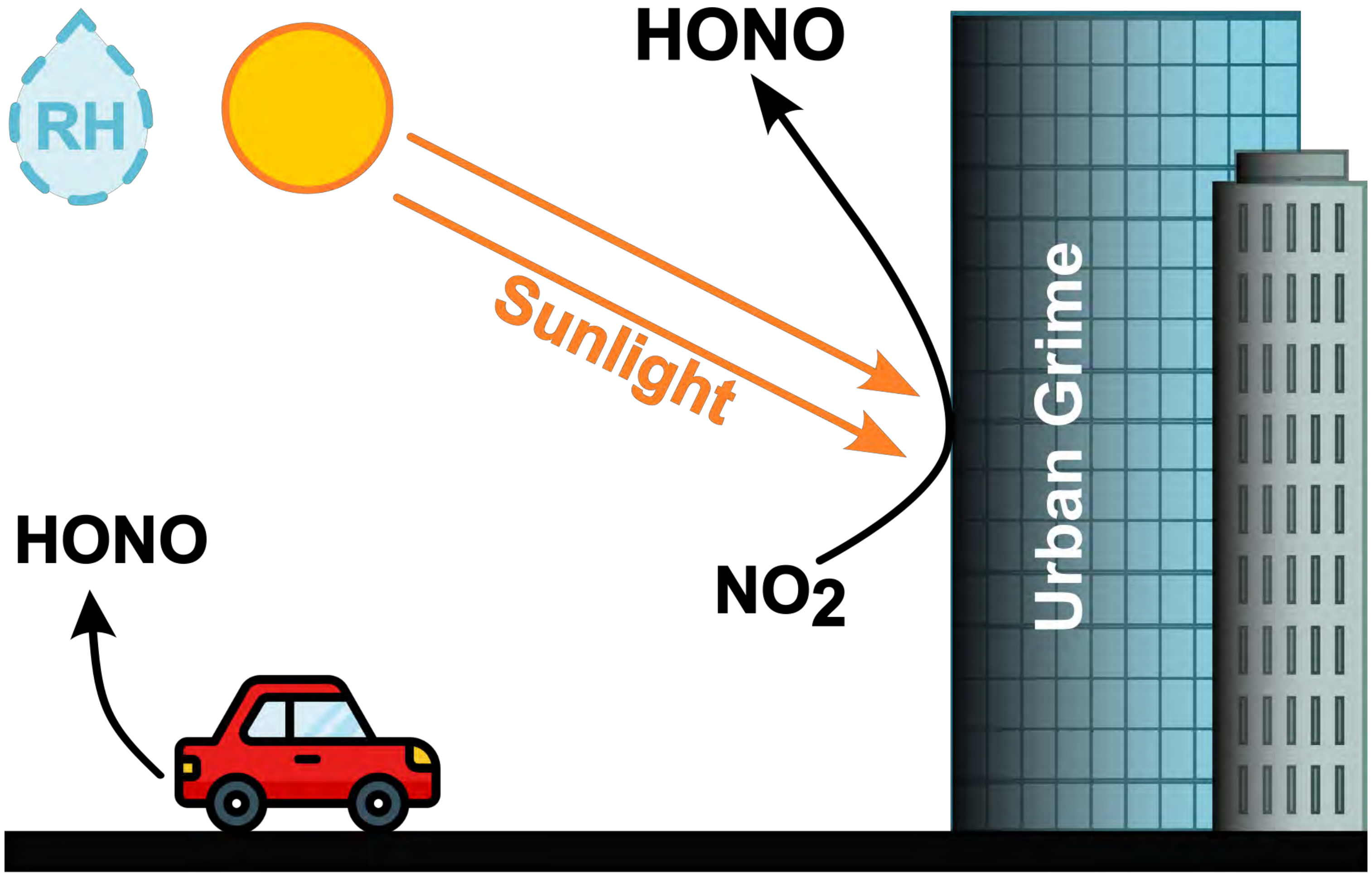
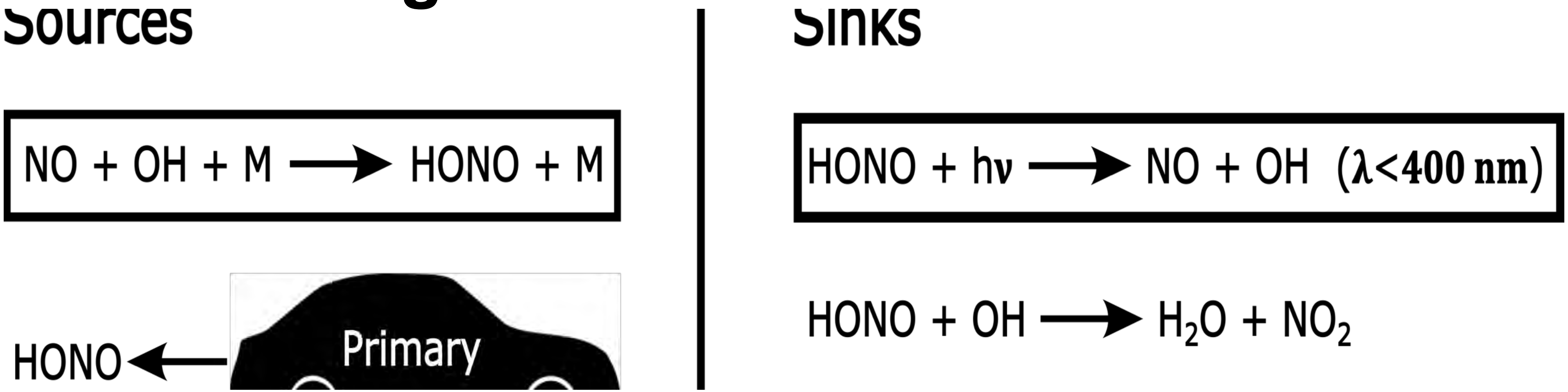
Multiphase HONO formation pathways in Central London

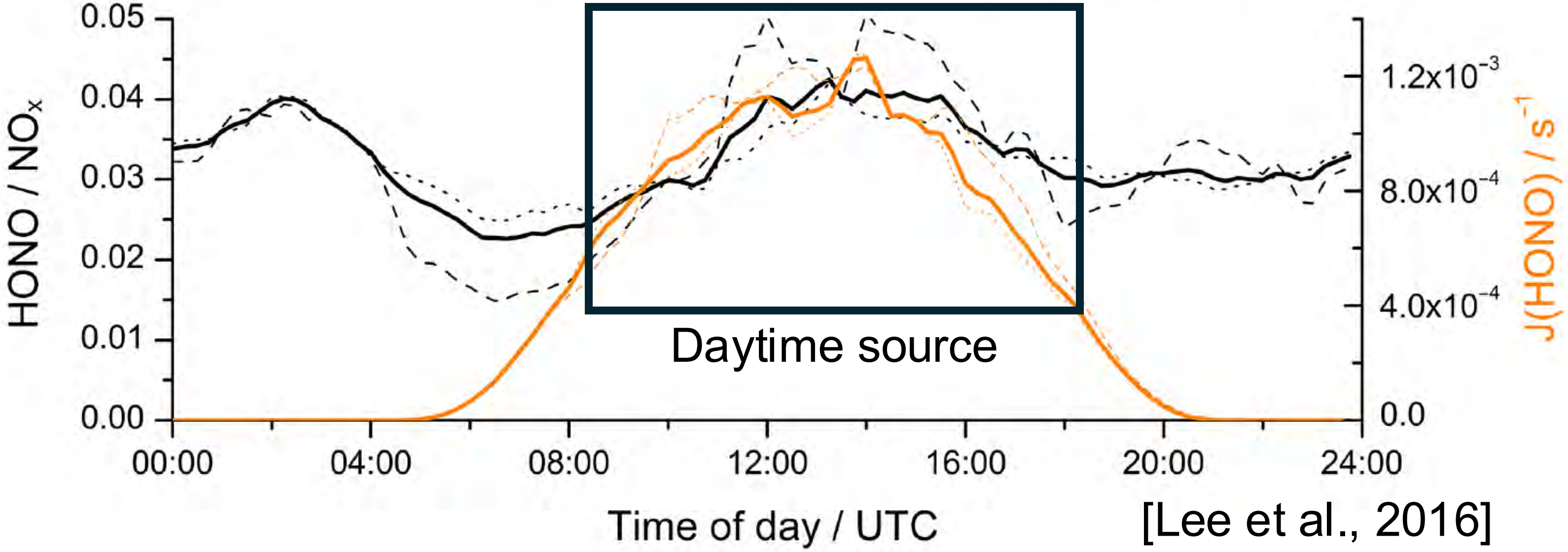


Eleanor Gershenson-Smith, E. A. Marais, R. G. Ryan, J.-L. Tirpitz, G. Lu

Knowledge of urban HONO is limited



Summer midday HONO detected in London with in situ instruments.

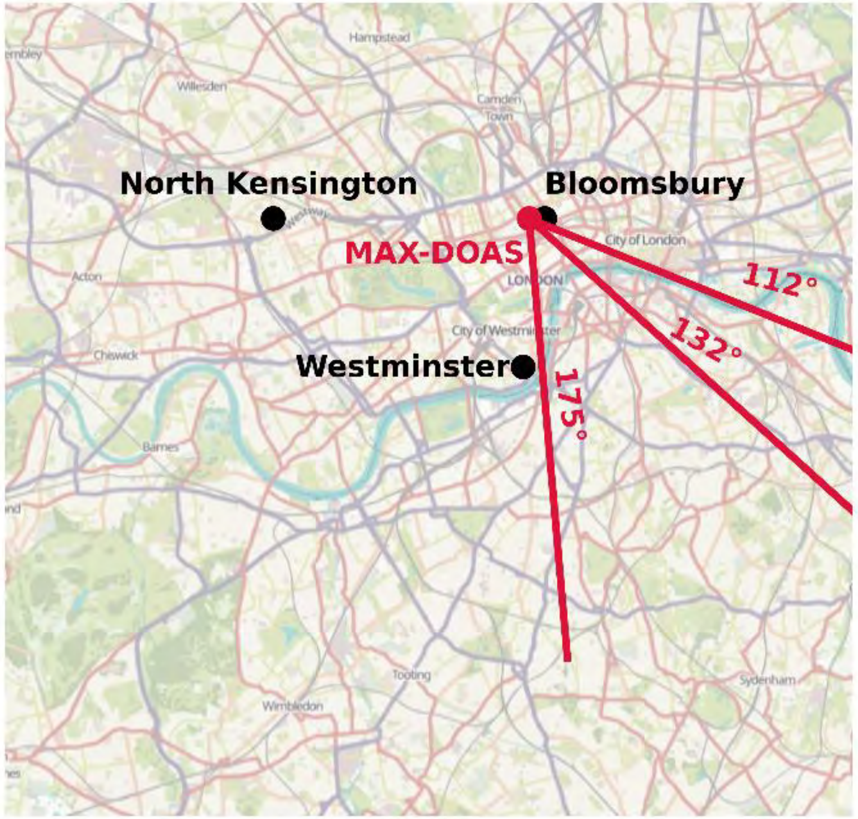


[Lee et al., 2016]

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

Measuring vertical profiles of HONO in Central London

The UCL MAX-DOAS and UK observation sites

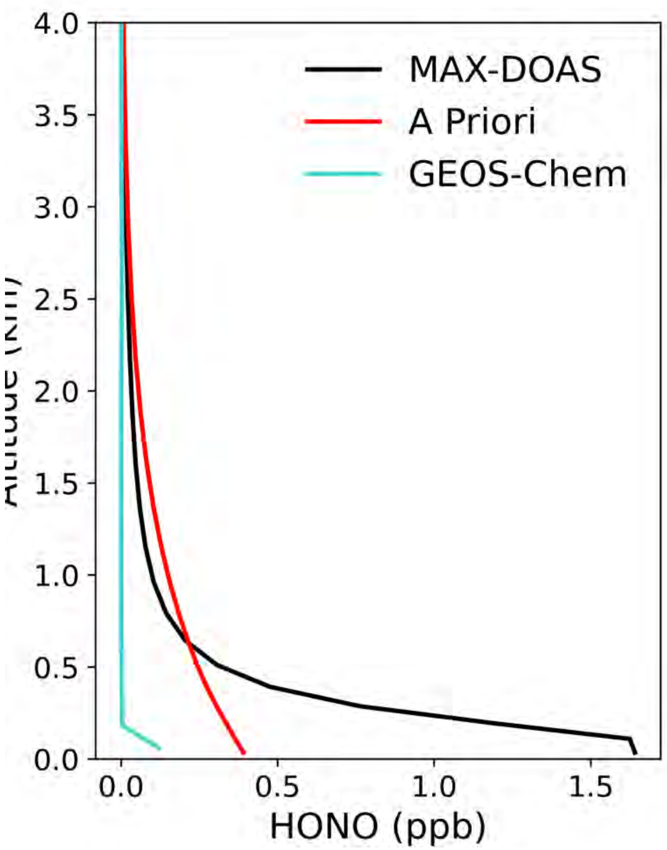


A priori is an exponential decay curve using a vertical column density of 1×10^{15} molec cm^{-2} and 1 km scale height.

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

Surface sites are used to assess MAX-DOAS observations.

