Improving the representation of HONO chemistry in CMAQ and examining its impact on haze in Beijing, China

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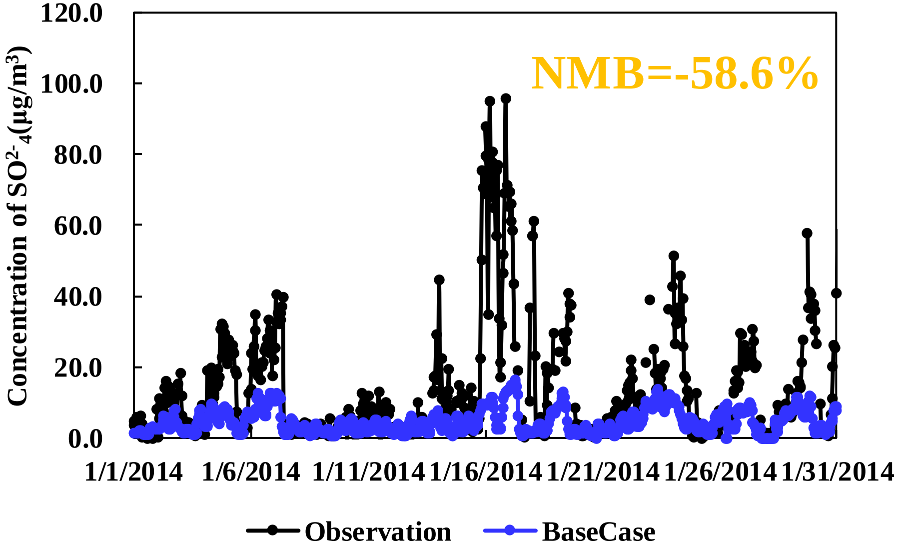
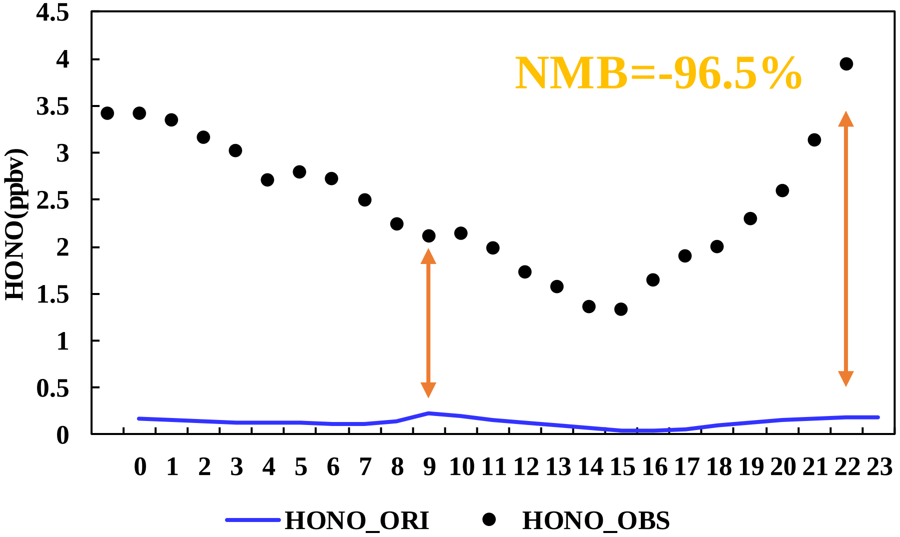
Background





- ☐ Secondary aerosol and HONO were seriously underestimated in previous studies
- ☐ HONO can photolyze to produce OH which can form secondary aerosol. However, the role of HONO in secondary aerosol formation has not been examined in model
- ☐ Here, we examine the role of HONO in secondary aerosol formation in Beijing, China

Field Campaign

- A field campaign was conducted in Beijing, China
  - Location: Tsinghua University Campus & Research Center for Eco-Environmental Sciences Campus
  - Duration: 11/22/2015 – 12/31/2015
  - Measured gaseous/aerosol species, meteorological parameters
- Major gaseous species: NO, NO_2, NO_x, SO_2, O_3, HONO
- HONO concentrations were measured
  - Using a custom made equipment - stripping coil equipped with ion chromatograph
  - The method was compared to three standard methods and produced similar results
  - Minimum detection of 4.0 ppt
- Major aerosol species: SO_4^{2-}, NO_3^-, NH_4^+, $PM_{2.5}$

Model configuration

- Chemical Transport Model: CMAQv5.3
- Meteorological Model: WRFv3.8
- Simulation Domain: China
- Simulation Time: 11/22/2015 – 12/31/2015
- Horizon Resolution: 27km×27km
- Vertical Resolution: 14 layers
- Emissions: Developed by Tsinghua University, 2015
- Chemical Options:
  - Gas-phase Mechanism: CB6r3
  - Aerosol Module: AERO7
- Number of Model Simulations:
  - ORI – simulation with the existing chemistry
  - REV - simulation with the revised chemistry

