Factors affecting urban HONO interpreted with a MAX-DOAS instrument and GEOS-Chem

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Knowledge of urban HONO is limited

Sources

$NO + OH + M \longrightarrow HONO + M$

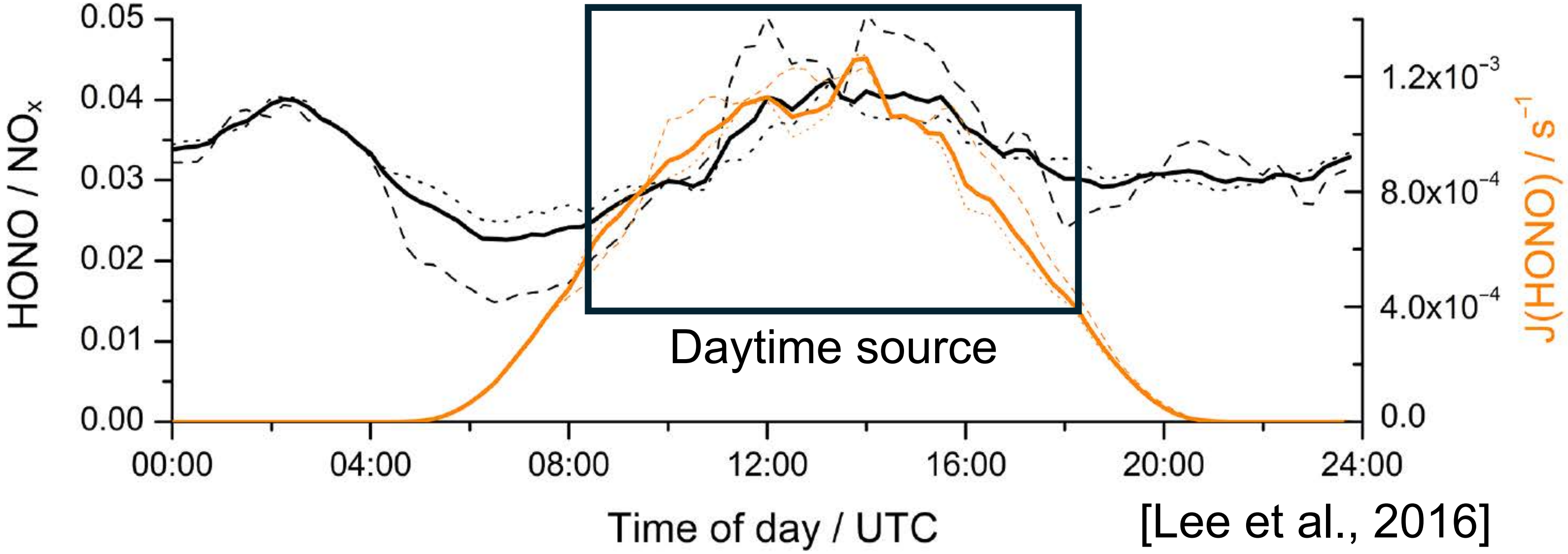
HONO ←

Sinks

$HONO + h\nu \longrightarrow NO + OH \quad (\lambda<400\ nm)$

$HONO + OH \longrightarrow H_2O + NO_2$

Summer midday HONO detected in London with in situ instruments.



[Lee et al., 2016]

Long-term measurements are required to improve understanding of HONO production and depletion in an urban environment.

