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 1

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 sub-sectional structuring, and some other text (e.g. abstract) of our manuscript as a consequence the revisions we describe above and below.

General comments

The paper describes the use of filter radiometer measurements of j(NO2) to derive photolysis rate coefficients and primary production rates of OH radicals (and Cl atoms) from various precursors at a site in Scotland for a period of one year. The study additionally uses clear sky TUV model calculations of actinic flux, local measurements of precursors and meteorological data including solar shortwave irradiance. The general idea is to utilize measured and clear sky modelled values of j(NO2) to calculate adjustment factors (MDAF), suitable to derive local photolysis rate coefficients for species other than NO2. These rate coefficients were then applied to determine radical production rates for some measured (and unmeasured) precursors. The MDAF approach is in principle sound. However, the study in my view has major deficiencies and should not be published in the present form. My main objections are listed below followed by some minor and technical comments.

We are pleased the reviewer thinks that the MDAF approach is sound. We highlight that the paper also presents our work in the context of discussing the basis for the use of in-situ photolysis measurements for long-term validation and local atmospheric chemistry studies. We have carefully considered the reviewer's comments on deficiencies and objections and taken forward many of the reviewer's suggestions. We think that the adjustments have significantly improved the manuscript and addressed the scientific issues raised.

To improve clarification of the aims of our study, we have revised the aims at the end of the introduction in the revised manuscript.

Section 1: "This study presents the first long-term j(NO₂) filter radiometer dataset in the UK (Auchencorth Moss, SE Scotland), its use in generating a measurement-driven

adjustment factor (MDAF) and how this can be applied to basic model estimations of j-values at a local site. The filter radiometer dataset is shown to account for variations in local meteorological conditions which impact $j(NO_2)$ (e.g. cloud cover, surface albedo), and how this information within the MDAF can be used as a point of model validation or education, with a minimal increase in computational cost. The impact of the MDAF on atmospheric chemistry is discussed in the context of unimolecular photolysis reactions, and hydroxyl (OH) radical production rates from precursor sources routinely measured at Auchencorth Moss (O_3, HONO and HNO_3). The scientific, and ultimately policy, value of incorporating filter radiometer measurements alongside existing long-term and spatially-resolved air quality monitoring networks is emphasised."

Major comments

Section 2.2: Filter radiometer: As is noted in the text (line 142 ff) and visible in Fig. 1, the filter radiometer instrument covering downwelling radiation reached signal voltages above 10 V that were not properly recorded, presumably because the range of the data logger was limited to 10 V. Even though this was noticed (at the latest) during the calibration in June, the problem was apparently not fixed. Basically this means that j(NO2) > 7E-3/s were not recorded (Fig. 1) which is well below expected clear sky maximum values of around 8E-3/s for the downwelling in summer. Moreover, under conditions of broken clouds there is the effect of short-term enhancements that can be observed for solar shortwave irradiance (e.g. Schade et al., 2007) but also for j(NO2). This probably led to occasional shortterm values greater than 7E-3/s even at lower sun elevations. Looking at one hour averages alone the effect may remain unnoticed but the data are nevertheless biased. So the problem is not limited to three weeks in June (that were probably for that reason taken out later in Figs. 3 and 6 without explanation). I think the authors have to go back to their original 1 s data set of FR and flag all data where within the one hour averaging periods 10 V values occurred. Consequently these periods have to be removed from the further data analysis and mean diurnal variations for spring and the summer periods may become disputable. Moreover, this will affect the correlation with the solar shortwave irradiance in Fig. 5 (see below).

We thank the reviewer for the detailed assessment, and we address the specific issues raised individually.

1) Handling and validation of 1 second data

We remind the reviewer that in calculating hourly average values of measured $j(NO_2)$, the original 1 second dataset was flagged as invalid where measurements in the downwelling dome exceeded the topping out threshold. This comprised 1.4% of the full dataset (line 147, submitted manuscript). For information, the distribution of invalid flagged data is shown in Figure AC1 below.

In our revised manuscript, an hourly average has *only* been quantified if the 1 second data collected within that hour met or exceeded 75% data capture, after all invalid flagged data has been excluded. The manuscript has been updated to detail the data handling procedures used.

Section 2.2: "These incidences of high $j(NO_2)\downarrow$ (>9 V) comprised 1.4% of all raw data collected, and were excluded from further analysis. An hourly average was only calculated if the 1 s data remaining within that hour met or exceeded 75% data capture. As a

consequence, maximum j(NO₂)↓ presented in this study is an underestimate (7-22% based on comparison to the spectroradiometer during calibration)."
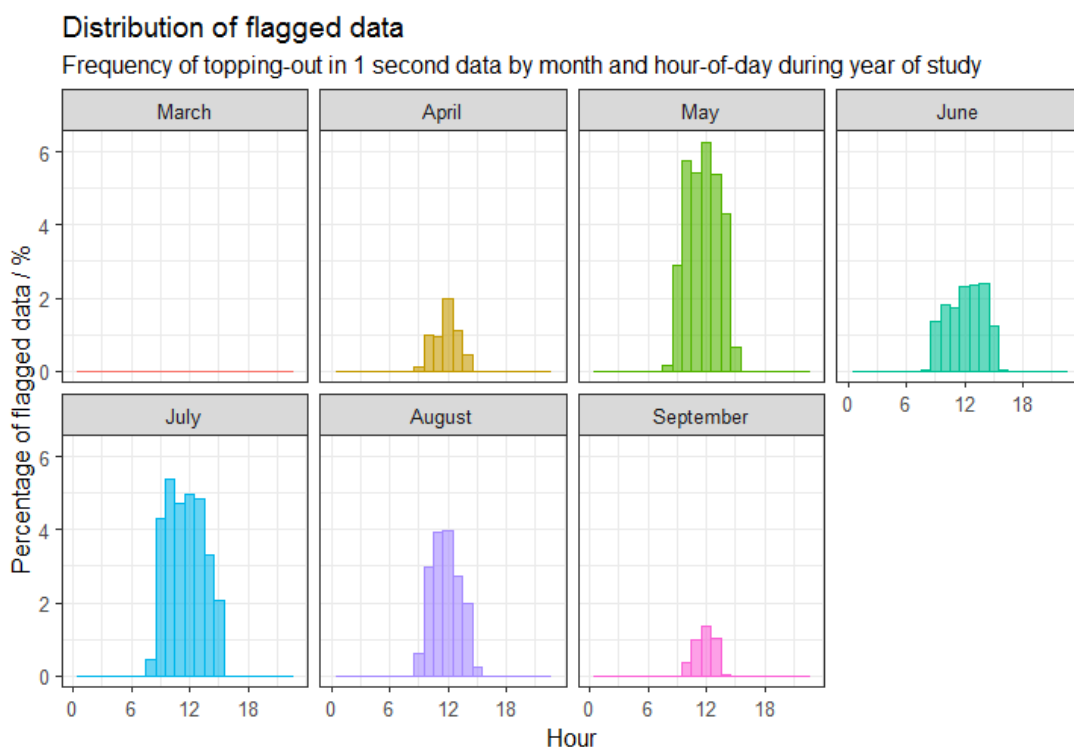

Figure AC1: The distribution of 1-second downwelling dome measurements by month and hour-of-day that were flagged for topping out (>9 V) in 2019. These comprised 1.4% in total of raw data collected.

