Atmos. Chem. Phys. Discuss., 14, C8545–C8558, 2014
www.atmos-chem-phys-discuss.net/14/C8545/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterisation of $J(O^1D)$ at Cape Grim 2000–2005" *by* S. R. Wilson

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Received and published: 28 October 2014

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Response to Referees

28 October 2014

I thank both referees for their very useful comments. In the following text my responses are in bold. The supplementary material contains an updated version of the paper (apologies for the formatting issues) with the additional discussion on errors appended.

1 Referee #1

Specific comments P 18390, lines 9-11: "Factors dependent on ...." The statement is unclear.

Altered

P 18390, line 17: Replace "at higher solar angles" by "larger solar zenith angles" to avoid confusion with high sun conditions.

Altered

P18390, line 18: The final sentence of the abstract is unclear.

Altered - confusion caused by the term "reduced" - now "adjusted"

P 18391, line 7: There is a work by Rohrer and Berresheim where continuous measurements of OH and J(O1D) over a five-year period are reported (Rohrer and Berresheim, Nature 442, 184-187, doi:10.1038/nature04924, 2006).

Thank you for the reminder! Included and text altered

P 18391, line 9: Use notation O(1D), as in (R1).

Missing brackets added.

P 18391, line 13: Even if you exchange (R2) and (R3) in that line, Q is not the branching ratio between reactions (R3) and (R2) but the contribution of the water reaction (R3) to the total loss rate constant of O(1D) (or the yield of OH if multiplied by two).

I have changed the wording to the more explicit description!

P 18392, line 1: The terms “actinic flux” including quotation marks and “solar flux” are perhaps misleading. In recent literature “spectral actinic flux density” is the preferred term for the first and “spectral radiance” for the latter quantity.

Willing to take the advice and have altered it.

P 18392, line 19: “If it is assumed ...”

Done

P 18393, line 20: The title of the subsection is misleading. The section describes basic approaches of spectral radiation measurements.

Title altered.

P 18394, line 6: The title is misleading. ”O(1D) production” is not a synonym for J(O1D). The product of J(O1D) with the ozone concentrations corresponds to the O(1D) production rate.

Changed - poor wording choice on my part.

P 18395, line 25 ff: At the end of section 2 there should be a clear statement regarding the accuracy of the measured global, diffuse, and (calculated) direct spectral irradiance that are later used for the conversion to spectral actinic flux densities. I think it is important to distinguish between the uncertainties of the measurements and those of the conversion. Both uncertainties are probably underestimated as also supposed by Referee 2. Moreover, the issue that scanning instruments can provide wrong spectra under variable external conditions (section 1.1.2) is further enhanced here where alternating, scanning measurements with low time resolution are used to derive the direct sun irradiance by subtraction.

Agreed. I have altered this section substantially, attempting to separate the various components to the total error budget.

P 18396, Eq. (7): The origin of the formula is unclear. Kylling et al., 2003 merely present values of a for various (clear sky) conditions in a figure. The value “2.01” implies a precision that is certainly not justified. In fact, 1.8±0.3 appears to be more appropriate if no distinction between different atmospheric conditions is made. It should also be noted that the isotropic a= 2 is closer to that for the Rayleigh atmosphere than to cloudy conditions (a $\approx$1.7).

Poorly phrased and interpreted by me. I have altered this section, and hopefully clarified the text and calculation sufficiently.

P 18397, line 22: The comparison with the filter radiometer data is not very convincing because it shows only three (typical?) days from a four-week period. Even when the accuracy of the filter radiometer is rather limited, a thorough comparison could reveal systematic differences between the two measurement principles. The filter radiometer data probably have a higher time resolution and by averaging over the scanning periods of SRAD, e.g. the scatter induced by changing cloud cover could be investigated in a correlation plot or the dependence on solar elevation in a plot of ratios against solar zenith angles.