Measuring vertical profiles of HONO in Central London

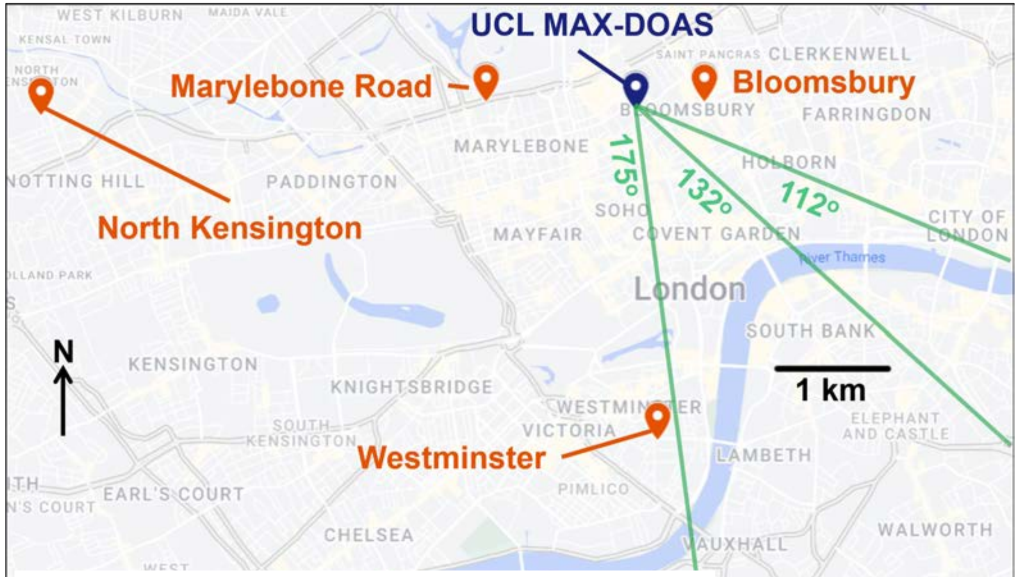
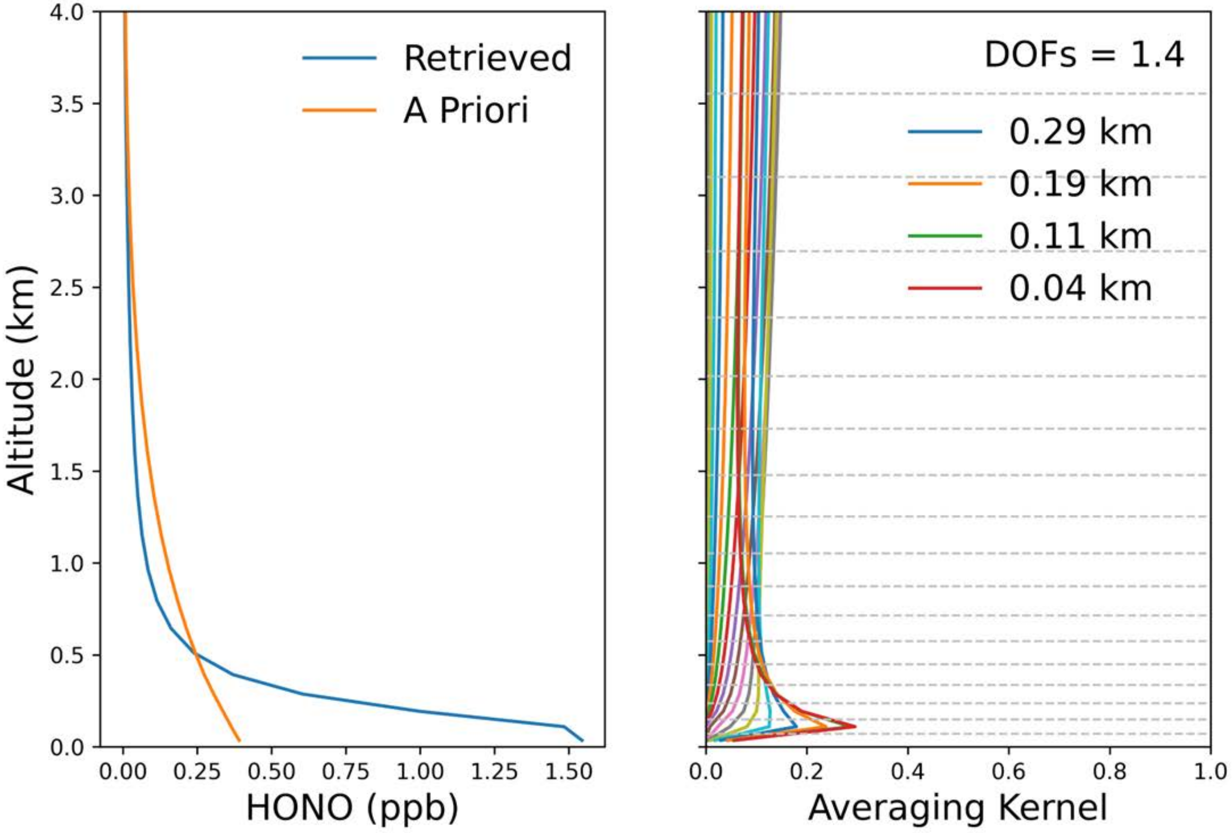


Image by Robert G. Ryan

3 optimized azimuth angles from a 60 m rooftop in Central London.

Surface sites are used to assess MAX-DOAS observations.

