S1 Stray light as convolution in wavelength space

To characterise the stray light in an instrument, we can define a spectral line-spread function (LSF) $f(\lambda', \lambda)$ representing the effect of the signal at input wavelength λ' on the irradiance measured at wavelength λ. When λ' and λ are sampled at discrete steps, f turns into a matrix, often called the spectral stray signal distribution matrix (Zong et al., 2006).

To determine $f(\lambda', \lambda)$, a tunable monochromatic source is needed, e.g. a tunable laser. Since this kind of equipment is not common to most laboratories, several studies approximate $f(\lambda', \lambda)$ as $f'(\lambda' - \lambda)$ and then use the resulting function, obtained from only one or a few laser scans, in a convolution with the true solar spectrum to provide the stray light spectrum. Such a method assumes that the stray light response to an input wavelength only depends on the spectral distance between that wavelength and the measurement wavelength, regardless of the exact region of the spectrum taken into consideration.

This procedure is not entirely correct, for example the LSF can slightly change with wavelength, as shown by Pulli et al. (2018). Additionally, some features of the Brewer stray light spectrum are not well represented in the wavelength space. To provide an example, we can consider the spectra shown in Fig. S1. While Fig. 1 in the main text depicts the count rates collected through slit 1 only, which is normally used for UV scans, Fig. S1 shows the results of a 325 nm laser scan through multiple slits (1–5). The data refer to the MkIV Brewer #066. When these curves are plotted as a function of the wavelength distance to the laser emission wavelength (Fig. S1a), they almost completely overlap in the shoulder region (i.e., within about 10 nm from the peak) for all slits. However, an increase in the stray light can be noticed far away (20–30 nm) from the peak, in the wing region, with best overlap among the slits if the count rates are plotted as a function of the grating position (micrometer step, Fig. S1b). This fact suggests that some specular reflections could originate in the monochromator depending on the grating position (maximum effect at about 1500 steps for the specific Brewer). This also indicates that stray light might not be fully represented as a simple convolution in the wavelength space.