HONO vertical profiles



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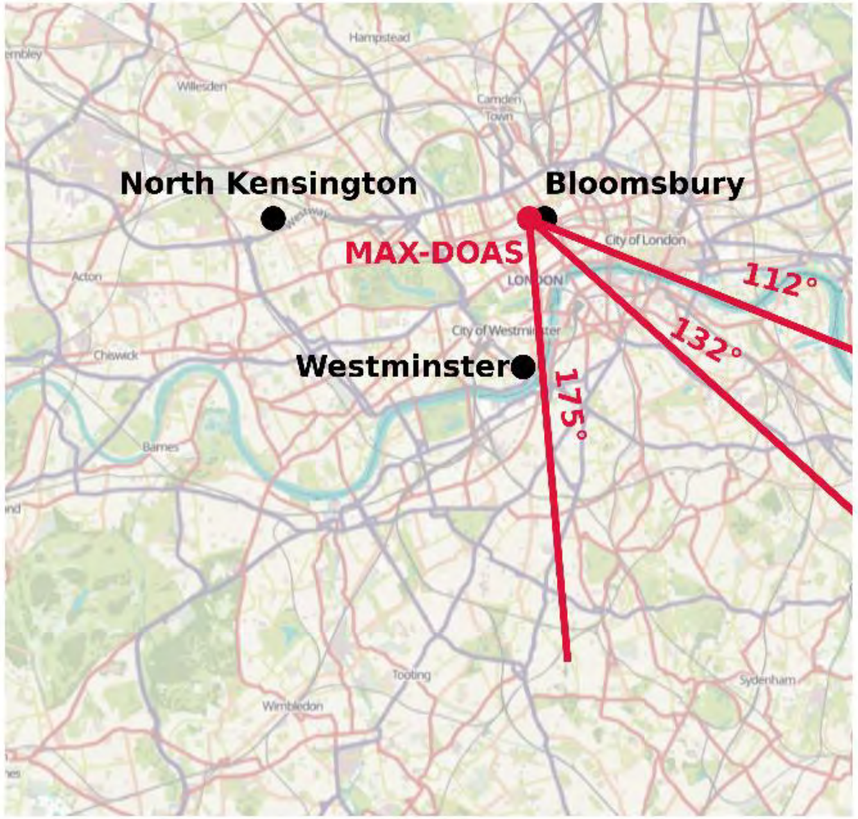

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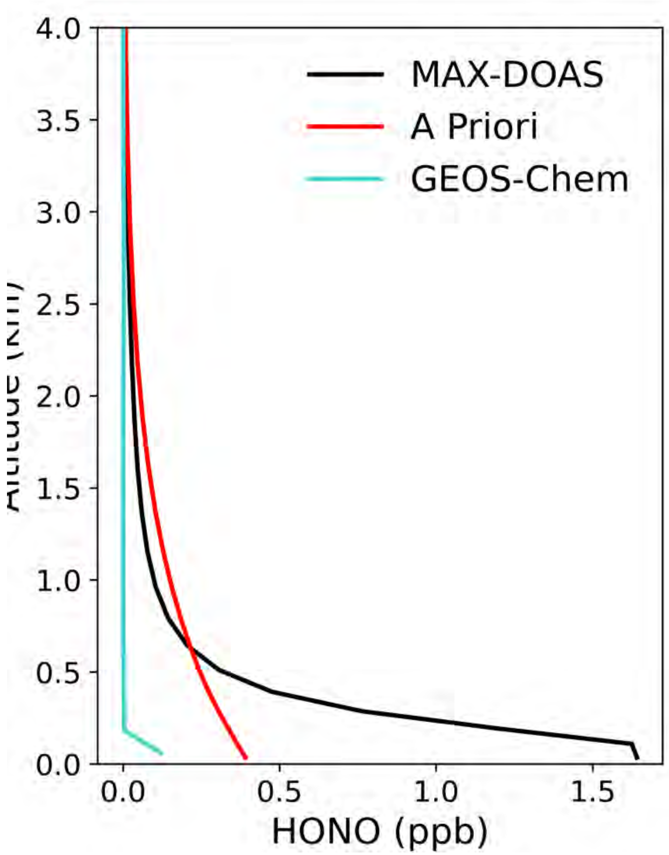

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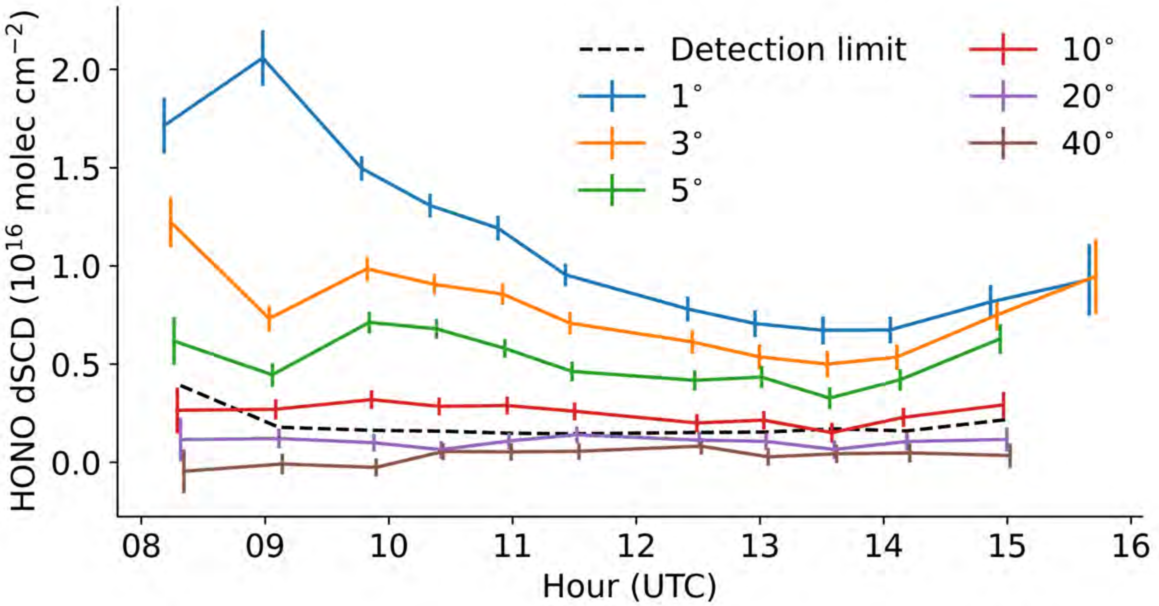
The UCL MAX-DOAS has provided vertical profiles of HONO since its June 2022 deployment.

Detecting HONO with the UCL MAX-DOAS

MAX-DOAS HONO dSCDs and detection limit



$$DL = \frac{2\ RMS}{\sigma_{max}}$$ High-confidence detection limit

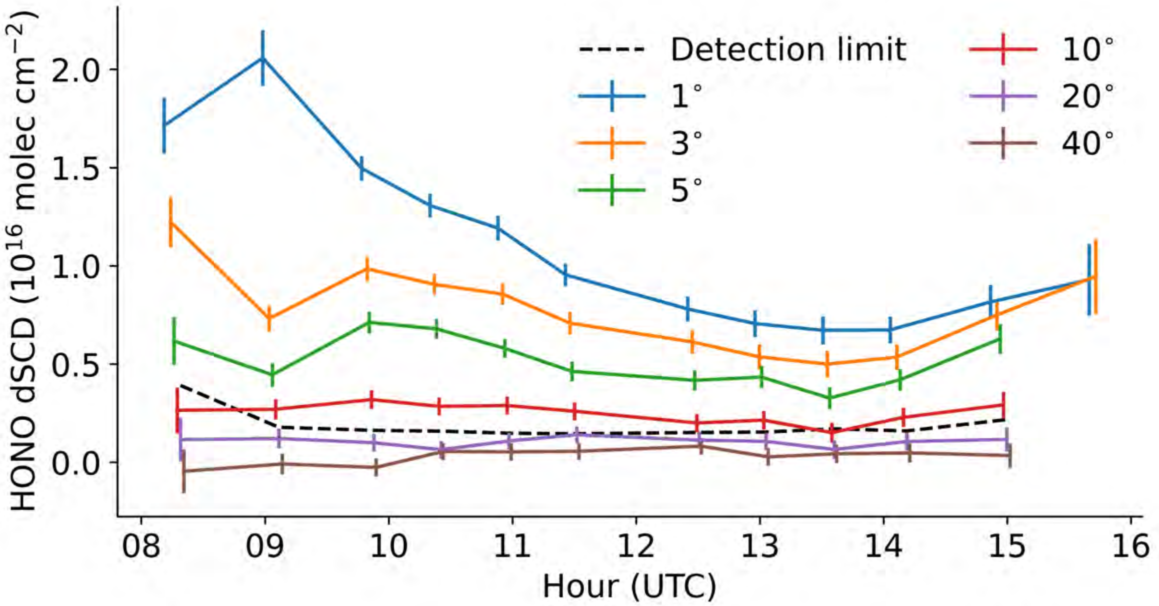
$$DL = \frac{RMS}{\sigma_{max}}$$ Medium-confidence detection limit

HONO is a weak absorber in the UV-vis.

High concentrations are required for detection.

Detecting HONO with the UCL MAX-DOAS

MAX-DOAS HONO dSCDs and detection limit



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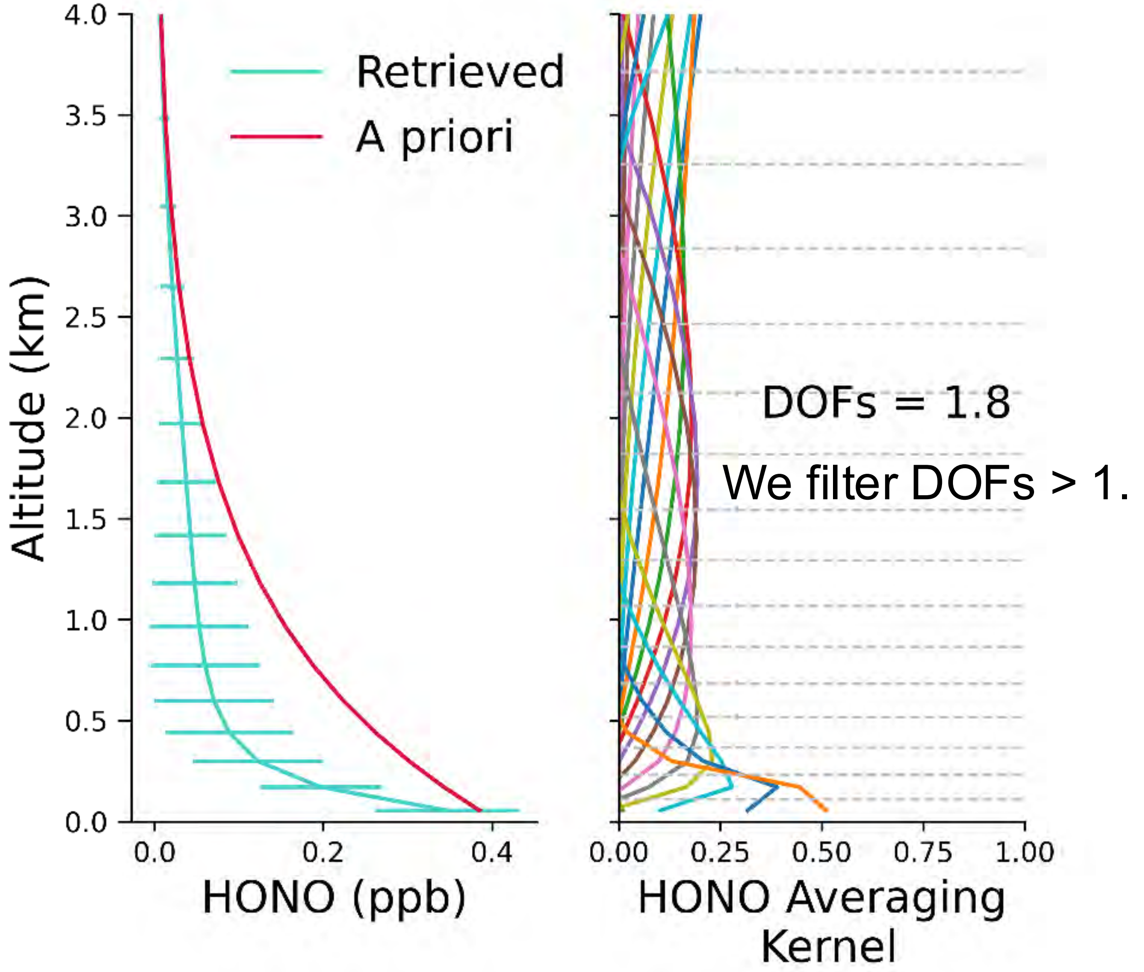
HONO vertical profiles and averaging kernels



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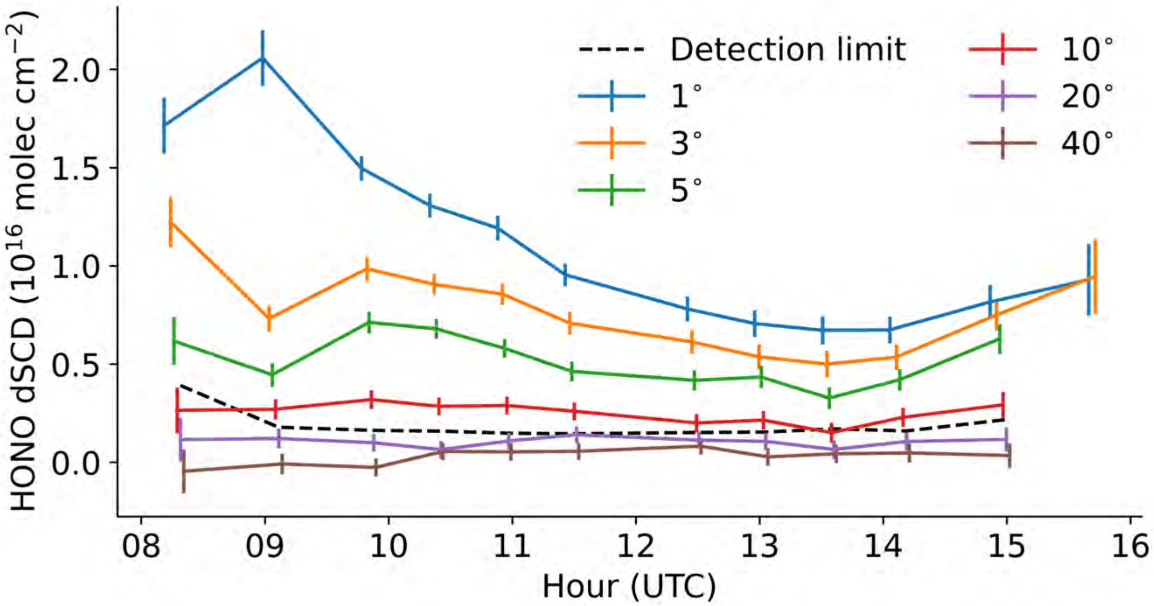

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13%-58% of days in a month are detect days and HONO is only detected by the UCL MAX-DOAS under specific conditions.

