Supplementary Information

Evaluation of local measurement-driven adjustments of modelled cloud-free atmospheric photolysis rate coefficients

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Figure S1: Diurnal cycles of the photodissociation rate constants (*j*-values) for the 12 photolysis reactions investigated in this study, as determined for the sunniest day of measurements (9 March 2021). As described in the main text, *j*-values were calculated from 1 min scans of actinic flux made by a spectral radiometer, using absorption cross-section and quantum yield values in Table 1.



Figure S2: Time series of daily mean temperature, aerosol optical depth (AOD) and ozone column used in the TUV v5.3 model input. Temperature data is measured on site by a Viasala HMP155. AOD is measured by a Cimel sun photometer and downloaded from the AERONET network (<u>https://aeronet.gsfc.nasa.gov/new_web/aerosols.html</u>). Ozone column measurements derive from the NOAA Ozone Monitoring Instrument on the NASA Aura satellite, and were downloaded from: <u>https://www.esrl.noaa.gov/gmd/grad/neubrew/SatO3DataTimeSeries.jsp</u>.



Figure S3: Hourly MDAF values for each photolysis reaction as a function of slant ozone column (calculated as = $(O_3 \ column \ in \ DU) / c \ os(SZA)$). Plots are presented in columns corresponding to the three groups of photolysis reactions obtained from the hierarchical clustering of MDAF time series described in the main paper.



Calculation of *p*(OH) at Chilbolton Observatory:

The rate of OH radical production from the photolysis of ozone (O₃),

$$\begin{array}{ll} 0_3 + hv \ (\lambda \leq 330 \ \mathrm{nm}) \rightarrow \mathrm{O}(^1\mathrm{D}) + \mathrm{O}_2 & \mathrm{SI \ R1} \\ \mathrm{O}(^1\mathrm{D}) + \mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{OH} & \mathrm{SI \ R2} \end{array}$$

is calculated using Equations S1 and S2.

$$p(OH)_{O_3} = 2 \times f \times j(O^1D) \times [O_3]$$
(Eq. S1)

$$f = \frac{k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]}{k_{\text{N}_2}[N_2] + k_{\text{O}_2}[\text{O}_2] + k_{\text{H}_2\text{O}}[\text{H}_2\text{O}]}$$
(Eq. S2)

In these equations, $j(O^1D)$ is the photolysis rate constant for O₃, and *f* is the fraction of O(¹D) atoms that react with water vapour to form OH, as opposed to their quenched removal by N₂ and O₂ molecules. Rate constants for the individual reactions of O(¹D) with H₂O, N₂ and O₂ $(k_{H_2O}, k_{N_2} \text{ and } k_{O_2}, \text{ respectively})$ were taken from Atkinson et al. (2004). Temperature dependence was included for the rate constants of the quenching reactions but not for k_{H_2O} , as the latter is stated to be independent of temperature measurements (Vaisala HMP155A humidity and temperature probe) were used to derive absolute H₂O concentrations, and hourly concentrations of ground-level O₃ measured at Chilbolton Observatory were downloaded directly from UK-AIR (https://uk-air.defra.gov.uk/data).

For the study period at Chilbolton Observatory, the mean \pm sd fraction f was $4.7 \pm 1.0\%$.

References

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of O_x, HO_x, NO_x and SO_x species, Atmos. Chem. Phys., 4, 1461-1738, 10.5194/acp-4-1461-2004, 2004.