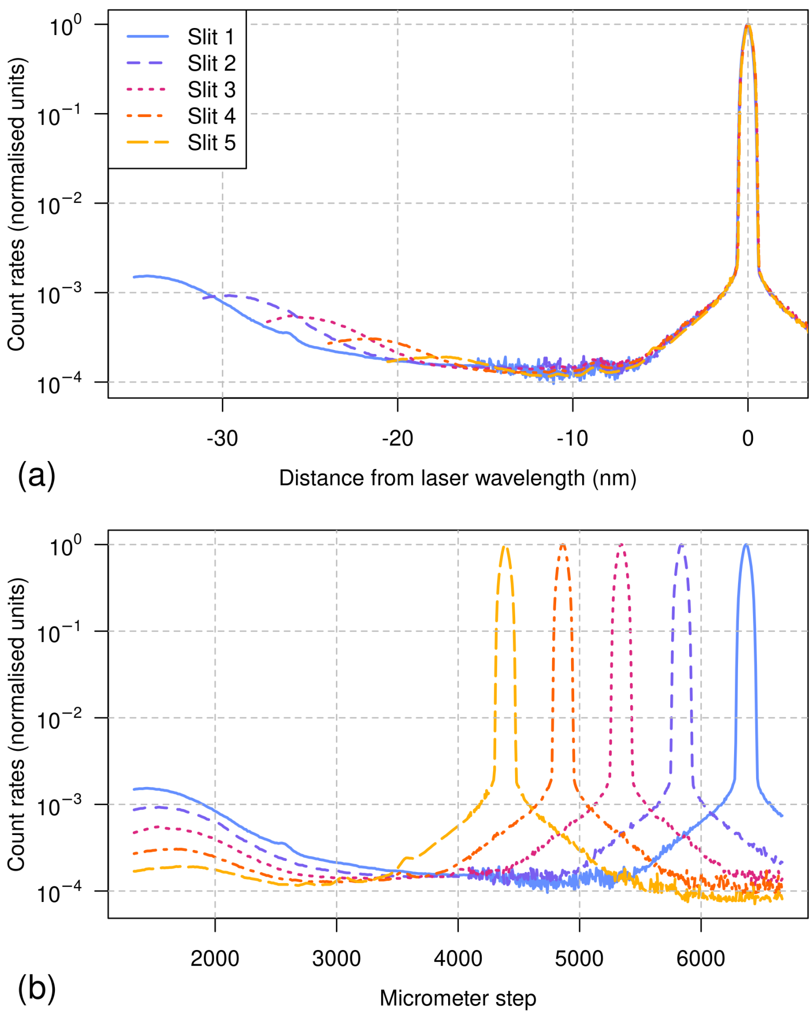
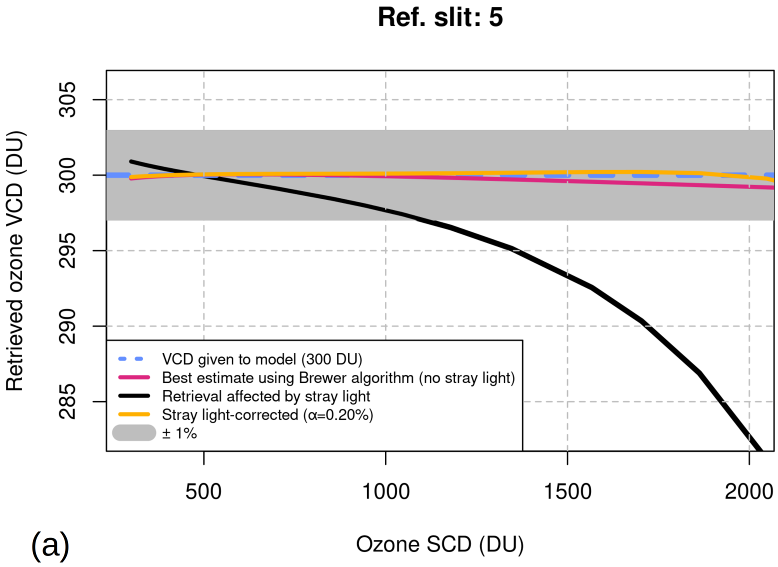


Figure S1: Laser scans for MkIV Brewer #066. The count rates for each slit, normalised to their respective peak values, are plotted against the wavelength distance from the laser excitation wavelength **(a)** and against the micrometer position, in term of steps **(b)**.

S2 Supporting information on radiative transfer calculations



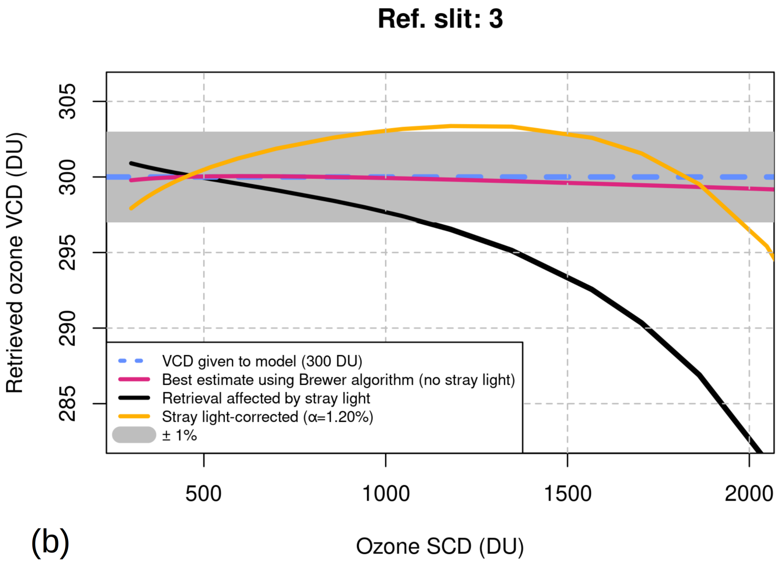


Figure S2: Comparison between the performances of two different stray light correction algorithms. **(a)** Method presented in the text, α being a percentage of count rates at slit 5 (320 nm). This subfigure corresponds to Fig. 3 in the main text. **(b)** Numerical experiment to prove that the method does not work if a percentage of slit 3 (313 nm) instead of slit 5 is employed to estimate the stray light contribution. In this case, α was increased to 1.20 % to allow matching, on average, between the corrected and the true ozone VCDs.

