Assessment of variability in urban HONO using MAX-DOAS measurements in Central London

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Knowledge of urban HONO is limited

Sources

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

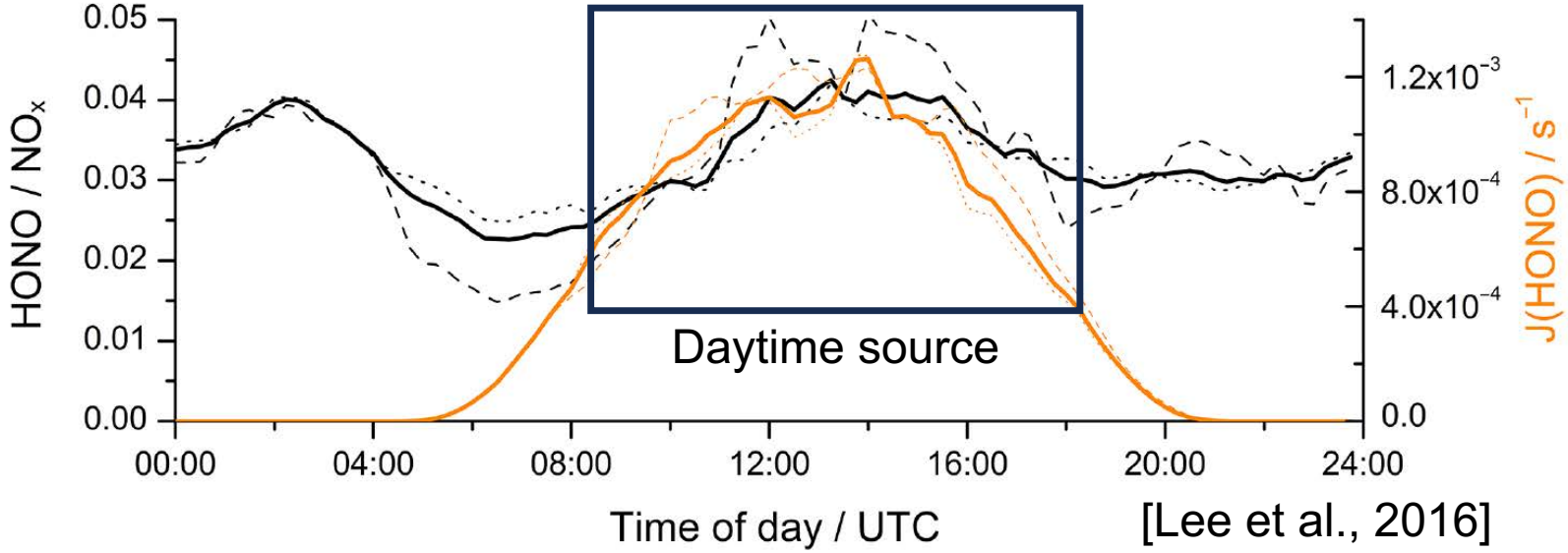
HONO ← 

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.

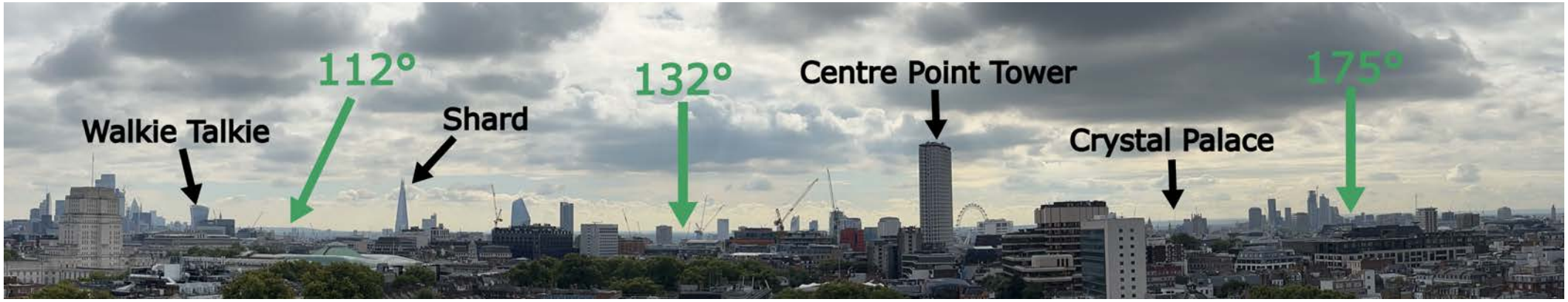


[Lee et al., 2016]