Agreed. I have actually looked into this in more depth, but unsatisfactorily. I have asked for the data from the Creasey paper and was directed to the BADC archive, which did not contain the published data record. I was unable to get further communication from the authors, and so limited my comparison to this one figure. I propose removing this comparison entirely.

iP 18398, line 9: I wonder if episodes of increased aerosol load could be responsible for the lower measured values. Moreover, also ozone column data from satellites have a limited spatial and temporal resolution that can be responsible for model/measurement differences. I presume that for the simulated J the same absorption cross sections and quantum yields were used (including the influence of ambient temperature).

Good thoughts - Aerosol scattering is unlikely, AOD < 0.09 . Note that their median AOD ranges between 0.1 - 0.3 (monthly) (mean 0.15 - 0.4). CG has 0.03 - 0.1 (median, 368nm) . Yes, the absorption cross section and cross sections are the same. Ambient temperature is used. I note regarding ozone columns that this is also calculated from the ground based observations, and there is not a large discrepency.

P 18399, line 3: There is a work by Gerasopoulos et al. (J. Geophys. Res. 117, D22305, doi: 10.1029/2012JD017622, 2012) also reporting about a five-year period of J measurements.

Apologies for not including this. It is now mentioned. Comment on the difference between the two sites in terms of AOD also included in the site description.

P 18402, line 11: What do you mean by "returned a significant value"? The fact that the returned error limit is small does not mean that the approach is correct in particular when the fit quality does not improve. The clear sky index probably ranged between 0.9 and 1.5 which means that scaling factors range between 1.02 and 0.93, far too small to describe the strong variations induced by clouds. Under conditions of scattered clouds there are enhancements as well as reductions of J(O1D) at indices probably already

well above unity. On the other hand, overcast conditions with low and high cloud optical thicknesses will all range around the maximum index leaving no room for cloud induced variations.

I agree and it was my intention with this wording to imply that the approach is not useful. I have made this comment more explicitly.

P18404, line 8: "... produced significant fits that did not significantly..." please rephrase.

Done

2 Referee #2

The comments of the reviewer are most constructive, and raise a number of very useful points. These are discussed in detail below with my comments in bold.

3 Error Analysis

My main criticism of the manuscript is that the uncertainty of the photolysis rate data derived from the author's OL752 spectroradiometer is not clearly and completely described. ... specified in the manuscript.

Agreed with apologies! The error estimates were for the calibration of global and diffuse irradiance, and clearly insufficient. I have therefore reworked the error analysis, which ended up a rather long document given the length of the rest of the paper. I have therefore created that as a separate document to be included as supplementary information. I have altered the text in the main document to include the primary conclusions - that the uncertainty in the overall value is approximately 23%. This reduces to 12% when comparing to the model,

where some of the sources of error are common.

Specific comments

P18390, L9: For clarity, the sentence should be changed to “Variations in solar zenith angle and total ozone column explain 87% of the observed variability in the measured photolysis rates.”

agreed - text altered.

P18392, L10: The title “Angular response” does not fit the contents of the subsection well. A better title would be: “Estimate of actinic flux from irradiance measurements”

Agreed - changed suggestion into the active tense though.

P18391, L11-13: Technically, the branching ratio Q is the ratio of Reactions (R3) and (R2) and not the ratio of Reactions (R2) and (R3). (Q is small when the H2O concentration is small). I suggest to reverse the Reaction equations (R2) and (R3), but leave line 13 as it is.

I have implemented a version of the recommendation of reviewer one that clarifies this issue.

P18393, L2-7: Eq. (6) is hard to understand intuitively. I suggest to replace Eq. (5) with: $F = aE\downarrow + E0 = a(E - mE0) + E0$ and replace the sentence “If the diffuse . . .from.” with: “Eq. (5) can be rearranged to the following form suggested by Kazadzis et al. (2004).”

Implemented.

P18393, L9. The sentence “The ratio a is reasonably well behaved” should be improved because “well behaved” is not a good quantitative term. A range for a should

be provided, or alternatively, Section 3.1 should be referenced, where the range of a is discussed.

Reference to section 3.1 inserted.

P18395, L4: Please describe how the diffuser is shaded. Is it shaded with a shadowband or a small disk, approximately the angular diameter of the Sun, that is moving with the Sun’s position?

Shaded with a small disk - text added and specific reference added to where more details may be found.