Existing HONO chemistry in CMAQ

- CMAQ contains several gas-phase reactions related to HONO
  - However, default gas-phase chemistry underestimate HONO (Sarwar et al., 2008)
- CMAQ also contains one heterogeneous reaction on ground/aerosol
  - Implemented in 2008 (Sarwar et al., 2008)
- Many HONO related articles have been published during the last 12 years which contain updated reactions
- Thus, HONO chemistry in CMAQ needs to be updated

Existing heterogeneous reaction producing HONO in CMAQ			
Reaction	K (1/s)	Surface area	Reference
NO2 →0.5HONO + 0.5HNO3 (ground)	$k = 1.6\times10^{-6} \times S/V_g$	**Urban surface areas are calculated from PURB. Leaf surface areas are also used**	Vogel et al., 2003
NO2 →0.5HONO + 0.5HNO3 (aerosols)	$k = 1.6\times10^{-6} \times S/V_a$	**Aerosol surface areas are used**	Vogel et al., 2003

* CMAQv53 accounts for HONO emissions from motor vehicles as 0.008 x NO_X emissions

Revised HONO chemistry in CMAQ

Pseudo-first-order reaction

$$k_i = \left(\frac{d_p}{2D_i} + \frac{4}{v_i \gamma_i} \right)^{-1} S_p$$

dp: effective diameter of particle
Di: gas diffusion coefficient
vi: mean molecular speed in gas phase
Sp: surface area per unit volume of air
γi: uptake efficient

γ is key parameter

K_{a_day}: heterogeneous reaction rate of NO_2 on the aerosol surface at day time

K_{a_night}: heterogeneous reaction rate of NO_2 on the aerosol surface at night time

K_{g_day}: heterogeneous reaction rate of NO_2 on the ground surface at day time

K_{g_night}: heterogeneous reaction rate of NO_2 on the ground surface at night time

PNO_3: photolysis reaction rate of nitrate

K_{HNO3}: production rate of the acid displacement reactions of HNO_3

K_{CL}: production rate of the acid displacement reactions of HCl

K_{EC}: production rate from the reaction of EC

J : NO_2 photolysis rate

$JHNO_3$: photolysis reaction rate of HNO_3

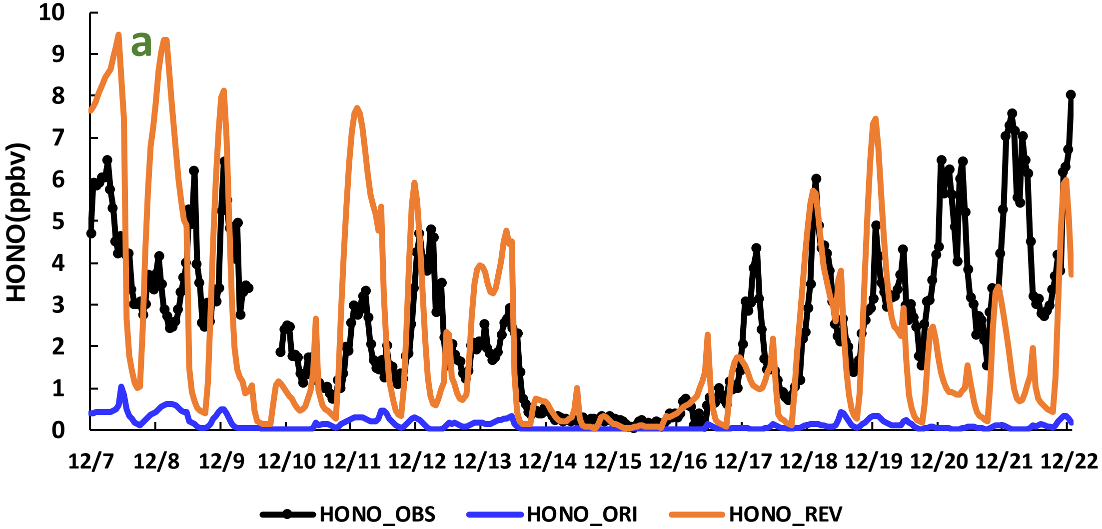
V_{dep_HNO3} : deposition velocity of HNO_3