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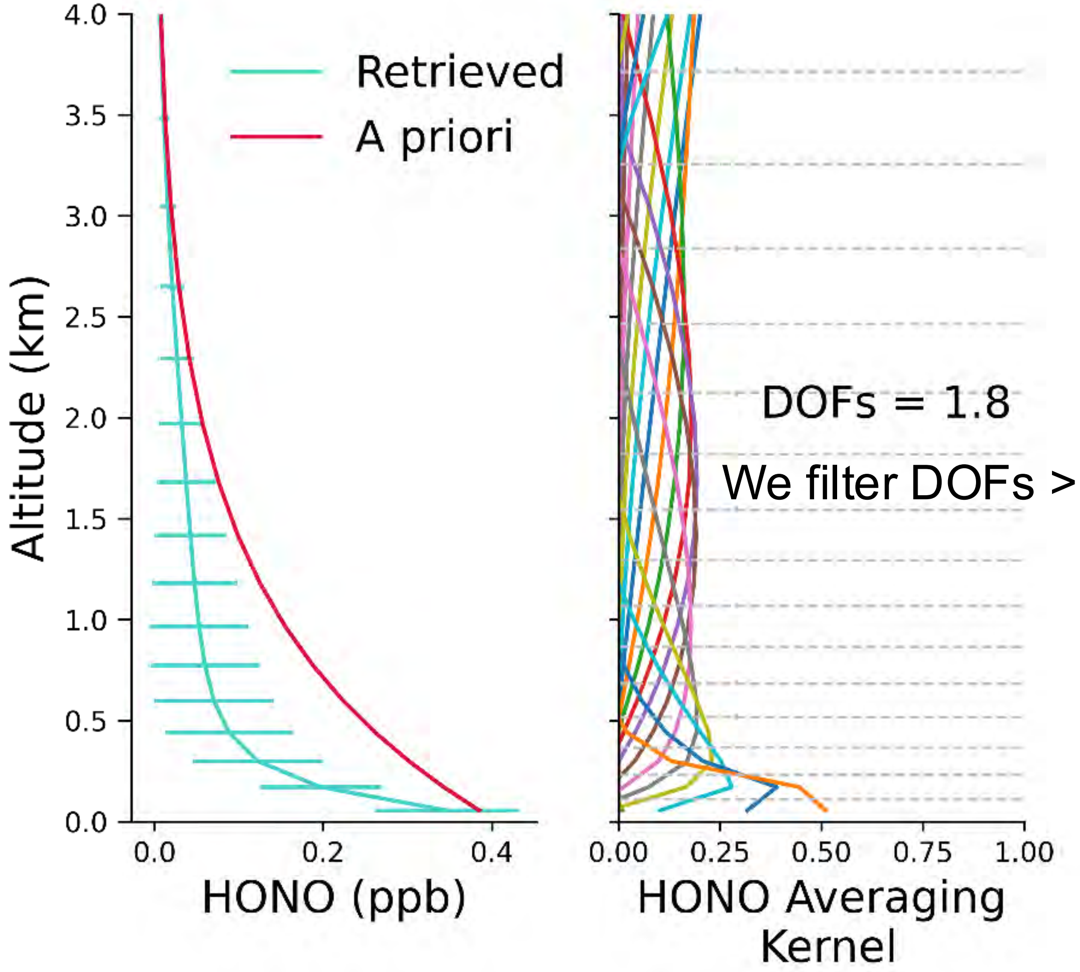
HONO vertical profiles and averaging kernels

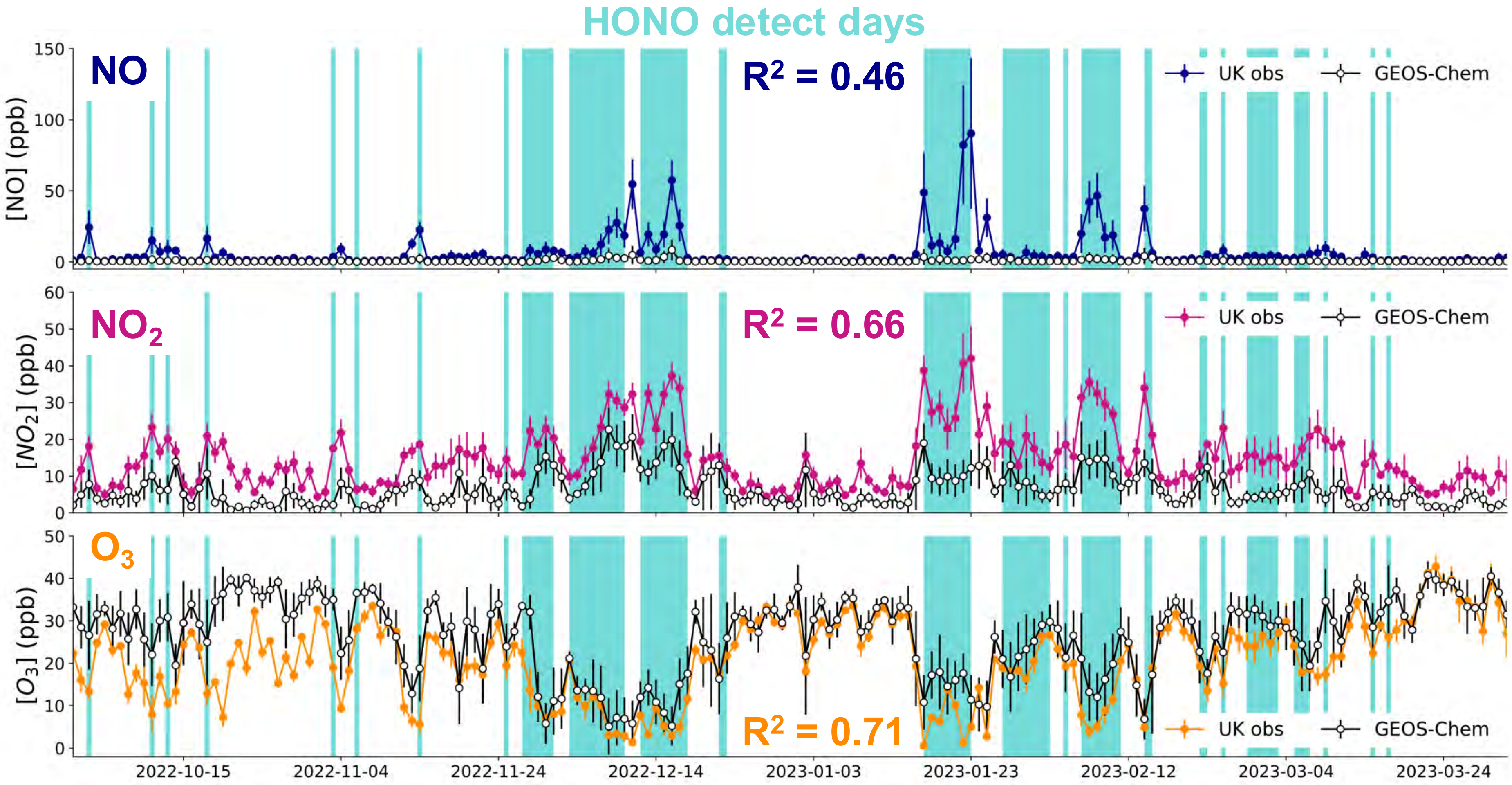


DOFs = 1.8

We filter DOFs > 1.

NO_x and O_3 determine HONO concentrations

Daily NO_x and O_3 concentrations from October 2022 to April 2023



High **NO_2 (>15 ppb)**, **NO (>20 ppb)** and low **O_3 (<27ppb)** optimal for HONO formation.

$NO + OH \rightarrow HONO$

$NO + O_3 \rightarrow NO_2 + O_2$

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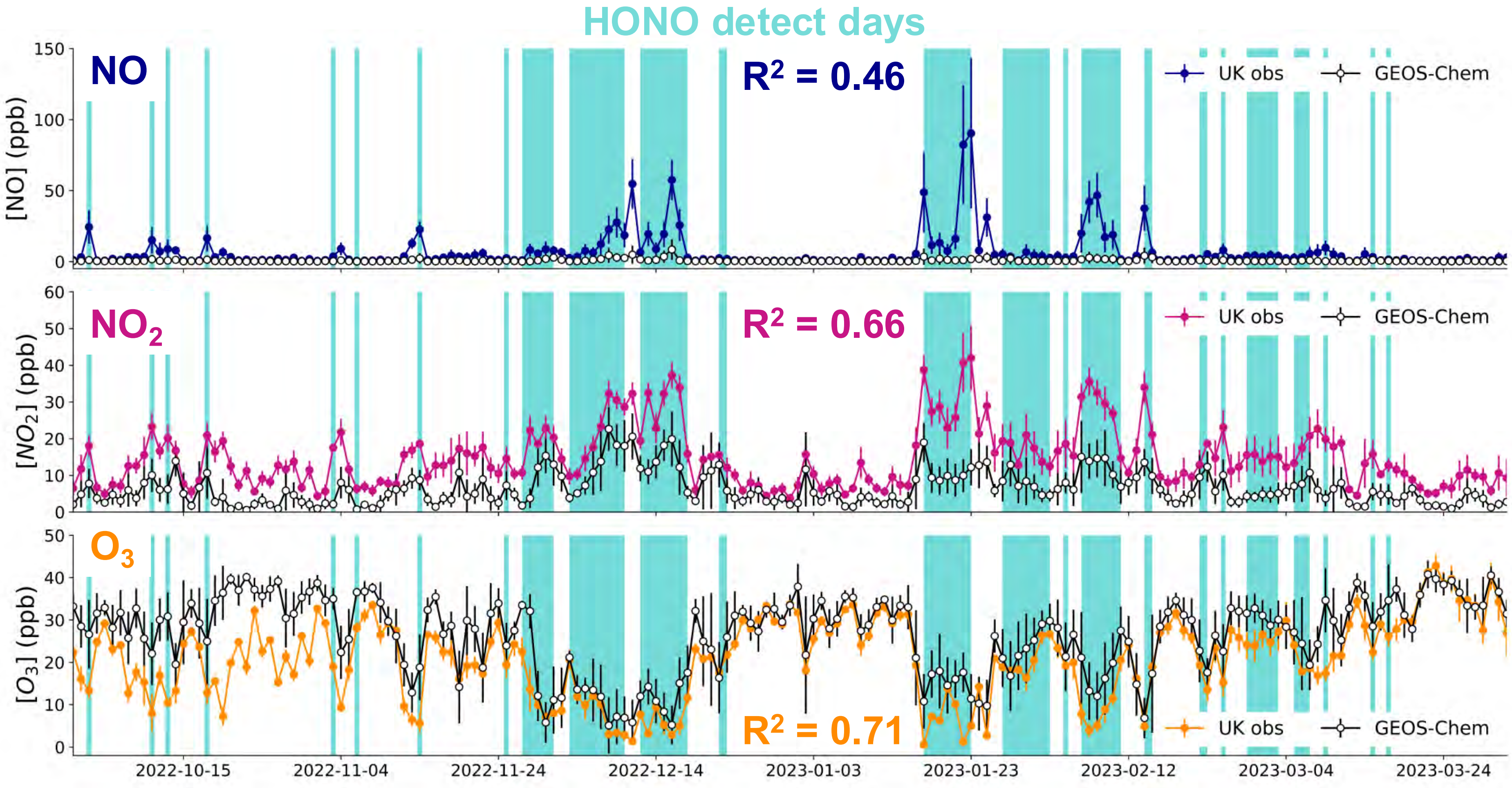

High NO_2 (>15 ppb), NO (>20 ppb) and low O_3 (<27ppb) optimal for HONO formation.