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

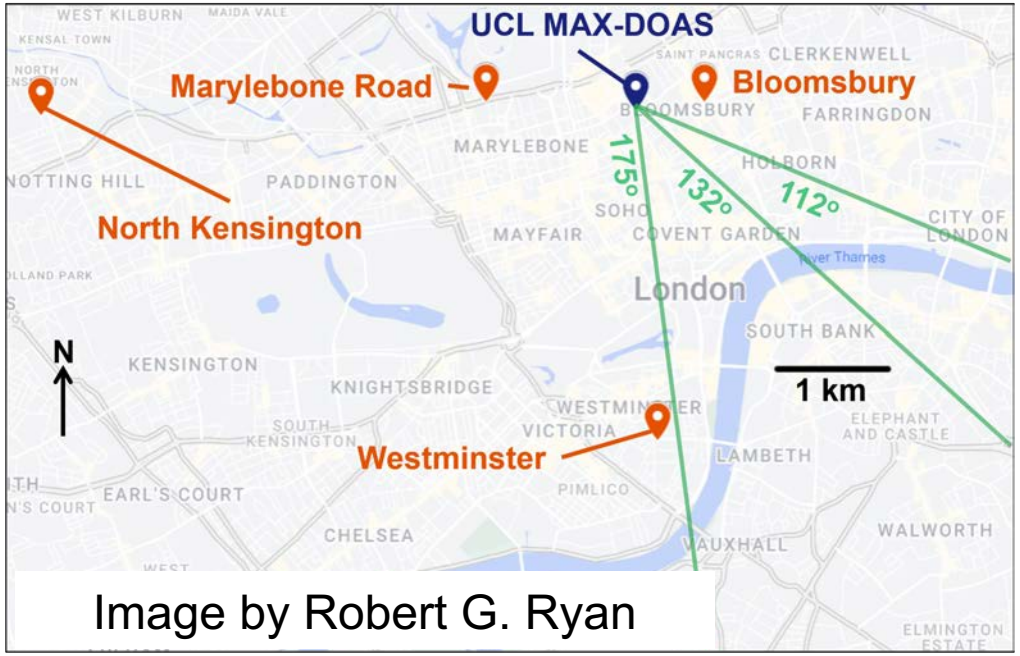
Measuring vertical profiles of HONO in Central London

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



GEOS-Chem used as an a priori.

Surface sites are used to assess MAX-DOAS observations.



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

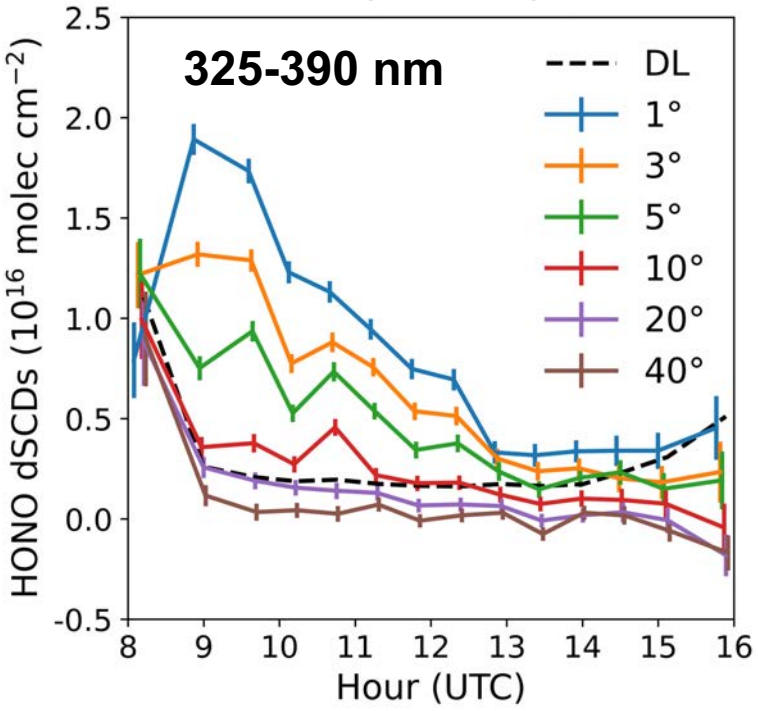
MAX-DOAS dSCDs retrieval optimized for HONO

HONO detection determined with conservative detection limit calculated using root mean square error (RMS) and maximum cross section:

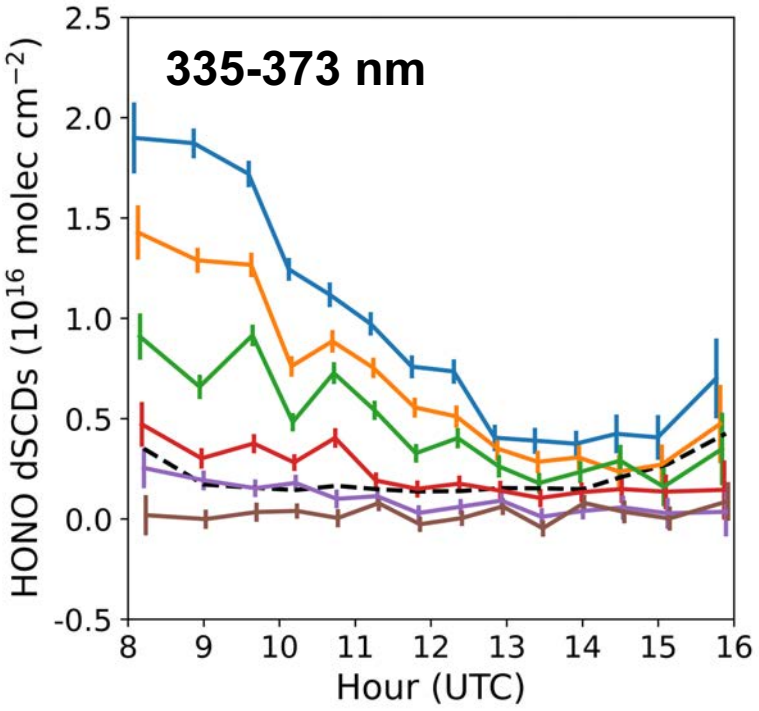
$$\text{Detection Limit (DL)} = 2\frac{\text{RMS}}{\sigma_{max}}$$