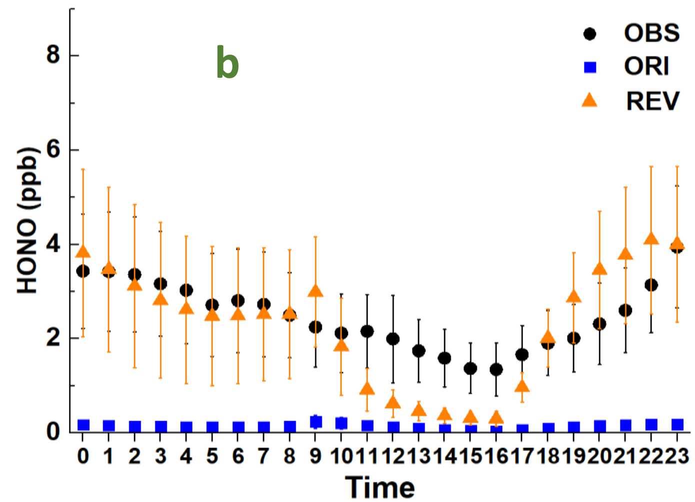
Revised HONO chemistry in CMAQ

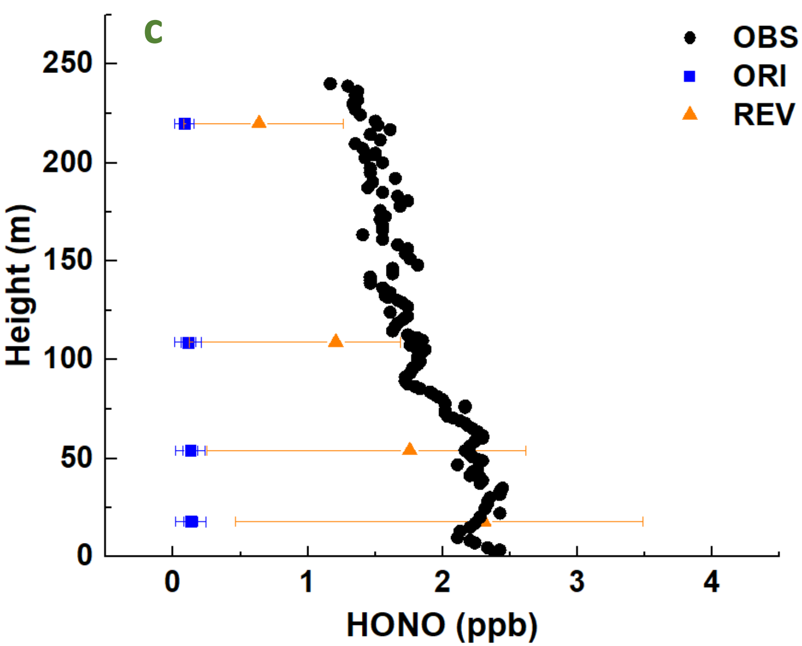
Reaction	K	Gamma	Reference
NO2 → 0.5HONO + 0.5HNO3 (night)	$K_{\mathrm{a\_night}} = \frac{1}{4}\gamma v_{NO2}\frac{S}{V_a}$	$\gamma_{an}=8\times10^{-6}$	(Liu et al., 2019)
NO2 → 0.5HONO + 0.5HNO3 (day)	$K_{\mathrm{a\_day}} = \frac{1}{4}\gamma v_{NO2}\frac{S}{V_a}\times\frac{\mathrm{J}}{J_{max}}$	$\gamma_{ad}=1\times10^{-5}$	(Li et al., 2018a; Liu et al., 2019)
NO2 → HONO (night)	$K_{\mathrm{g\_night}} = \frac{1}{8}\gamma v_{NO2}\frac{S}{V_g}$	$\gamma_{gn}=4\times10^{-6}$	(Liu et al., 2019)
NO2 → HONO (day)	$K_{\mathrm{g\_day}} = \frac{1}{8}\gamma v_{NO2}\frac{S}{V_g}\times\frac{J}{J_{max}}$	$\gamma_{gd}=6\times10^{-5}$	(Liu et al., 2019)
NO3 (aero) → 0.67HONO + 0.33NO2	PNO3=30×JHNO3		(Romer et al., 2018)
HNO3 → HONO	$K_{HNO3}=0.06V_{dep\_HNO3}/H$		(Spataro and Ianniello, 2014)
HCL → HONO	$K_{HCl}=0.2V_{dep\_HCl}/H$		(VandenBoer et al., 2015)
NO2 + EC → 0.61HONO + 0.39NO	$K_{\mathrm{EC}} = \frac{1}{4}\gamma v_{NO2}\frac{S}{V_{\mathrm{EC}}}$	$\gamma_{EC}=2\times10^{-6}$	(VandenBoer et al., 2015)