2) Missing data in June

It is important to note that data was unavailable in June was not a result of the topping out issue of the filter radiometer, but because the instrument was relocated to the University of Manchester for calibration between the 13-25th of that month.

The manuscript text and captions for Figs. 3 and 6 (Figs. 2 and 5 in the revised manuscript, respectively) have been updated to reflect this more clearly, as follows:

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…."

3) Effect of topping-out on Fig. 5 and $p(OH)$ values

We agree with the reviewer that the filtering may have resulted in an underestimate where the downwelling measurements exceed the topping-out threshold, particularly during midday hours or where broken cloud conditions resulted in short-term enhancements in j(NO₂). We have provided a quantification for this underestimate (7-22%; line 146, submitted manuscript)

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using the calibration comparison to the spectroradiometer in June at the University of Manchester.

As mentioned in part 1 of this comments response, hourly averages of the filter radiometer measurements were only calculated if data capture in the hour exceeded 75%, once all data that topped out had been removed. As is demonstrated in Figure AC1, these mostly occur during the middle of the day. In total, this data capture threshold resulted in 3.5%, 6% and <1% of hourly average measurements not being included in spring, summer and autumn diurnal cycles, respectively. No hours were affected in the winter months. This means that a small fraction of spring and summer data could be underestimated by up to 22% during hours of full daylight, for both $p(OH)_{O_3}$ and $p(OH)_{HONO}$ rates. However since MDAF is determined separately for each hour of data, both values will be underestimated by the same quantity, resulting in the overall trends being comparable to those in the submitted manuscript.

We have revised the manuscript to emphasise that rates of $p(OH)$ from photolysis of O₃, HONO and HNO₃ discussed are estimates, due to this potential source of error limiting the upper values. Quantification of uncertainties are discussed in response to the reviewer's comments on Section 2.4.1.

Section 3.5: *"The maximum rates reached for both photolysis reactions presented here are underestimated, owing to the exclusion of the largest measurements of j(NO₂) because of the downwelling dome of filter radiometer periodically topping-out (Sect. 2.2). As these excluded measurements occur primarily during midday hours in the spring and summer months, this underestimation is likely to impact production rates of OH from the photolysis of O₃ more than from HONO. However, in this dataset the topping-out only affected 6% of summertime hours. If it is assumed all of these values are underestimated by the upper limit expected (22%; Sect. 2.2), the maximum rate of $p(OH)_{O_3}$ would increase by less than 2x10⁴ radicals cm⁻³ s⁻¹. Consequently, the overall trends observed in Fig. 8 would remain the same. Uncertainty in the seasonal estimates of $p(OH)_{HONO}$ are driven by that of measured concentrations being near the MARGA detection limit, observed in Fig. 8 with and without MDAF applied to j(HONO). For $p(OH)_{O_3}$, uncertainty from concentration measurements is much lower, but when MDAF is applied a significant amount of uncertainty is inherited (see Sect. 3.3). This combination results in less distinction between MDAF adjusted $p(OH)_{O_3}$ and $p(OH)_{HONO}$ during the full day in autumn and midday hours in spring, where these rates are comparable."*

"Table 3. Estimated mean production rates of OH from the photolysis of O₃, HONO and HNO₃ during each meteorological season, using j-values directly output from the cloud-free TUV model and those adjusted using the MDAF metric. Means are calculated using only daytime measurements, and are reported with corresponding uncertainties discussed in Sect. 3.3. The % decrement in production rate for the MDAF data is the average decrement across the season."

We discuss the impact of this topping-out on Fig. 5 in response to the reviewer's comments on Section 3.2 below.

Section 2.3: Model approach: The use of an annual mean value of ozone columns as a TUV model input (line 162) is an unnecessary simplification. The ozone column is a major factor influencing j(O1D) and j(HNO3) which is not covered by the j(NO2) measurements and is therefore not included in the MDAFs. Ozone columns are highly variable, especially during spring time in Europe and are apparently available for the site on a daily basis (or from satellite observations).

We agree with hindsight that the inclusion of the ozone column (and temperature) should have been undertaken in a more complex but realistic approach. To address this, and similar comments from Reviewer 2, we have rerun the TUV model to include measured O_3 column and ambient temperature as input. The temperatures used are the daily average of those already presented in the manuscript (Figure 3, submitted manuscript, now Figure 2, revised 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, 2020). Good agreement was determined between these ($R^2 = 0.75$), so we opted for the satellite data due it measuring at the correct latitude and longitude, and its higher rate of data capture. These changes have been reflected in the manuscript text, figures and other associated data.

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 O_3 column measurements were missing used the measurement from the following day."*

Figure 2: *"…in this study. 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…"*

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.

Section 2.3: Model approach: Modelled j(O1D) should also take into account ambient temperature which mainly affects the quantum yields of O(1D). The temperature effect was considered for ClNO2 (mentioned later in line 206). It's unclear why it was neglected for the more important j(O1D).

We thank the reviewer for this comment, and appreciate the impact temperature can have on the quantum yield of O(^{1}D) from the photolysis of O_3. This was not discussed in the submitted manuscript because the Φ(O^{1}D) values used by the TUV model include a temperature dependence (Matsumi *et al.*, 2002) applicable to all temperatures measured during this study (267-302 K), that is currently recommended by IUPAC (Atkinson *et al.*, 2004). On the other hand, the temperature dependence of σ(ClNO₂) reported by Ghosh *et al.* (2012) was included in the IUPAC recommended preferred values (line 168, submitted manuscript), but not in the TUV model. Consequently there are large differences to the model output for ClNO₂, as we discussed in our submitted manuscript.

We have addressed the inclusion of temperature in the model input in our response to the previous comment.

Section 2.3: Model approach: It is also not explained why MDAFs were derived in the first place for an unimportant precursor like HNO3 and an unmeasured precursor like ClNO2 but not for a species like HCHO, a well-known and important primary radical source in this case of HO2.

The focus of the lead author's research is oxidised nitrogen chemistry, therefore focus has been placed on NO_y effects. 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.

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 O_3 (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)."*

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 in this work because HNO_3 is part of the suite of long-term measurements at the site. However, following comments from both Reviewer 1 and 2, we now exclude from the revised manuscript the presentation of rates of Cl production ($p(Cl)_{ClNO_2}$) from the photolysis of estimated concentrations of $ClNO_2$.

Section 2.4.1: Adjustment factor: The quality of the applied adjustment factors (MDAF) remains unclear and is not investigated even though it is a key parameter of this work. For example, the calculated clear sky-photolysis rate coefficients j(NO2) and j(O1D) will generally not correlate well because of the different spectral regions where the photolysis takes place which results in different dependencies on solar elevation. In addition j(O1D) is affected by temperature and ozone columns while j(NO2) is not (or very little). The uncertainty of the MDAF should be carefully estimated for each photolysis rate coefficient dependent on solar elevation and atmospheric conditions including cloud effects. Without such sensitivity studies the uncertainties of the adjusted j-values remain unclear, as well as the benefits of the whole approach.

We thank the reviewer for this response and acknowledge that we should have included a discussion of error around the application of MDAF in the submitted manuscript. In response to this, we have compared our originally $j(NO_2)$-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).