HONO vertical profiles and averaging kernels

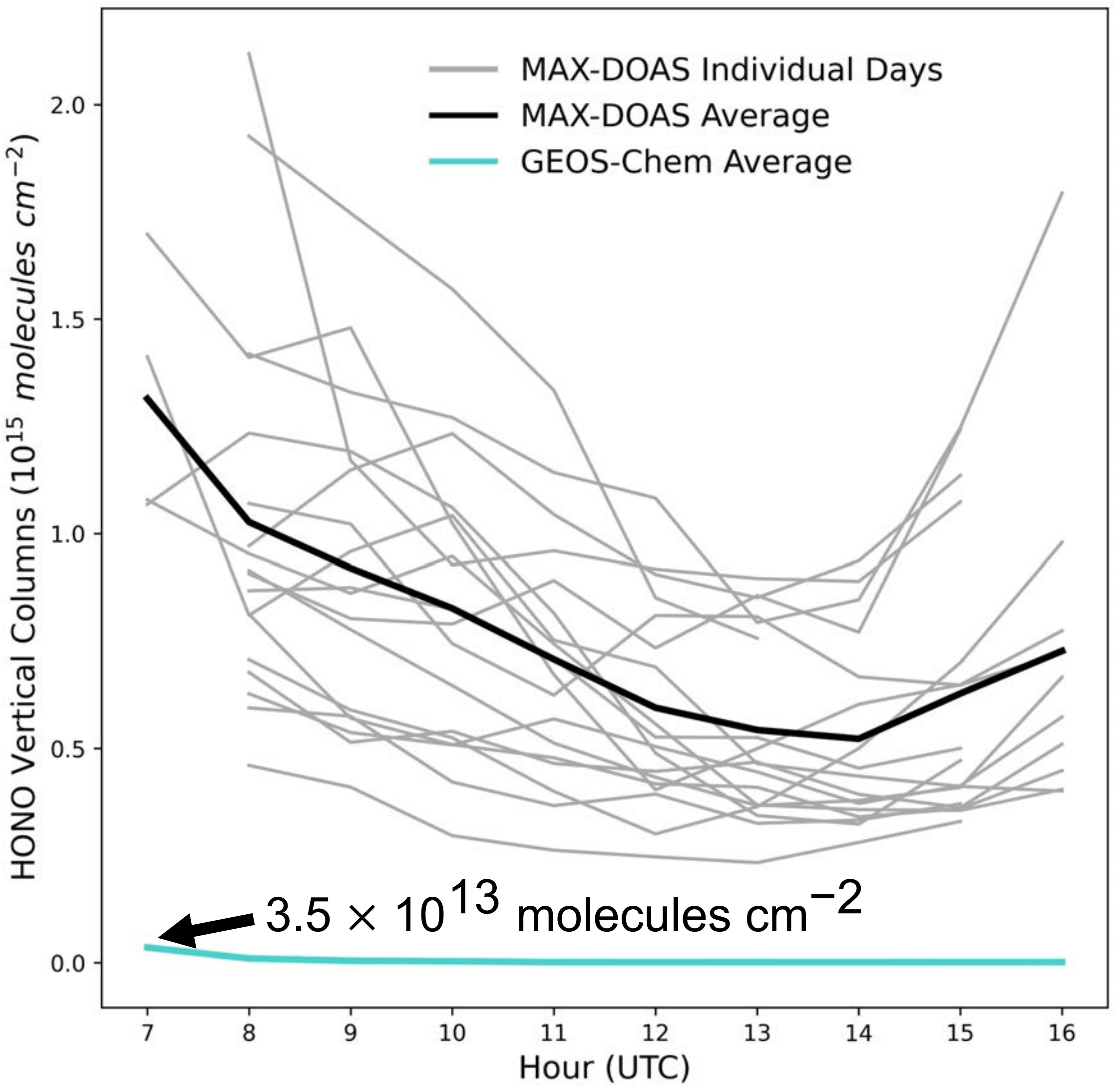


A priori is an exponential decay curve using a vertical column density of $1{\times}10^{15}$ molec cm^{-2} and 1 km scale height.

The UCL MAX-DOAS has provided vertical profiles of HONO since its June 2022 deployment.

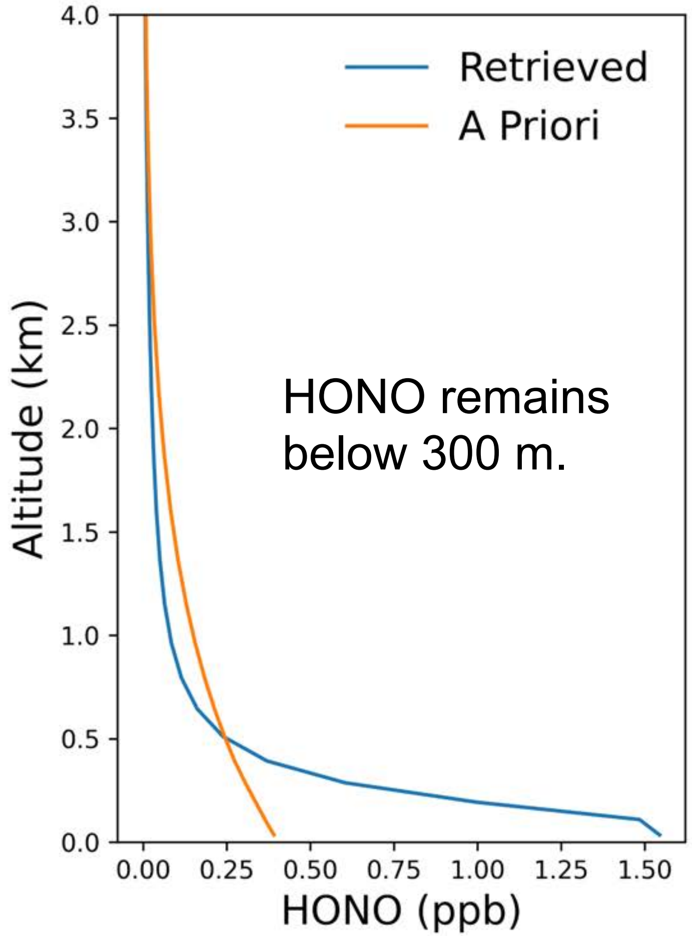
MAX-DOAS observations of HONO diurnal variability

Diurnal variations in HONO columns



Similar to Beijing (July 2008 - April 2009) [Hendrick et al., 2014].

Half of that in Madrid (winter 2016) [Garcia-Nieto et al., 2018].



MAX-DOAS HONO follows expected diurnal variability and is concentrated in the lowest 300 m. GEOS-Chem HONO is almost 2 orders of magnitude less than MAX-DOAS HONO