$$NO + OH \rightarrow HONO$$

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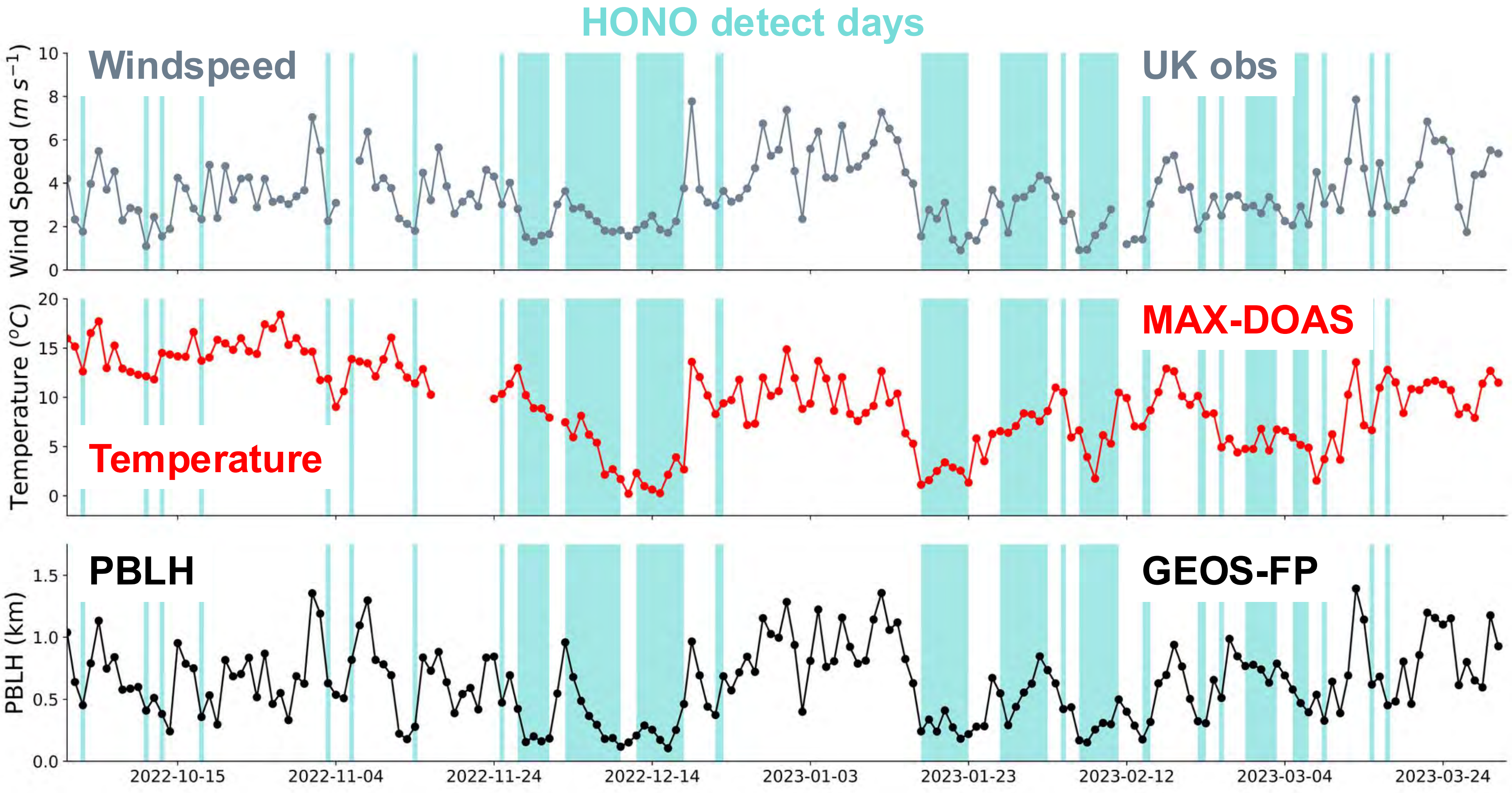
Under low O_3 conditions, the formation of HONO outcompetes the reaction between O_3 and NO.

Meteorological conditions that favour HONO detection

Daily meteorological conditions from October 2022 to April 2023



Clear days allow for HONO detection.

Meteorological conditions that favour HONO detection

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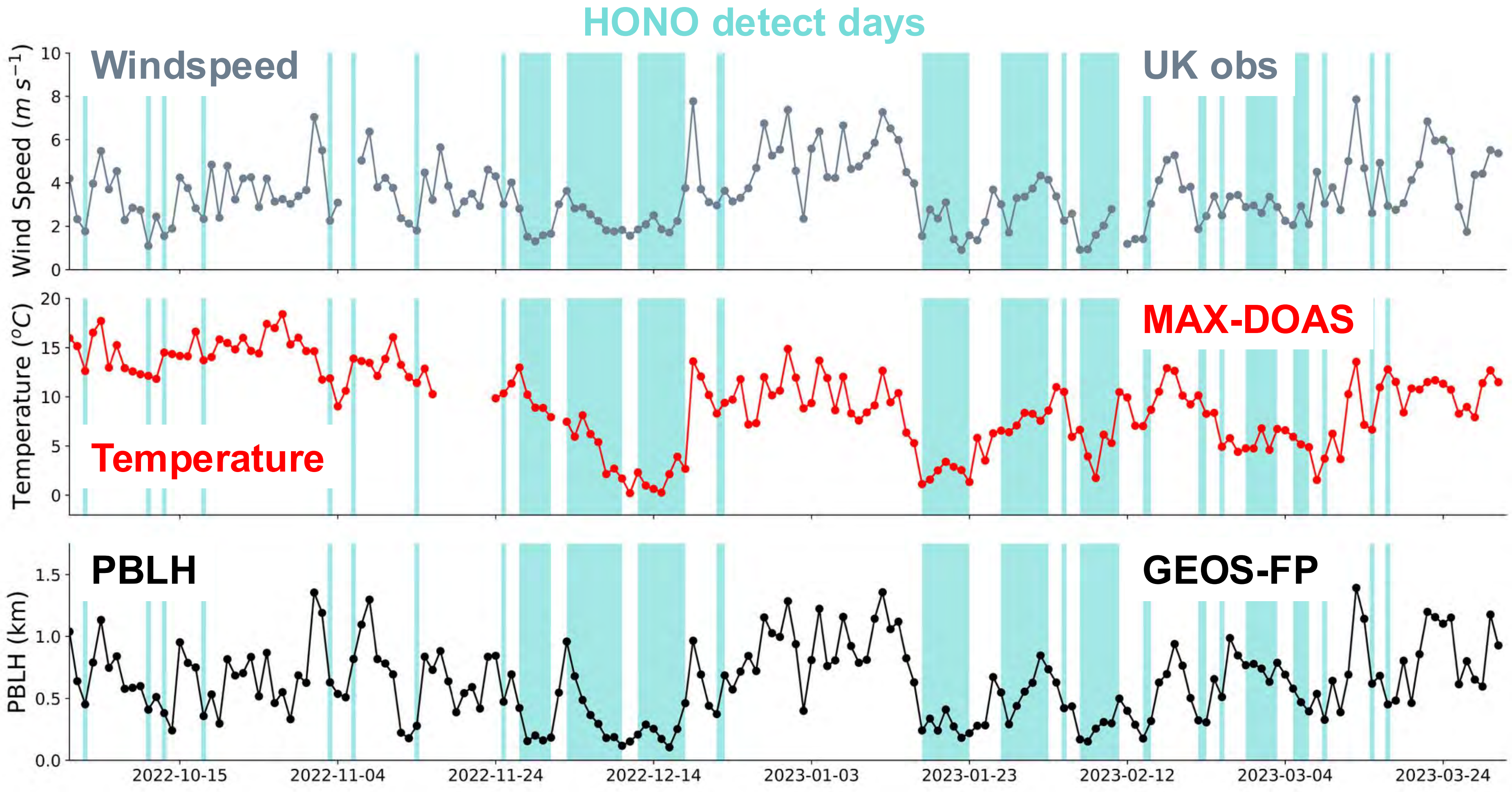
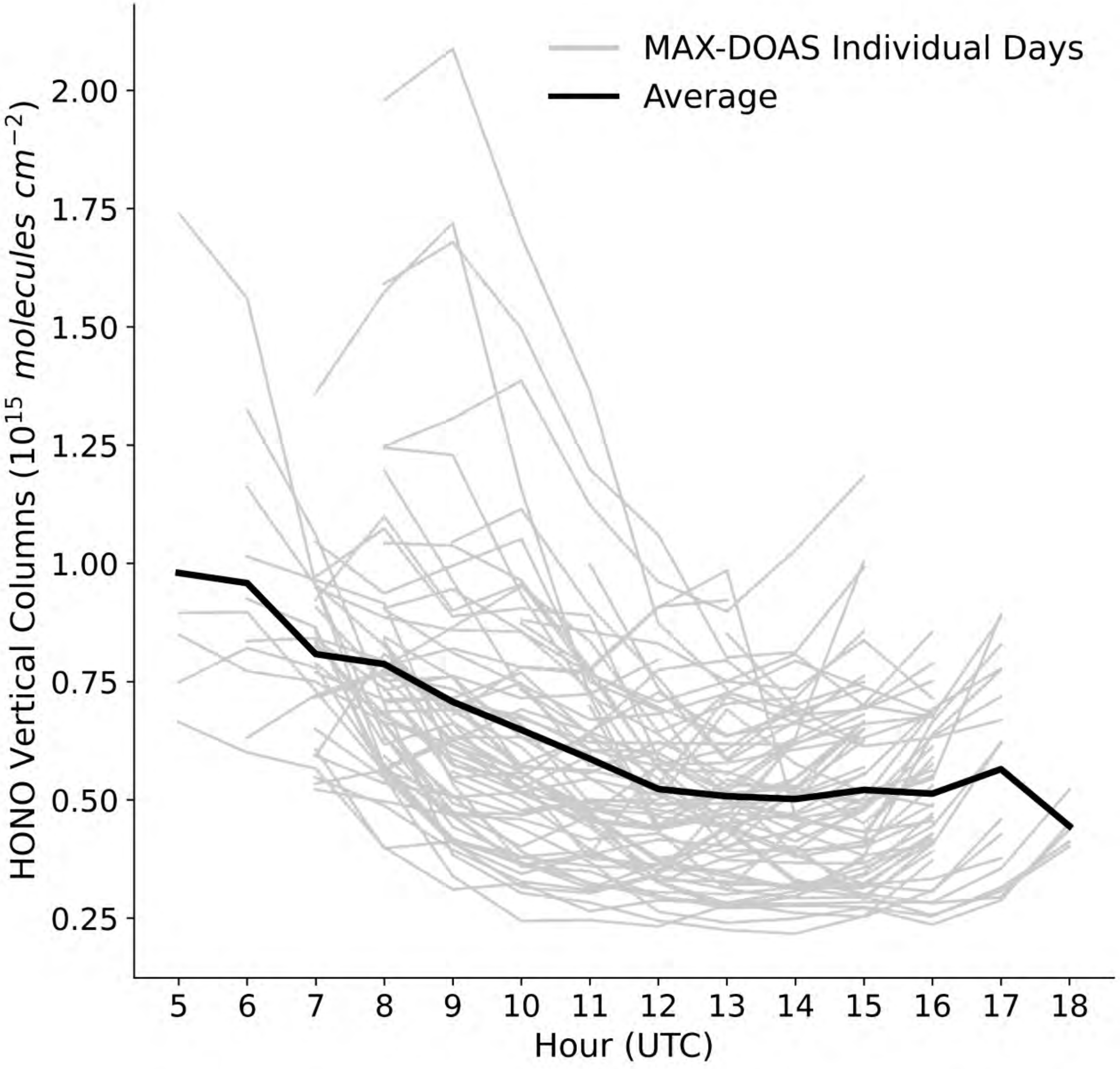


Clear days allow for HONO detection.

Low windspeeds (<6 ms^{-1}), cold conditions (<13°C), depressed PBL (<500 m) optimal for HONO detection.

MAX-DOAS observations of HONO diurnal variability



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

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

HONO peaks in the early hours of the morning, depletes as the sun rises and increases from approximately 2 pm (UTC).

GEOS-Chem is almost **2 orders of magnitude lower** than MAX-DOAS HONO.

