Response to Referees

November 27, 2014

I thank both referees for their very useful comments. In the following text my responses are in bold. The page numbers listed are those that are relevant for the included textdiff.pdf document. I enclose also an updated version of the paper and a "supplementary material document" with the additional discussion on uncertainty estimates. With this second document I am unsure of the correct formatting.

For the textdiff.pdf document there are two places where "latexdiff" failed that I could not repair. I have flagged those explicitly in the file.

1 Referee #1

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

Altered in accordance with the suggestion of reviewer 2. Page 2 line 9

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

Altered. Page 2, line 17

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

Altered - confusion caused by the term "reduced" - now "adjusted". Page 2, last line of the abstract.

P 18391, line 7: There is a work by Rohrer and Berresheim where continuous measure- ments 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. Page 3, line 8

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

Missing brackets added. Page 3, line 10

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. Page 3, line 15

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. Page 4 line 3, as well as elsewhere in the text - see heading 1.1 for example

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

Done. Page 4 line 22

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

Title altered. See page 6, heading 1.1.2

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) pro- duction rate.

Changed - poor wording choice on my part. Page 6 - heading 1.2

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 irradi- ance 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 section 3.1 substantially, attempting to separate the various components to the total error budget. I have included "additional material" to cover this in much more depth, and have removed some of the text in the main paper. Page 8 line 16+ and the additional pdf.

P 18396, Eq. (7): The origin of the formula is unclear. Kylling et al., 2003 merely present values of α 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 $\alpha = 2$ is closer to that for the Rayleigh atmosphere than to cloudy conditions ($\alpha \approx 1.7$).

Poorly phrased and interpreted by me. I have altered this section, reprocessed the data and hopefully clarified the text and calculation sufficiently. Page 8, line 16, new figure 1.

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. Removed figure 1 and associated text. Page 10 - heading 4.1 and the following text removed.

P 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 optical depth for the two days shown (UVA) varies between 0.01 (Feb 2000) and 0.16 (4 Oct 2003). Other days where the deviation between model and observation is observed the AOD lies within this range. I note the work of Gerasopoulos reports this effect for the Mediterranean. Their median AOD ranges between 0.1 - 0.3 (monthly) (mean 0.15 - 0.4). CG has 0.03 - 0.1 (monthly median, 368nm - there is a seasonal variation).

Yes, the absorption cross section and cross sections are the same. Ambient temperature is used.

Regarding ozone column errors. This could also be an issue. I have checked a number of days, using both the value derived from the midday calibration and the derived ozone column. The differences are up to 10DU, and not obviously in the direction that would explain the discrepancy. I have added words to this effect to the text (Page 10, bottom of the page).

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. Page 11 line 24

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. Page 15 - line 15

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

Removed the first 'significant', as recommended by referee 2, Page 17 - Conclusions line 7.

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 additional material information. I have altered the text in the main document to include the primary conclusions - that the uncertainty in the overall value is approximately 25%. This reduces to 12% when comparing to the model, where some of the sources of error are common. Page 9 paragraph 2 and the bottom of page 9.

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. Page 2 line 10

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. Page 4 heading 1.1.1 and including terminology recommendation from referee 1

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. Page 3 line 15

P18393, L2-7: Eq. (6) is hard to understand intuitively. I suggest to replace Eq. (5) with: F = αE↓ + E0 = α(E − μE0) + 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. Page 5 – line 6 and 8

P18393, L9. The sentence "The ratio α is reasonably well behaved" should be improved because "well behaved" is not a good quantitative term. A range for α should be provided, or alternatively, Section 3.1 should be referenced, where the range of α is discussed.

Text deleted and reference to section 3.1 inserted. Page 5 line 11

P18395, L4: Please describe how the diffuser is shaded. Is it shaded with a shadow- band 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. Page 7 line 10.

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. Page 7 line 13

P18395, L15: Change "alternative" to "alternating"

Agreed and implemented. Page 7 last paragraph - first line

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 - However, in response to the comments from both referees on the SOAPEX comparison I have deleted this comparison (and associated figure 1. Therefore no change is needed.