GEOS-Chem simulations over Central London

Model Input

NASA GEOS-FP assimilated meteorology

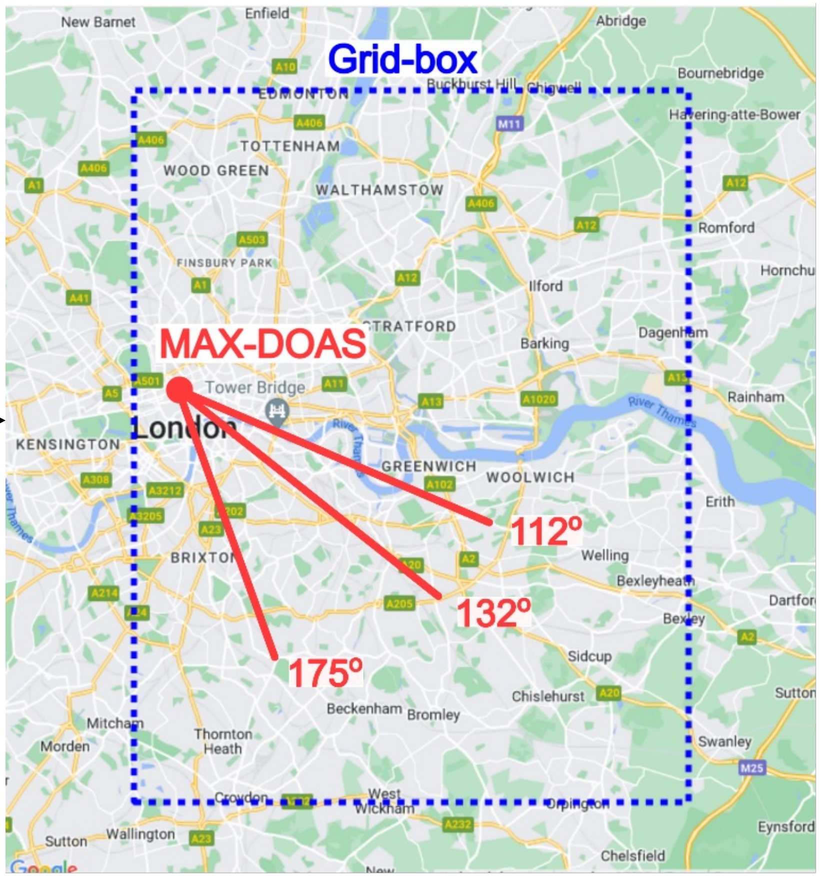
CEDs v2

MEGAN

GEOS-Chem 14.1.0

0.25°×0.3125° over Central London with 4°×5° boundary conditions.

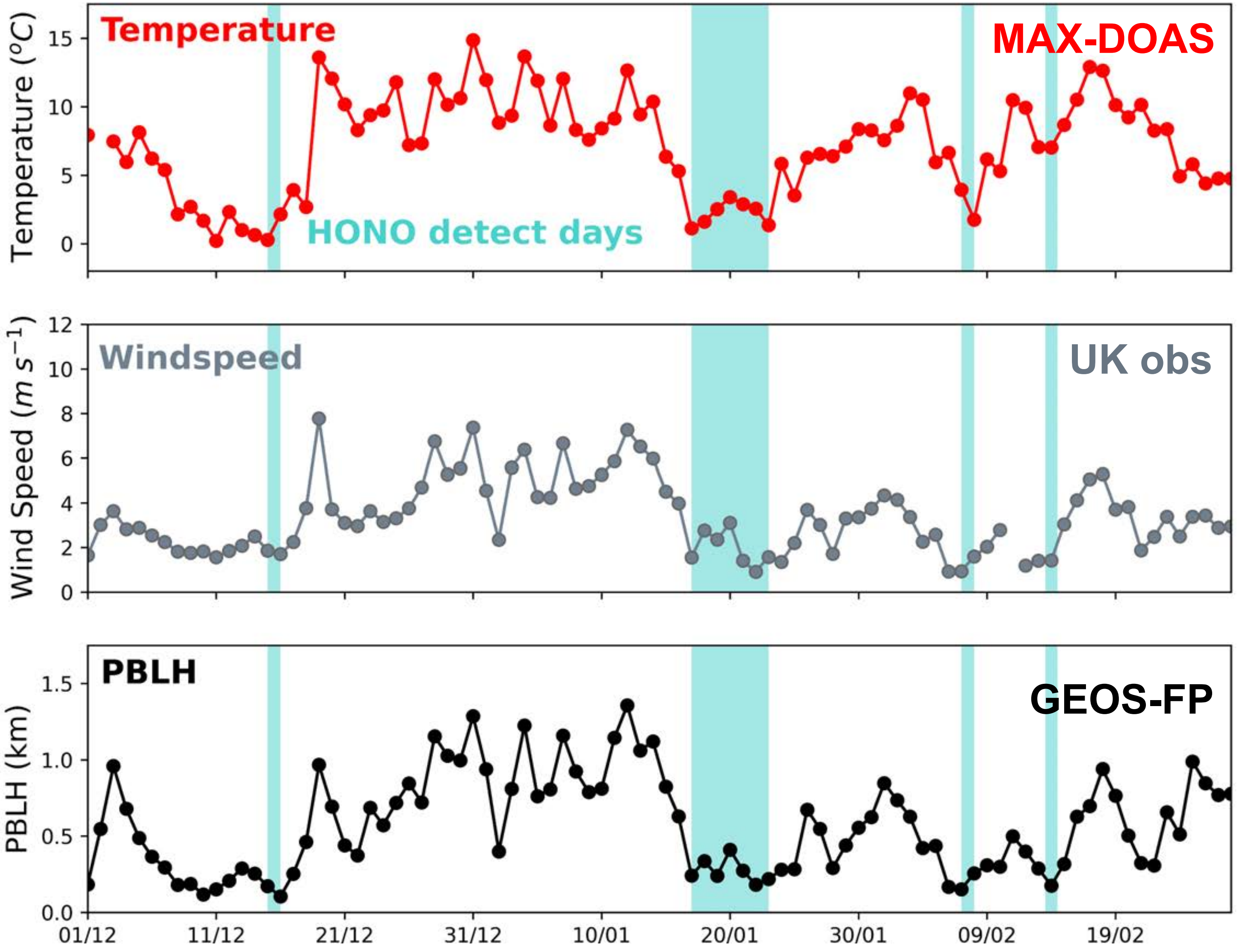
Model and MAX-DOAS coincidence



GEOS-Chem simulations are compared to MAX-DOAS observations to assess the best understanding of urban HONO.