The Figure AC2 below shows the results of this comparison: with our $j(NO_2)$ filter radiometer-derived 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 solar zenith angle (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. AC2) is now included in the revised manuscript (as Fig. 6), and the caption used is the same as given here.
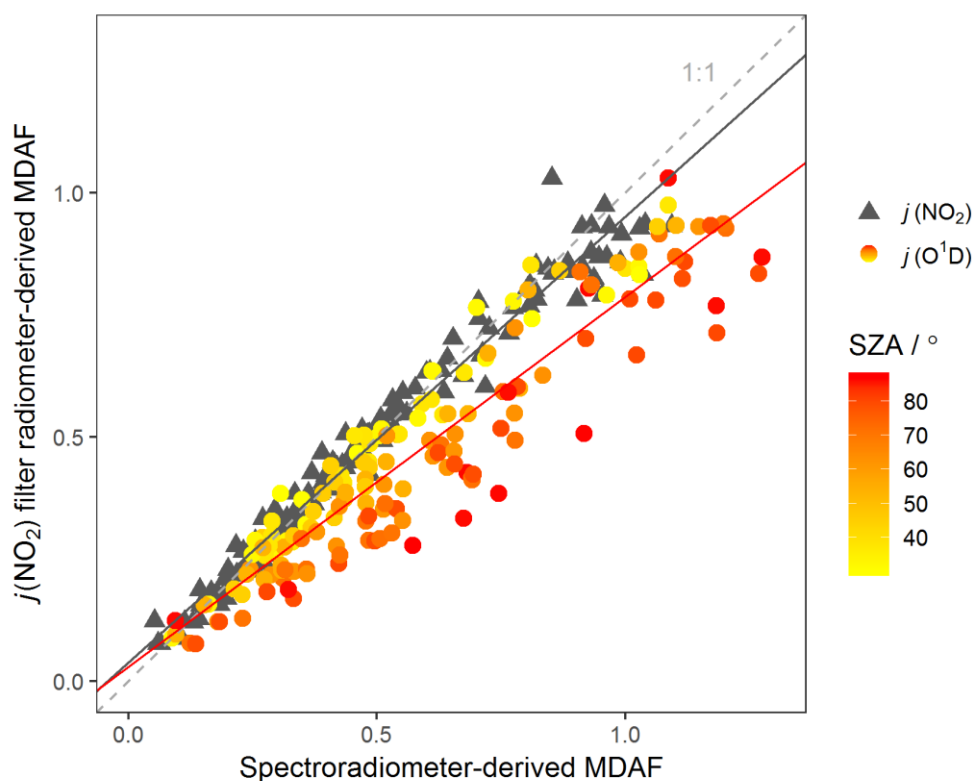

Figure AC2: "*Comparison between $j(NO_2)$ filter radiometer-derived MDAF and MDAF calculated using spectroradiometer-derived $j(NO_2)$ and $j(O^1D)$, at the University of Manchester (13-25 June 2019). MDAF derived using $j(NO_2)$ measurements are represented by dark grey triangles, and $j(O^1D)$ are circles coloured by the solar zenith angle (SZA), with linear regressions in dark grey and red, respectively. The 1:1 line 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 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 O_3 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. AC3 below (Fig. 8 of revised manuscript). The same figure caption text is used in the revised manuscript.
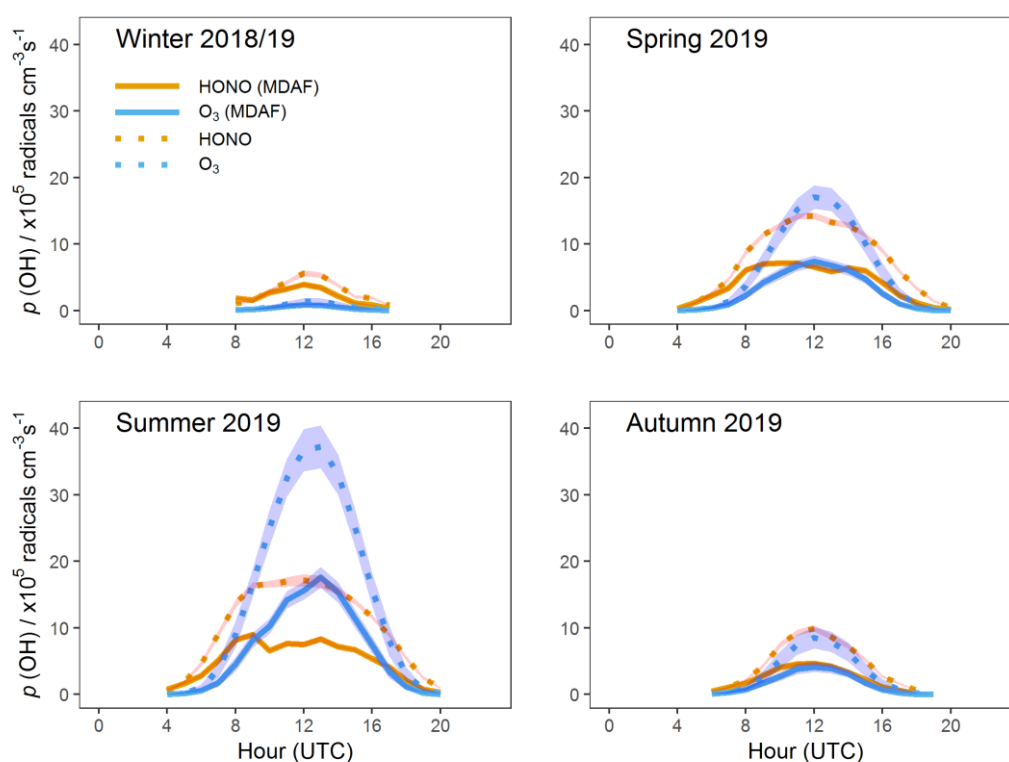

Figure AC3: "*Diurnal variations in seasonally-averaged hourly mean $p(OH)$ rates from O_3 and HONO photolysis. Dotted lines show rates calculated using j-values directly from the cloud-free TUV model, while solid lines show rates where j-values were first corrected by the MDAF metric, as described in 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(NO₂) 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(NO₂) 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 $j(NO_2)$-derived MDAF to modelled $j(O^1D)$ 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 $j(O^1D)$, as the photolytic spectral range of NO_2 overlaps significantly with that of HONO (Kraus and Hofzumahaus, 1998) and $ClNO_2$ (Ghosh et al., 2012). Uncertainty in these overlapping regions ranges from ≤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 $j(NO_2)$, 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."

Section 2.4.3 Production rate of Cl atoms: ClNO2 was not measured at the site (line 211). There is no reason to assume that ClNO2 concentrations are similar to those measured in Weybourne unless at least NOx and O3 levels are comparable (not shown), let alone to consider a constant mean concentration or a seasonably independent mean diurnal concentration. Consequently, the results presented later in Sect. 3.5 are pure speculation. j(ClNO2) should of course be considered as an important photolysis rate coefficient but the attempt to apply it for the site without ClNO2 measurements is pointless (see below).

We accept the reviewer's comment on this section of our manuscript, and it has now been removed. Further information regarding this is included in response to the reviewer's comments on Section 3.4 and 3.5.

