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

Eleanor Gershenson-Smith (eleanor.smith.18@ucl.ac.uk)[1], Eloise A. Marais[1], Robert G. Ryan[2], Jan-Lukas Tirpitz[3], Gongda Lu[1]

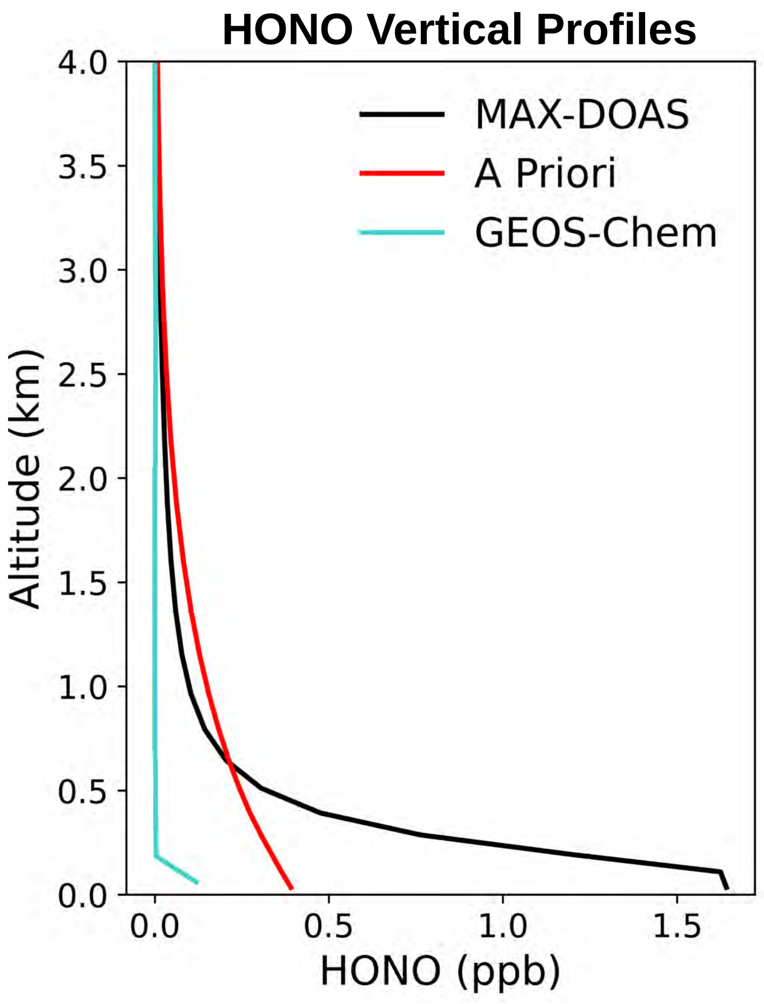
[1]Department of Geography, University College London, London, UK

[2]School of Geography, Earth and Atmospheric Sciences, University of Melbourne, Melbourne, Australia

[3]Joint Institute for Regional Earth System Science and Engineering, University of California, Los Angeles, USA

1. Background and motivation

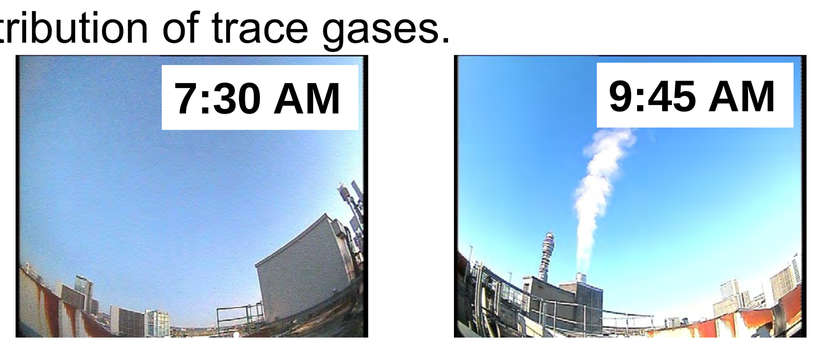
- Nitrous acid (HONO) is a major early morning source of the hydroxyl radical (OH), which influences atmospheric reactivity and the production of ozone.
- HONO is generally underestimated in models and sources of urban HONO need to be identified to improve the current understanding of urban air quality.
- Here we parameterize vehicle emissions of HONO and the heterogeneous conversion of NO_2 to HONO on urban grime in the GEOS-Chem model.