Meteorological conditions that favour HONO formation

Daily meteorological conditions from December 2022 to January 2023



MAX-DOAS camera shows clear days

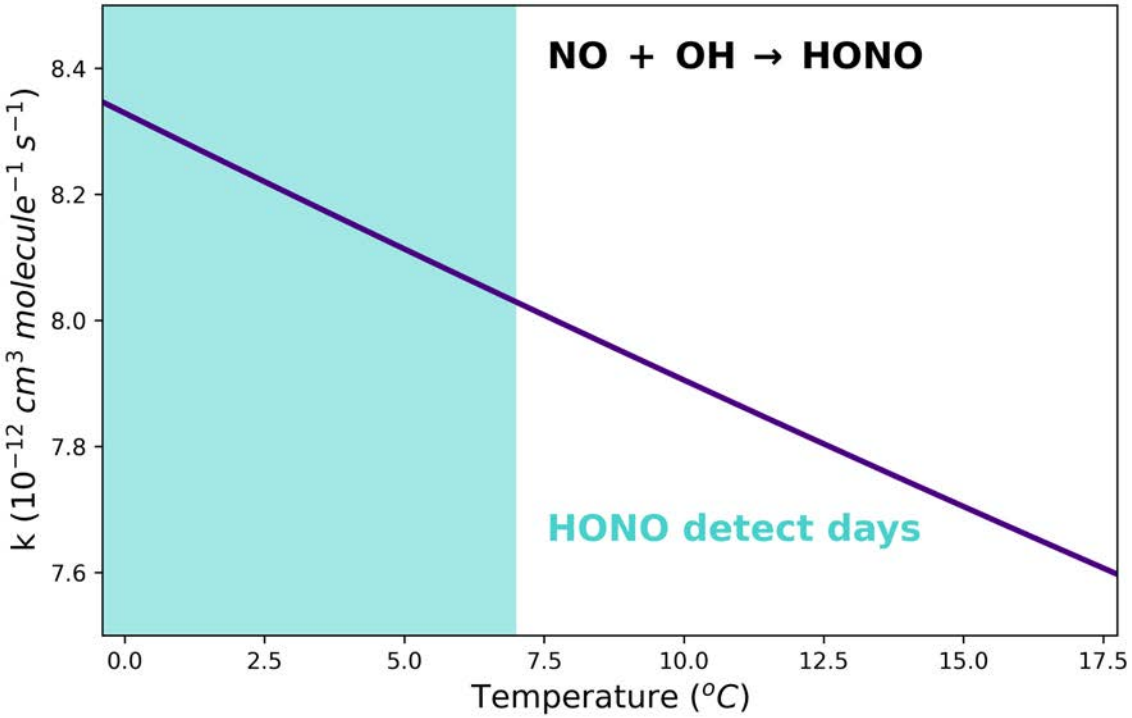
7:30 AM

9:45 AM

Low windspeeds (<4 ms^{-1}), cold conditions (<7°C), depressed PBL (<300 m) optimal for HONO formation.

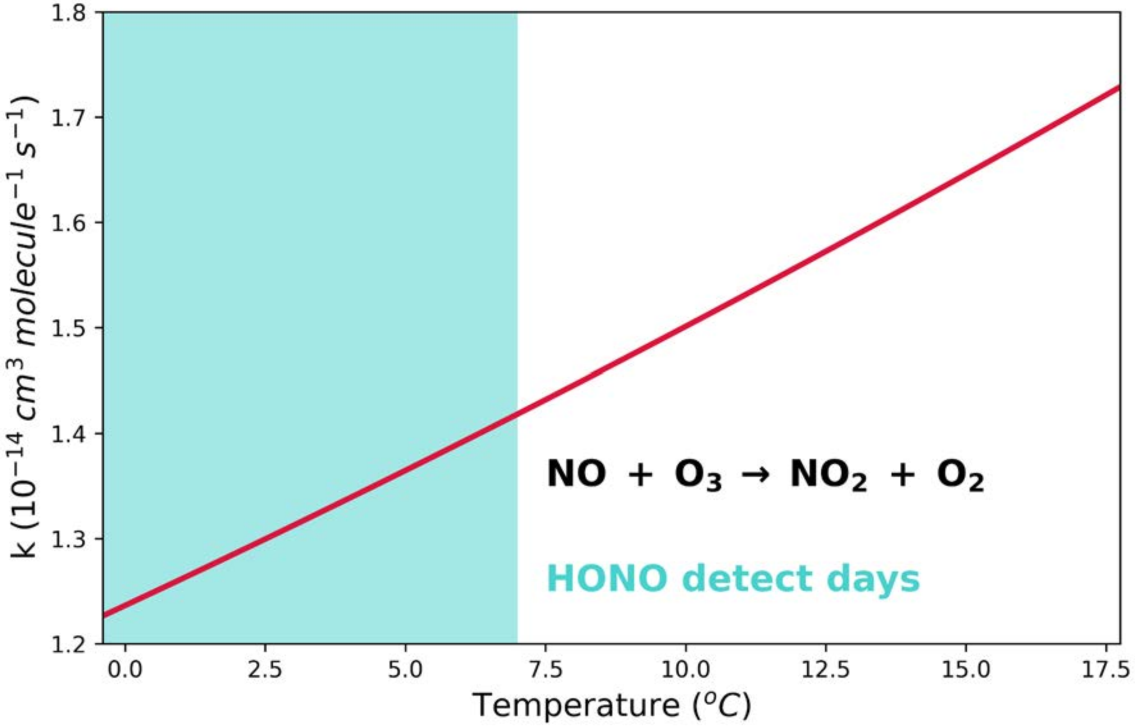
Temperature dependence of HONO formation

Rate of HONO formation reaction



HONO only detected in winter (10 detect days from December 2022 to January 2023).

