amt-2020-219: Use of filter radiometer measurements to derive local photolysis rates and for future monitoring network application (Walker *et al.*)

Responses to Reviewer 2

The authors thank Reviewer 1 for their time spent conducting a careful review of our paper, and providing constructive comments. We hope that our comments and corresponding revisions to the original manuscript are satisfactory.

The major revisions to the manuscript after comments from both Reviewer 1 and 2 include the following.

- Re-running of the TUV model to include measurements of daily average ozone column and ambient temperature (see our response to comments on Section 2.3).
- Estimates of $p(Cl)_{ClNO_2}$ rates have been excluded and Section 3.5 (*"Production rate of Cl atom radials"*, submitted manuscript) has been removed (see response to Section 2.4.3 and 3.4/3.5).
- A new section has been introduced (*"Section 3.3: MDAF derivations"*, revised manuscript) to detail methods of determining the uncertainty arising from applying a *j*(NO₂)-derived MDAF, as we present here, to other species *j*-values (see response to Section 2.4.1).

Our responses to individual points raised by the review are listed below. The suggestions and comments made by the reviewer are listed in **black font**, and our responses highlighted in blue, with any relevant manuscript changes indicated in *blue italic*. We have also amended the subsectional structuring, and some other text (e.g. abstract) of our manuscript as a consequence the revisions we describe above and below.

General comments

The work ratios long-term filter radiometer jNO2 measurements to a cloud-free radiative transfer model (TUV) to calculate a measurement-driven adjustment factor (MDAF). Modeled jO3, jHONO, jCINO2 and jHNO3 are then multiplied (presumably) by the MDAF correction factor to determine the environmentally impacted local values. Combining these rates with local measurements, the authors calculate radical products and find a significant reduction in OH compared with the cloud-free modeled products. The authors suggest that such local radiation measurements would significantly improve chemical model calculations of important species. The local impact of clouds, aerosols and changing albedo on photolysis rates and the resulting impacts on radical chemistry require additional validation in models. The long-term dataset discussed provides the opportunity to examine a range of conditions to test model sensitivity to changes in local conditions and the incentive to set up additional jNO2 measurement locations. The paper is relevant but lacks rigor in some areas. With revisions and additional discussion the paper would be worthy of publication.

We are pleased that the reviewer has identified the relevance of this method. The authors would like to thank the reviewer for the overall positive review, and their constructive comments. We have taken forward most of the reviewer's suggestions, and think that the adjustments we have made have significantly improved the manuscript and addressed the scientific issues raised.

Specific comments

Line 13: 40% lower OH production rate compared to what? Presumably compared to the cloud-free model. Best for clarity to be explicit. Some discussion of cloud-free vs cloud resolving models would be useful.

The reviewers' interpretation of this statement is correct, and we agree with their statement. We have revised the text in the manuscript accordingly.

Abstract: "The MDAF resulted in these rates being ~40% lower than the cloud-free model output over the entire year."

Line 35: I suggest an alternative PAN reference:

Singh, H. B., Herlth, D., O'Hara, D., Zahnle, K., Bradshaw, J. D., Sandholm, S. T., Talbot, R., Crutzen, P. J., and Kanakidou, M.: Relationship of Peroxyacetyl nitrate to active and total odd nitrogen at northern high latitudes: Influence of reservoir species on NOx and O3, J. Geophys. Res, 97, 16523–16530, 1992.

The reference for PAN contributing to regional pollution has been updated to include the suggested citation, and a modelling study which also determined the importance of PAN in redistributing NO_x .

Section 1: "...and atmospheric reservoirs of NO₂ such as peroxyacetyl nitrate (PAN), which contribute to long-range and regional pollution (Singh et al., 1992; Moxim et al., 1996)."

Line 70: Many molecules include a pressure dependence. I suggest adding pressure (p) to equations.

We agree that pressure is another variable influencing molecule-specific parameters used to determine the *j*-values, and Eq. (2) in the revised manuscript has been updated to reflect this. We did not originally include pressure in Eq. (2) as the IUPAC and JPL-recommended absorption cross-section and quantum yield values used in our calculations did not include quantified pressure dependencies. For example, Sander *et al.* (2006) state that the effects of variation in NO₂ absorption cross-sections with total pressure is only observed when measured at spectral resolutions higher than 0.01 nm, which is greater than that used in our calculations (1 nm). Similarly, Burkholder *et al.* (2019) present evidence that no pressure dependence has been experimentally observed for the O₃ absorption cross-section.