P18395, L7: The paper by Forgan (1998) describing the ratio-Langley technique was published in a CSIRO report and is not easily accessible. Instead (or in addition to), the Applied Optics paper (Wilson and Forgan, 1995) should be cited.

For simplicity changed to Wilson and Forgan (1995) - I agree that this is much easier to find and the original work is cited within the 1995 paper.

P18395, L15: Change “alternative” to “alternating”

Agreed and implemented.

P18395, L21. What input diffuser is described here? According to Lines 12-14, two diffusers were in use and the first diffuser was replaced in October 1999.

Agreed - both diffusers were made from PTFE and the comment applies to both. I have therefore changed the text to reflect this.

P18396, L3: The measurements are affected by the cosine error of the instrument’s diffuser. Hence, a correction is necessary before Eq. (5) can be applied. It should be briefly described how this is done.

A brief paragraph is included in the methods to explain.

P18396, L11: I presume this formula refers to clear sky. If so, please specify. a for

cloudy sky is in the order of 1.65 to 1.75, see Figure 3 of (Kylling et al., 2003) and Table 2 of (Kazadzis et al., 2004). Considering that clouds are the norm at Cape Grim, a value in this range should be applied most of the time. It is not clear whether this was done. When calculating a with Eq. (7), the solar zenith angle has to be larger than 80$\circ$ for a to become smaller than 1.75. So if Eq. (7) was used for all conditions, a would be too large in the majority of cases (i.e., cloudy conditions).

Agreed. This section of the text is modified to reflect this. (And the software modified and all data recalculated.)

P18396, L12: Please quantify "small". As mentioned earlier, the effect of the uncertainty of a on the total uncertainty of F should be quantified.

This is now explicitly included in the error analysis section and the text here modified to reflect this. Note that the fuller details are provided as supplementary indormation.

P18396, L20: The calibration of SRAD has likely a considerably uncertainty below 305 nm due to the limitations of the ratio-Langley technique below this wavelength. If ignoring measurements below 298 nm may cause an error of up to 5% in J(O1D), the (rather uncertain) contribution from the range between 298 and 305 could conceivably cause systematic errors in F of larger than 5%. This should be quantified.

This has now been included in the error analysis section.

P18396, L26: The sentence "The calibration uncertainty of the measurements ...diffuse irradiance" is not clear. What does the "calibration uncertainty" of 5% include? Is it the uncertainty in finding the intercept with airmass zero of the Langley analysis, the uncertainty of the extraterrestrial spectrum, or the combined uncertainty of both components? What is the uncertainty (in %) caused by the "variability in the calibration observed from the multiple calibrations carried out during the 6 years"? Please specify the uncertainties of the three components separately plus the combined uncertainty.

As mentioned in my general comments, I suspect that the combined uncertainty is larger than 8% if all error sources are taken into account.

An error analysis is now included as supplementary material, with a summary table of uncertainties.

P18397, L23: The good agreement of the results of SRAD and the filter radiometers is a bit surprising considering that the uncertainty of the filter radiometers is quoted to be 20-30%, and the uncertainty of the SRAD data is likely larger than the quoted uncertainty 8% and also biased low by 5% because of the omission of spectral measurements below 298 nm (P18396,L24). So the good agreement could be serendipity. Figure 1 only shows results for a 3-day period. Were the results similar for the rest of the campaign?

The agreement with this dataset remains good across the 30 days. However, in light of the comments of both reviewers I have removed this comparision (1 paragraph and 1 figure). Despite repeated attempts to obtain the data presented in Creasey I have been unable to get a copy of the calibrated data. (A copy of data does reside in the campaign database, but it is not the same).

P18398, L8: If the disk of the Sun is unobstructed, and clouds are in the vicinity of the Sun, radiation is typically enhanced, not reduced.

True - and the wording has been altered to allow for changes in both directions

P18398, L16-20: If there are no instrument failures, I would expect at least 120 data records in each 24 hour bin per month (30 days times 4 records per hour). I would assume further that instrument failures would impact several consecutive hours or days. I therefore don't understand how there can be bins with no data that are between adjacent bins with data. This would mean that there is not a single measurement in a given hour for an entire month but enough measurements in the bin associated with the hours before and after the given hour. Please clarify.