2. The UCL MAX-DOAS

The UCL MAX-DOAS was installed mid-June 2022 on a 60 m altitude rooftop in Central London.

3 optimized azimuth angles along the horizon (112°, 132°, and 175°). 8 elevation angles (1°, 2°, 3°, 5°, 10°, 20°, 40°, and 90°) probe the vertical distribution of trace gases.



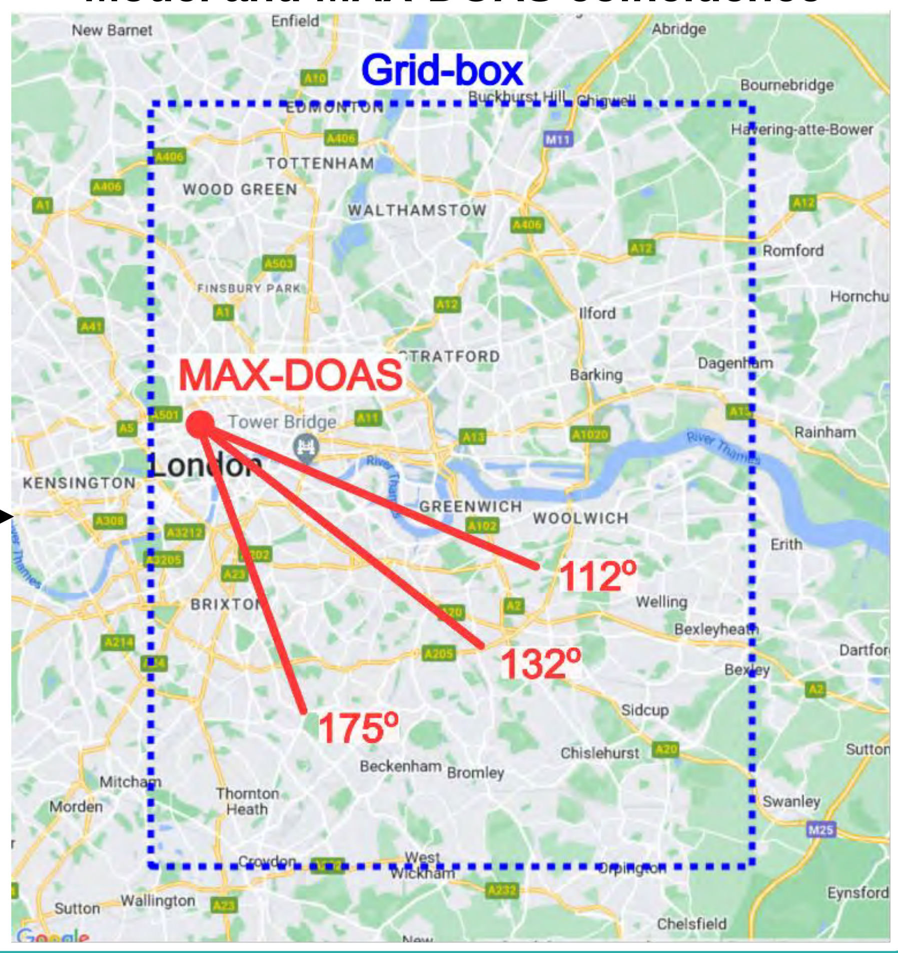
We only detect HONO on cold (< 7°C), still (windspeed < 4 ms^{-1}), clear winter (December-February) days.