Section 1: Eq. (2): $j = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda, T, p) \phi(\lambda, T, p) F(\lambda) d\lambda$

Line 72: The definition attributed to Madronich is confusing. Actinic flux is more simply the spherically integrated radiation through a sphere or the radiant energy density incident on a unit spherical surface.

We thank the reviewer for highlighting this issue with the wording of our definition of actinic flux. We have simplified the text in the manuscript to convey the message more clearly.

Section 1: "The actinic flux (F) is the spherically integrated radiation available to a molecule in the atmosphere, which upon absorption results in photodissociation (Madronich, 1987)."

Line 78: Here and throughout the paper, the authors refer to applying or using the MDAF. However, I don't see the "application" is ever explicitly defined. I am left to presume (perhaps obviously) that MDAF is a simple multiplication factor. That should be stated here.

There is no mention of MDAF at or around line 78; instead we believe that this comment was intended for line 178, where we agree with the reviewer, and thank them for noticing this omission. The process of applying MDAF, as correctly presumed by the reviewer, has been included in more detail in Section 2.4.

Section 2.4: "Adjustment factors like MDAF can be derived from other spatio-temporally coincident measured and modelled j-values, such as j(O¹D). The product of MDAF and the initially modelled (cloud-free) j-values are referred to as "adjusted j-values". These factors have only occasionally been applied both spatially and temporally (Stone et al., 2012; Bannan et al., 2015)..."

Line 86: This seems like an odd line noting that jNO2 instruments have "limited potential to estimate the photolysis frequencies of other atmospheric species." Isn't that the point of this paper? I think you are saying that they cannot *directly* measure the other species without MDAF or a similar correction.

The interpretation presented by the reviewer is the point which we intended to make. To provide more clarity, we have rephrased this sentence to include the word "directly".

Section 1: "However, they remain reliant on absolute calibrations to directly quantify j-values from recorded voltages. Each instrument is only applicable for its specified photolysis reaction, and cannot be used to directly estimate the photolysis frequencies of other atmospheric species. Filter radiometers most commonly measure j(NO₂) and j(O¹D)."

Line 103: This is an incorrect oversimplification. The Palancar data was screened for clouds and included PBL heights in addition to AOD and NO2 concentrations.

We thank the reviewer for spotting this. We have added further clarification to the citation of Palancar *et al.* (2013) to better reflect the study and avoid possible misinterpretation.

Section 1: "Palancar et al. (2013) demonstrate that when parameters measured within the planetary boundary layer (PBL) are included in model input (including AOD, O₃ column, single scattering albedo and NO₂ concentrations), actinic flux is reasonably well predicted on cloudless days, and the main source of uncertainty is then attributable to σ and ϕ ."

Line 127: The difficulties of a 4 pi spectrometer should be discussed. In particular, the upwelling can be significantly influenced by the support tower, any nearby equipment and the local albedo (e.g. a bush or rock below the tower). This can add significant uncertainty, particularly when the upwelling is large (e.g. snow). Also, the errors in the two 2-pi optics are particularly large near the horizion. This is noted throughout the literature (e.g. Hofzumahaus, et al, (2002) doi:10.1029/2001JD900142 and references therein). See the comment at lines 258-61.

We thank the reviewer for this constructive comment. As the Auchencorth Moss site comprises lots of instrumentation, these potential sources of uncertainty and bias in the filter radiometer measurements were carefully considered during set-up. We agree that many of the issues associated with the filter radiometer placement can introduce error to the measurements, but due to logistical issues (e.g. the necessity of a mast and a finite cable length) are sadly unavoidable. To compensate we have included these features in the description of the filter radiometer in Section 2.2. We appreciate the reviewer drawing our attention to the Hofzumahaus *et al.* (2002) study, and we now include a small discussion of these principles in this section. Errors associated directly with the inlet optics of our filter radiometer are discussed with the response to the reviewer's comments at lines 258-61.