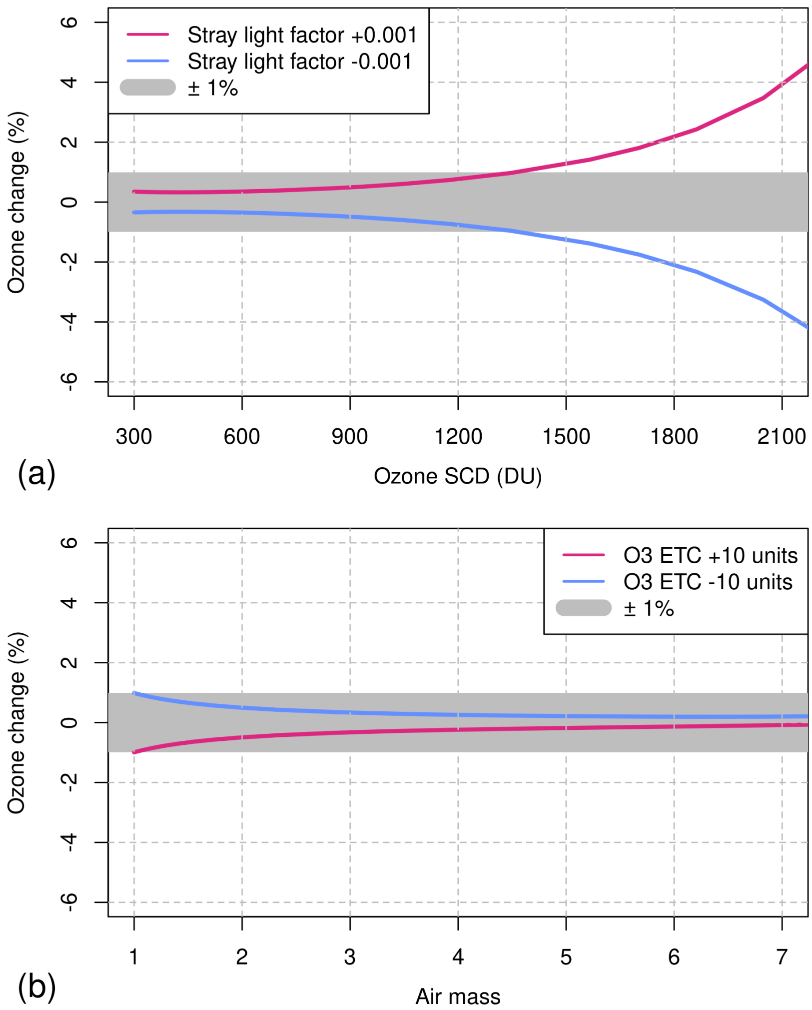


Figure S3: Sensitivity analysis on ozone retrievals for changes in **(a)** the stray light correction (the original α value of 0.2 % was changed to $\alpha_+ = 0.3$ % and $\alpha_- = 0.1$ %) and **(b)** the ozone ETC (10 units were added or subtracted to the original value). The ozone VCD set for these calculations is 300 DU.