3. GEOS-Chem simulations

We use GEOS-Chem v14.1.0 nested grid simulations (0.25°×0.3125°) centered over Greater London (49.25°N−59.5°N, 9.375°W−3.75°E) as the state-of-knowledge of HONO and compare it to our MAX-DOAS observations.

Model inputs are NASA GEOS-FP simulated meteorology and anthropogenic emissions from the Community Emissions Data System version 2 (CEDS v2).

Model and MAX-DOAS coincidence

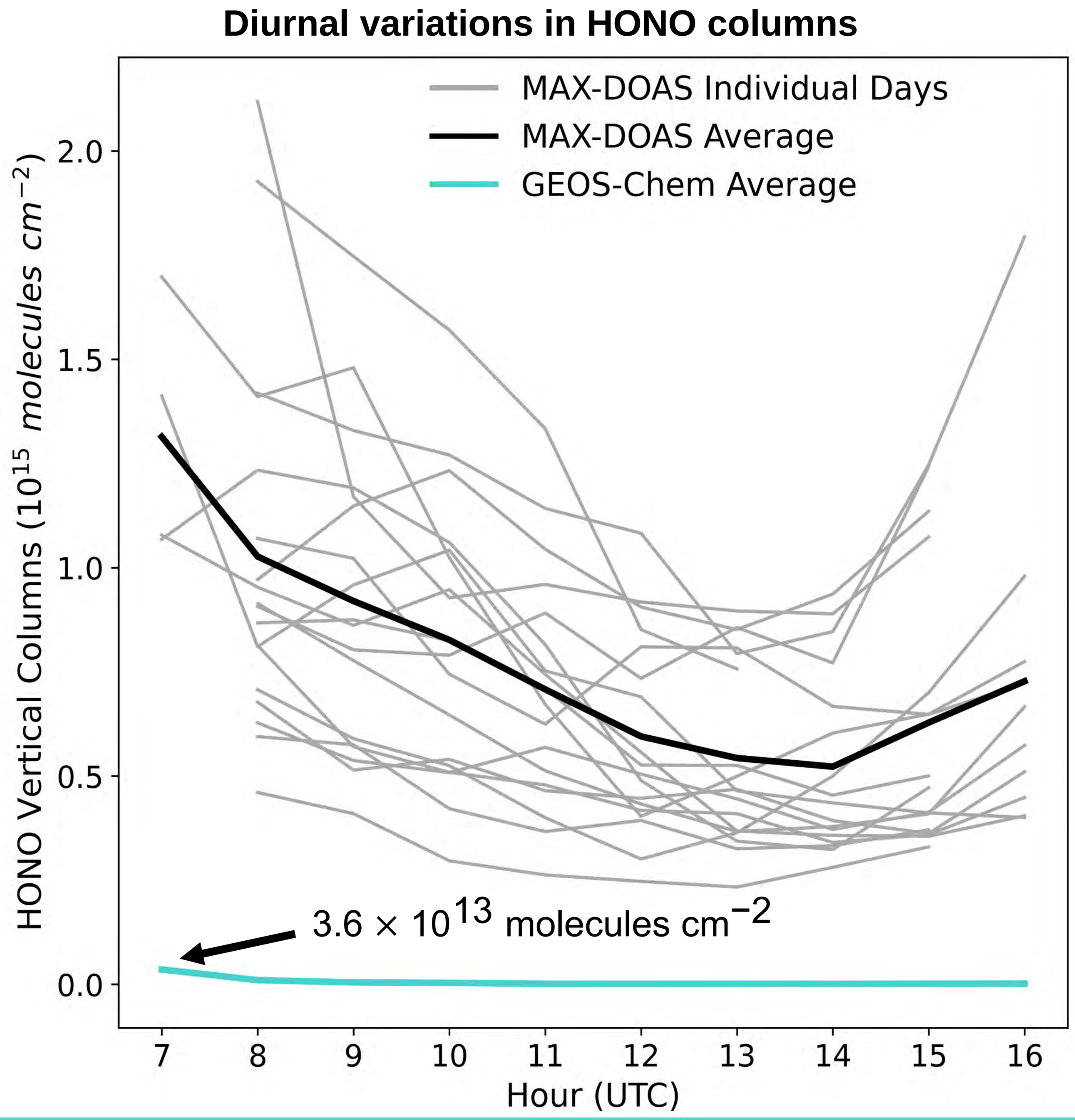


4. MAX-DOAS observations of HONO diurnal variability

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.

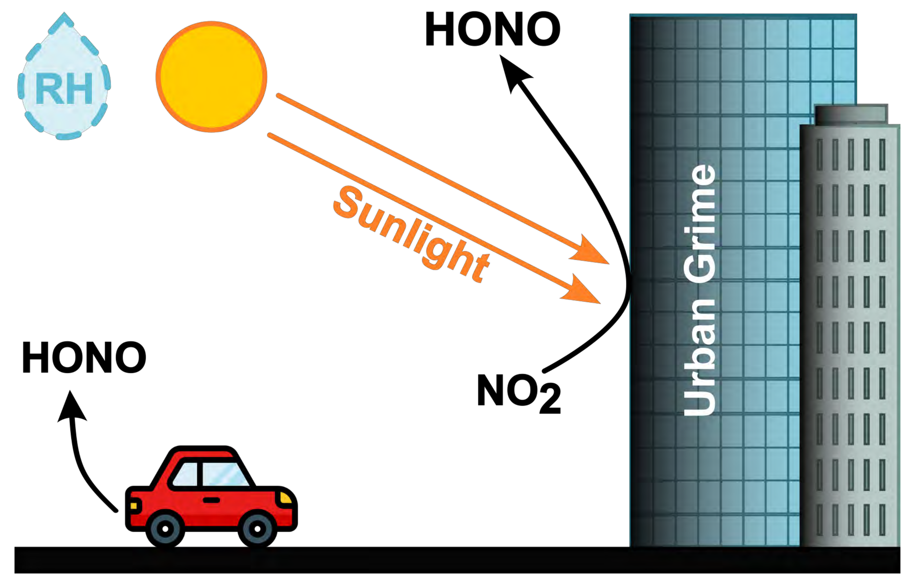
Diurnal variations in HONO columns



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

5. Parameterizing HONO sources in GEOS-Chem

The direct emission of HONO from vehicles and the heterogeneous conversion of NO_2 to HONO on urban grime are not represented in GEOS-Chem.



We parametrize the uptake of NO_2 on urban grime (γ) as functions of relative humidity ($[RH]$), NO_2 concentration ($[NO_2]$) and light intensity according to Yu et al.[2].

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

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

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

The largest γ at a given time is used to represent the uptake of NO_2 on urban grime in the model.

The rate of NO_2 loss to urban grime is assumed to be pseudo first order.