Section 3.2 Filter radiometer measurements: Because of the limitations of the measurement technique as discussed above (Sect. 2.2), the current j(NO2) dataset does not seem suitable to derive an empirical relationship between j(NO2) and solar shortwave irradiance. Fig. 5 clearly shows that data points above the instrument's limit are missing. Moreover, as noted, some of the 1h averages shown may be biased low. So the agreement with the parametrization by Trebs et al. may in fact be better than implied by the blue line. The authors seem to recognize that because they reproduce the empirical formulas from previous studies in the text but not their own.

Figure 5 in the submitted manuscript (now Figure 4) presenting the different parameterisations between $j(NO_2)\downarrow$ and G was only intended to demonstrate that the data collected by the filter radiometer in our study is in line with literature relationships, rather than imply that the current work was an updated equation for future use. The nature of the bias introduced from the 1.4% of topped-out data is discussed above (response to comments on Sect. 2.2). The missing data has affected this relationship, and as the reviewer correctly identified, is the reason we have not included our own parameterised relationship. The instrument will be renovated to improve its performance for future data collection. However this does not invalidate our approach, and our demonstration of a method that the reviewer has stated above to be a sound idea.

We have revised the text in Section 3.2 of the manuscript to reflect this, and removed the empirical formulae which could be interpreted as a comparison of equations, as picked up by the reviewer.

Section 3.2: *"A direct comparison between the co-located downwelling filter radiometer and G measurements for the duration of the study is presented in Fig. 4. The relationship between the two measurements is linear until G≈450 W m^{-2} above which a slight curvature is observed. A quadratic fit to this data yields predicted values of j(NO$_2$) that lie between two previously published parameterisations between these two measurements: lower than Trebs et al. (2009) for values of G >90 W m^{-2}, but higher than Bahe et al. (1980) until the larger downwelling j(NO$_2$) measured during the year. Trebs et al. used co-located G and spectro- or filter radiometer measurements from 9 sites worldwide to derive an empirical relationship between them. They show differences of up to 50% between their results, and the linear relationship proposed by Bahe et al. (1980). Trebs et al. suggest that one possible reason for the lack of curvature observed by Bahe et al. was that they did not include measurements at SZAs <30° However Auchencorth Moss is at a higher latitude than any of these sites, with a minimum SZA of ~32° in June. Curvature of the plot of j(NO$_2$) against G is still observed, although there is still a moderate amount of scatter."*

Due to the topping-out of the downwelling dome of the filter radiometer (discussed in Sect. 2.2), the data presented from this study is likely to be an underestimate; particularly at higher G, where measurements above the instruments limit have been excluded. Despite this, Fig. 4 demonstrates that the downwelling dome of the filter radiometer can account for changes in local conditions as well as the pyranometer, in accordance with other literature at an hourly resolution."

Section 3.2 Filter radiometer measurements: The employed pyranometer also requires more attention. The SKS 1110 is not a standard pyranometer. It has a fairly limited spectral response range much more narrow than the solar range and is probably calibrated by the manufacturer by comparison with a reference pyranometer in the field. According to Coyle et al., 2019, the instrument was running for more than 20 years at the site without a follow-up calibration. Such a calibration was suggested by Coyle et al., 2019. Was it made and implemented in the current work?).

The SKS1110 is a "secondary standard grade" sensor commonly used in agro/environmental research as it provides a relatively large signal output without amplification, and is stable and reliable. The range is similar to other equivalent pyranometers (LI-COR LI-200R, Apogee Instruments SP-110 and SP-230; see links in References below). It was monitored alongside a new sensor by UKCEH for 18 months at Auchencorth Moss in 2016/17, then returned to the manufacturer and calibrated on 20 April 2018. The pyranometer was within 5% uncertainty of

a WMO Secondary Standard Pyranometer, traceable to the World Ratiometric Reference. This paper uses calibrated pyranometer data.

> Section 2.1: *"Long-term instrumentation deployed at Auchencorth Moss utilised in this study is detailed in Table 1. Solar global irradiance (G) measurements were calibrated in April 2018, and certified to be within 5% uncertainty of a traceable WMO Secondary Standard Pyranometer."*

Section 3.3 Estimates of j(HONO) and j(ClNO2): The discussion of the empirical relationship between j(NO2) and j(HONO) by Kraus et al. is misleading. The fact that this older parametrization gives higher values than the TUV model is not a result related with the j(NO2) measurements of the present study. It's just a property of the TUV model which used more recent recommendations of absorption cross sections and quantum yields. Qualitatively the discrepancy is explainable because Kraus et al. used recommendations from 1998: smaller quantum yields for the NO2 photolysis and greater absorption cross sections for HONO. What is more important for this study is that j(NO2) and j(HONO) from TUV probably correlate linearly in good approximation which justifies the use of the MDAF concept for j(HONO).

We agree that the comparison to this older parameterisation highlights how the relationship can change when the molecular-specific values are updated. We also agree that a bit more explanation is needed, and have adjusted the text to include the different molecular-specific values used in each calculation to better reflect the point that Reviewer 1 makes, and ensure it is not misleading.

> Section 3.4: *"…consistent over all seasons. This is likely to be attributed to the updated molecule-specific parameters used by the TUV model, c.f. Kraus and Hofzumahaus (1998) for both NO_2 and HONO. Absorption cross-sections (σ) are different for both species. σ(HONO) varies the most, with an agreement of better than 10% between the JPL recommended values used in the TUV model (Sander et al., 2011) and the results of Bongartz et al. (1994) used by Kraus and Hofzumahaus (Burkholder et al., 2019). For $\sigma(NO_2)$, results of Harwood and Jones (1994) used by Kraus and Hofzumahaus are 6−8% below most other studies (Burkholder et al., 2019), including that of Vandaele et al. (1998) and Mérienne et al. (1995) used in this study (in the TUV model and spectroradiometer calculations in Sect. 2.2, respectively). The quantum yield for HONO photolysis is assumed to be unity in both calculations, but $\Phi(NO_2)$ used by the TUV model (and in spectroradiometer calculations; Troe, 2000) are on average 4% greater than the combination of Gardner et al. (1987) and Roehl et al. (1994) used by Kraus and Hofzumahaus."*

Section 3.3 Estimates of j(HONO) and j(ClNO2): For j(ClNO2) a similar problem arises: The result that TUV overestimates j(ClNO2) has again nothing to do with the j(NO2) measurements. It's simply because the implemented absorption cross sections are obviously outdated as noted in Sect. 2.3 of the paper. How much greater the values are is secondary for the current study but it could of course be mentioned in the text as a friendly reminder for the TUV developers to update their input.

The reviewers' observation is correct. We feel this is a valuable addition to the science, as both TUV developers and other atmospheric chemistry modellers should understand when parameters are in need of review. We have added a sentence to the manuscript to emphasise this, and made the discussion of these parameterisations more general.