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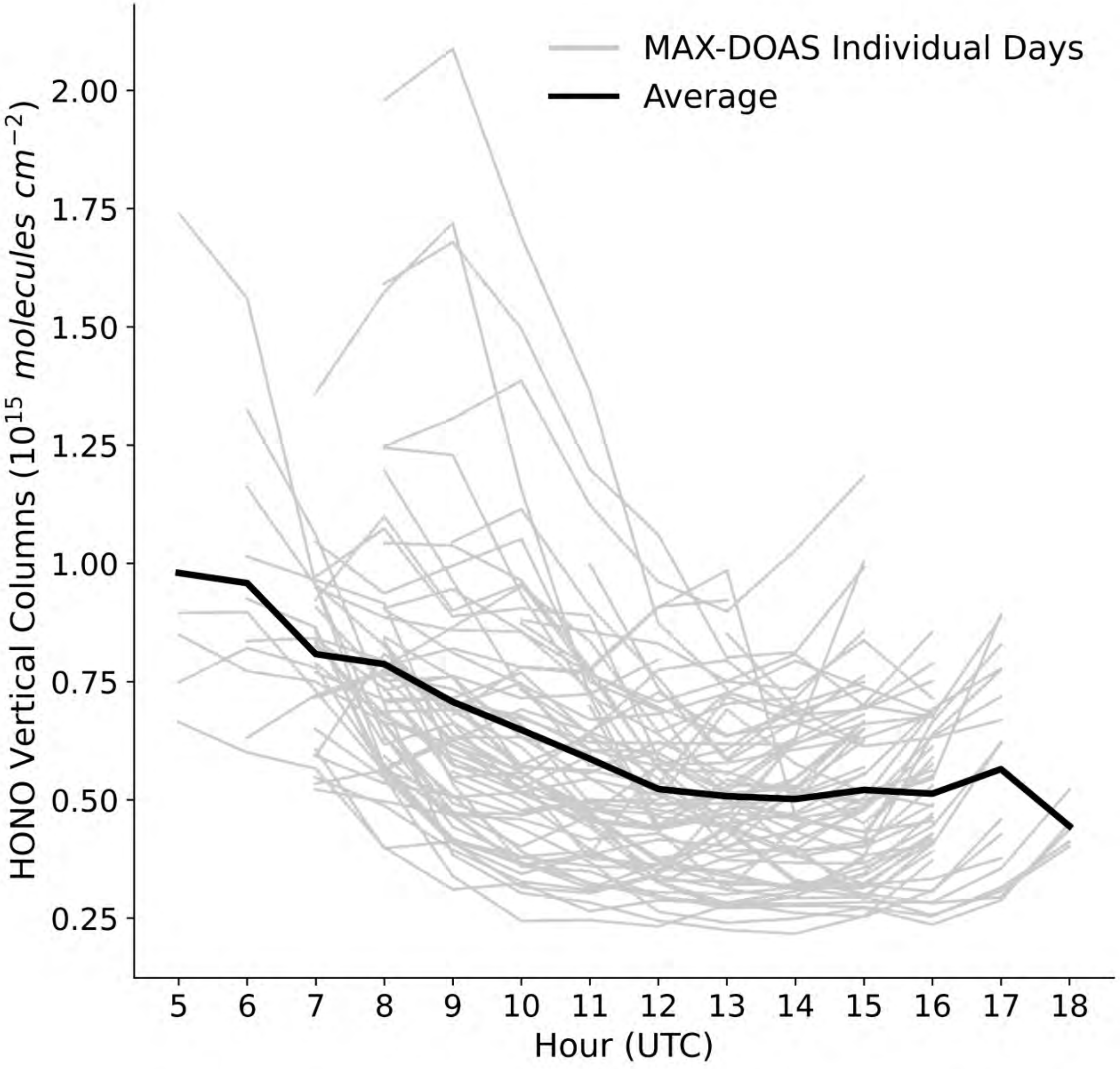

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GEOS-Chem is almost **2 orders of magnitude lower** than MAX-DOAS HONO.

GEOS-Chem underestimates HONO concentrations and does not reflect the observed diurnal variation of HONO.

GEOS-Chem simulations over Central London

Model Input

NASA GEOS-FP assimilated meteorology

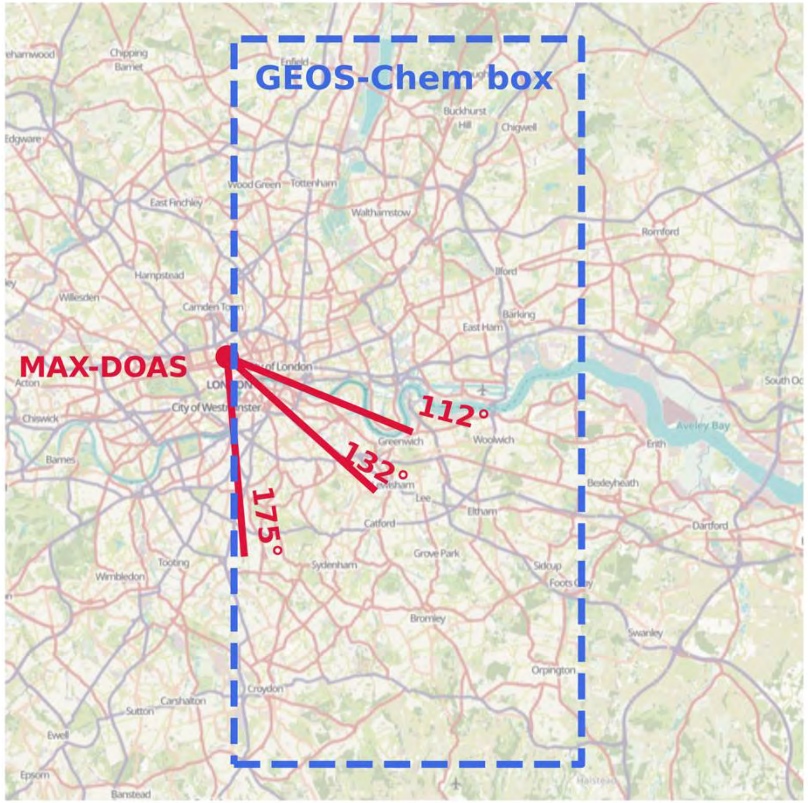
CEDs v2

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.

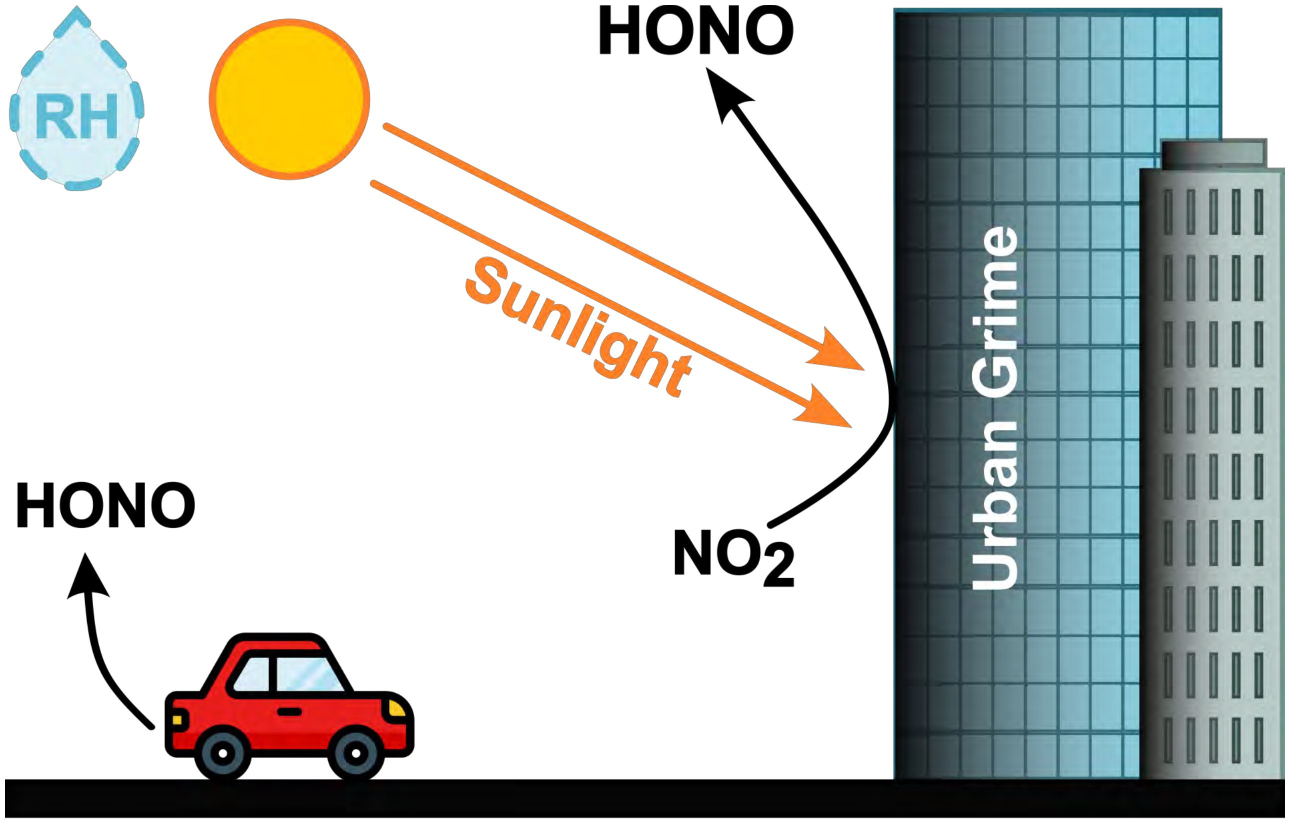
Parameterising new HONO sources

$$\gamma = 4.8 \times 10^{-8} \times [light\ intensity](W\ m^{-2}) + 1.3 \times 10^{-6}$$

$$\gamma = \frac{1}{9.9 \times 10^{3} \times [NO_2](ppb) + 1.4 \times 10^{5}}$$

$$\gamma = -4.4 \times 10^{-10} \times ([RH]\ (\%))^{2} + 6.2 \times 10^{-8} \times [RH](\%) - 6.1 \times 10^{-7}$$

The uptake of NO_2 on urban grime is represented as functions of **light intensity**, **NO_2 concentration** and **relative humidity**.



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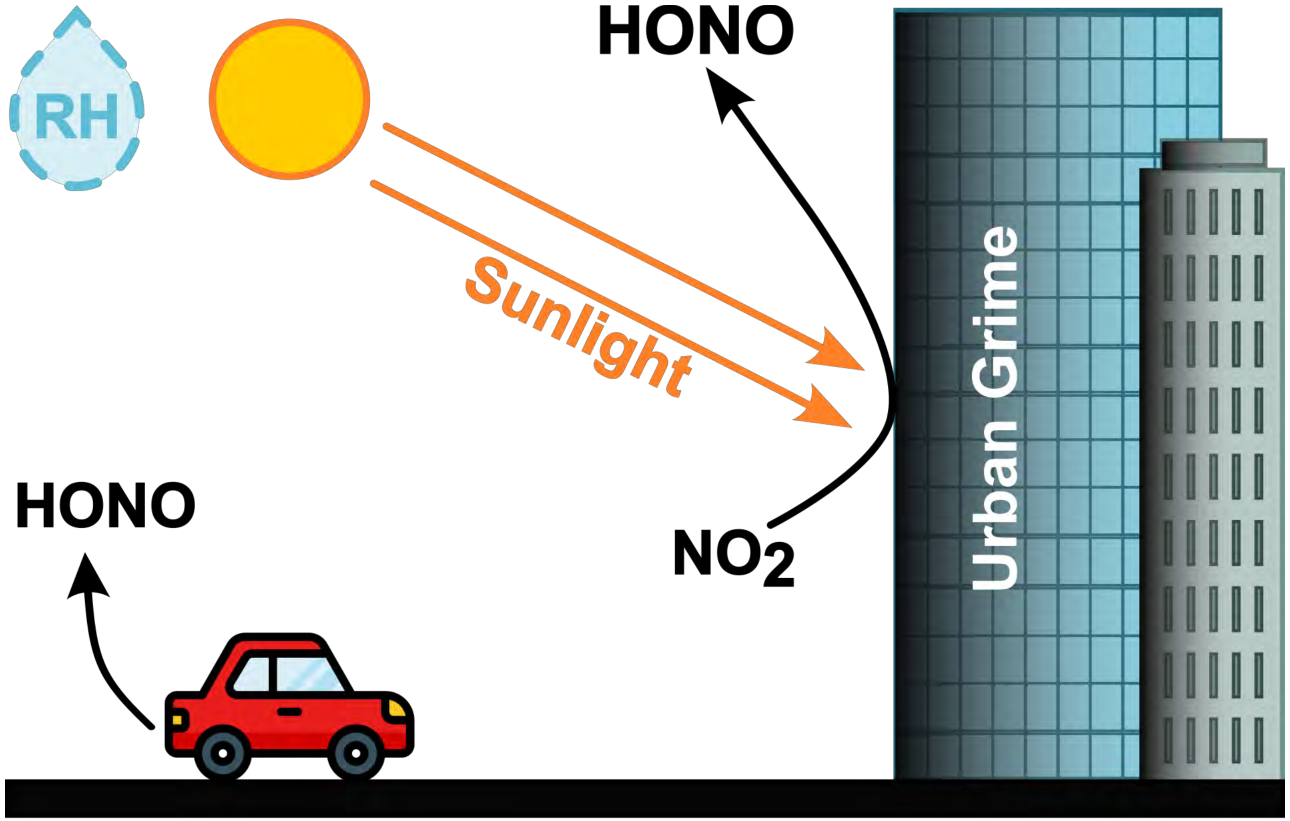
The uptake is used to calculate the pseudo 1st order loss rate of NO_2 on a surface.