Section 2.2: "The 4- π filter radiometer (Metcon, Meteorologie Consult GmbH, Germany) was mounted ~3 m above the ground, recording measurements at 1 s time resolution for a full year (21 November 2018 – 20 November 2019). The position of the instrument was carefully considered to minimise potential sources of interference from the site. Situated at the outskirts of the site, the filter radiometer was directed away from all other objects. Its supporting mast had a matte black coating to reduce any reflection that wouldn't otherwise occur. The ground cover beneath the instrument was largely long grasses, where features that could increase surface albedo (e.g. snow) were quite evenly distributed. The closest change in these features (approx. 5 m behind the supporting mast) is a wooden slatted path covered in black non-slip mats. This could contribute some uncertainty to upwelling measurements, particularly during conditions with a large surface albedo, but is deemed minimal due to its distance and how it is often obscured by vegetation growth. The inlet optic of each dome is designed to have a near-uniform angular response through use of a guartz diffusor (Bohn et al., 2004). Each optical inlet is surrounded by a light shield to provide an "artificial horizon", restricting the field-of-view for each dome to one hemisphere (Volz-Thomas et al., 1996). This restriction is not perfect as increased sensitivity can be observed near the horizon in $4-\pi$ systems due to contribution from the opposite dome. Hofzumahaus et al. (2002) show that this bias is partially compensated by the reduced sensitivity in individual 2- π inlets, resulting in a maximum overestimation of their actinic flux of 4% (between 0-12 km altitude)."

Lines 146-9: I recommend being explicit about the averaging for clarity. The filter radiometer is broadband and continuously measures the full jNO2 spectrum. The scanning spectrometer measures one narrow wavelength band linearly in time over the 3 minute duty cycle. Thus, the measurements are not equivalent in rapidly changing conditions.

We agree with these comments made by the reviewer. During a 3 minute scan where conditions are changeable, the bandpass measurements made by the filter radiometer would not be equivalent to the sum of the wavelengths scanned by the spectroradiometer. This is why we used the standard deviation of measured 1 s filter radiometer measurements as an

estimate of how changeable the conditions were during each scan. Any time this standard deviation in filter radiometer measurements during the relevant 3 minute interval was exceeded, that comparison point was removed from the calibration dataset. We have revised the text in the manuscript to detail this process.

Section 2.2: "During the calibration, broadband measurements made by the filter radiometer (1 s) during each spectroradiometer scan (actinic flux measured in each narrow λ band sequentially; 3 mins) were averaged to obtain a comparison point. Large standard deviations associated with these mean values were used to remove calibration points where actinic flux was highly variable during the scan (e.g. rapidly changing cloud cover), which would result in inconsistent conditions between λ bands and render an unrepresentative comparison to the filter radiometer. This range was primarily within ±5% of the mean calculated."

Line 158: Be consistent TUV 5.3 or 5.3.1 (as noted in the abstract).

We thank the reviewer for identifying this inconsistency. The TUV model is now referred to as v5.3.1 throughout the manuscript.

Line 161: The model is not technically "clear-sky" because aerosols are included. I suggest using "cloud-free" throughout.

We have changed all references of the "clear-sky model" to "cloud-free" as suggested.

Lines 163-4: List the default values for albedo and aerosols (presumably 0.10 and the Elterman (1967) continental aerosol profile).

L. Elterman UV, Visible and IR Attenuation to 50 Km, AFCRL-68-0153, Environ. Res. Papers, (No. 278) (1968), Bedford, Mass.

The values mentioned by the reviewer are correct, and are now directly cited in the revised manuscript. Following comments from both Reviewers 1 and 2, the TUV model has been rerun to include daily average ozone column and ambient temperature in the model input, in order to more accurately estimate modelled $j(O^{1}D)$. These alterations have also now been mentioned in Section 2.3 and in response to the reviewers' comments on line 295.

Section 2.3: "The model was set up for the location and height of the filter radiometer at Auchencorth Moss, and assumed to have cloud-free conditions. Daily average ozone column measurements were accessed via the OMI satellite (NOAA, 2020b), and calculated for air temperature from measurements made on site (Table 1). Days where O₃ column measurements were missing used the measurement from the following day. Default TUV values for surface albedo (0.10) and AOD at 500 nm (Elterman, 1968) were used."

Lines 168-9: I believe default TUV uses a different cross section (Vandaele et al., 1998). According to JPL 2015, Vandaele and Mérienne are within 2-3% across their measurement spectral range.