Section 3.4: *"Overall, the TUV model yields the greatest annual mean $j(ClNO_2)$ values (Fig. 7, middle panel), exceeding the others by 16-26%, with the maximum difference at midday. Both Young et al. (2014) and Riedel et al. (2014) demonstrate reasonable agreement to the updated $j(ClNO_2)$ results, suggesting this difference is in part contributed by outdated $\sigma(ClNO_2)$ used in the TUV model. The inclusion of $j(O^1D)$ in the parameterisation by Young et al. appears to result in smaller predicted $j(ClNO_2)$ values c.f. Riedel et al., particularly in the morning hours (04:00-10:00 UTC). However, these results are within the uncertainty associated with applying the MDAF metric (Sect. 3.3), and consequently distinctions between these cannot be made with great certainty."*

Section 3.3 Estimates of j(HONO) and j(ClNO2): A discussion of j(O1D) is completely missing here. The points raised in Sect. 2.3 and 2.4.1 should be considered and a reasonable uncertainty estimate should be derived for all photolysis rate coefficients. The MDAF concept is far more complicated and error-prone in particular for j(O1D) than currently implied in the paper.

The comments here have been taken on board by the authors. We did not include $j(O^1D)$ estimations in Section 3.3 of the submitted manuscript as this was not also compared to parameterisations that estimate $j(O^1D)$. However we agree with the comments made by the reviewer, and acknowledge that not including this discussion elsewhere in the manuscript was inappropriate.

In our revisions we have renamed this section and revised the text to include $j(O^1D)$, and included a new panel in Fig. 7 (Fig. AC4 below, the caption of which is also used in the revised manuscript) to show its annual average diurnal cycle where MDAF has been applied, with associated uncertainty. This uncertainty attributable to using a $j(NO_2)$-derived MDAF on modelled $j(O^1D)$ has been derived in response to the reviewers comments on Section 2.4.1 and 3.4/3.5, and in the new section in the revised manuscript (Sect. 3.3: MDAF derivations).

"Section 3.4: Estimates of j(HONO), $j(ClNO_2)$ and $j(O^1D)$

The annual average diurnal cycle of $j(O^1D)$ output by the TUV model is presented in the bottom panel of Fig. 7, alongside the uncertainty associated with applying MDAF to these results, determined for each SZA bin before averaging (Sect. 3.3). The uncertainty is greatest during sunrise (04:00-07:00 UTC) and sunset hours (18:00-20:00 UTC), at 35-42%, but results in largest range of $j(O^1D)$ during midday hours (~15% uncertainty). This is almost twice as much uncertainty as attributed to either j(HONO) or $j(ClNO_2)$."
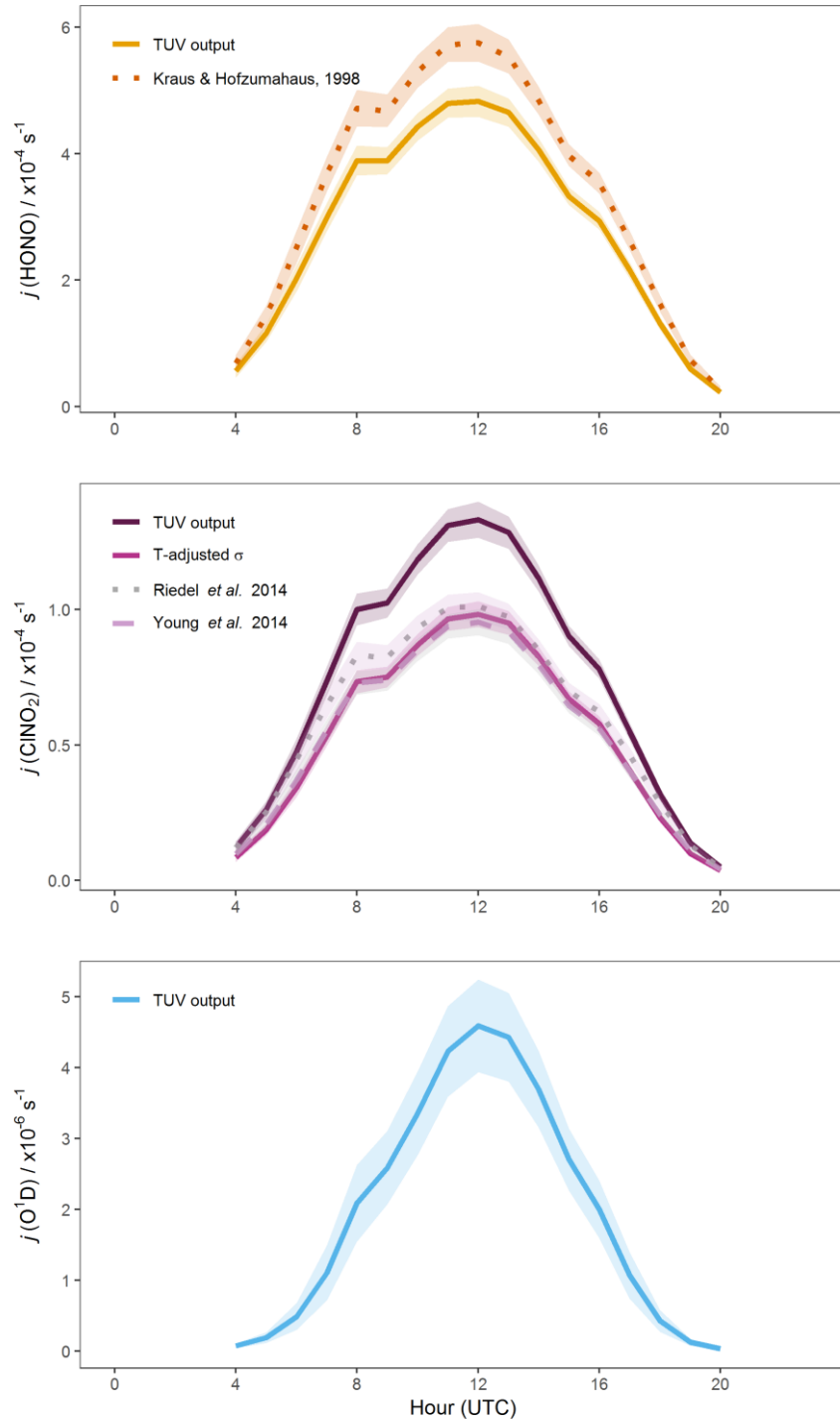
Figure AC4: "***Top:** Annual average diurnal cycle of j(HONO) at Auchencorth Moss calculated by the TUV model and using the Kraus and Hofzumahaus (1998) parameterisation. **Middle:** Annual average diurnal cycle of j(ClNO$_2$) estimates for Auchencorth Moss, using the direct TUV model output and updated j(ClNO$_2$) values (accounting for daily average temperature), and parameterisations presented in Riedel et al. (2014) and Young et al. (2014). **Bottom:** Annual average cycle of j(O^{1}D) at Auchencorth Moss, calculated by the TUV model. All values of j(HONO), j(ClNO$_2$) and j(O^{1}D) are the annual mean of each hour with the MDAF metric applied, to account for local influence on solar fluxes. Shading for all data represents the uncertainty determined from MDAF derivation methods, discussed in Sect. 3.3.*"

Section 3.4 and 3.5: Production rate of OH radicals / Production rate of Cl atoms: That HNO3 photolysis is insignificant (line 290) as an OH precursor is by no means new information and could have been estimated from clear sky summer maximum OH production rates alone. The impression is that HNO3 was included in this study only because it was measured.