Rate of reaction between NO and O_3

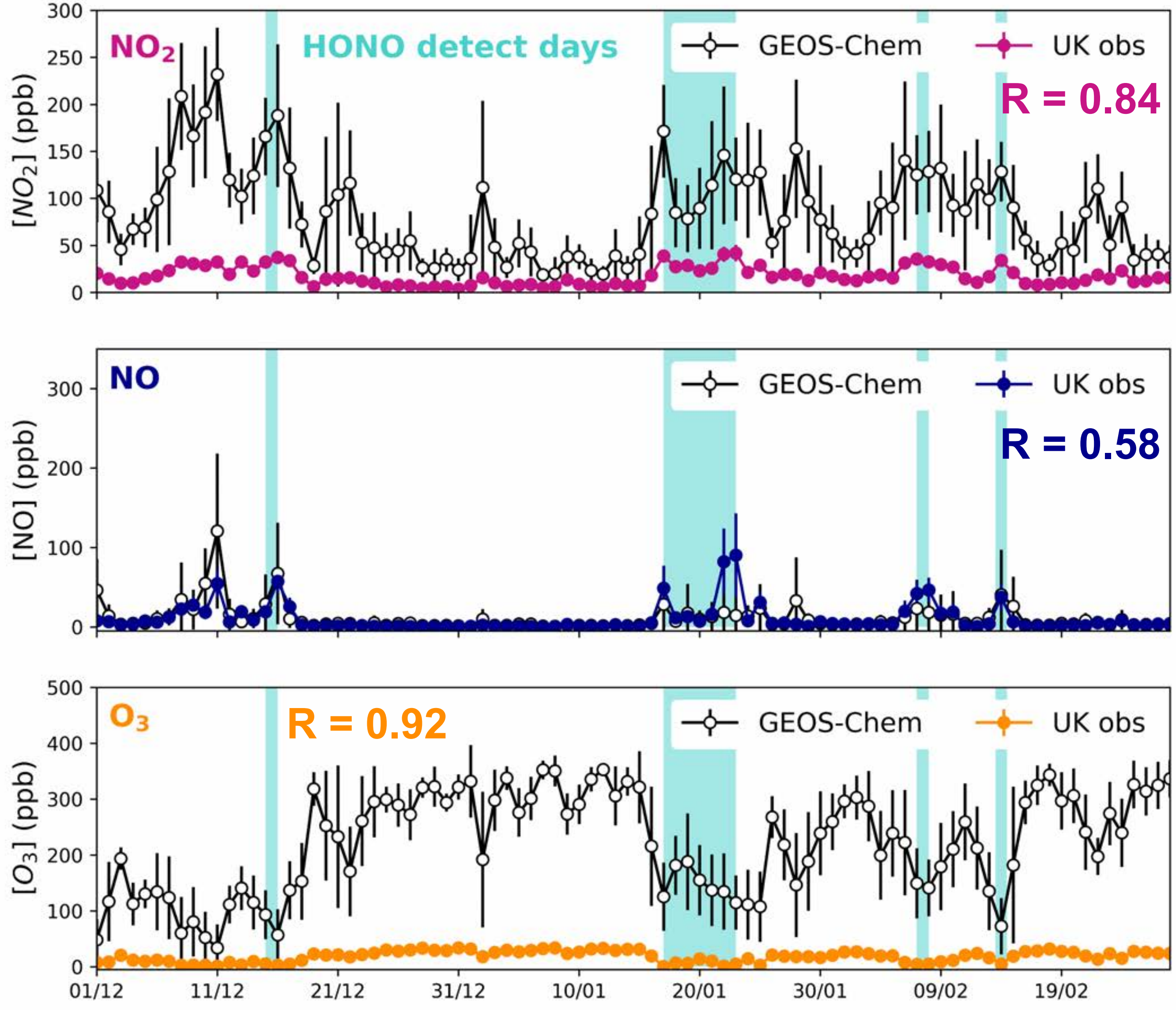


NO + OH is competitive with NO + O_3.

Low temperatures are kinetically favourable for HONO formation.

NO_x and O_3 determine HONO concentrations

Daily NO_x and O_3 concentrations from December 2022 to January 2023



High **NO_2 (>20 ppb)**, **NO (>20 ppb)** and low **O_3 (<24ppb)** optimal for HONO formation.

GEOS-Chem consistently overestimates **NO_2 (385 %)** and **O_3 (1659 %)**.

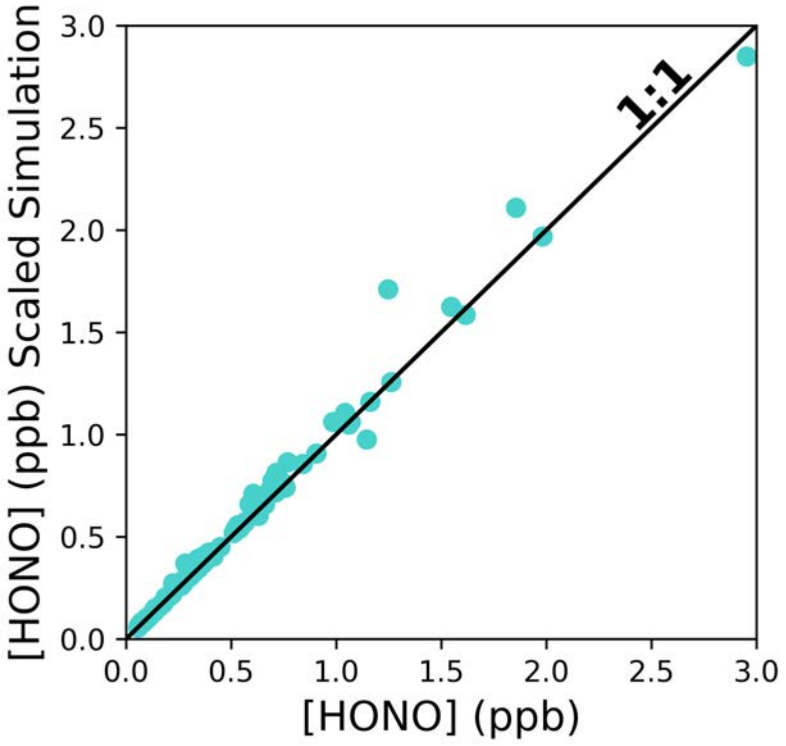
The effect of O_3 and NO_2 overestimation can be diagnosed by implementing an exaggerated sink.