We appreciate the reviewer highlighting this error in the manuscript. We were mistaken in this particular aspect of the TUV model based on our interpretation of the source code. The revised manuscript now includes this reference, and a comparison to the absorption cross-sections used in our calculations.

Section 2.3: "It should be noted that for j(NO₂) calculations, the NO₂ quantum yield used by the TUV model is the same as that used in the calibration of the filter radiometer (Troe, 2000), while the absorption cross-section uses measurements made by Vandaele et al. (1998), which differ from the values used in calibration (Mérienne et al., 1995) by 2-3% at room temperature (Burkholder et al., 2019)."

Line 190: Describe kH2O, kN2 and kO2.

These parameters have now been identified in the description of Eq. (6) in the revised manuscript.

Section 2.5: "In these equations, $j(O^1D)$ is the photolysis rate constant for O_3 , and f is the fraction of $O({}^1D)$ atoms that react with water vapour to form OH, as opposed to their quenched removal by N_2 and O_2 molecules. Rate constants for these individual reactions between $O({}^1D)$ and H_2O , N_2 and O_2 (k_{H_2O} , k_{N_2} and k_{O_2} , respectively) were taken from Atkinson et al. (2004). Temperature dependence was included for quenching reactions but not k_{H_2O} , as it is stated to be independent of temperature between 200-350 K."

Line 207: Eq 2 is specific to jNO2. One option would be to make Eq 2 generic and adjust the ("in this case") text in line 75.

Equation 2 was made specific to $j(NO_2)$ for relevance to the context in which it is first presented in the introduction. However the reviewer correctly points out this is less applicable where it is referenced later in the manuscript. The equation (and subsequent explanation) has been updated to ensure it remains generic and relevant for all instances to which it is referred.

Section 1: Eq. (2): $j = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda, T, p) \phi(\lambda, T, p) F(\lambda) d\lambda$

This section of text (describing the updated *j*(CINO₂) calculations) has been moved to Section 2.3, as Section 2.4.3 has been removed from the manuscript (described further in response to comments on line 215).

Section 2.3: "Since the dataset presented by Ghosh et al. includes the temperature dependence of $\sigma(CINO_2)$, values in this study were parameterised according to the daily mean temperature measured at Auchencorth Moss prior to use in Eq. (2). Henceforth, $j(CINO_2)$ calculated with these values are referred to as "updated $j(CINO_2)$ ". It should be noted that for $j(NO_2)$ calculations..."

Line 215: Discuss expected seasonal variation in CINO2 as Sommariva was summertime only.

This would be a good addition to provide context to the $p(Cl)_{ClNO_2}$ calculations. However following the combination of feedback we received from Reviewers 1 and 2, we have decided that this section of the manuscript should be removed due to the lack of physical measurements of ClNO₂ at the Auchencorth Moss site. (We initially decided $p(Cl)_{ClNO_2}$ would be a useful additional example of radical production routes at the site, but we now acknowledge that its inclusion contains too much conjecture.)

Line 258-61: A figure would be helpful to understand the SZA relationship to MDAF. At low sun, the angular response of the radiometer optics will contribute significantly to the MDAF. How does the filter radiometer data compare to the Bentham at low sun? In addition, the model will be particularly sensitive to the aerosols applied in TUV (Elterman). These will generally differ from the actual profile (including the PBL height). I expect the MDAF analysis is not particularly effective at very low sun (perhaps >85 deg sza). This topic should be addressed and perhaps such data needs to be excluded.

We agree with this assessment of MDAF in relation to SZA. In comparison to the Bentham spectroradiometer, we have coloured the data points in the calibration data (Fig. 1) by the SZA measured by the spectroradiometer (see Fig. AC1, below). The plot below is a magnification of the figure in the discussion manuscript so as to focus on the higher SZA (range of filter radiometer from 10 V to 3 V, and spectroradiometer from $8 \times 10^{-3} \text{ s}^{-1}$ to $3 \times 10^{-3} \text{ s}^{-1}$. The caption for this figure is that now used in the revised manuscript. The maximum SZA observed for down- and upwelling domes were 91.69° and 91.34°, respectively. From this we have assumed that from this calibration, SZA measured by each dome up to 90° are within the error of its calibration.