$\sigma_{max} = 5.21\times10^{-19}$ cm^2 [Stutz et al., 2000]

dSCDs with DOASIS default wavelength range:



dSCDs with Wang et al. [2020] optimized range

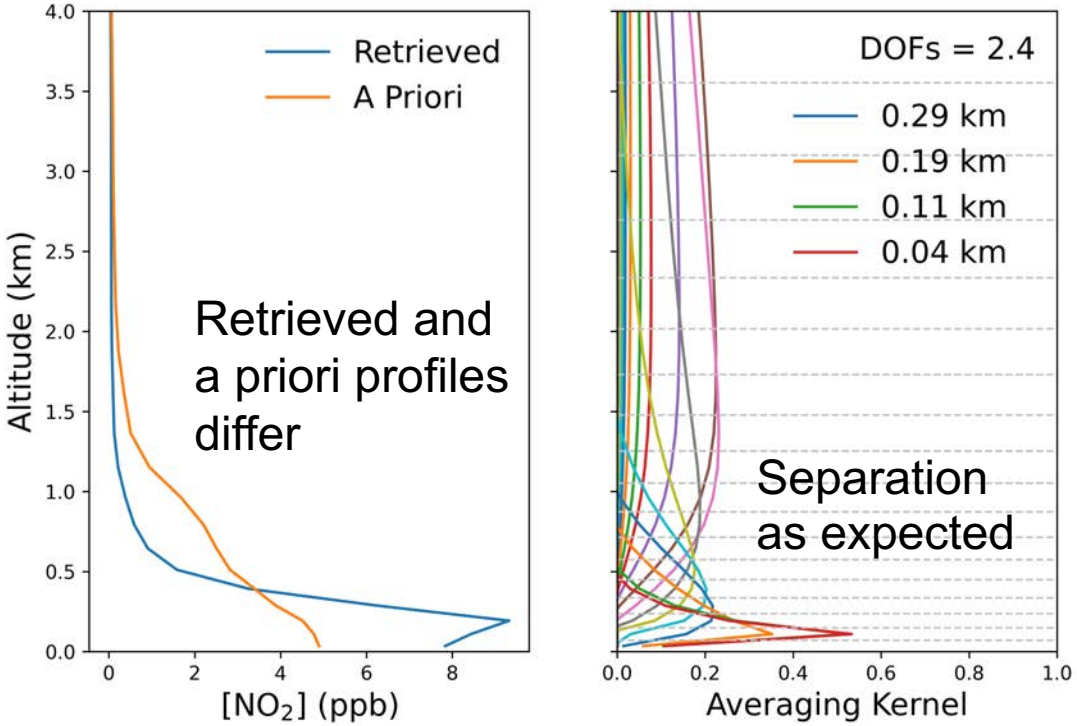


Optimized wavelength range achieves far superior dSCDs separation. HONO only detected in winter (10 detect days from December 2022 to January 2023)

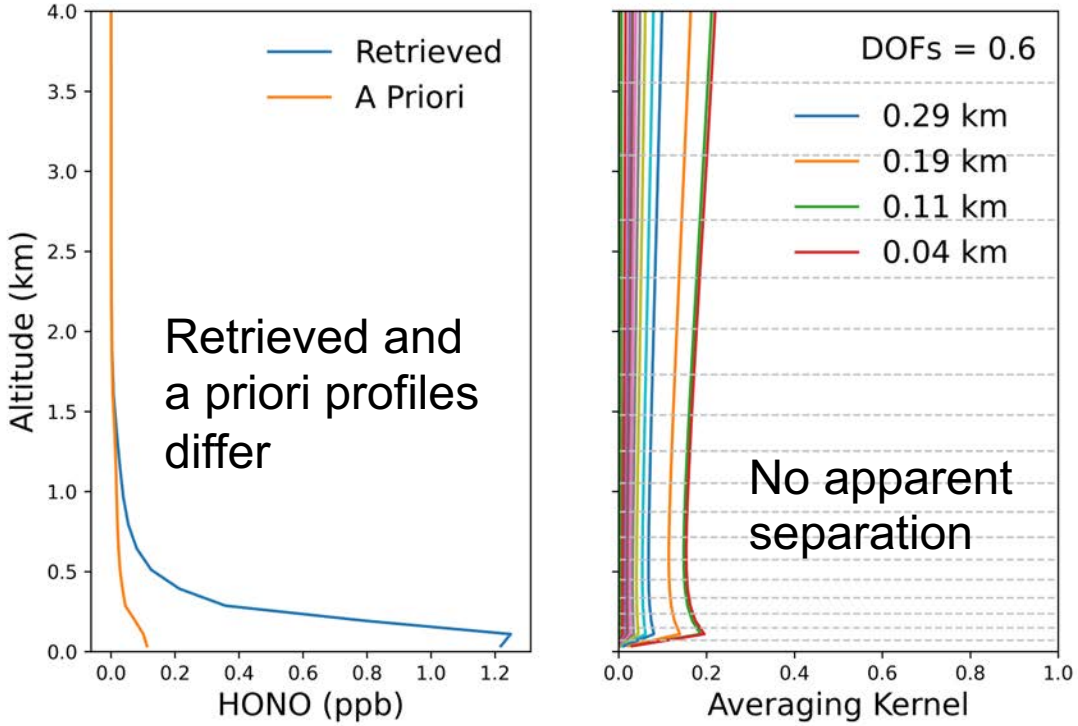
Vertical profile retrieval issues still to resolve

