

POINT-BY-POINT RESPONSES

Ms. Ref. No.: EGUSPHERE-2023-24, doi:10.5194/egusphere-2023-24.

Title: Measurement Report: MAX-DOAS measurements characterise Central London ozone pollution episodes during 2022 heatwaves

Journal: Atmos. Chem. Phys. Measurement Report

Responses to RC#2:

Ryan et al. presented a valuable report about the ozone pollution episodes during 2022 heatwaves in Central London via the MAX-DOAS measurements. NO₂ and HCHO VCDs of TROPOMI were firstly validated by ground-based MAX-DOAS. In addition, lowest layer retrieved NO₂ and HCHO from MAX-DOAS were compared with in-situ NO₂ and isoprene, respectively. Regarding the daytime ozone production, VOCs-limited regime is identified for non-heatwave days according to the MAX-DOAS HCHO-to-NO₂ tropospheric vertical column ratios. Temperature favors the biogenic isoprene emissions and further the increase of ozone concentrations exceeding the regulatory standard. Influenced heavily by traffic emission, the compliance status may be changed under the conditions that stricter controls on NO_x vehicle emissions and frequenter and severer heatwave. Overall, the paper is well organized and written, however, there still some comments need to be addressed before it can be considered to be accepted for ACP journal.

Main Concerns:

Since the vertical profiles of NO₂ and HCHO can be obtained by the RAPSODI algorithm, why only the column density and lowest layer results were used to discuss in the paper? I would like to suggest the authors present the characteristics of the vertical pattern of NO₂ and HCHO during heatwave days and non-heatwave days at least.

Thank you for the suggestion. We chose to focus on the surface and the tropospheric column, as the goal of the study is to interpret surface ozone air pollution and assess tropospheric column density retrievals from the widely used TROPOMI instrument. Vertical profile information from MAX-DOAS is limited to ~3 pieces of information for NO₂ and ~2 for HCHO during the TROPOMI overpass, as stated in the manuscript when reporting on typical DOFS (line 317).

Moreover, considering the air mass transport described in Line 48-49, the HCHO-to-NO₂ ratio may also be analyzed in different heights.

This is surface air advected from continental Europe. We now state “surface” to ensure this is clear (line 56).

Minors:

1. Line 45-47, It's better to also provide background information about the VOCs emission in Central London, when discuss the ozone production there.

We now include a brief discussion of the mix of summertime VOCs sources in London measured during a field campaign in London and postulate that volatile chemical products (VCPs) likely also contribute to enhancements in emissions in the morning (lines 51-54).

2. Line 115-120, in addition to the DLs of individual DSCDs, the authors should provide a more detailed table for the spectral analysis configurations. Besides, the performance of the spectral analysis should be evaluated, such as the range of RMS? DSCDs errors? An example plot of spectral fitting? And any filtering of the DSCDs before be introduced into the profile retrieval?

We now include Table 1 (screenshot pasted below) to summarize additional fit parameters not given in the text (Section 2.2, lines 130-134). The lineshapes for HCHO, NO₂ and O₄ are well documented in the MAX-DOAS literature in the spectral fitting example plots, so instead of reproducing these, we evaluate the spectral analysis by presenting the mean dSCD errors (<5 % for all trace gases, line 292) and the mean residual RMS of 4×10^{-4} for all fitting windows (line 299); corrected from 4×10^{-5} in the original manuscript. No other filtering is applied to the dSCDs.

Table 1. Cross section fittings for retrieving NO₂, HCHO, and O₄ dSCDs.

Absorber	Temperature [K] ^a	I_0 correction [molecules cm ⁻²] ^b	Reference
NO ₂	220, 294	1×10^{15}	Vandaele et al. (1998)
HCHO	298	5×10^{15}	Chance and Orphal (2011)
O ₄	293	3×10^{43}	Finkenzeller and Volkamer (2022)
O ₃	223, 246, 293	1×10^{18}	Serdyuchenko et al. (2014)
BrO ^c	223	1×10^{13}	Fleischmann et al. (2004)

^a Temperatures used for cross section fit. More than one temperature given for trace gases with substantial contribution from the warm troposphere, cold upper troposphere and stratosphere, ^b Solar reference intensity (I_0) correction, ^c Bromine monoxide.

3. Fig. 4, why datasets of elevation 20° not be presented?

Data for the 2° elevation angle were also not shown. This was merely to avoid showing a cluttered figure. We now show in Figure 4 all elevation angles. On updating the plot, we also identified a plotting issue with the NO₂ dSCDs that has been addressed. Updated plot and caption pasted below.

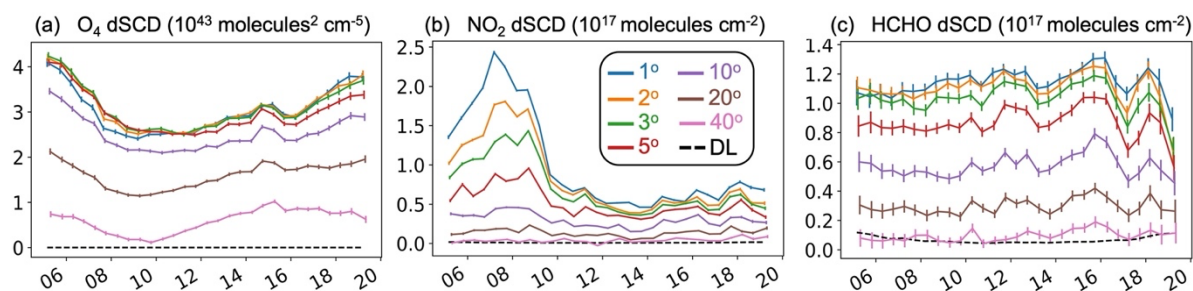


Figure 4. Time series of O₄, NO₂ and HCHO differential slant column densities (dSCDs) on 18 July 2022. DOASIS retrieved dSCDs of O₄ (a), NO₂ (b) and HCHO (c) at 1° (blue), 2° (orange), 3° (green), 5° (red), 10° (mauve), 20° (brown) and 40° (pink) elevation angles at the 132° azimuth angle (Figure 1). Error bars are dSCD uncertainties. Black dashed lines are detection limits (*DL*) at 1° elevation (see text for details).

4. Fig. 6, MAX-DOAS HCHO:NO₂ is VCD to VCD or lowest layer to lower layer? Same comments on Fig. 8.

It already states in the legend for panel (c) that this is the ratio of the columns. For clarity, we now add “vertical column density ratios” in “MAX-DOAS HCHO:NO₂ vertical column density ratios (c)” to the Figure 6 caption. Figure 8 also already states that the panels in Figure 8 are the same as those in Figure 6.

5. Fig. 8 and related discussion, the dependency of isoprene-to-HCHO ratio to NO₂ need to be investigated, also isoprene-to-NO₂ ratio.

We assume the reviewer is referring to the dependence of HCHO yields from isoprene oxidation on NO_x concentrations. In London, the NO_x concentrations far exceed the threshold between low- and high-NO_x oxidation conditions (~1 ppbv; Marais et al., ACP, doi:10.5194/acp-12-6219-2012, 2012), due to sustained large emissions of NO_x from vehicles. As such, we do not expect dependence of HCHO yields from isoprene oxidation on NO_x in London in 2022. We now clarify this is the case in the text (lines 508-509).