We agree that the demonstration here that HNO_3 photolysis is a minor OH production pathway is not new; however given this study was looking at NO_y, the authors feel that it is not irrelevant to include. As mentioned in our response to previous comments, this parameter has not yet been estimated at Auchencorth Moss, and since its concentration is already an established long-term measurement at this site, it has been included, alongside its propagated uncertainty (including that from concentration measurements and MDAF derivation).

Section 3.4 and 3.5: Production rate of OH radicals / Production rate of Cl atoms: The explanations in lines 297-305 regarding the different seasonal dependencies of p(OH) from O3 and HONO are not reproducible. Cloud effects may be a factor but the main seasonal difference is that j(O1D) and j(HONO) depend differently on solar elevation. The diurnal variations of p(OH) from O3 are probably not the same in summer and winter (line 303). The authors will notice that when they multiply the winter data with 25 (line 304).

We thank the reviewer for pointing out this inaccuracy. We have revised this paragraph in the manuscript to more accurately reflect the likely explanation for these differences, attributing them to solar elevation *c.f.* the presence of overcast cloud. The mention of the diurnal variation of $p(OH)_{O_3}$ was not intended to imply that the diurnal cycles were completely identical in summer and winter, as we are aware this is not the case. We aimed to illustrate the point that for all seasons, the diurnal cycle of $p(OH)_{O_3}$ has broadly the same bell shape, tracking the solar intensity (*c.f.* $p(OH)_{HONO}$ which is larger in the morning). This has been rectified in our revised manuscript.

Section 3.5: *"…Despite this, the greatest rates of $p(OH)$ are still observed in the summer, with seasonal average peak in $p(OH)_{O_3}$ at 13:00 (UTC), at approximately 1.7 x10⁶ radicals cm⁻³ s⁻¹, around half the rate observed in Melbourne, Australia in March (Ryan et al., 2018). These rates are comparable when a MDAF is not applied, due to similar concentrations of O₃ (~54 µg m⁻³ average in Australia). In the same season at Auchencorth Moss, $p(OH)_{HONO}$ reaches a maximum, approximately half that of $p(OH)_{O_3}$, at 09:00 (UTC; ~5 hours after sunrise). As concentrations of HONO are higher in Melbourne than at Auchencorth Moss, $p(OH)_{HONO}$ is around 8 times greater. A similar pattern is observed in spring (Fig. 8), where $p(OH)_{HONO}$ is greater in the early morning hours (~04:00-09:00 UTC), before $p(OH)_{O_3}$ increases to a comparable level in the middle of the day, closely following the diurnal cycle of light intensity and peaking when shorter wavelengths of light are more prevalent. This broadly similar diurnal pattern of $p(OH)_{O_3}$ is observed in all seasons, but a difference of ~20 is observed between peak $p(OH)_{O_3}$ in summer and winter, despite similar concentrations of O₃ (61.0 µg m⁻³ and 57.1 µg m⁻³, respectively). This is a consequence of the change in solar elevation between the two seasons. During this study, the minimum SZA (complementary to the solar elevation angle) in winter is 64° c.f. 32° in summer, meaning the sun is further from the zenith and lower in the sky. This results in a longer path length of light through the atmosphere, and increases the probability that light will be scattered or absorbed (e.g. by clouds or aerosols) before reaching the point of observation. Consequently the shorter wavelengths of light necessary for O₃ photolysis (≤ 340 nm) readily scatter before reaching ground-level, c.f. the longer wavelengths*

required for HONO photolysis ($305 \leq \lambda \leq 420$ nm). For this reason, over all daylight hours in winter, $p(OH)_{HONO}$ consistently exceeds $p(OH)_{O_3}$ by a factor of ~5."

Section 3.4 and 3.5: Production rate of OH radicals / Production rate of Cl atoms: The comparison of the obtained p(OH) with those from a single study in Australia is arbitrary. That HONO photolysis is a significant or even dominant OH precursor (at ground level) is well known and was discussed in many well designed studies before. The current paper gives little new insight as the quality of the HONO measurements remains unclear as well as local NOx levels that could classify the results.

We agree with the reviewer that HONO as a source of OH at ground level is not a new finding, and although there are numerous studies showing this, these rates have not yet been quantified at Auchencorth Moss. Long-term HONO measurements are spatially infrequent (particularly *c.f.* O_3), making this an important dataset (unique in the UK) with which to test our understanding of this photolysis reaction, and the application of MDAF. The comparison to the recent work by Ryan *et al.* (2018) in Melbourne, Australia was deliberately included as context for our results, since these authors explicitly present $p(OH)_{HONO}$ and $p(OH)_{O_3}$ rates calculated using the same methodology as this study. We have reduced this discussion to a short comparison between peak rates reached (see revision in quote from Section 3.5 in response to previous comment).

We appreciate the suggestion made by the reviewer to include further discussion of the concentration measurements used. We have revised the manuscript to include further discussion of the quality of the gaseous MARGA measurements used (see quote from Section 3.1 below), as well as annual average NO_x concentrations measured at Auchencorth Moss, from a manuscript currently in preparation about NO_x measurements at the site.

Section 3.1: *"Annual average concentrations of NO_2 and NO were 2.84 and 0.18 µg m^{-3}, respectively (Thermo Scientific 42C NO-NO_2-NO_x analyser, ThermoFisher, USA; Cowan et al., in prep.)."*

Cowan, N., Leeson, S. R., Twigg, M. M., Jones, M. R., Harvey, D., Simmons, I., M., C., and Braban, C.: Assessing the bias of molybdenum catalytic conversion in the measurement of NO_2 in rural air quality networks, in preparation.

Section 3.1: *"Median HONO concentrations show far less diurnal and seasonal variation, but a greater interquartile range of concentrations for each hour in the summer. Larger concentration episodes were observed in the spring and summer months, particularly July, reflected by the largest seasonal mean and median concentrations occurring in summer (0.065 and 0.096 µg m^{-3}, respectively).*

MARGA measurements are predicted to overestimate HONO concentrations, as a result of heterogeneous chemistry of NO_2 on inlet surfaces and the wet rotating denuder (WRD). This potential overestimate has not yet been quantified at Auchencorth Moss, but the nearest geographical comparison (~8.5 km NE at Easter Bush) showed that a Gradient of Aerosols and Gases Online Registrator (GRAEGOR, ECN, NL; with the same sampling and analytical method as MARGA) recorded measurements ~6% higher than a co-located Long Path Absorption Photometer (LOPAP), an artefact-free HONO measurement method (Ramsay et al., 2018). In contrast, MARGA measurements in Melpitz, Germany (Stieger et al., 2018), show this artefact to be 58% (Ren et al., 2020). The length of the inlet plays a large role in the

artefact potential, with the longer inlet at Melpitz providing a greater surface area for heterogeneous reactions of NO₂ to occur. The inlet length at Auchencorth Moss lies between that used at Easter Bush and Melpitz, so it is anticipated that the potential interference in concentration is likely to be between these two values.