Clear separation of dSCDs supports presence of HONO, but retrieval algorithm (RAPSODI) issues still to resolve.

NO_2 vertical profiles of DOFs



HONO vertical profiles of DOFs

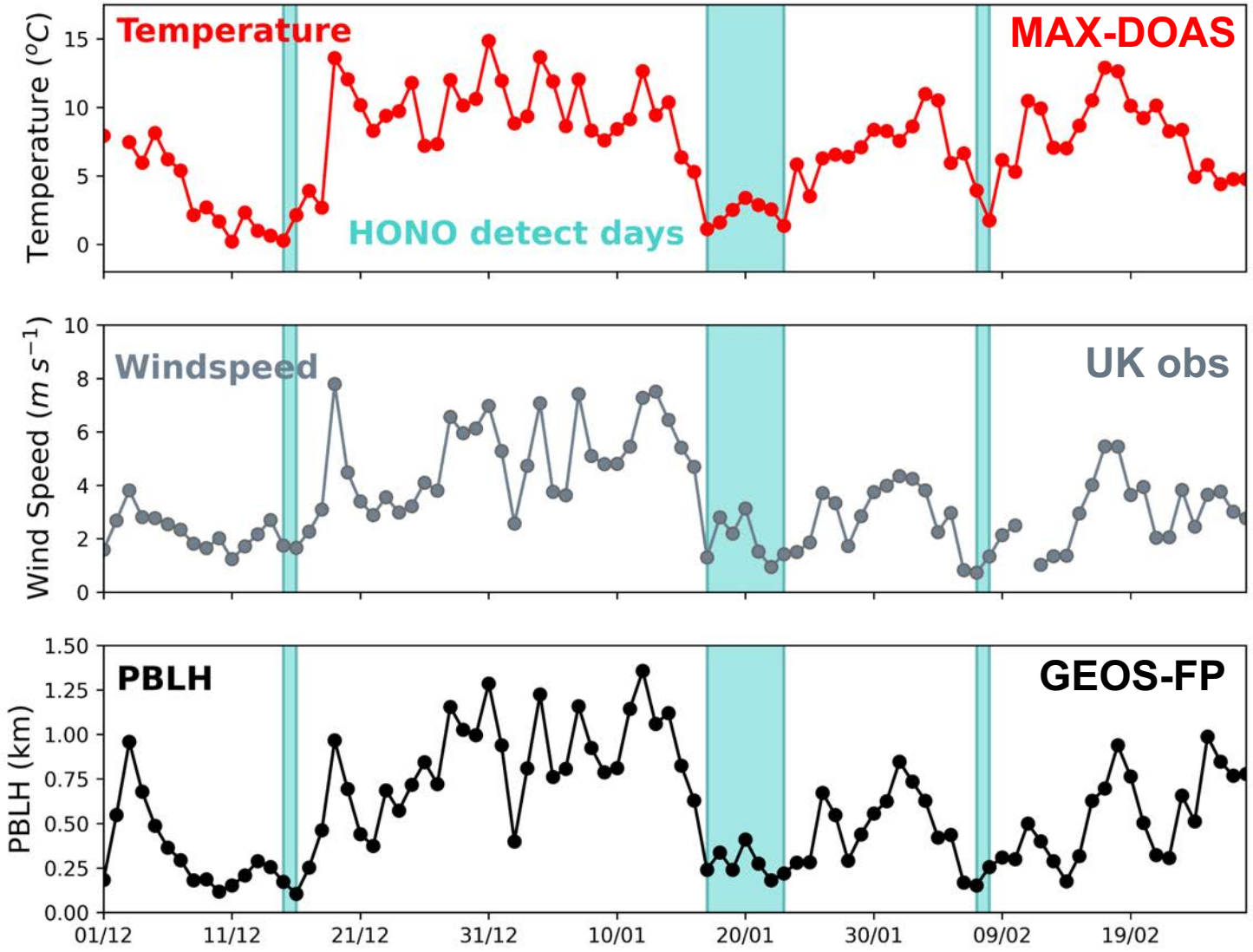


The issue is the a priori (inferior first guess from GEOS-Chem).

Ongoing work to address this issue.