Figure AC1: "Calibration of both filter radiometer optical inlets against a Bentham DTM300 spectroradiometer at the University of Manchester from 13-25 June 2019. Filter radiometer measurements (1 s) are averaged to equal the scan duration of spectroradiometer (approx. 3 mins), and data where conditions were highly variable for this period (e.g. cloud cover), have been excluded. Points are coloured by the solar zenith angle (SZA) measured by the spectroradiometer (30–91°). Relationships used for subsequent conversion of filter radiometer measurements are presented in black."

This version of Fig. 1 has magnified both axes close to the origin to demonstrate the agreement at high solar zenith angles. The version included in the revised manuscript is shown in Fig. AC3 below.

In Fig. AC2 below we have plotted the hourly calculated MDAF against the SZA, before any data was filtered out. A log_{10} scale is used to include all data points. A huge uptick in MDAF is observed at highest SZA, which was found to be primarily driven by extremely small values of *j*(NO₂) calculated by the TUV model and slightly higher measurements due to actinic flux at low solar elevation being measured simultaneously by both domes (model as low as ~10⁻¹³ s⁻¹ at times when ~10⁻⁵ s⁻¹ was measured).



Figure AC2: Hourly filter radiometer $j(NO_2)$ -derived MDAF values as a function of hourly SZA determined by the TUV model prior to data filtering, on a log₁₀ scale. The vertical line indicates an SZA of 90°, where measurements made by the filter radiometer are within the error of calibration against the University of Manchester Bentham DTM300 spectroradiometer.

In our submitted manuscript, filter radiometer measurements below the detection limit were excluded from MDAF calculations. MDAF was also not calculated if modelled $j(NO_2)$ was below the detection limit. This resulted in MDAF values calculated at a maximum SZA of 93°. Following this comment made by the reviewer, the approach has been changed in the revised manuscript to use the SZA calculated by the TUV model ($R^2 \ge 0.99$ when compared to that measured by the spectroradiometer we calibrated against). The filter radiometer is accurate within the error of calibration to 90°, which also bisects the curve in Fig. AC2 before modelled values result in a fast increase in MDAF with SZA. Therefore we excluded MDAF values where SZA was >90°.

- Section 2.2: "...this mid-summer period was selected to provide calibration over the maximum range of ambient incident radiation, between solar zenith angles (SZA) of 30-91°."
- Section 2.2: "...calibration error of each dome. Overall errors for down- and upwelling domes were 13% and 12%, respectively for SZA between 30° and 91°."
- Section 2.4: "In this study at Auchencorth Moss, MDAF values were excluded if they were calculated at a SZA >90°, as these conditions are likely to result in more significant uncertainty in measurements, and were not observed during calibration."



Figure AC3: "Calibration of both filter radiometer optical inlet domes against a Bentham DTM300 spectroradiometer at the University of Manchester from 13–25 June 2019. Filter radiometer measurements (1 s) are averaged to equal the scan duration of spectroradiometer (approx. 3 mins), and data where conditions were highly variable for this period (e.g. cloud cover), have been excluded. Points are coloured by the solar zenith angle (SZA) measured by the spectroradiometer (30.1–91.69° downwelling; 30.1–91.34° upwelling). Relationships used for subsequent conversion of filter radiometer measurements are presented in black."

Line 287: The discussion of HNO3 is a bit odd. Either it should be given the full analysis of the other molecules or it should excluded because it is not relevant to the OH analysis. The low OH production from HNO3 is not even mentioned in the conclusion, perhaps because it is not an interesting finding of the study. If HNO3 is included, why not a list of other photolysis frequencies?

The focus of the lead author's research is oxidised nitrogen chemistry, therefore focus has been placed on NO_y effects. We acknowledge that HNO_3 is not an important precursor for OH radicals, although this has not yet been quantified at Auchencorth Moss. It was included because HNO_3 is part of the suite of long-term measurements at the site. We have revised the conclusion to mention HNO_3 .

Section 4: "The enhanced contribution of HONO photolysis in the colder months is a consequence of the lower solar elevation in winter (minimum SZA of 64° c.f. 32° in summer), reducing the shorter wavelengths available for O₃ photolysis, relatively more than the longer wavelengths contributing to HONO photolysis. In all seasons, $p(OH)_{HNO_3}$ is negligible compared to $p(OH)_{O_3}$ and $p(OH)_{HONO}$, reaching seasonal average rates 10³ radicals cm⁻³ s⁻¹ lower."