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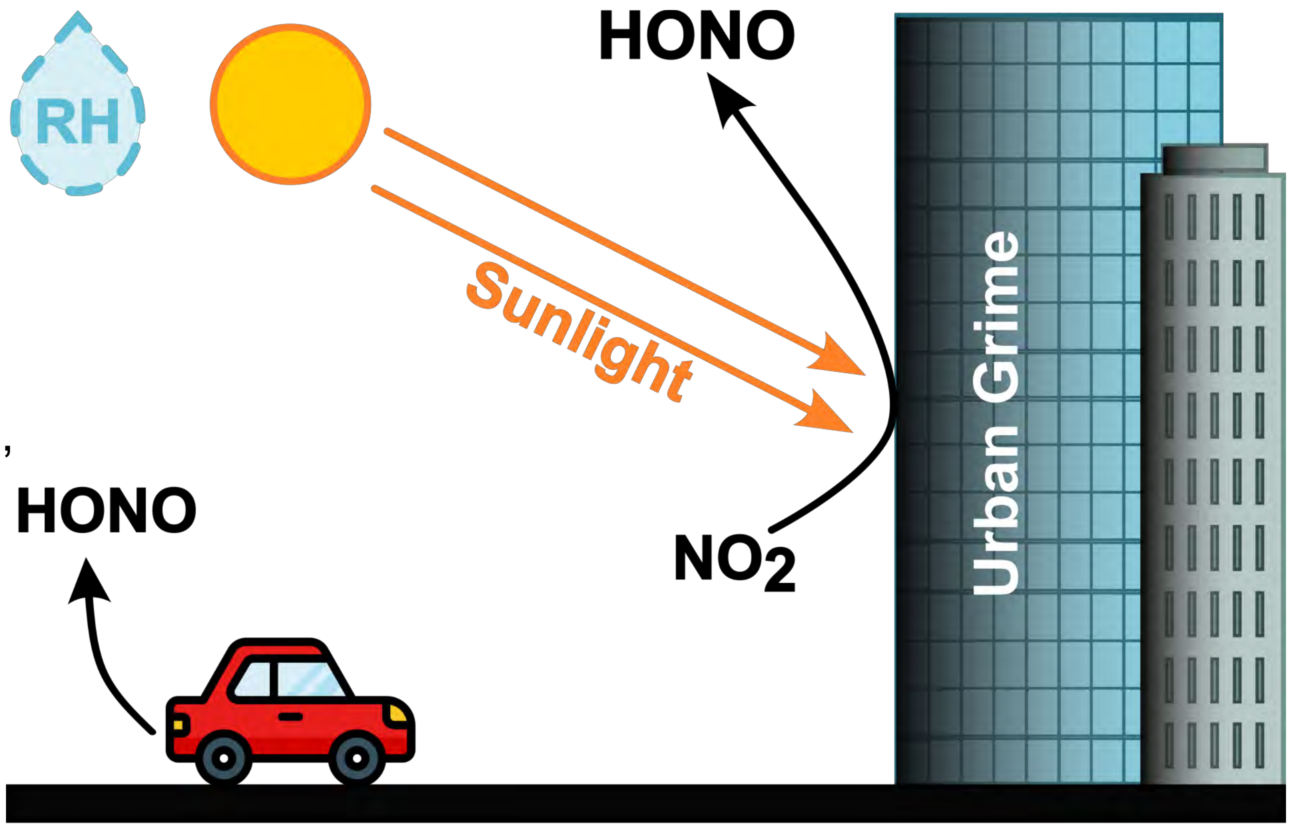
Vehicle emissions are calculated as **0.85 % of NO_x emissions** according to a road tunnel study in Birmingham, UK.

$$\Delta HONO/\Delta NO_x = 0.85\ \%$$



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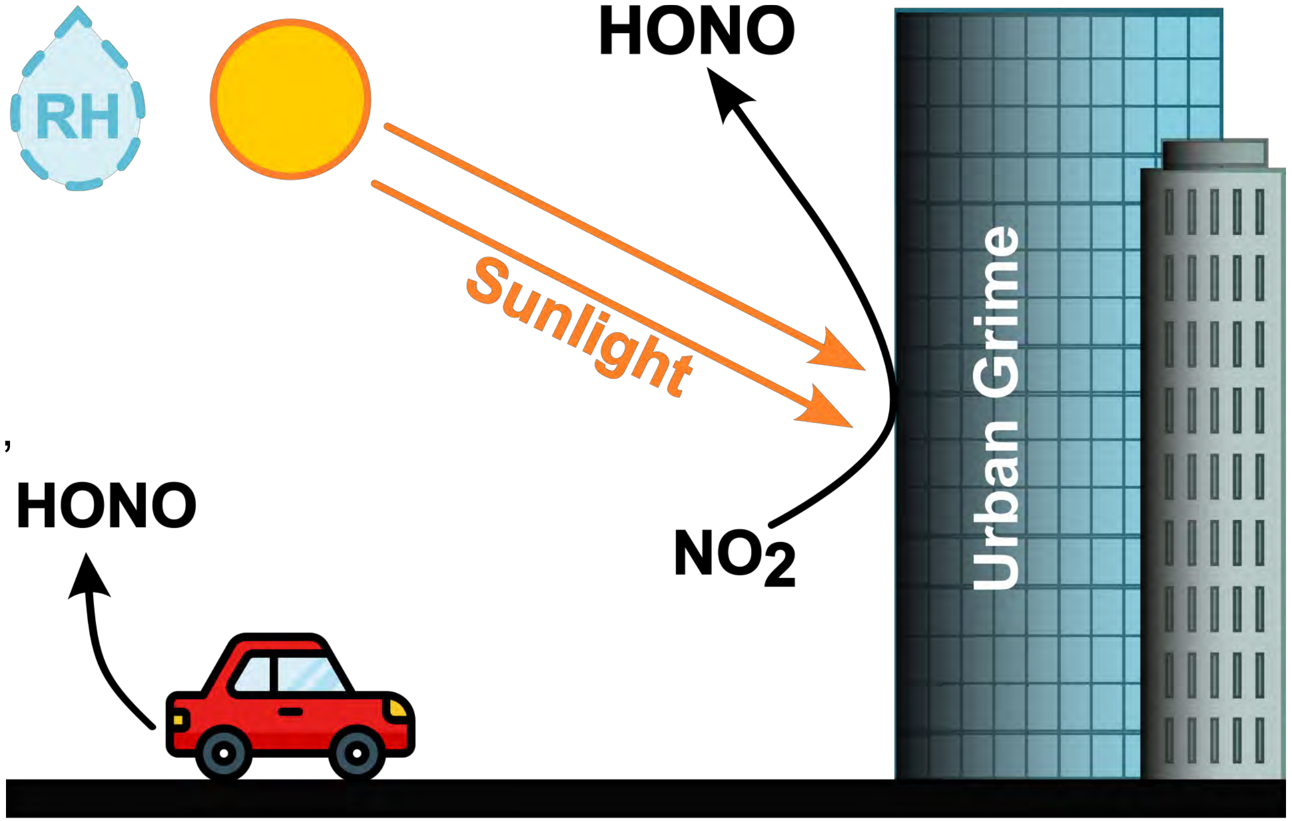
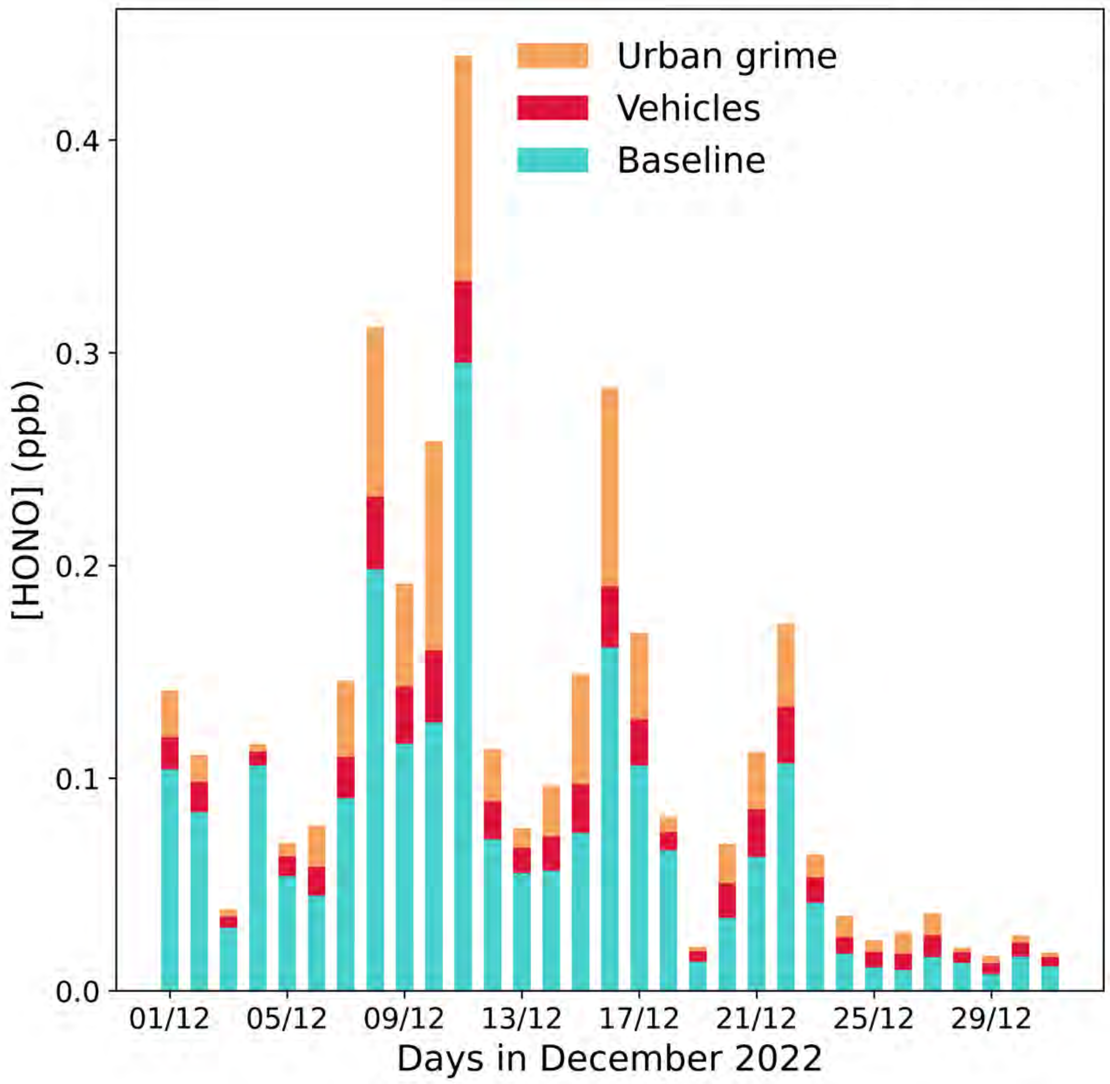
Here we parameterise the conversion of NO_2 on urban grime using laboratory observations.

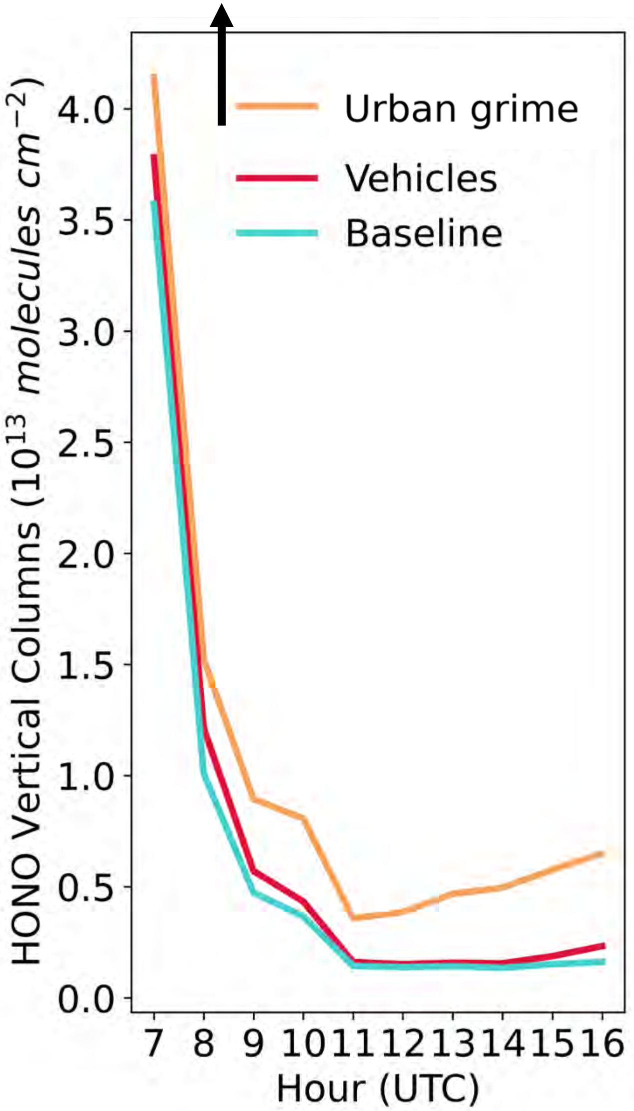


HONO concentrations with new sources

Lowest model layer concentrations and HONO vertical columns with updated sources



$20 - 210 \times 10^{13}$ molec cm^{-2}



The inclusion of vehicle emissions and urban grime production increases the average daily HONO concentration by 60 %.

GEOS-Chem still underestimates HONO.