Meteorological conditions that favour HONO formation

Daily meteorological conditions from December 2022 to January 2023

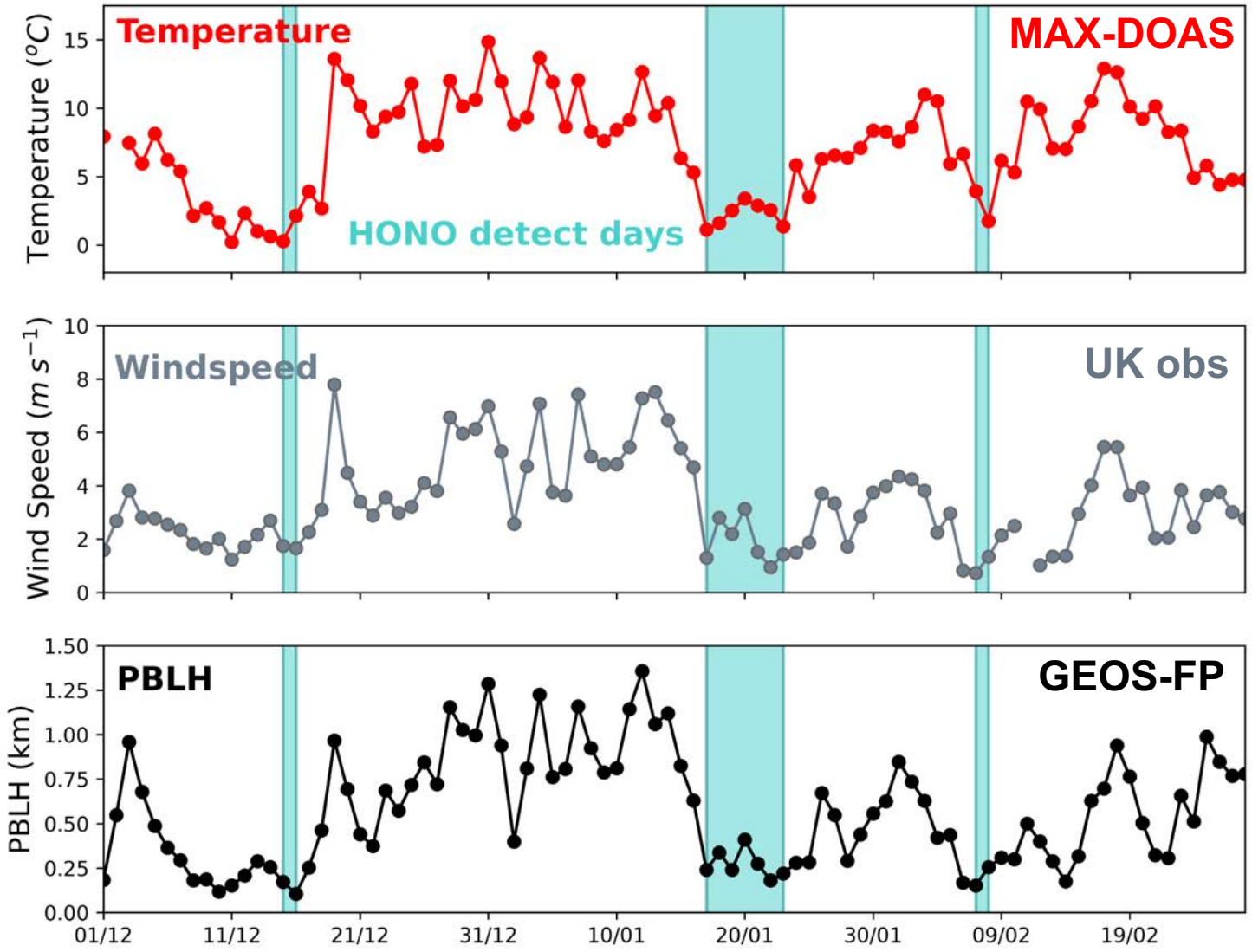


7:30 AM

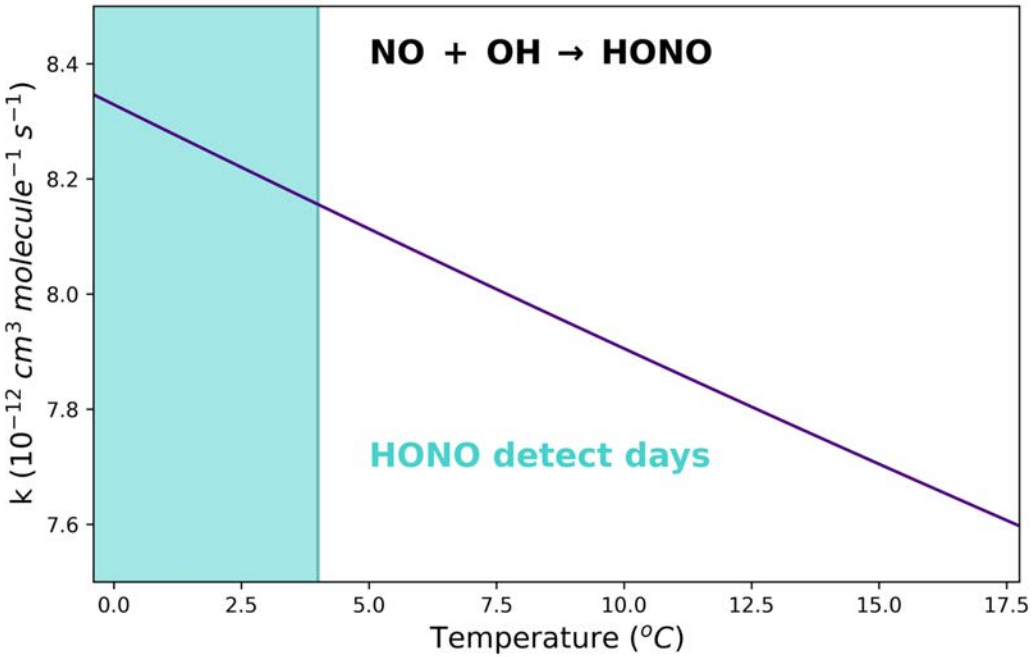
9:45 AM