- Added five heterogeneous chemistry updates for HONO

Impact on HONO Concentration

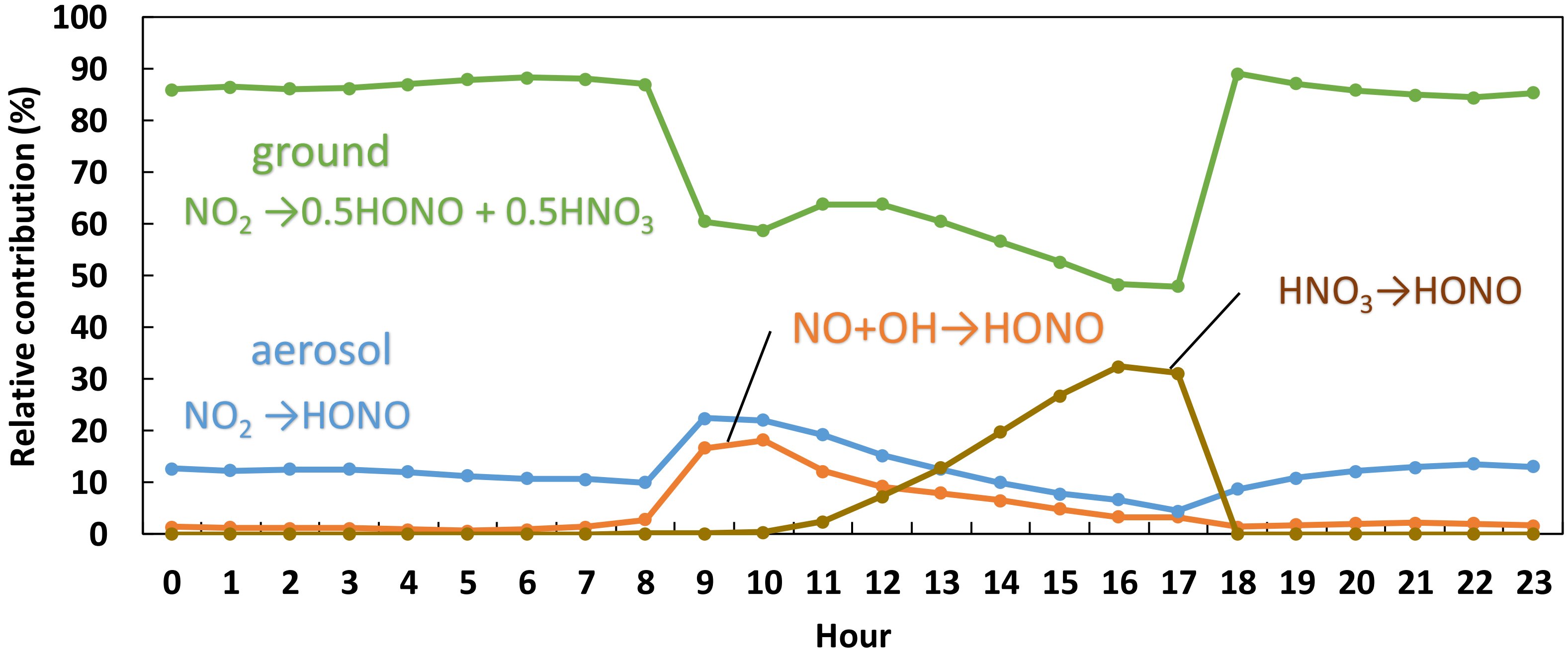






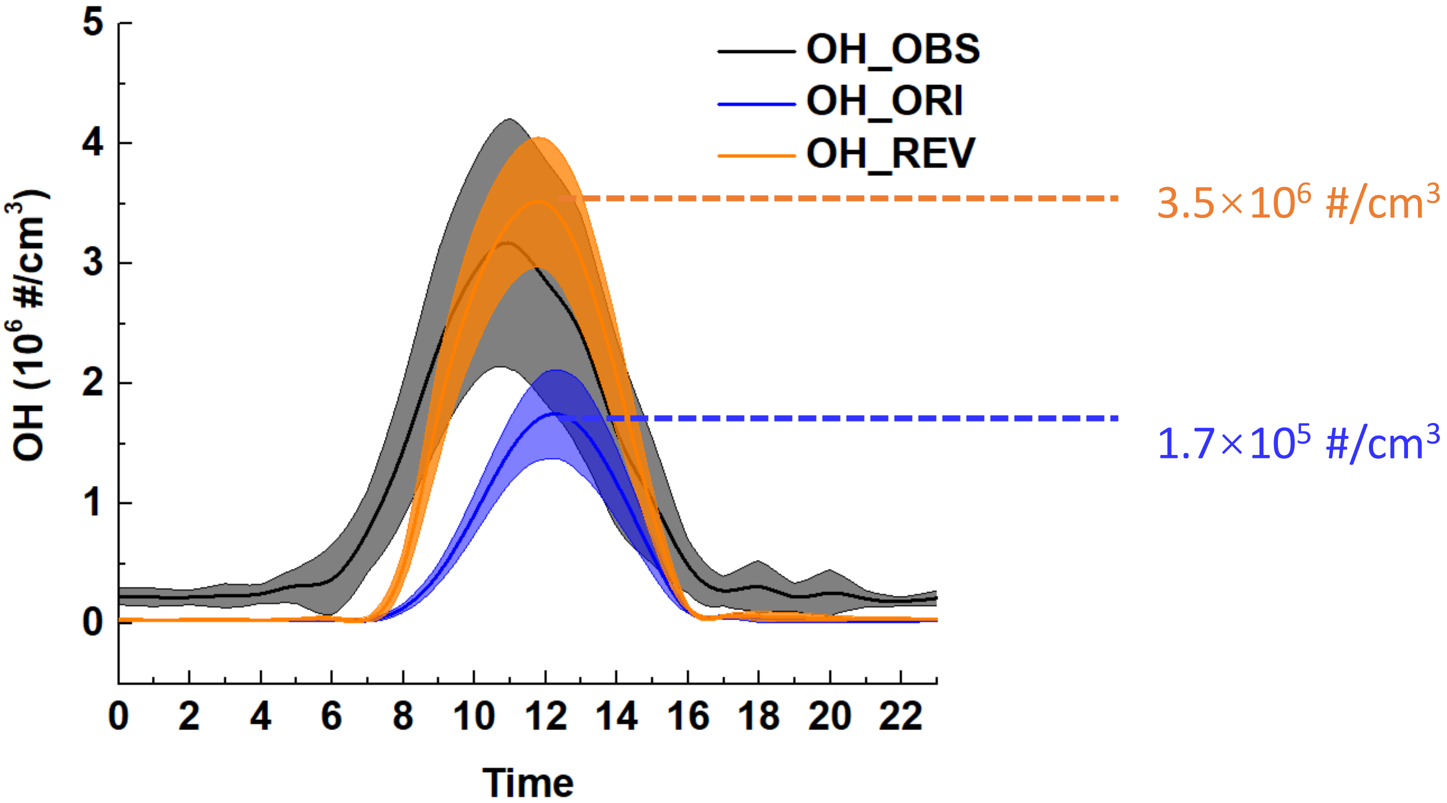
- Predicted HONO with ORI are too low; REV enhances HONO concentrations which compare more favorably with observed data
- Average HONO increases from ~0.1 ppb with ORI to ~2.3 ppb with REV and NMB is reduced from -96.5% to -4.8%
- REV enhances diurnal HONO concentrations similar to the observations
- REV enhances HONO concentration aloft also