There are a significant number of organic species which are radical sources, including important precursors like HCHO, but these are not the focus of this study. However, to address this we have now expanded the discussion in Section 3.6 to include the potential application of this metric for other photolysis reactions at the site, including potential caveats for this, and some possible solutions (see our response to the Reviewers comments on Line 364-70).

Line 289 and Table 3: I think this must state "cloud-free TUV" for clarity.

Yes, these corrections to references to the TUV model output have been updated in the manuscript as suggested in response to the reviewer's previous comment.

Line 295: jNO2 and jO3 cover significantly different spectral ranges resulting in differing diurnal profiles and interactions with clouds and aerosols. More importantly, jO3 is highly dependent on the O3 column. Applying the MDAF to jO3 will result in significant uncertainty and I question whether it is a valid method. For more, see Lefer et al., 2003 (doi:10.1029/2002JD003171). The jCINO2 and jHONO have spectral parameters similar enough to jNO2 that MDAF is likely ok. The paper lacks any discussion of uncertainties resulting from the MDAF results for each of the molecules.

We fully agree with this comment, and a similar point raised by Reviewer 1. Consequently, we have now re-run the TUV model to include the daily average measured O_3 column and ambient temperature as input. The temperatures used are the daily average of measurements already presented in the manuscript (Figure 3, submitted manuscript). Daily average ozone column measurements were compared between the Dobson photometer measurements at Lerwick in the Shetland Islands (Defra, 2020), and the NOAA OMI satellite data measured over Auchencorth Moss (NOAA, 2020b). Good agreement was determined between these ($R^2 = 0.75$), so the satellite data was used due to it measuring at the correct latitude and longitude, and its higher rate of data capture. Both time series can be seen in Fig. AC4 below (Fig. 2, revised manuscript), with the same caption used in the revised manuscript.

Section 2.3: "Daily average ozone column measurements were accessed via the OMI satellite (NOAA, 2020b), and calculated for air temperature from measurements made on site (Table 1). Days where O₃ column measurements were missing used the measurement from the following day."

Overall, the use of the TUV model in this paper is not intended to perfectly predict actinic flux or the *j*-value at any given location, but demonstrate the use of applying MDAF approaches to basic models, to account for local meteorology changes that impact atmospheric chemistry which are difficult to replicate in models.



Figure AC4: "Time series of mean hourly trace gas concentrations (O_3 , HONO, HNO₃) and meteorological parameters (solar global irradiance (G), air temperature, relative humidity and wind speed (ws)) for the year of data included in this study (21 November 2018 to 20 November 2019). Satellite O_3 column measurements over Auchencorth Moss used in model input (NOAA, 2020b) are shown as daily values, with missing data replaced by the measurement from the following day. The *j*(NO₂) measurements reported are the hourly mean of summed down- and up-welling components; the missing data in June are when the filter radiometer was removed from the site for calibration."

We have also compared our original $j(NO_2)$ -derived MDAF to a version using $j(O^1D)$. For this we used the spectroradiometer measurements of actinic flux made at the University of Manchester to determine $j(O^1D)$, and TUV model runs for this location and time. The model set-up was the same as it was for Auchencorth Moss, apart from the changes made to location-based data (e.g. lat/long, altitude, O_3 column, temperature etc).

Figure AC5 below shows the results of this comparison: with our $j(NO_2)$ filter radiometerderived MDAF against MDAF calculated using spectroradiometer-derived $j(NO_2)$ and $j(O^1D)$. As anticipated, agreement between $j(NO_2)$ -derived MDAF's are good (grey triangles), while there is a positive bias to $j(O^1D)$ -derived MDAF (mean of 23%) (coloured circles). The bias increases with SZA, where the largest difference to $j(NO_2)$ -derived MDAF (69%) occurs at high SZA (>79°). This is likely attributable to the differences in scattering between the two different spectral regions of $j(NO_2)$ and $j(O^1D)$ as a result of both aerosol and cloud effects. This figure (Fig. AC5, below) is now included in the revised manuscript (as Fig. 6), and the caption used is the same as given here.