Meteorological conditions that favour HONO formation

Daily meteorological conditions from December 2022 to January 2023



Rate of HONO formation reaction

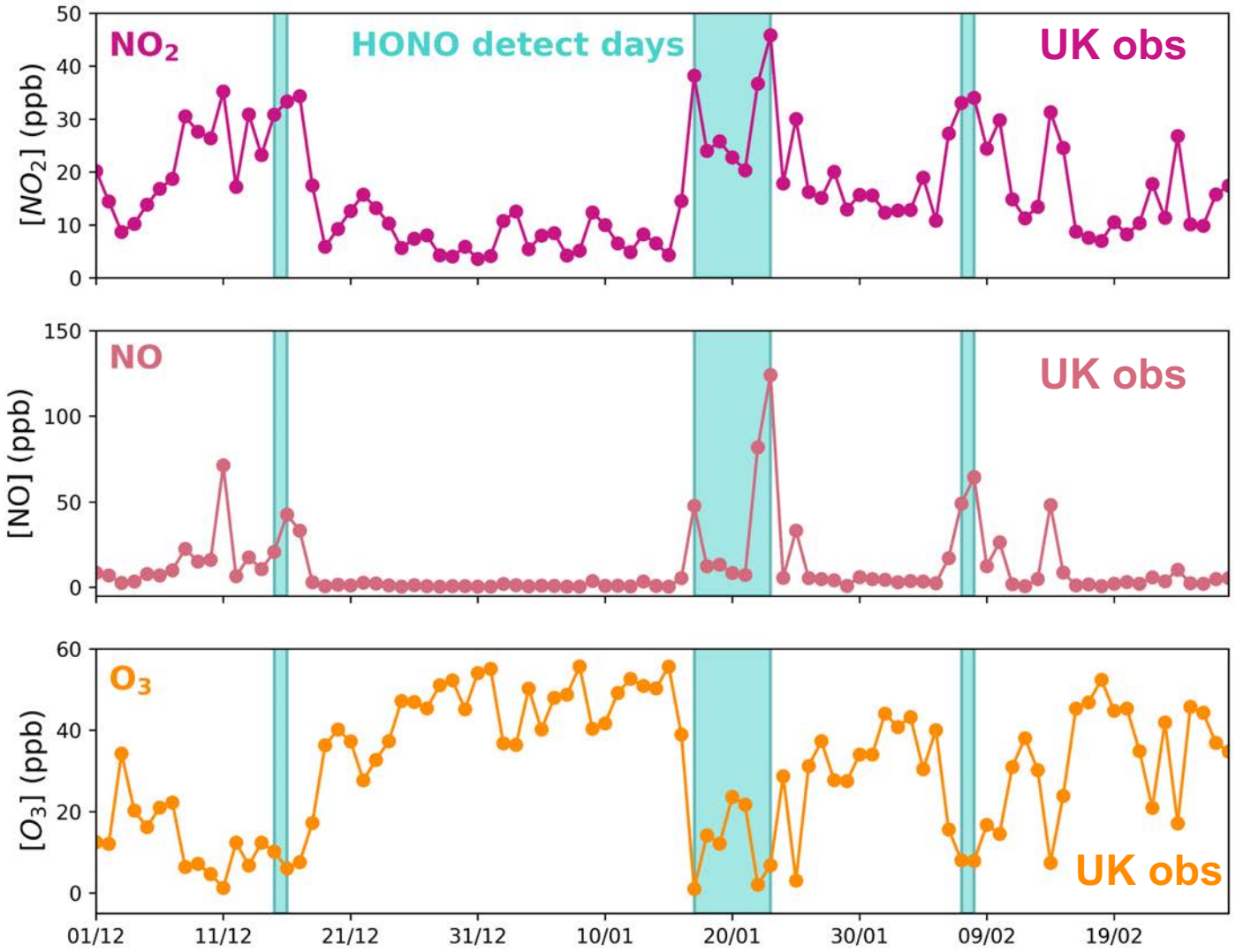


Low temperatures are kinetically favourable for HONO formation.