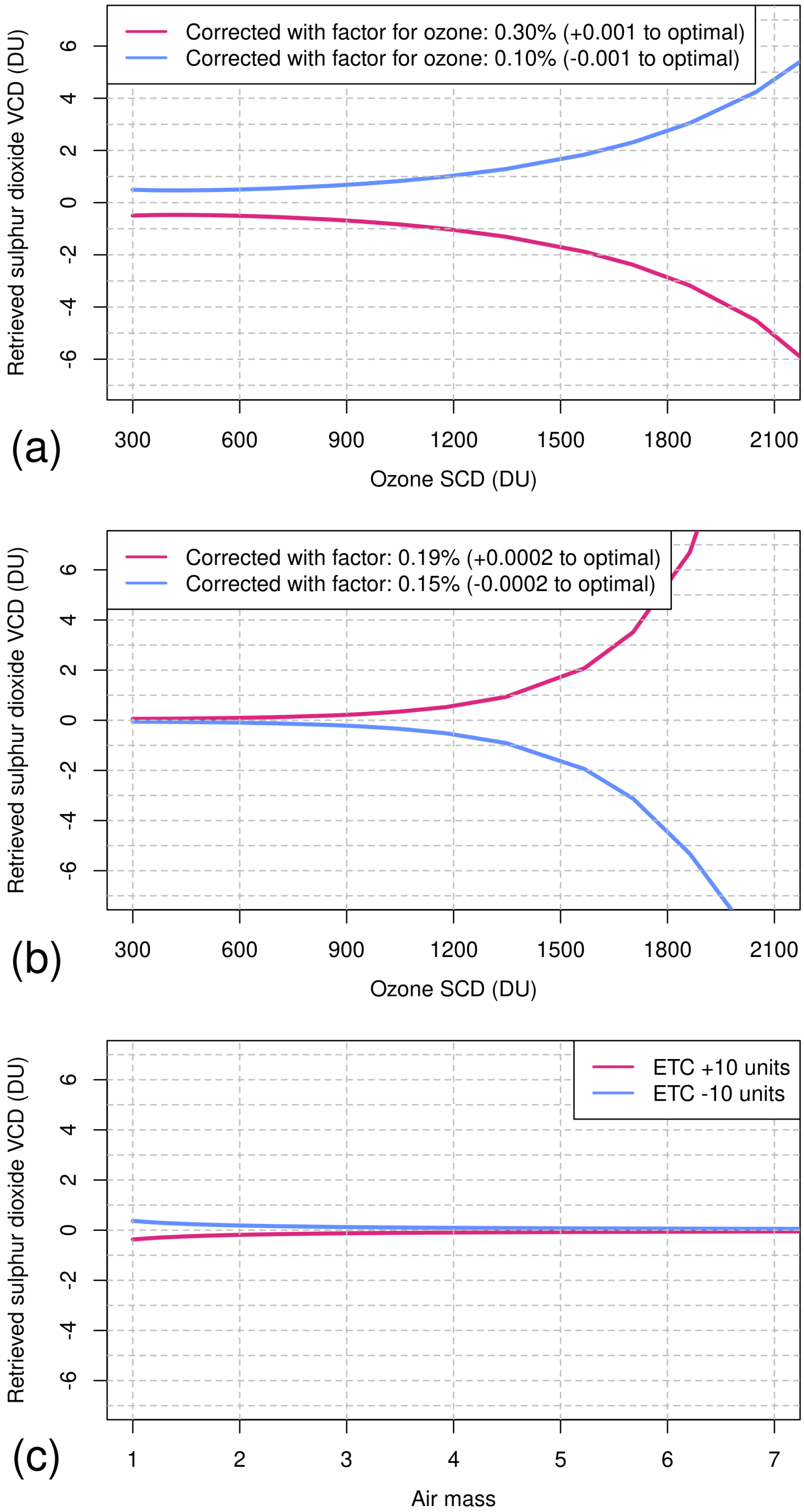


Figure S4: Sensitivity analysis on sulphur dioxide retrievals for changes in **(a)** the ozone stray light correction coefficient (the original α value of 0.2 % was changed to $\alpha_+ = 0.3$ % and $\alpha_- = 0.1$ %), **(b)** the sulphur dioxide stray light correction coefficient (the original β value of 0.17 % was changed to $\beta_+ = 0.19$ % and $\beta_- = 0.15$ %) and **(c)** the sulphur dioxide ETC (10 units were added or subtracted to the original value). The sulphur dioxide VCD set for these calculations is 0 DU. Notice that absolute changes are represented on the y scale.