HONO concentrations with new sources

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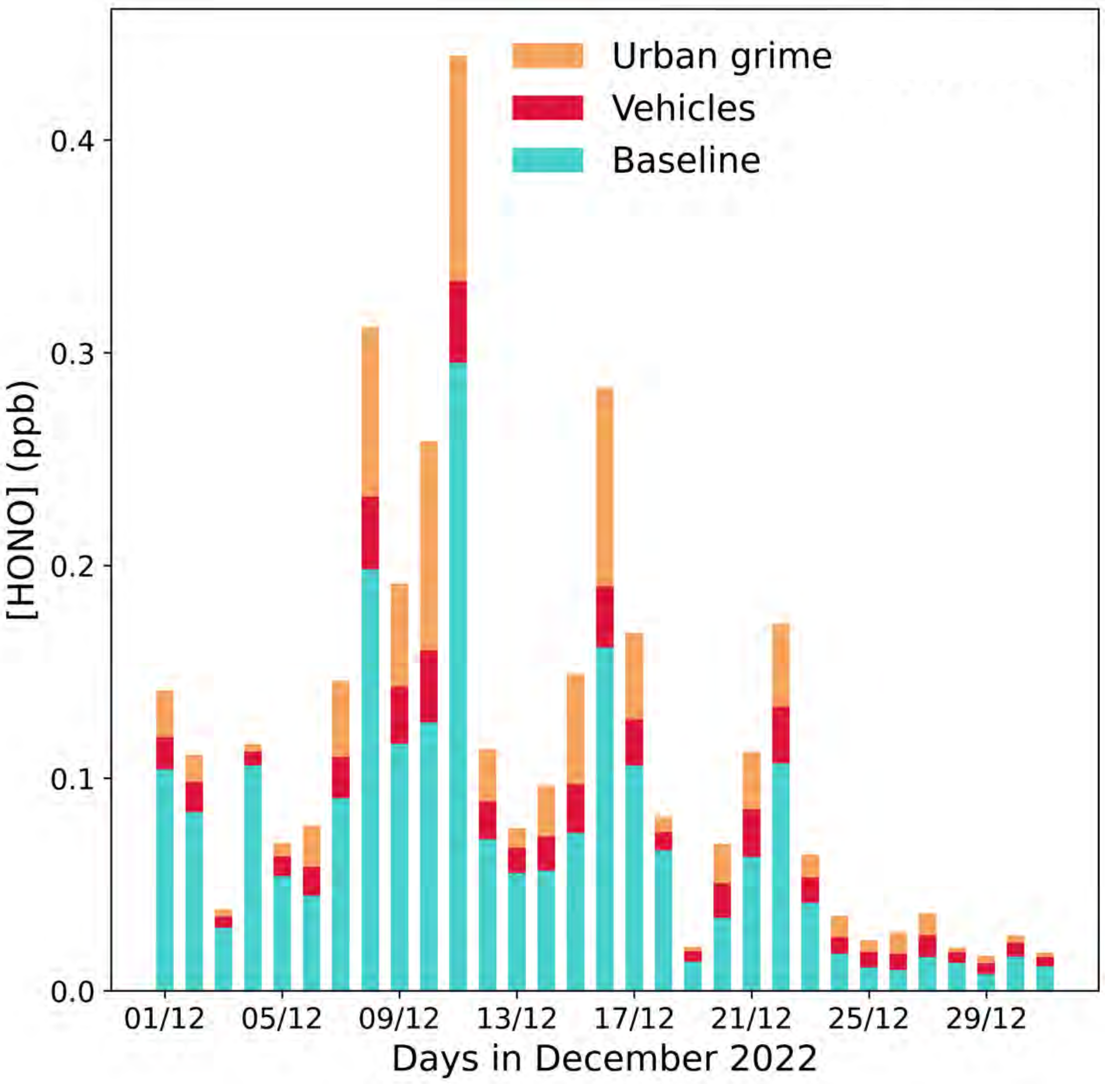

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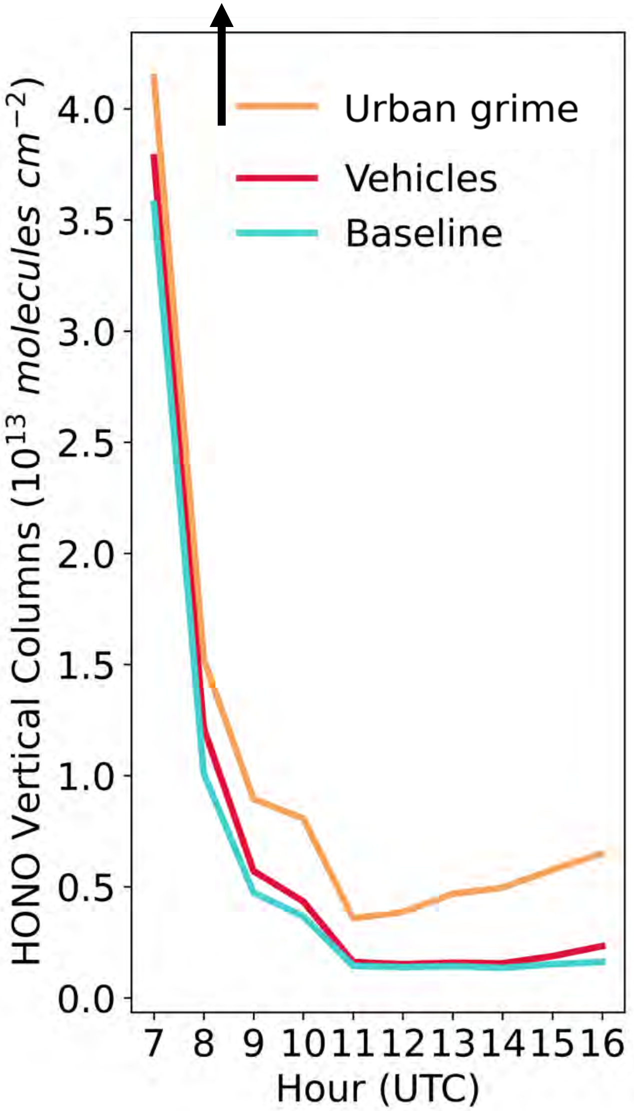

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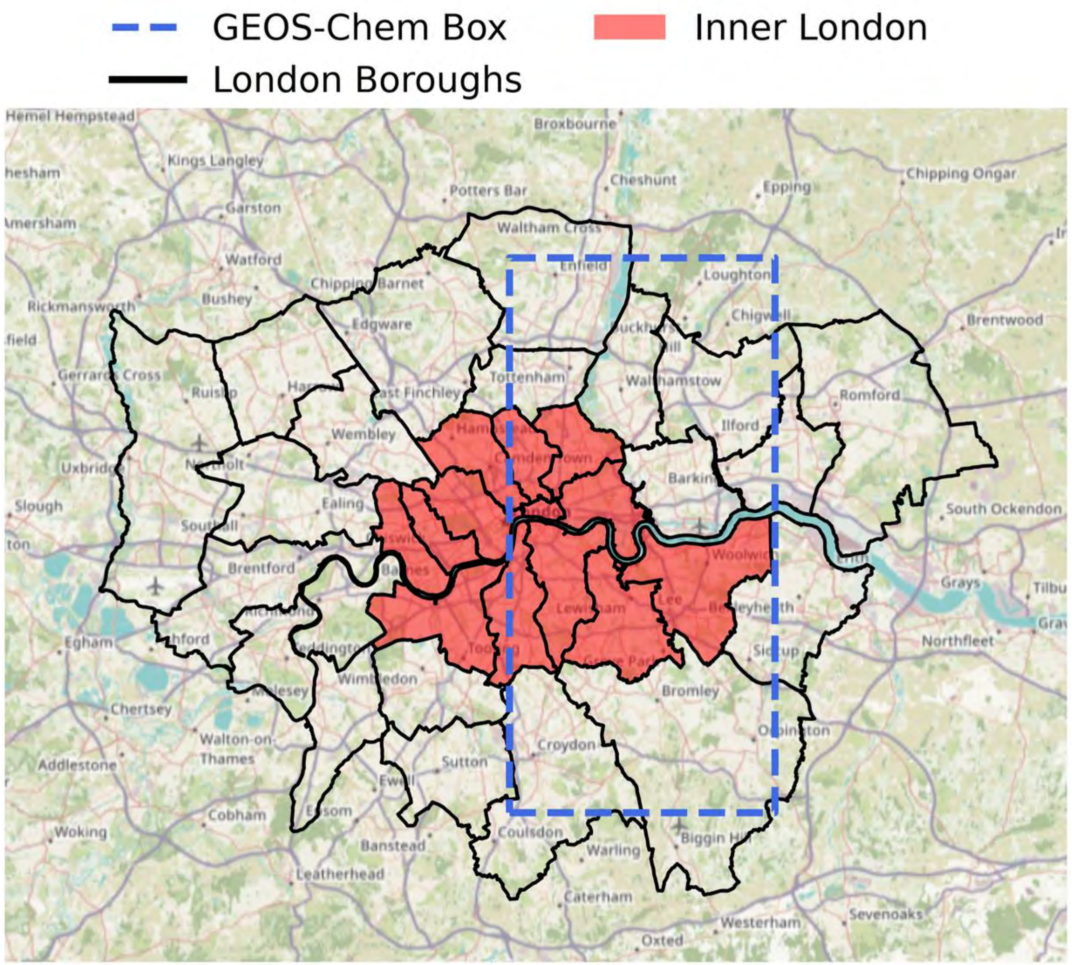
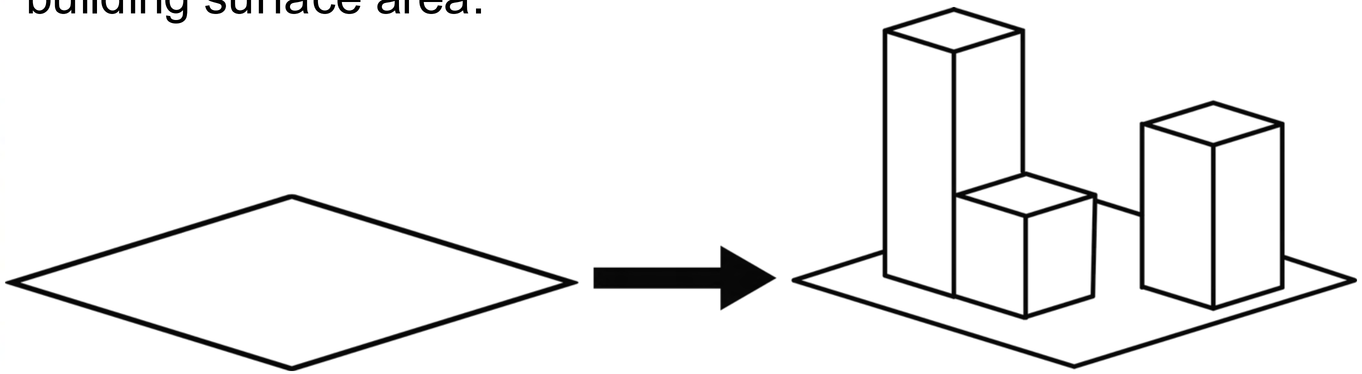
Including these new sources increases HONO concentrations, but the parameterisations require improvements.

We aim to calculate the value of uptake needed for the model to reflect observations.

Accounting for buildings



GEOS-Chem assumes London is flat and does not account for building surface area.



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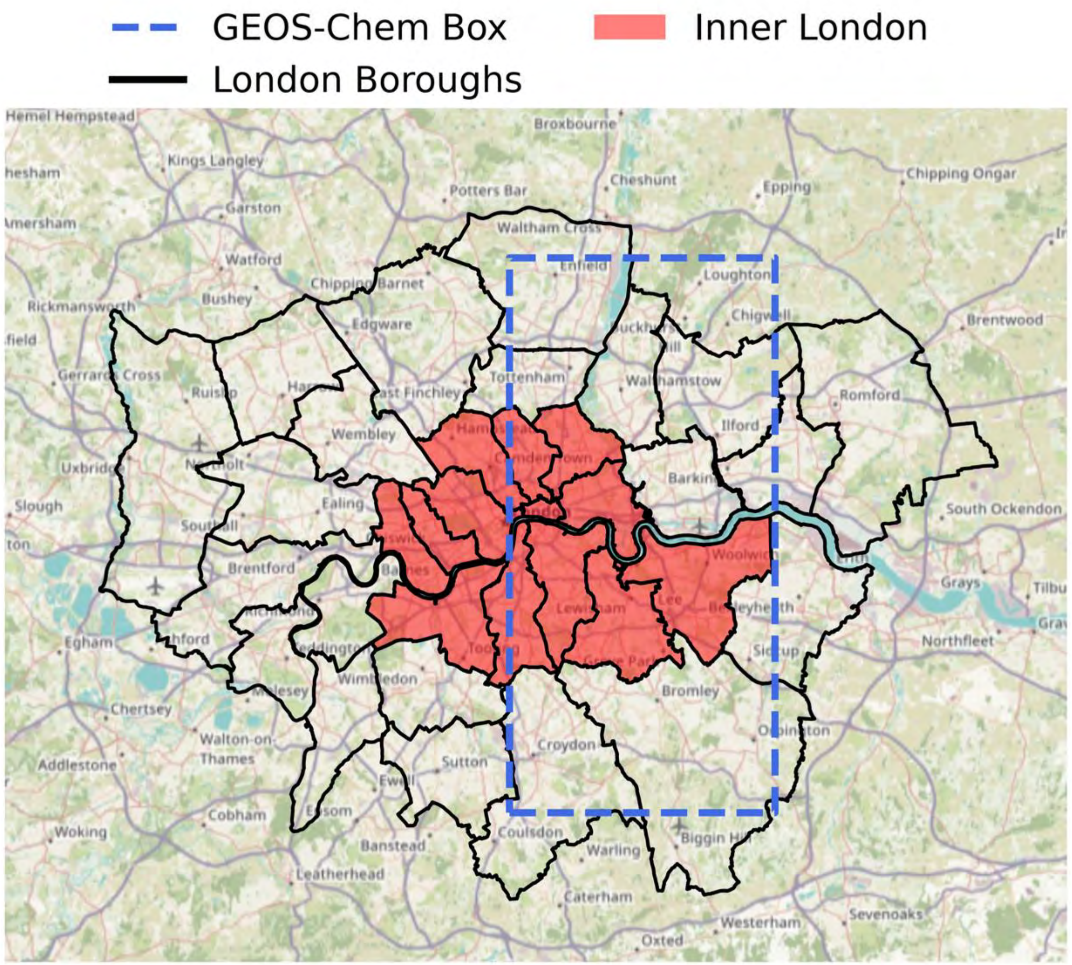