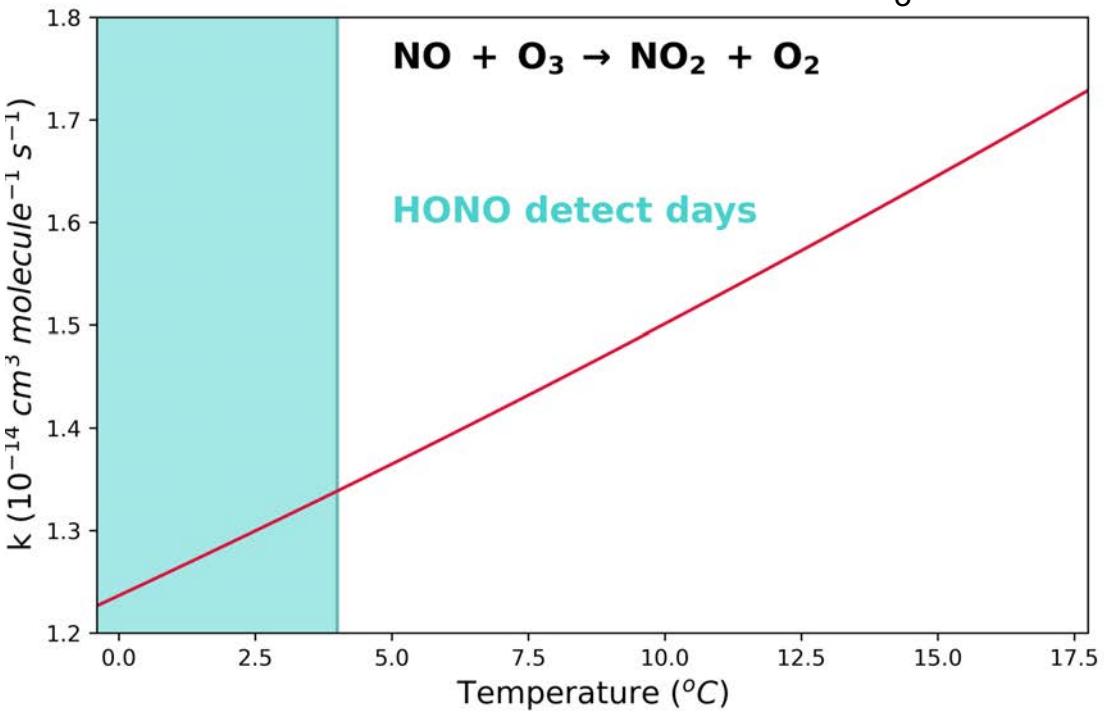
Low windspeeds (< 4 ms^{-1}), cold conditions (<4°C), depressed PBL (<300 m) optimal for HONO formation.

NO_x and O_3 determine HONO concentrations

Daily NO_x and O_3 concentrations from December 2022 to January 2023



Rate of reaction between NO and O_3

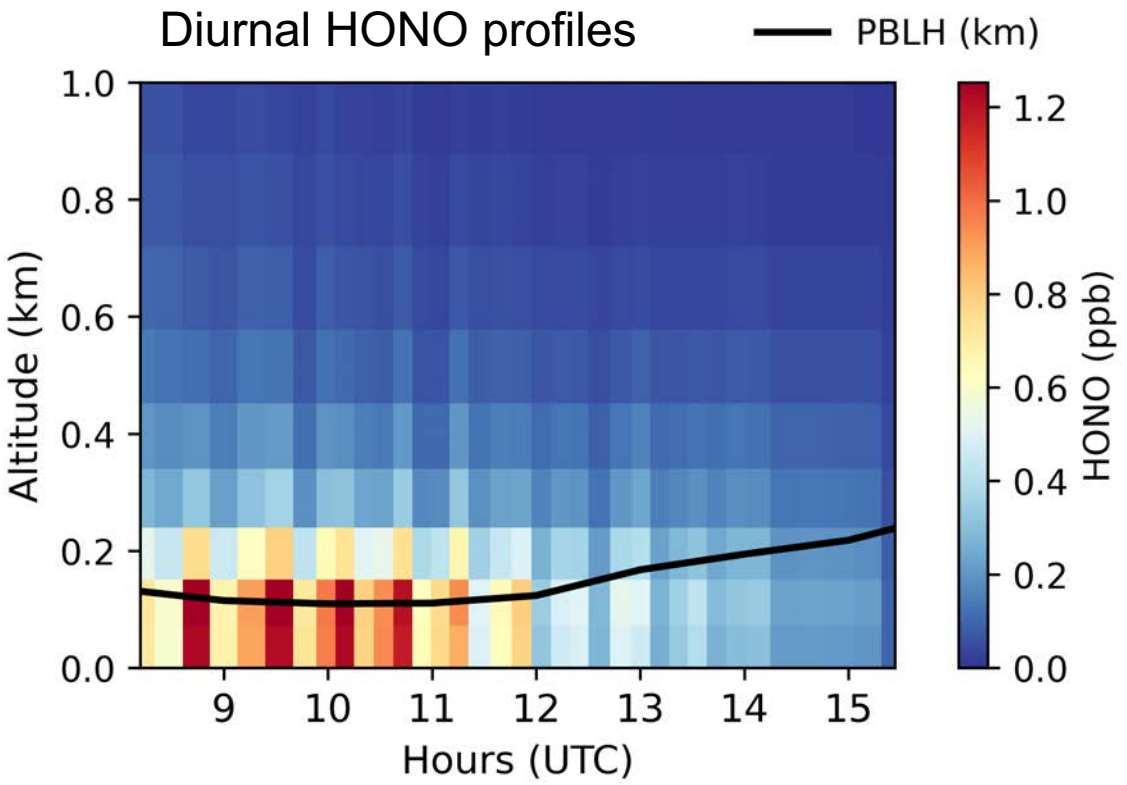


NO + OH is competitive with NO + O_3.