Mean and median HNO₃ concentrations were largest in the spring (0.16 and 0.10 µg m⁻³, respectively), due to a large peak in mid-April reaching a maximum of 1.45 µg m⁻³. Daytime HNO₃ is likely to be underestimated, as it is expected that there will be losses of HNO₃ to the inlet, although the magnitude of this loss at Auchencorth Moss has not yet been quantified. A study using a similar set-up to Auchencorth Moss reported that HNO₃ was ~50% less than a standard filter method for sampling HNO₃ (Makkonen et al., 2014). Nocturnal MARGA measurements of HNO₃, on the other hand, have been shown to include positive interference from the heterogeneous hydrolysis of N₂O₅ (Phillips et al., 2013). However since nocturnal filter radiometer measurements are below the detection limit at night, this interference is not predicted to affect $p(OH)_{HNO_3}$ rates presented in this study."

Section 3.4 and 3.5: Production rate of OH radicals / Production rate of Cl atoms: As was noted already in Section 2.4.3 the discussion of Cl production rates based on devised diurnal concentrations is too speculative. So the lengthy discussion on possible diurnal or seasonal variations of Cl production at the site is not productive. That ClNO2 photolysis can lead to an increased VOC oxidation in particular during morning hours has been discussed in a number of previous studies, however based on ClNO2 measurements. ClNO2 concentrations are typically extremely variable. Compared to that potential uncertainties related with photolysis rate coefficients seem to be a minor problem. The final sentence in line 345 intended to emphasize the (potential) impact of Cl atoms for the radical budget at the site is also misleading. The fact that Cl atoms react faster with many VOCs than OH is secondary. Ultimately they both react mostly with VOCs and what counts are the production rates.

We would like to thank the reviewer for this input. Although we were aware of the limitation of using estimated ClNO₂ concentrations we had originally decided that inclusion of a $p(Cl)_{ClNO_2}$ rate estimation would provide useful additional comparison with the other radical production rates derived for the Auchencorth site. However, following comments from both Reviewer 1 and 2, we accept that there is too much conjecture in these estimations of Cl radical production. Therefore this section and its associated figures (Sect. 3.5 and Figs. 2 and 10, submitted manuscript) have been removed from the revised manuscript.

Section 3.4 and 3.5: Production rate of OH radicals / Production rate of Cl atoms: Overall the sections on the radical production rates are not very conclusive. The production rates are important parameters but they are just a small fraction of production and destruction rates during daytime that make up tropospheric photochemistry. So the absolute numbers are difficult to interpret unless you run a box model for comparison or you manage to extract these parameters from an operational model for this location. Moreover, this work is not about the concentrations of the precursors and whether or not they are represented correctly in current models. If you would just discuss the photolysis rate coefficients, a very similar picture would emerge regarding the importance of local effects on radiation. In accordance with that, the whole introduction is concerned with radiation, not with radical production rates.

The purpose of including these radical production rates was to demonstrate the impact that MDAF can have on further calculations of photochemical parameters, as well as a potential useful application of long-term *j*-value measurements at a site (in this case, Auchencorth Moss). The absolute quantities of $p(OH)_{O_3}$ and $p(OH)_{HONO}$ may be difficult to interpret alone, but are useful for comparison against one another and similar studies where these values are necessary.

Although the production rates compared here (from HONO and O_3 photolysis) comprise a small fraction of the overall tropospheric photochemistry taking place at the site, they are fundamentally important as sources of local OH radical formation. It is therefore crucial that these are determined accurately in a chemical reaction scheme to prevent propagation of large errors in further calculations. As we show in our study, application of MDAF reduced both $p(OH)$ rates determined for Auchencorth Moss by ~40% throughout the year compared to a basic cloud-free model representation, which is a very significant. Inclusion of this metric provides a minimal contribution to computational cost *c.f.* an extensive radiative transfer scheme that also needs accurate cloud cover, making it a useful alternative. We have revised the manuscript to improve clarity of these points.

Section 2.5: *"The impact of a locally-driven MDAF is demonstrated here through the context of OH radical production rates at Auchencorth Moss, from the photolysis of sources in existing long-term measurements at the site including O_3 and two NO_y species: HONO and HNO_3."*

Section 3.6: "*Accurate j-values are integral to accurate assessment of air quality, in particular to photolytic production of radicals and subsequent secondary pollutants which negatively impact both human and environmental health, including tropospheric O_3 and particulate matter. Radiometer measurements will consequently have immense value in supporting atmospheric chemistry measurement and modelling. A demonstration of the application of MDAF at Auchencorth Moss (Sect. 3.5) shows that where concentrations of relevant atmospheric precursors are co-located with long-term filter radiometer measurements, other metrics like the production rate of OH radicals can be quantified. These can provide additional routes for model validation and assessment, as these parameters are fundamental in model representations of tropospheric photochemistry.*"

Section 3.6 and 3.7: Implications of the MDAF metric / Conclusions: The paragraph following line 351, "In contrast, Sommariva et al. report: : :." is confusing: MCM parametrizations, different altitudes, and different seasons all mixed together. I don't think this arbitrary citation is necessary to emphasize the need for locally measured photolysis rate coefficients for a proper analysis of field data.

We agree with the reviewer about the lack of clarity in our original phrasing. However we do believe this citation is relevant as it provides a view of the discrepancies that can occur when measurement and model locations are not the same, in contrast to this study. We have reworded this section of the manuscript to improve clarity.

Section 3.6: *"This work, together with the recent study by Sommariva et al. (2020), highlights the importance of coincident measurement and model locations when generating a local MDAF metric."*

Section 3.6 and 3.7: Implications of the MDAF metric / Conclusions: The paragraphs line 364-370 and 387-390 where "long-term multi-site radiometer measurements" (line 364) are suggested, apparently draft a main conclusion of the study which is also implied in the title. However, I don't think such an investment would be justified based on the current analysis.

The investment justification is an opinion rather than a critical comment on the science presented, and the reviewer may have a different opinion to the authors.

Section 3.6 and 3.7: Implications of the MDAF metric / Conclusions: The authors themselves show that a fairly compact empirical relationship exists between j(NO2) and solar shortwave radiation (Trebs et al., 2009). Even though this parameterization is not perfect, it will nevertheless cover a large fraction of the most important local cloud effects.

Although the empirical relationship is good, it is also valuable to understand the accurate details of local atmospheric chemistry, particularly as pollutants such as NO_2 are changing with policy or air quality management interventions. Operation of filter radiometers are straightforward to set-up and operate, and would provide a valuable dataset at sites in existing long-term networks, such as the EMEP network.

Section 3.6 and 3.7: Implications of the MDAF metric / Conclusions: As the authors also state, pyranometers are already used within existing networks and have a high degree of standardization. So to "provide a higher spatial density of model-measurement jvalue comparison points in the UK" (line 387) a first step could be to use these already available long term data from many stations to evaluate the model data and to investigate the impact of potential shortcomings of model-predicted j-values. If it then turns out that the j(NO2) derived from the pyranometer data are not accurate enough for this purpose you would have a point. But I doubt this will be the case.

The authors thank the reviewer for their comments and thoughts on the future work.

For "supersites" like Auchencorth Moss, having a long-term on-site set of radiometer measurements would greatly improve model representations of the site for the many campaigns or studies that take place there on account of the quantity of instrumentation co-located there. Similar sites in existing air quality networks would also benefit from this addition. Pyranometer measurements can be used in local photochemistry modelling, however these are approximations with varying degrees of accuracy. To understand or validate model chemical mechanisms at given sites, *j*-values measurements are better. A UK-wide study using the pyranometer network would be very interesting.