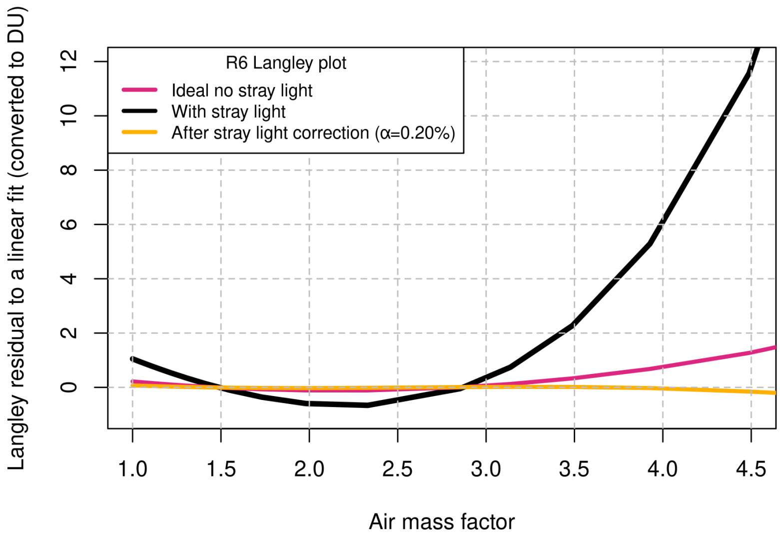


Figure S5: Residuals to a linear fit of the R_6 linear combination (Appendices A2–A3 of the main text) as a function of air mass. The calculations are based on the experimental characterisation of Brewer #009. The residuals were converted to DU for ease of understanding.

S3 Additional experimental data

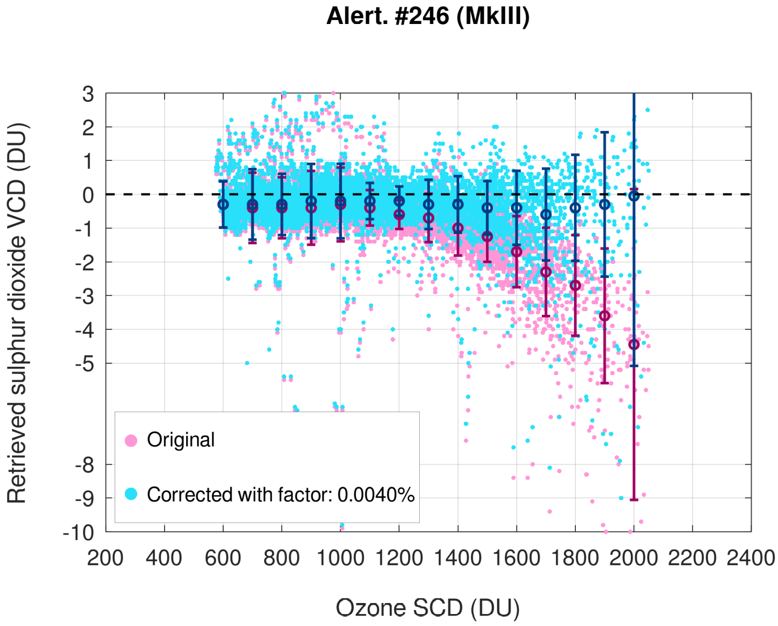


Figure S6: Sulphur dioxide retrievals at Alert from MkIII Brewer #246, before and after PHYCS implementation.

References

Pulli, T., Karppinen, T., Nevas, S., Kärhä, P., Lakkala, K., Karhu, J. M., Sildoja, M., Vaskuri, A., Shpak, M., Manoocheri, F., Doppler, L., Gross, S., Mes, J., and Ikonen, E.: Out-of-Range Stray Light Characterization of Single-Monochromator Brewer Spectrophotometers, Atmosphere-Ocean, 56, 1–11, https://doi.org/10.1080/07055900.2017.1419335, 2018.

Zong, Y., Brown, S. W., Johnson, B. C., Lykke, K. R., and Ohno, Y.: Simple spectral stray light correction method for array spectroradiometers, Appl. Opt., 45, 1111–1119, https://doi.org/10.1364/AO.45.001111, 2006.