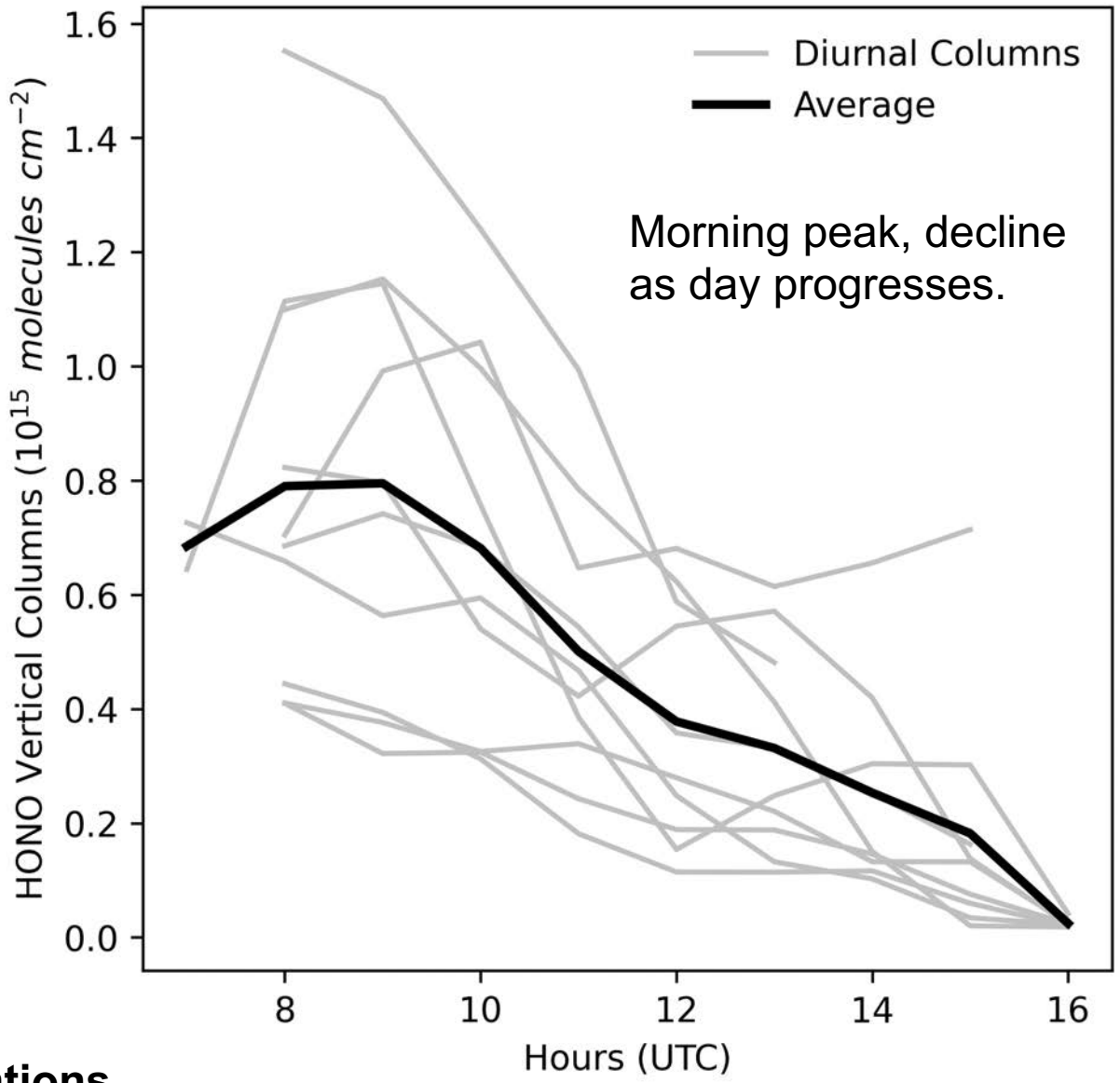
Low NO_2 (>20 ppb), NO (<20 ppb) and O_3 (<24ppb) optimal for HONO formation.

HONO concentrations peak in the morning

HONO remains below 300 m due to fast photolysis.



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].

We do not observe an afternoon peak in HONO concentrations.

Summary and further work

HONO is only detectable in London on cold (**< 4°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 throughout the day.

Continue to optimise the retrieval.

Process MAX-DOAS observations for 2023-2024.

Investigate spatial variability in HONO by analysing individual azimuth angles.

Assess best understanding of urban HONO as simulated with GEOS-Chem.

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