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Interactive comment on "Use of filter radiometer measurements to derive local photolysis rates and for future monitoring network application" *by* Hannah L. Walker et al.

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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 However, the study in my view has major deficiencies and should not be published in the present form.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.

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 short-term 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).

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). 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). 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.

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.

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).

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. 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?

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).

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.

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.

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.

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).

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.

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.

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.

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.

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 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. 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 j-value 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.

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.

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).

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.

Line 134: Give a reference where the Bentham instrument and its uncertainties are

described or provide more information.

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

Line 223: “UK seasons are defined. . .” Is this definition useful with regard to radiation measurements?

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

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.

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.

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

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.

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

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.

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

References

N. H. Schade, A. Macke, H. Sandmann and C. Stick, Enhanced solar global irradiance during cloudy sky Conditions, Meteorologische Zeitschrift, Vol. 16, No. 3, 295-303 (June 2007)

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