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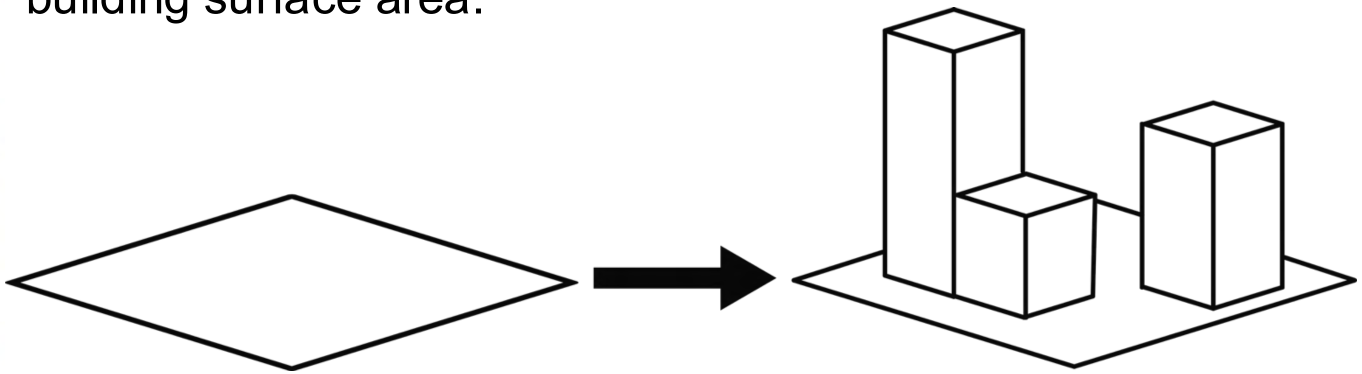
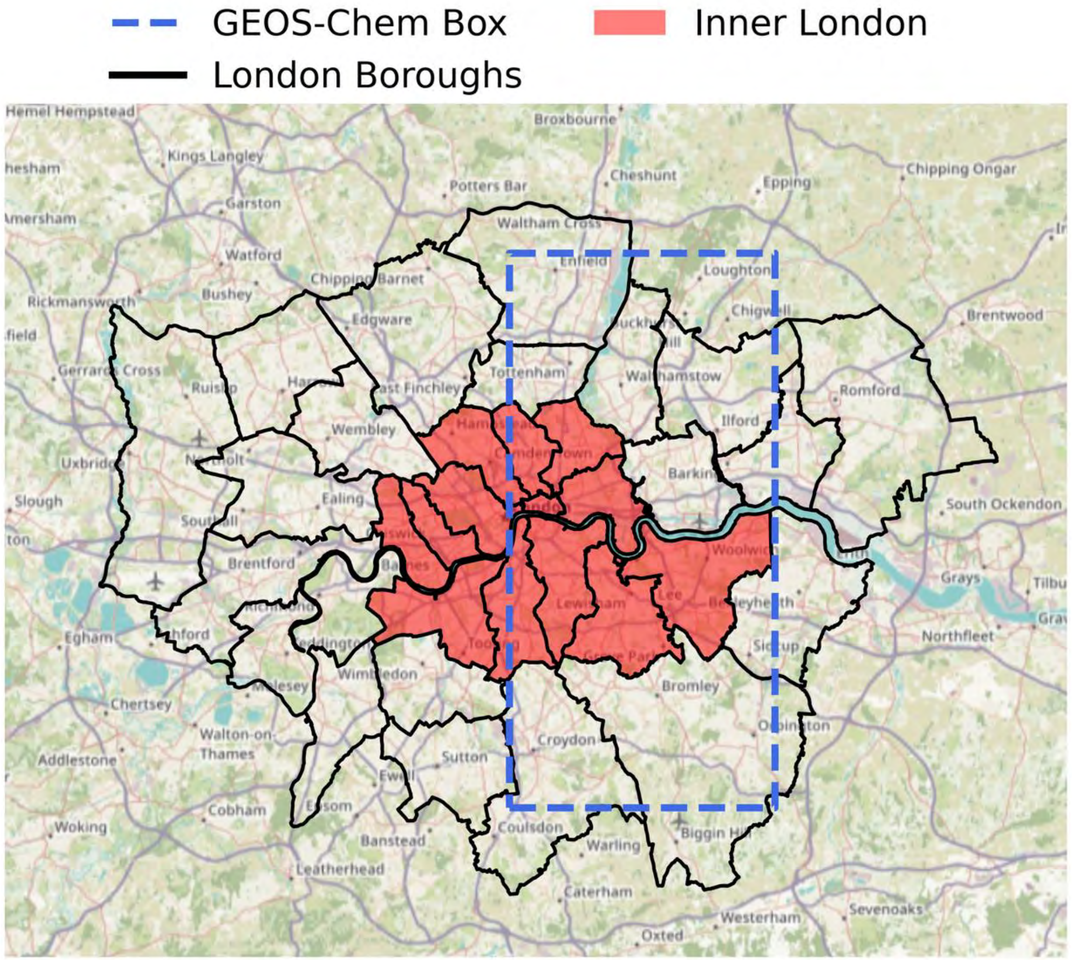


We use 3DStock, a building stock model, to estimate the exposed wall area in **Inner London**.

The addition of exposed wall area increases the surface area of **Inner London** by **28% - 50%.**

3DStock still underestimates surface area.

Accounting for buildings



Our **simulations** encompass **62%** of **Inner London** as well as Greater London and beyond.

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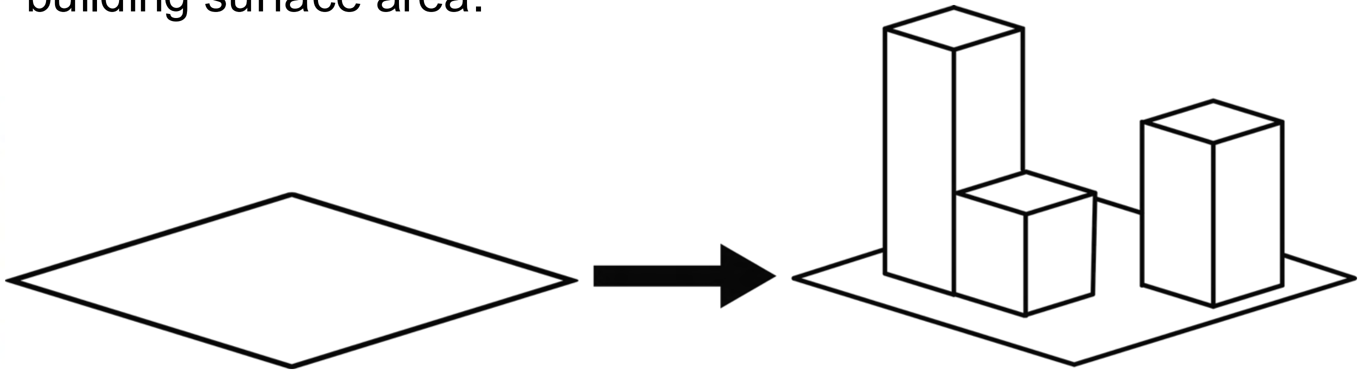

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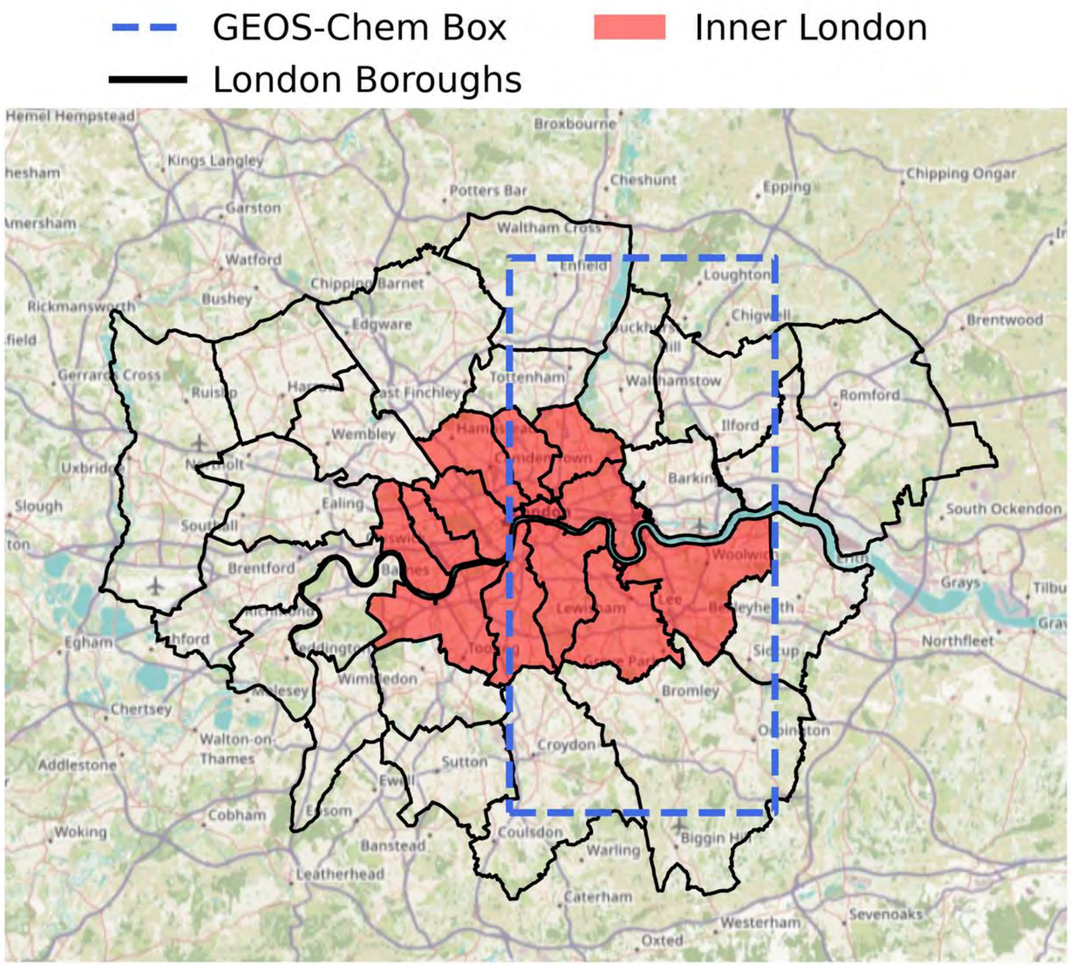

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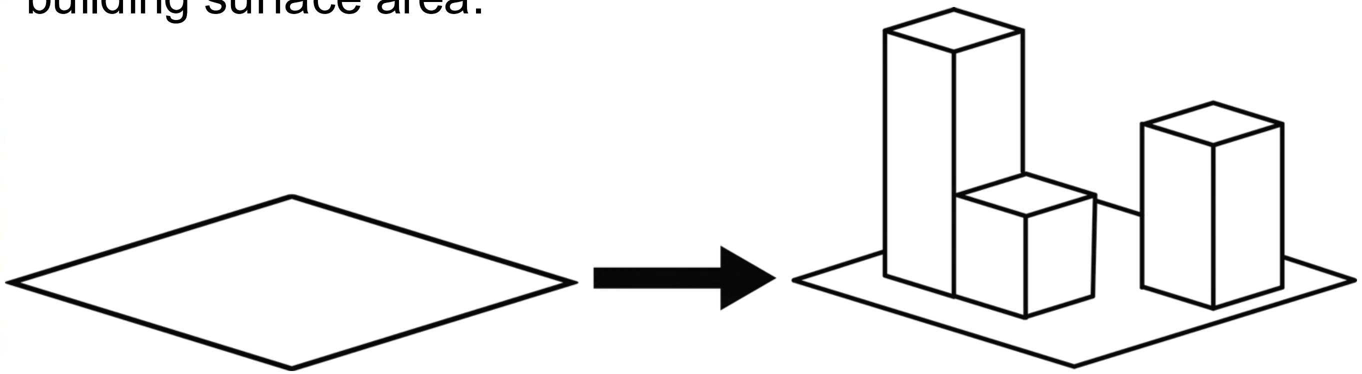

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Assuming building density and height decreases outside Inner London, we scale the surface area within the GEOS-Chem box by 28 % to account for the built environment.

Summary and further work

GEOS-Chem severely underestimates urban HONO.

Heterogeneous sources of HONO are significant and require parameterization.

However, the addition of car and urban grime emissions are not sufficient to match observations without scaling.

Incorporate building surface area estimates.

Assess the magnitude of uptake required to match observations.

Incorporate the observation-informed uptake value and assess the role of HONO in urban air quality.

Evaluate atmospheric oxidation capacity after finalisation of HONO sources in the city.

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