Relative Strength of Different HONO Sources



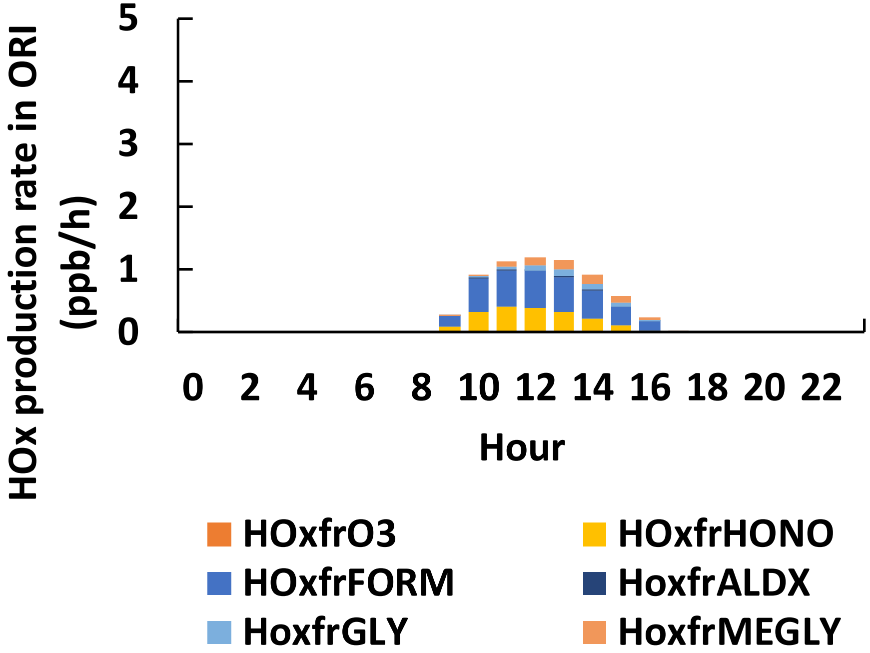
- Heterogeneous reactions on the ground surface at night is the largest contributor representing ~86% of the predicted HONO
- Heterogeneous reactions on aerosol surface at night is the second largest contributor representing ~12 % of the predicted HONO

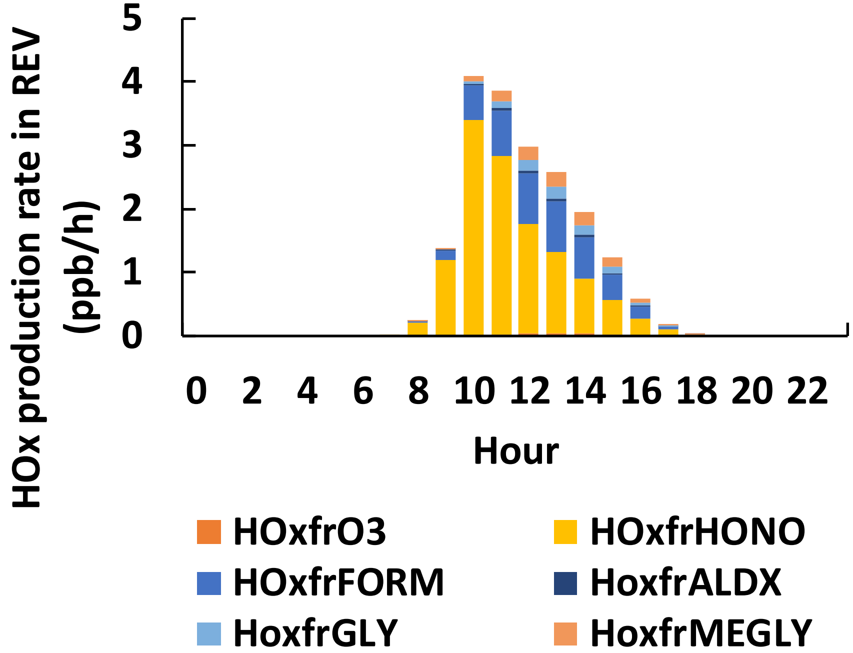
Impact on OH



- REV enhances OH and improves the underestimation of OH which is the primary atmospheric oxidant

