs and sinks of NOx.** This has large impacts on daytime air quality concerns (Figure 1). We compared the NO_2 concentrations calculated using two different heterogeneous chemistry schemes to assess the impact of this chemistry.

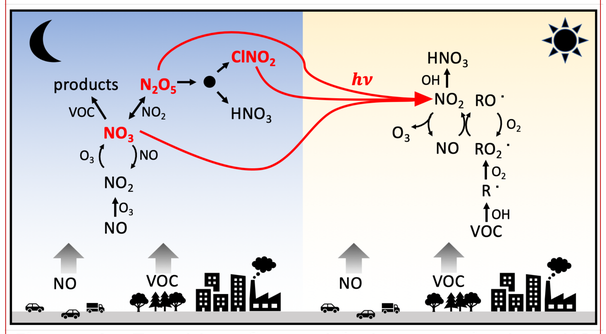

Figure 1. *Transition from nighttime to daytime NO_x chemistry. The species NO_3, N_2O_5, and $ClNO_2$ all affect daytime NO_x-O_3 chemistry because they will break down to form NO_2 once the sun comes up.*

Modeling approach

We tested two heterogeneous chemistry schemes in the Community Multiscale Air Quality (CMAQ) model version 5.3.2. More information about the chemical mechanisms is in the "Heterogeneous Chemistry Schemes" section.

Time period: Jan 1, 2016 – Feb 1, 2016 (plus 10 day spin-up period)

CMAQ domain: US CONUS on a 12 km x 12 km grid, 1 hr time steps

References

1. Bertram, T. H., & Thornton, J. A. (2009). Toward a general parameterization of N2O5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride. Atmospheric Chemistry and Physics, 9, 8351–8363. www.atmos-chem-phys.net/9/8351/2009/

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Updated heterogeneous NO_x chemistry increases ambient NO_2 concentrations across the US in wintertime

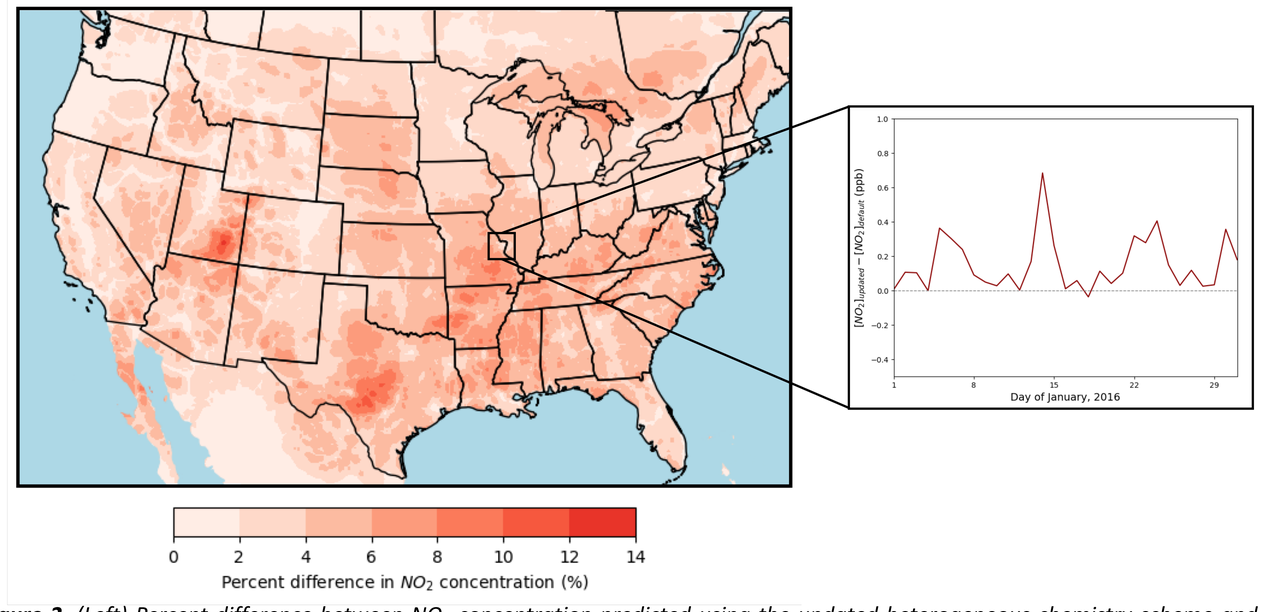

Figure 2. *(Left) Percent difference between NO_2 concentration predicted using the updated heterogeneous chemistry scheme and the default heterogeneous chemistry scheme, averaged over the entire month of January 2016. Red means the updated scheme predicts a higher NO_2 concentration, with darker shades indicating greater difference. Greater differences are generally predicted over the southeastern US. (Right) Time series of the difference between update and default chemistry schemes, where locations were aligned with EPA monitors in the St. Louis region.*