Testing the sensitivity of HONO to O_3

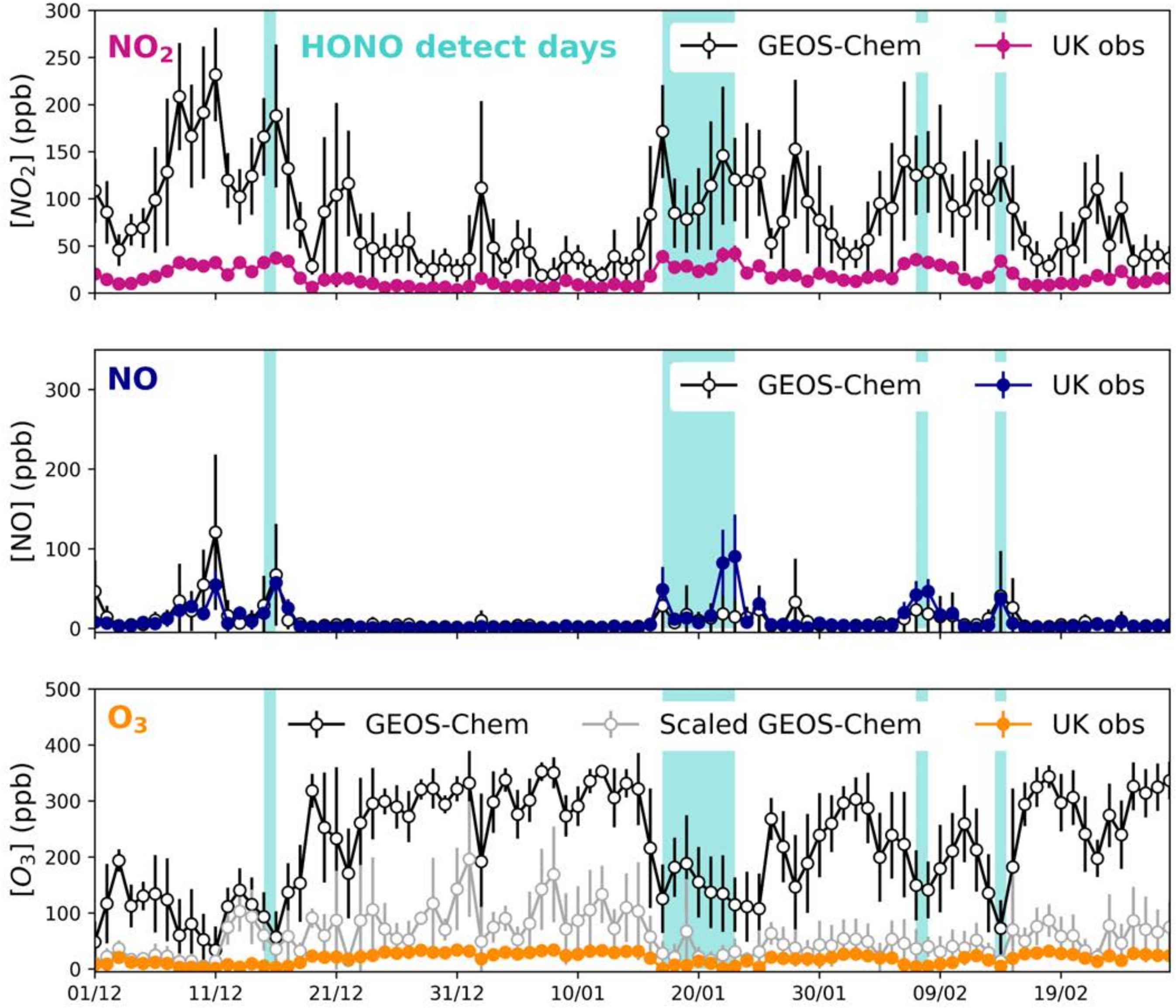
O_3 dry deposition velocity scaled up by a factor $\times 10^2$.

Scaling has minimal effect on NO_2 and NO.

O_3 concentrations decreased significantly.



Daily NO_x and O_3 concentrations from December 2022 to January 2023



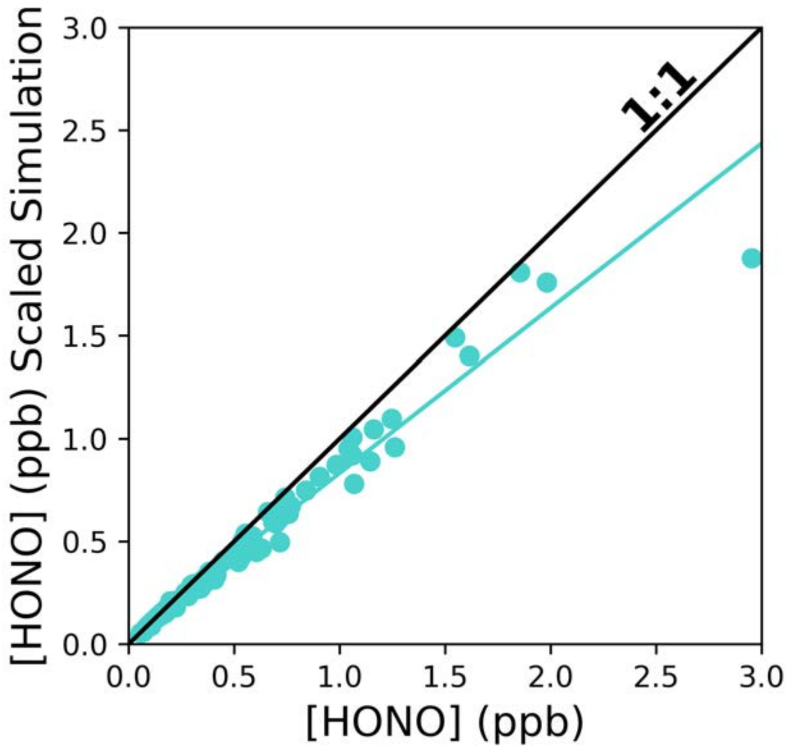
HONO is not sensitive to changes in O_3 concentration in GEOS-Chem.