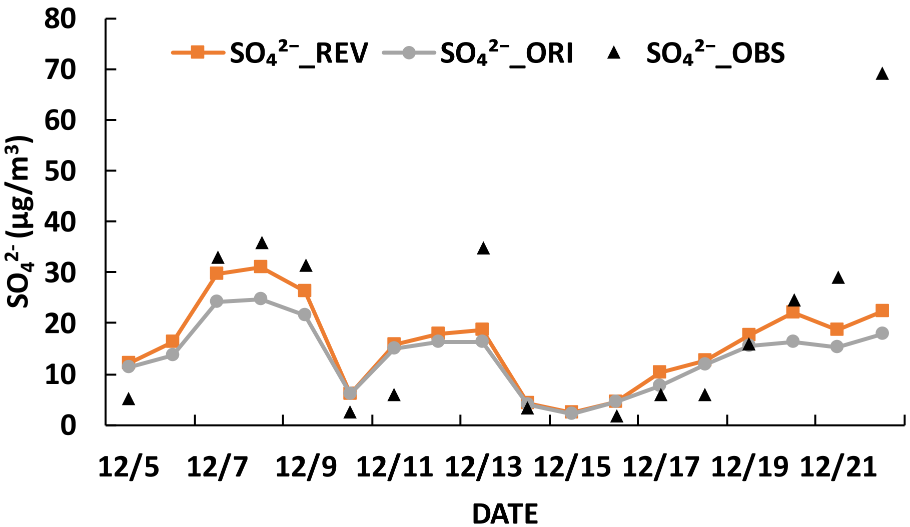
Relative Strength of Different Photolytic HO_x Sources

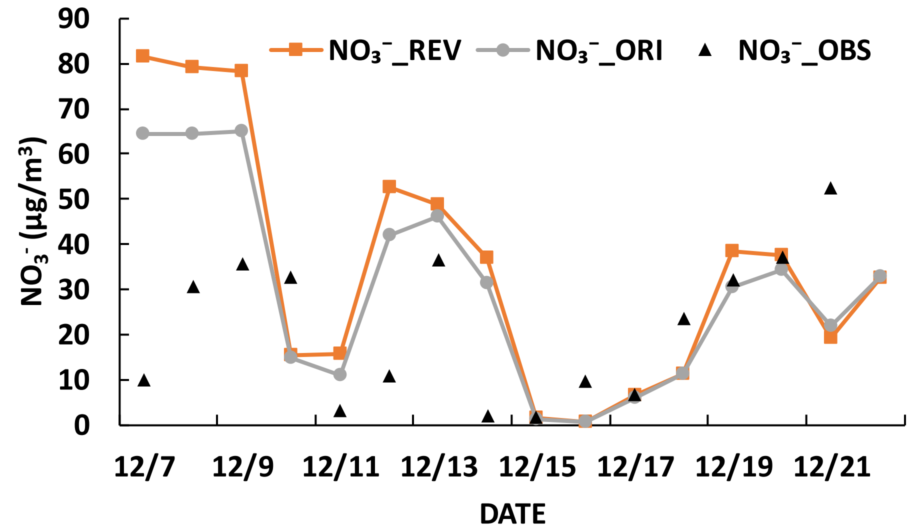




- In ORI, production of HO_x is dominated by the photolysis of HONO and formaldehyde
- In REV, production rates of HOx are much higher than those in ORI due to much larger contribution from HONO