Figure AC5: "Comparison between $j(NO_2)$ filter radiometer-derived MDAF and MDAF calculated using spectroradiometer-derived $j(NO_2)$ and $j(O^1D)$, at the University of Manchester (13-25 June 2019). MDAF derived using $j(NO_2)$ measurements are represented by dark grey triangles, and $j(O^1D)$ are circles coloured by the solar zenith angle (SZA), with linear regressions in dark grey and red, respectively. The 1:1line is included in dashed grey for comparison."

Section 2.4: "An MDAF metric was also determined for $j(O^1D)$), in a calculation analogous to Eq. (3), using spectroradiometer measurements of actinic flux made during calibration at the University of Manchester, $\sigma(O_3)$ from Daumont et al. (1992) and $\Phi(O^1D)$ from Matsumi et al. (2002) in Eq. (2). The TUV model was run with the same input data sources as Section 2.3, except air temperature was as measured at Manchester Airport (NOAA, 2020a). The model utilises the same values of $\Phi(O^1D)$ but sources of $\sigma(O_3)$ differ, with the TUV model using data from Malicet et al. (1995). There is generally good agreement between this data (<2-3% difference at room temperature; Burkholder et al., 2019)."

These derivations have been used to estimate the uncertainty in applying MDAF to other species *j*-values, propagated through where MDAF is applied (e.g. determination of p(OH))

rates). Since the bias between $j(NO_2)$ and $j(O^1D)$ MDAF derivations is highly variable with SZA, the bias between these two variables has been divided into 5° SZA bins. An average bias has been determined for each SZA bin, and used as the uncertainty in MDAF for that SZA bin, when applied to calculations involving O₃ photolysis. The same procedure is used for the photolysis of all other species investigated, except the error in MDAF is quantified from the difference between $j(NO_2)$ measurement methods used to derive each version of MDAF (spectro- vs. filter radiometer). This has been illustrated for calculation of p(OH) rates in Fig. AC6 below (Fig. 8 of revised manuscript). The same figure caption text is used in the revised manuscript.



Figure AC6: "Diurnal variations in seasonally-averaged hourly mean p(0H) rates from O_3 and HONO photolysis. Dotted lines show rates calculated using *j*-values directly from the cloud-free TUV model, while solid lines show rates where *j*-values were first corrected by the MDAF metric, as described in the text. Shading represents the propagated uncertainty discussed in Sect. 3.3."

"Section 3.3: MDAF derivations

The MDAF values calculated as per Eq. (3) from the measured and modelled $j(NO_2)$ at Auchencorth Moss were largest during the sunrise and sunset hours, where SZA exceeded 80°. This is presumed to be a combined result of the model predicting incredibly small values of $j(NO_2)$ during these hours, and radiation measured simultaneously by both domes of the filter radiometer, due to the direction of incoming radiation at high SZAs.

Figure 6 provides a comparison between MDAF derived from filter radiometer measurements of $j(NO_2)$, and that calculated using $j(NO_2)$ and $j(O^1D)$ measured by the spectroradiometer at the University of Manchester (Sect. 2.4). There is strong

agreement between $j(NO_2)$ MDAF derivations (R^2 = 0.97), with a mean difference of 6.9%, while there is a positive bias between $j(NO_2)$ filter radiometer and $j(O^1D)$ spectroradiometer derived MDAF values ($R^2 = 0.87$; mean = 23%). This bias is driven by increasing SZA (Fig. 6) with good agreement at low SZA (30-40°), reaching a maximum at lowest levels of solar elevation (69% at 87° SZA). This positive bias is attributed to the lack of significant overlap in spectral ranges where the photolysis of O_3 and NO_2 occur, as the wavelengths are scattered differently in the presence of atmospheric variables (e.g. clouds and aerosols). Consequently, the application of a $i(NO_2)$ -derived MDAF to modelled $i(O^1D)$ results in the potential for a large level of uncertainty. Given that SZA is a driving factor in this uncertainty, the different MDAF derivations were divided into 5° SZA bins. In each bin, the mean bias from the filter radiometer-derived MDAF was quantified, and used to estimate the uncertainty of MDAF in further calculations in which that species and SZA range are used. Uncertainty in $j(O^1D)$ ranges from 8% (30–35° and 35–40° bins) to 43% (85–90°). This is unique to $i(O^1D)$, as the photolytic spectral range of NO₂ overlaps significantly with that of HONO (Kraus and Hofzumahaus, 1998) and CINO₂ (Ghosh et al., 2012). Uncertainty in these overlapping regions ranges from $\leq 5\%$ (all bins between 30–70°) to 19% at high SZA (85–90°). Overall, uncertainty is lowest where photolytic spectral regions overlap with that of measured j(NO₂), and at low SZA. In order to minimise this uncertainty in future work, MDAF should be applied to modelled j-values that photolyse in a similar wavelength region to the species measured."