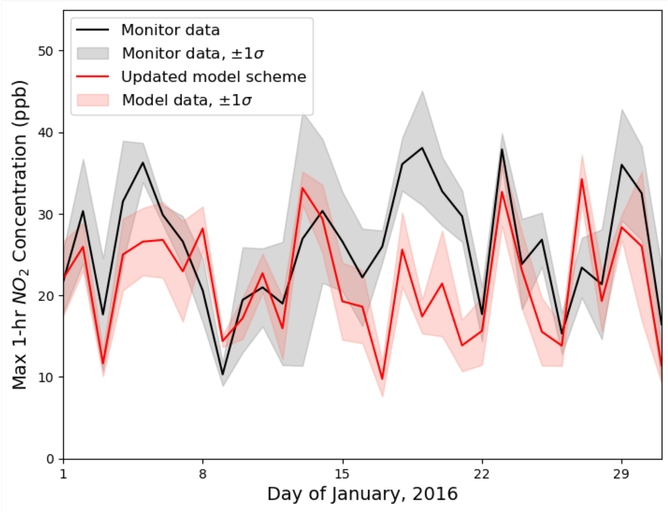

Figure 3. *Time series of the average daily maximum 1 hour NO_2 concentration in St. Louis, MO. There were five active EPA NO_2 monitors in the St. Louis area in 2016. The updated model data was aligned with these monitor locations to assess model performance. Solid lines are the daily average of the 1 hr maxima from the five monitor locations, and the shaded regions represent ± 1 standard deviation from this mean.*

How does the chemistry compare?

1. The updated chemistry scheme results in higher NO_2 concentrations across the US during January (Figure 2).
2. Differences vary over time (Figure 2, St. Louis zoom), but the updated scheme tends to predict higher daily NO_2.
3. This implies concentrations of reservoir species are higher in the updated chemistry scheme.
4. Despite the increases in the updated chemistry scheme, the model still tends to under-predict compared to monitor data ($NMB = -17\%$) in the St. Louis area during January, 2016 (Figure 3).
5. There is moderate model accuracy for the prediction of average daily maximum 1 hr NO_2 concentration in St. Louis ($RMSE = 8.0\ ppb$).

Questions?

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Heterogeneous Chemistry Schemes

We tested two chemistry schemes with combinations of N_2O_5 uptake $\gamma(N_2O_5)$ and $ClNO_2$ yield $\Phi(ClNO_2)$:

Default in CMAQ

$\gamma(N_2O_5)$**:** Depends on aqueous-phase composition, temperature and RH (Bertram & Thornton, 2009; Davis, et al. 2008).

$\Phi(ClNO_2)$**:** Depends on particle water and chloride (Sarwar, et al. 2012).

Updated mechanisms

$\gamma(N_2O_5)$**:** Includes the resistive effects of organic coatings on uptake. Depends on organic composition, aqueous phase composition, and RH (Gaston, et al. 2014).

$\Phi(ClNO_2)$**:** Includes competitive effect of sulfate, and depends on particle water, chloride, and sulfate (Staudt, et al. 2019).

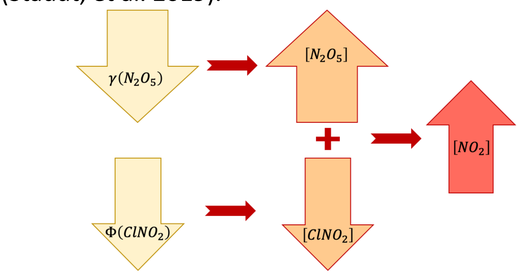

Figure 4. *Expected impacts of the updated chemistry on NO_2 morning concentrations. An organic coating will decrease $\gamma(N_2O_5)$ in the updated scheme, resulting in higher ambient N_2O_5 concentrations. Competition by sulfate will decrease $\Phi(ClNO_2)$ in the updated scheme, resulting in lower $ClNO_2$ production. We predict that the increase in N_2O_5 will be a greater effect than the decrease in $ClNO_2$, resulting in slightly higher NO_2 concentrations.*

Future Work

1. Compare summertime conditions.
2. Identify driving factors affecting the two chemistry schemes in each season.
3. Assess the relative impact of changes to $ClNO_2$ and N_2O_5 concentrations.
4. Validate NO_2 concentrations with satellite data.

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