I agree entirely - this situation only arises when there are significant instrument failures during the particular month of a particular year, leading to very low data amounts. This occurred for 2 hours, leading to insignificant changes in the data as presented here. I propose deleting the phrase.

P18398, L20: It would have been better if the sum rather than the average of the 24 hourly averages had been calculated. Using the sum, the result would be a daily dose. Using the average makes results harder to interpret because day lengths are different in the summer than during winter.

The sum is 24 times the average, given that all 24 hours are included in the average calculation. I suspect that I have not understood the reviewers wishes here.

P18399, L5: How is the variability defined? Is it standard deviation to average?

Yes, and words added to state that for clarity.

P18401, L2-9: It can have several reasons when measurements exceed the clear sky model value: enhancement by clouds (as described in this paragraph), measurements that are too large, model results that are too small, or a combination. While Figure 2 indicates that clear sky measurements agree well with the model, the difference at large solar zenith angles (small J(O1D) values) is difficult to see. It would therefore be good to describe the bias between measurements under clear sky and the associated model values as a function of solar zenith angle. The apparent increase of cloud enhancement as a function of solar zenith angle (Line 7) could be an artifact of a solar zenith angle dependent change in the bias between measurement and model.

While I had mentioned this broadly at line 20, it perhaps needs stating earlier - so I have included that comment from earlier on. I agree the "clear sunny days analysis could be informative, but with the two days shown in figure 2 you get conflicting results - 3 October you get good agreement (within the difference

between morning and afternoon) and on the 1 February 2000 the model values lie some 15 % low.

P18401, L12: Change "greater" to "smaller"

Agreed and done.

P18402, L11: Why "reduced R2"? The sentence indicates that inclusion of the "Clear-sky Index" term improved the fit (albeit by not by a lot), so R2 should have increased, which is also suggested by the phrase in the parenthesis "(increases of 0.0005)".

Statistical jargon taken from the analysing software. The "reduced R2" is the R2 adjusted for the changes in degrees of freedom. I have changed the wording to "adjusted R2" which is more common (and less ambiguous). I have also altered the wording in the abstract.

P18402, L20: Please explain what is meant with "the chemical outcome".

Changed wording to "The impact of the photolysis measured here on the chemical composition of the atmosphere"

P18407, L20: The Cape Grim station is located on a cliff. Is the station often shrouded in clouds while the ocean below is not, and could that lead to a systematic difference in J(O1D) compare to locations close to the ocean surface?

Not sure of the page number. Cape Grim is very rarely shrouded in cloud as cloud base is typically at or above 800m. I have included a statement to that effect.

P18403, L13-15: I don't understand the sentence "The reduction . . .cloud." For example, what does "at the average cloud factor of 0.8 to 0.9" mean?

Wording altered to clarify the terminology.

P18416 (Figure 5): The line for 350 DU is not "solid" but broken (and red).

Fixed!

Technical corrections Expressions such as “higher solar angles” (e.g., P18390, L17) are confusing. “Higher solar angles” means “higher solar elevation” (i.e., the angle measured from the hori- zon) for most people, while a larger angle measured from the zenith is meant here. I suggest to use only “large” and “small” in combination with “zenith angle” such as “. . . at larger zenith angles. . .” throughout the paper.

Agreed and implemented.

The word “cloud” is consistently used in singular. For example: “there can be cloud well away from the Sun” or “due to cloud”. Use of the plural would be more in line with other publications.

Altered.

P18394, L20: Change title to “Experimental setup”

Done

P18398, L12: Replace “of over” with “over”

Done

P18400, L6: I would say this the other way round: “. . .functions of the following form were fitted to the measured J(O1D) values.”

Done

P18400, L24: Change “low solar zenith angle” to “small solar zenith angle” (see also comment above)

Done

P18402, L12: Change “due the” to “due to the”

done

P18403, L12: Change “but close to” to “but the impact is close to”

Agreed

P18404, L8: Delete “significant”

Agreed