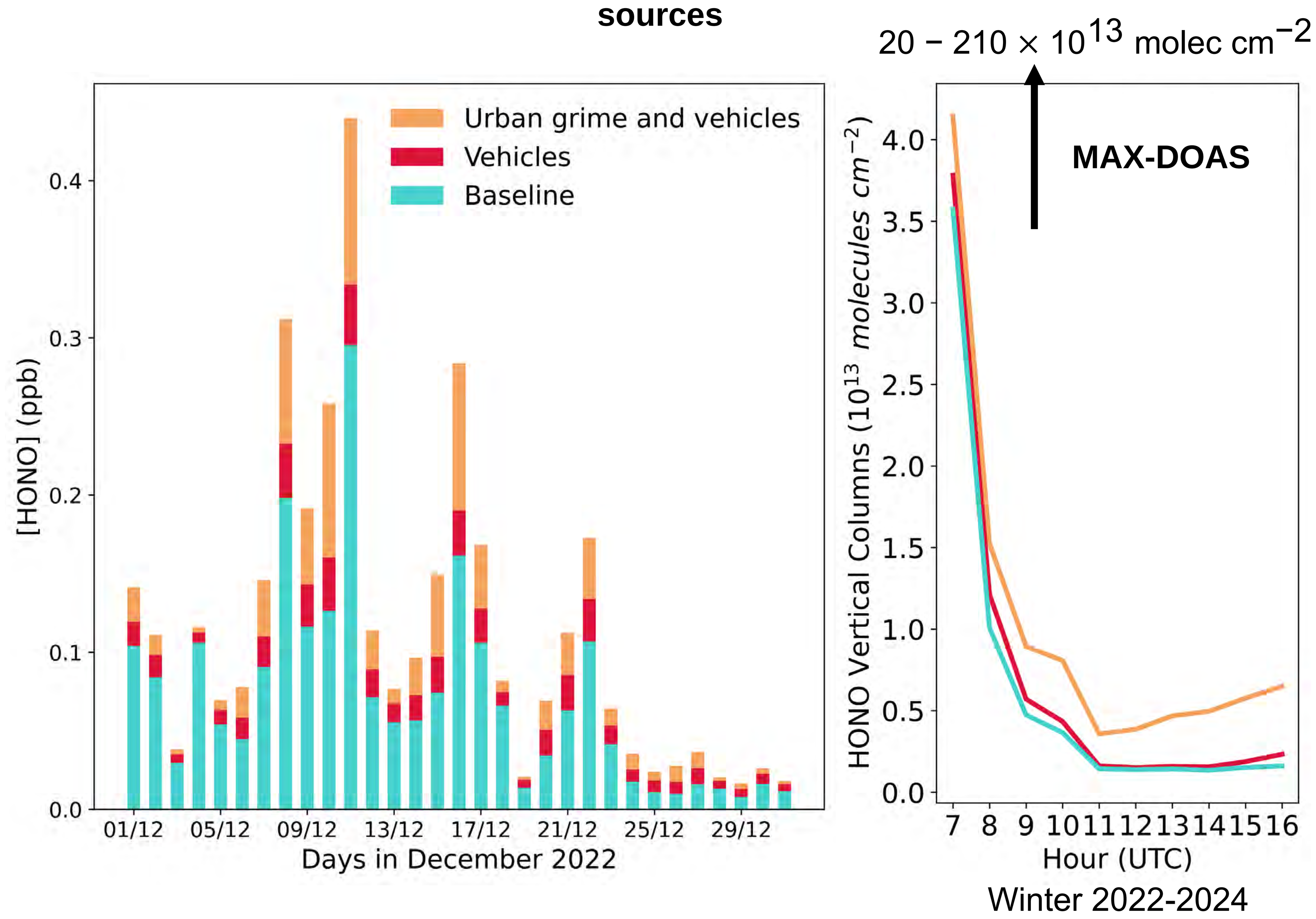
We add vehicle emissions as 0.85 % of the total NO_x emissions[1].

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

6. HONO concentrations with new sources

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

Lowest model layer concentrations and HONO vertical columns with updated sources



HONO columns decrease from sunrise, then increase at 12 pm (UTC).

GEOS-Chem still underestimates HONO concentrations relative to observations.

Ongoing work

- Improve the parameterisation of HONO emissions from urban grime in GEOS-Chem.
- Include emissions from dew in the model.
- Investigate the impact of increased HONO concentrations on OH concentrations, atmospheric reactivity and O_3 concentrations in the model.

References

[1] Kramer et al. (2020), doi: 10.5194/acp-20-5231-2020 **[2] Yu et al.** (2022), doi: 10.1021/acsearthspacechem.2c00054