Specific comments

Line 5: "In this paper, locally representative photolysis rate constants (j-values) for these molecules are shown to be critical for quantifying and understanding the rate of radical production in a local atmosphere." Is this a new insight? j-values are routinely measured since decades during photochemical campaigns for exactly that reason.

Although *j*-values have been measured in campaigns for decades, long-term measurements are much rarer and provide the volume of data to address chemistry in a changing physical and chemical atmosphere. We agree that this is not a new insight as a standalone phrase, and so have reworded the abstract accordingly.

Abstract: "*Locally representative photolysis rate constants (j-values) for these molecules are critical for quantifying and understanding the rate of radical production in a local atmosphere.*"

Line 55: "Cl radicals are extremely reactive…, Cl has a significant effect on local tropospheric oxidation." I think this statement is misleading. Low Cl concentrations may be a result of the high reactivity of Cl but the importance of Cl depends on its production rate. That it's more reactive than OH is unimportant (moreover, OH is regenerated which makes it the key oxidant).

We had included this statement to emphasise that Cl should not be ignored when considering the oxidising capacity of the local atmosphere. However, we agree with the points made by the reviewer, so to avoid any further potential misinterpretation, we have revised this part of the manuscript.

Section 1: "*Along with OH, Cl radicals are extremely reactive with VOCs, where rate constants can be up to an order of magnitude greater than equivalent reactions with OH (Monks, 2005; Young et al., 2012). Therefore, even in low abundances, Cl plays an important role in local tropospheric oxidation (Riedel et al., 2014; Bannan et al., 2015) but this varies with its production rate, as Cl is not as easily regenerated as OH.*"

Line 102: "…when measured AOD and NO2 concentrations are included in model inputs, actinic flux is reasonably well predicted…" It should be clarified that this statement probably refers to clear-sky conditions.

We agree with this comment, and have revised the statement referencing to Palancar *et al.* (2013) accordingly.

Section 1: "*Palancar et al., (2013) demonstrate that when parameters measured within the planetary boundary layer (PBL) are included in model input (including AOD, O_3 column, single scattering albedo and NO_2 concentrations), actinic flux is reasonably well predicted on cloudless days, and the main source of uncertainty is then attributable to σ and Φ.*"

Line 134: Give a reference where the Bentham instrument and its uncertainties are described or provide more information.

Publications where the Bentham spectroradiometer used for calibration were also deployed are now referenced, and the overall measurement uncertainty has been detailed and cited in the text.

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. This mid-summer period was selected to provide calibration over the maximum range of ambient incident radiation. The direction of the filter radiometer was turned 180° mid-way through this period, in order to calibrate each dome separately. Overall uncertainty in the spectroradiometer measurements was ±5%, the sum in quadrature of uncertainties in instrumental parameters (including cosine and actinic head responses), measured wavelength and general setup."*

Line 170: Why is Section 2.4 entitled "Theoretical calculations"? In this Section you combine measured data with those from the TUV model.

This section was primarily titled as theoretical as it includes the production rate of Cl atoms from $ClNO_2$, which at present has not been measured at the site, making all estimates of production rates theoretical. This section header has now been removed completely (see response to previous Section 3.5), and all subsections within it have been changed to individual sections.

Line 223: "UK seasons are defined…" Is this definition useful with regard to radiation measurements?

We included this clarification to ensure that all readers would be able to easily identify exactly which data were included in each of the seasonal averages presented.

Line 247, Eq. (9): Convert to units used in this work.

This comment is no longer applicable, as this equation has been removed from the revised manuscript (see response to comments on Section 3.2).

Line 258: "The MDAF values…was largest during sunrise and sunset hours" This is explainable by an instrumental artefact. At low sun direct radiation can strike the upper and the lower dome simultaneously unless your "artificial horizon" is large enough to prevent this. For the common Metcon instruments it is not.

We are aware of these artefact potentials in total filter radiometer measurements from 4-π instruments. However we believe, as we mention in the submitted manuscript, that the large MDAF values are largely due to extremely small non-zero values during these hours, where *j*-values are expected to be small and filter radiometer measurements are very close to the detection limit. Following a similar comment by the Reviewer 2, we have stated this potential

interference in the filter radiometer section of the methods (Section 2.2), and at this later point in the manuscript, which is in Section 3.3.

Section 2.2: *"This restriction is not perfect as increased sensitivity can be observed near the horizon in 4-π 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)."*

Section 3.3: *"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."*

Line 260: "..the adjustment factor was greatest in the morning and steadily decreases throughout the day until sunset". Is there an explanation for this behaviour? The mean diurnal variations of j(HONO) and j(ClNO2) in Fig. 7 don't show this.

The decrease referred to was from the annual average MDAF values, and was a small difference between sunrise and sunset. We do not have an explanation for this, so to avoid any misleading interpretations, we have removed this section from the manuscript.

Line 294: I do not see the 71% decrease in Fig. 8. It looks more like the overall 40% decrease stated in line 293.

The stated 71% decrease referred to the hourly values, where the maximum reduction in $j(O^1D)$ through the year was 71% in the summertime measurements, not the average decrease of ~40%. We appreciate the reviewer asking for clarification of this, and have updated the sentence accordingly.

Section 3.5: *"The largest decrease in measurements as a result of MDAF application occurs in the summer months (~50%; see Table 3), as the cloud-free model conditions are an inaccurate representation of summertime conditions at Auchencorth Moss."*

Line 385ff: "The enhanced contribution…" Please reconsider this statement taking into account the different dependencies of j(O1D) and j(HONO) on solar elevation. The clear-sky TUV results will show the same effect.

We agree with the comment made by the reviewer, and have addressed this in our response to comments on Sections 3.4/3.5. We have revised the text in the conclusion to reflect this.

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 O_3 photolysis, relatively more than the longer wavelengths contributing to HONO photolysis."*

Figure 3: The gap in the j(NO2) data should be noted in the caption.

The relocation of the filter radiometer to Manchester for the calibration (see response to Section 2.2) has been specified in the caption to Fig. 2 in the revised manuscript (Fig. 3, submitted manuscript).

Figure 2: "…The $j(NO_2)$ 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 6: What can be recognized in this figure are daily maximum values rather than hourly data. A correlation would perhaps be more insightful. The gap in the data requires an explanation.

Plotting a correlation would be a useful interpretation; however we plotted this figure (Fig. 5 in revised manuscript) to illustrate the temporal variation in both measured and modelled $j(NO_2)$ throughout the year, and to show occasions where measured $j(NO_2)$ exceeded the cloud-free TUV model estimates. The main example of this is in early February where upwelling contributed more due to the larger surface albedo, shown by the inset Phenocam image. These aims would be harder to present as easily in a correlation plot. The gap in data, due to the relocation of the filter radiometer (see response to Section 2.2), has been addressed in the revised caption for this figure.

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…."

Figure 7, 8, 9: The 95% confidence intervals are virtually invisible and it's unclear what they represent.

Following the inclusion of Section 3.3 (revised manuscript), we have revised the figures in the revised manuscript. The shading now represents the total error in each of these values, propagated from errors in concentration measurements, and error in MDAF application (see response to Section 2.4.1).

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