Impacts on sulfate and nitrate

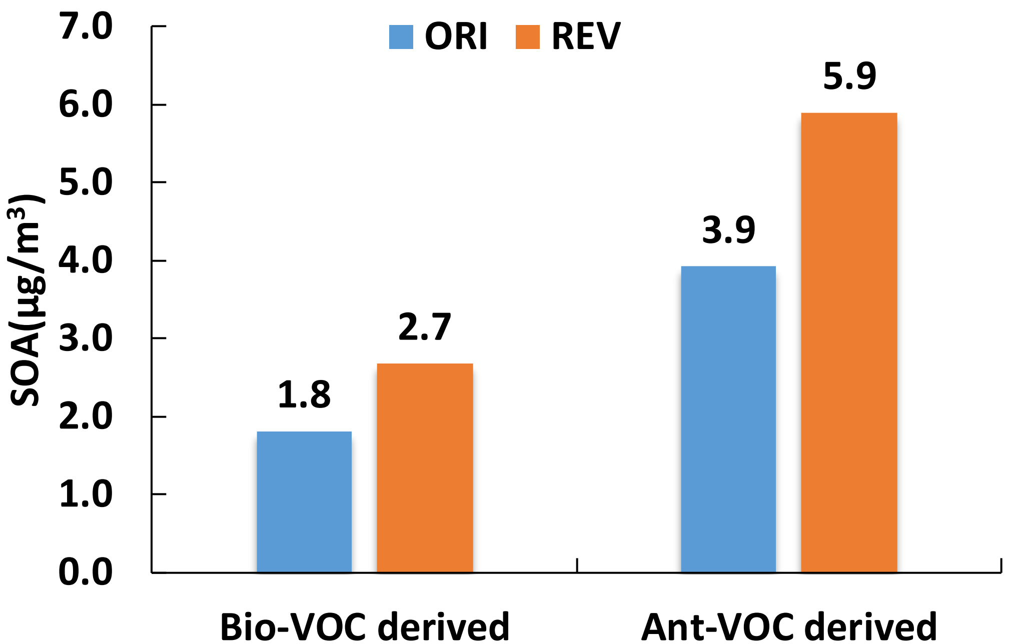




Chemical pathway	Sulfate average concentration in ORI (μg/m³)	Sulfate average concentration in REV (μg/m³)
SO_2 + OH	2.23	3.99
S(IV) + H_2O_2	0.25	0.41
S(IV) + O_3	0.02	0.02
S(IV) + O_2 (TMI)	0.61	0.50
S(IV) + MHP	0.01	0.01
S(IV) + PAA	<0.01	<0.01

- REV increases sulfate and nitrate concentrations
- Average reaction rate of SO_2 + OH increases by ~80% and of S(IV) + H_2O_2 by 64%
- Predicted sulfate compare better with observed data

Impacts on SOA formation



- Additional HONO chemistry updates enhances SOA production rate
- No observed data are available for comparison

Conclusion

- Implemented five additional HONO chemistry updates in CMAQ which significantly enhance and improve HONO concentration
- HONO production is primarily controlled by the heterogeneous reactions on ground and aerosol surfaces
- Additional HONO chemistry updates increase OH and production of secondary aerosols: sulfate, nitrate, and SOA

Future plan

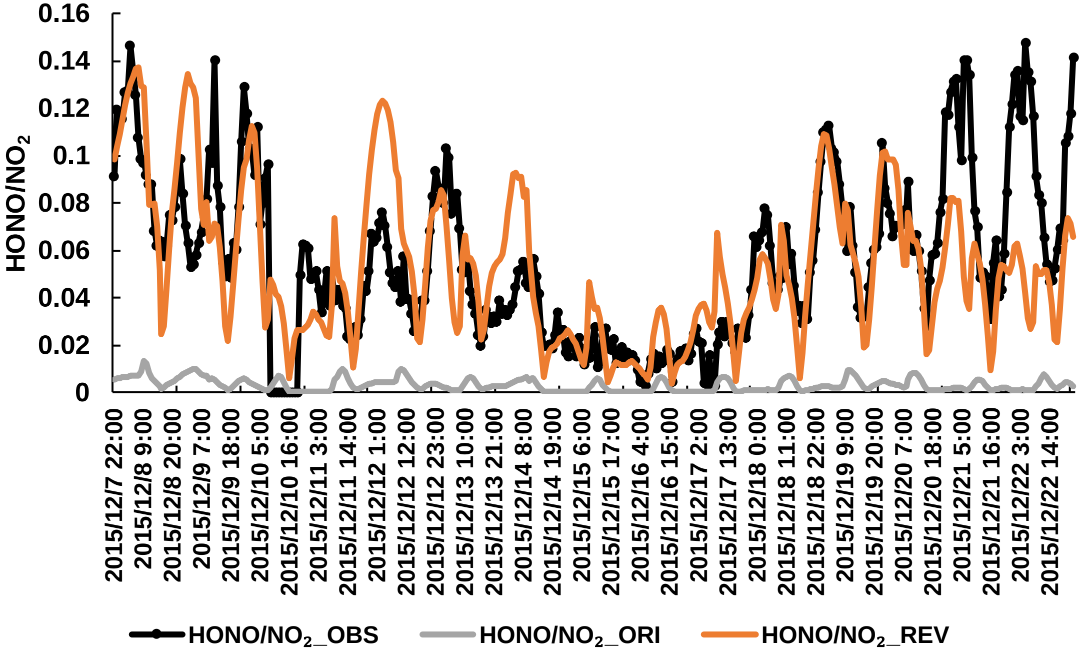
- Examine the impact of HONO chemistry updates in other seasons
- Examine the impact of HONO chemistry updates on O_3 formation

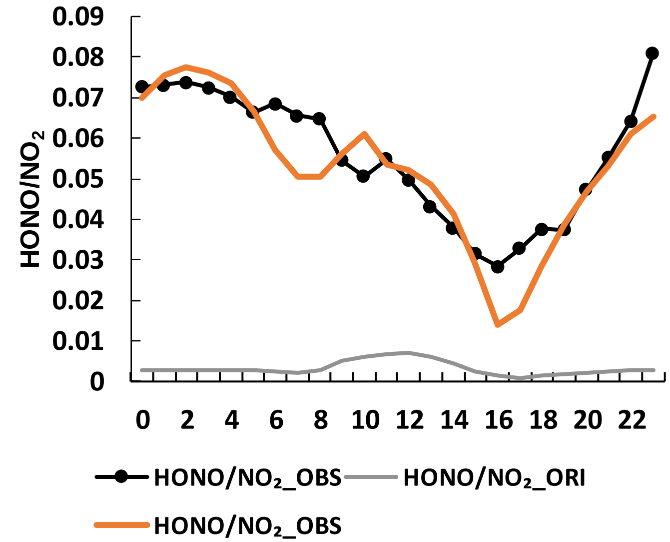
Thank you very much!