Lines 364-70: This would be a good place to discuss using MDAF for an expanded set of photolysis frequencies beyond those listed in this paper. The metric would be useful for other studies.

We thank the reviewer for this suggestion. We have updated the manuscript to briefly expand upon the potential of this method for other photolysis reactions, including potential caveats and some possible solutions.

Section 3.6: "MDAF application is not limited to the j-values presented in this study. There are a significant number of organic species which are radical sources, including other important HO_x radical precursors like HCHO, where this method could easily be implemented. The TUV model, for example, has the capacity to calculate over 110 separate photolysis reactions. The primary shortcoming of the MDAF method is that using a $j(NO_2)$ -derived MDAF metric means measurements lack full spectral overlap with photolysis wavelengths of some important species like O₃ (Sect. 3.3), contributing some uncertainty. However this can easily be minimised by use of other molecule specific radiometers (e.g. $j(O^1D)$ filter radiometer), or measurement of actinic flux across a wider wavelength range with a spectroradiometer. The latter sacrifices temporal resolution and some ease of measurement for the ability to quantify the specific j-value required for each individual study (where σ and Φ are available)."

Fig 6: What happened in June? Does this affect the annual averages shown in figure 7?

The missing data in June is because the filter radiometer was relocated from the Auchencorth Moss site to the University of Manchester for calibration. The text in Section 2.2 and the

caption for Figs. 3 and 6 (Figs. 2 and 5 in the resubmitted manuscript) have been updated to inform readers of this. This missing data could result in underestimated annual and summertime averages, however since both parameterisations and TUV output are both modified by MDAF that will not be calculated for missing $j(NO_2)$ measurements, the discussed difference between these values is likely to remain the very similar.

We also expect the underestimation due to missing data to be small, as measured solar global irradiance (G) and monthly averaged downwelling filter radiometer measurements were at a similar level. We also have no reason to believe that the upwelling component would vary much during this period, since conditions are remain broadly similar at the site.

- Section 2.2: "Output signals from the filter radiometer were calibrated at the University of Manchester against a Bentham DTM300 scanning spectroradiometer (Webb et al., 2002a; Thiel et al., 2008) between 13 and 25 June 2019.
- Figure 2: "...The j(NO₂) measurements reported are the hourly mean of summed down- and up-welling components; the missing data in June are when the filter radiometer was removed from the site for calibration."
- Figure 5: "...as measured by the filter radiometer at Auchencorth Moss for the year of study. The filter radiometer was removed from the site for calibration between 5 and 26 June 2019...."

Technical corrections

- Line 76: Change "and temperature" to "temperature (T) and pressure (p)
- Line 144: Shouldn't this be ">9V"
- Line 166: Perhaps, note that is is below, "shown in Eq. (3) (below in Section 2.4.1)"
- Lines 174-5: Remove "it has been demonstrated that" and change "could" to "can"
- Line 258: Change "was" to "were"
- Line 316 and Fig 10: Previously used only "p(CI)CINO2" but now shortened to "p(CI)". I suggest sticking to the long version.
- Line 328-9: Reword for clarity "compared with when the diurnal cycle of CINO2 is unaccounted for" to "compared with the constant CINO2 concentration"
- Fig 8: Legend should say "HONO (cloud-free TUV)" and "O3 (cloud-free TUV)" for the dotted values

These technical corrections have been updated as suggested in the revised manuscript, except for the caption of Fig. 8, which has been reworded as follows:

Figure 8: "Diurnal variations in seasonally-averaged hourly mean p(OH) rates from O₃ and HONO photolysis. Dotted lines show rates calculated using j-values directly from the cloud-free TUV model, while..."

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