Testing the sensitivity of HONO to NO_2

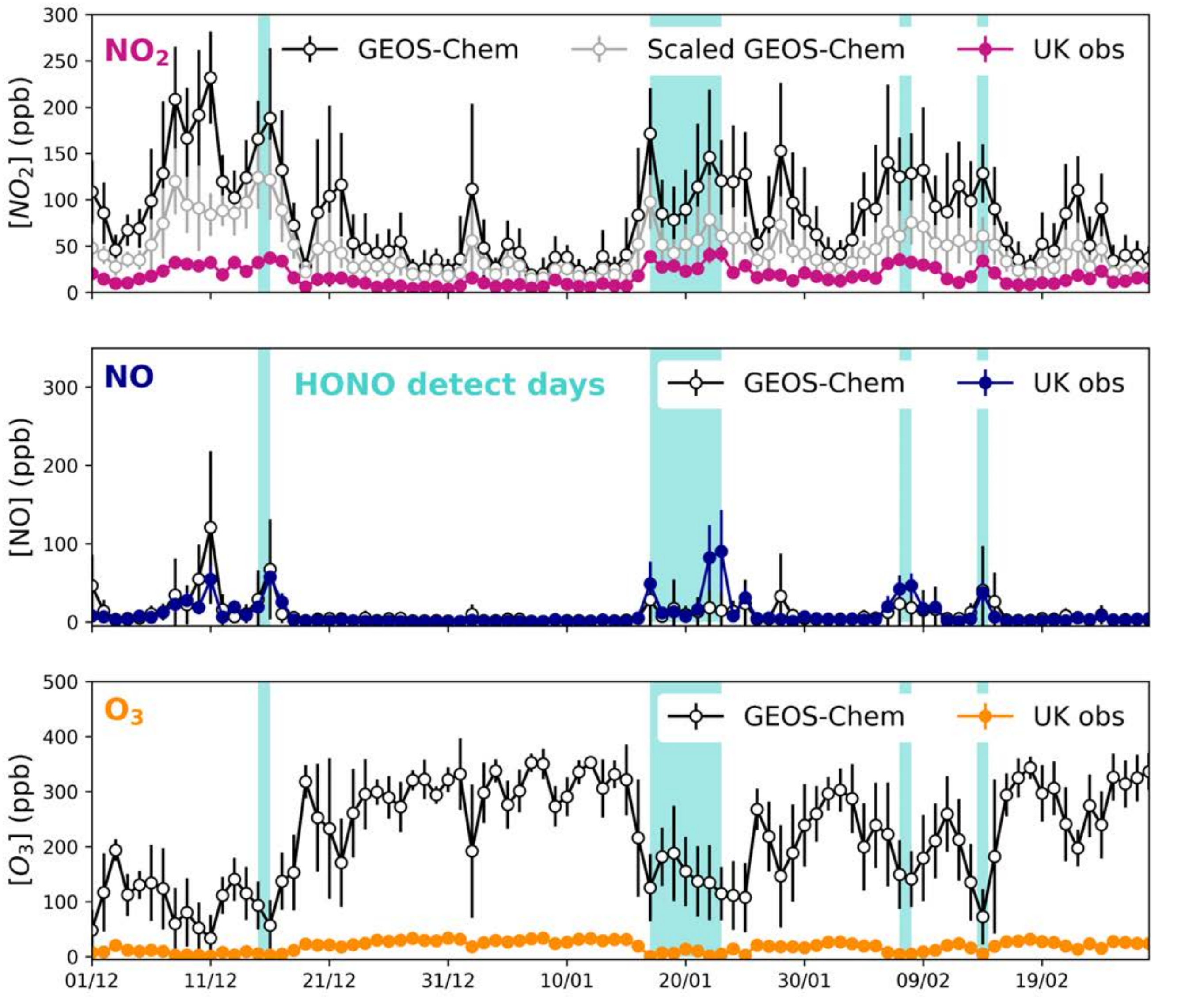
NO_2 dry deposition velocity scaled up by a factor $\times 10^2$.

Scaling has minimal effect on **NO** and O_3.

HONO concentrations decreased by 10%.



Daily NO_x and O_3 concentrations from December 2022 to January 2023



HONO is sensitive to changes in NO_2 concentration in GEOS-Chem.

Summary and further work

HONO is only detectable in London on cold (**< 7°C**), clear, still (**windspeeds < 4 ms^{-1}**) days.

NO_x must be high (**[NO], [NO_2] > 20 ppb**) and O_3 must be low (**< 24 ppb**).

Concentrations **peak in the morning** and deplete until 14:00 when concentrations increase again.

HONO is **not sensitive to a large overestimate in surface O_3** in GEOS-Chem.

HONO is **sensitive to a large overestimate in surface NO_2** in GEOS-Chem.

Investigate spatial variability in HONO by analysing individual azimuth angles.

Use an exaggerated source of HONO to assess its sensitivity to emissions.

Continue to test the sensitivity of HONO to NO_2.

Questions, suggestions, comments, please contact me at: eleanor.smith.18@ucl.ac.uk