The views expressed in this presentation are those of the authors and do not necessarily represent the views or policies of the U.S. EPA.

Extra slides

Results-Improved simulation of $HONO/NO_2$ ratio



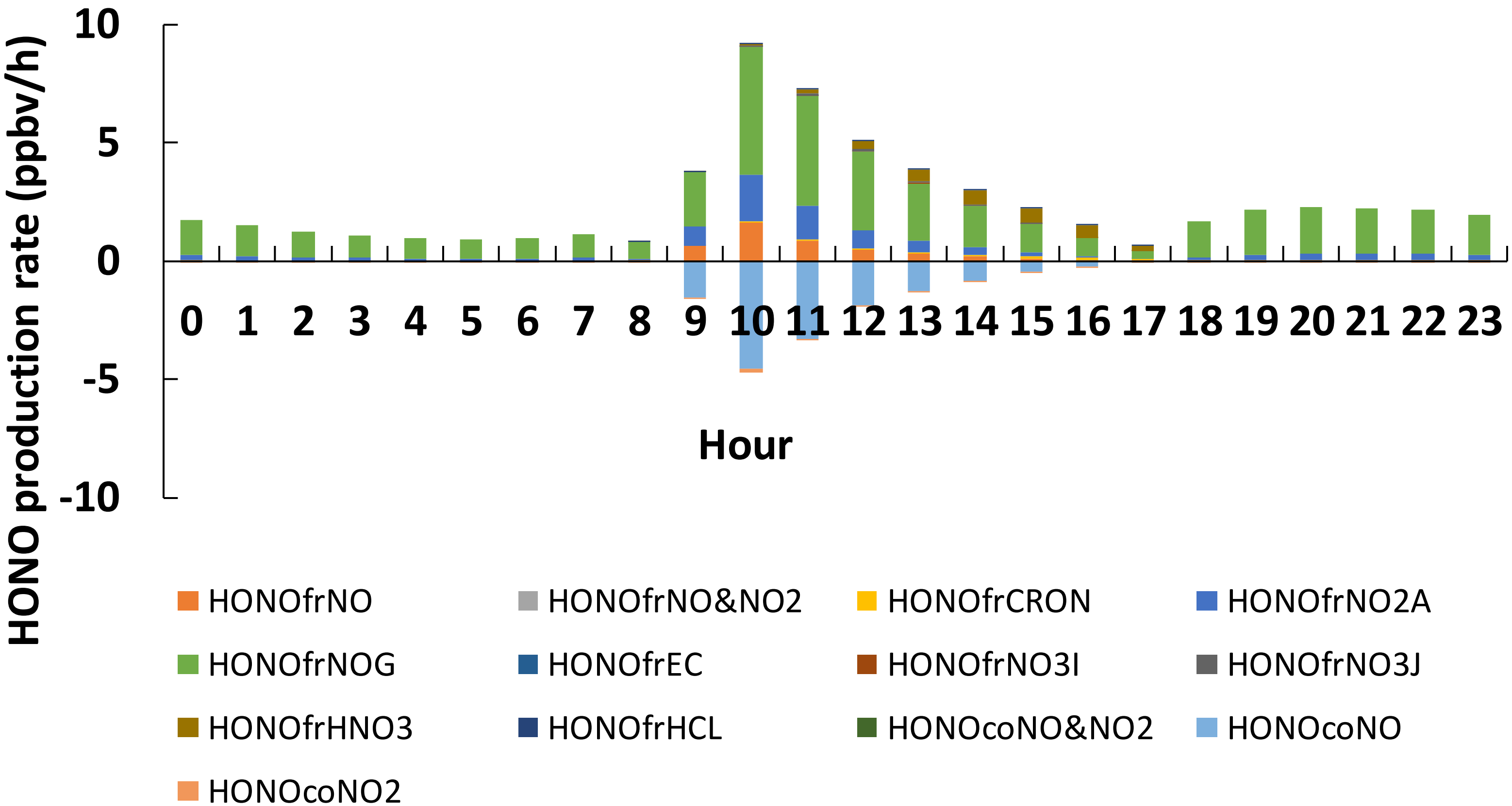


✓The $HONO/NO_2$ ratio is an index to estimate the efficiency of heterogeneous NO_2–HONO conversion.

✓The significant change of $HONO/NO_2$ ratio indicated that HONO production was mainly governed by secondary mechanisms.

✓Simulation finally were in well agreement with the observation.

Results-The budget of HONO



- The pathway of heterogeneous reaction on the ground surface (HONOfrNOG) dominated HONO increase with HONO formation rate of 1.8ppb/h at night time and 2.05ppb/h at day time.
- Most HONO photolysis into NO+OH.

Impact on spatial distribution