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 experimental section to explain. It is also mentioned in the additional material. See page7 paragraph 2

P18396, L11: I presume this formula refers to clear sky. If so, please specify. α 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 α with Eq. (7), the solar zenith angle has to be larger than 80◦ for α to become smaller than 1.75.

So if Eq. (7) was used for all conditions, α 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.) See page 8, First paragraph of 3.1 and also new figure 1.

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

This comment has been deleted. The uncertainty in α is now explicitly included in the error analysis section (additional information) and the text here modified to reflect this. Page 8 first paragraph of 3.1.

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. page 9, second paragraph and additional information

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 additional 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 mea- surements 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). (Page 9 last paragraph) 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 as the published figures).

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 from "reducing" to "altering" to allow for changes in both directions. Page 11 line 1

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. Page 11 - line 11.

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. Page 12 line 3.

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 changed "implies" to "suggests" (line 3 of section 4.4, page 14) and added two sentences to the bottom of the paragraph. included that comment from earlier on. While I agree the "clear sunny days analysis could be informative, but with the two days shown in figure 2 I 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. Hence the alternative approach presented at the bottom of the paragraph,

looking if the behaviour is consistent with what is known.

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

Agreed. Used "less than" rather than "smaller". Page 14 Second paragraph of section 4.2, line 3.

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. Page 15 line 14, and page 2, end of the abstract.

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

Changed wording to "The impact on atmospheric chemistry of the photolysis measured here on the chemical composition of the atmosphere". Page 16 line 4.

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?

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. Page 16 line 13.

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. I have now used estimates from the papers quoted by Calbo et al. for 50% cloud cover. Page 16, last line.

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

Fixed! Caption of now figure 4

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. Changes throughout the text. Particular example quoted see page 2, line 19

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. All mentions of cloud changed to clouds when not modified. Particular example is on page 10, line 15

P18394, L20: Change title to "Experimental setup"

Done. Page 7, header section 2.

P18398, L12: Replace "of over" with "over"

Done. Page 11 Section 4.2 Line 2.

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

Done. Page 13 just before equation 7

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

Done Page 13, line 20

P18402, L12: Change "due the" to "due to the"

done. Page 15, line 15

P18403, L12: Change "but close to" to "but the impact is close to"

Text altered. Page 16 , third paragraph line 3

P18404, L8: Delete "significant"

Agreed. Page 17 , conclusions line 7

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Characterisation of $J(O^1D)$ at Cape Grim 2000–2005

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Abstract

Estimates of the rate of production of excited oxygen atoms due to the photolysis of ozone $J(O^1D)$ have been derived from radiation measurements carried out at Cape Grim, Tasmania (40.6° S, 144.7° E). The measurements have a total uncertainty of < 25 %. These estimates agree well with ~~measurements made during SOAPEX-II and with~~ model estimates of clear sky photolysis rates. Observations spanning 2000–2005 have been used to quantify the impact of season, ~~cloud~~ clouds and ozone column amount. The annual cycle of $J(O^1D)$ has been investigated via monthly means. These means show an inter-annual variation (monthly standard deviation) of 9 %, but in midsummer and midwinter this reduces to 3–4 %. ~~Factors dependent upon~~ Variations in solar zenith angle and ~~satellite derived total ozone column explain 87~~total column ozone explain 86 % of the observed ~~signal variation of the individual measurements~~variability in the measured photolysis rates. The impact of total column ozone, expressed as a Radiation Amplification Factor (RAF), is found to be ~~~ 1.45~~~ 1.43, in agreement with model estimates. This ozone dependence explains 20 % of the variation observed at medium solar zenith angles (30–50°). The impact of clouds results in a median reduction of ~~14~~22 % in $J(O^1D)$ for the same solar zenith angle range. At all solar zenith angles less than 50° approximately ~~10~~1 % of measurements show enhanced $J(O^1D)$ due to cloud scattering and this fraction climbs to 25 % at ~~higher solar~~ larger solar zenith angles. Including estimates of cloudiness derived from Long Wave Radiation measurements resulted in a statistically significant fit to observations but the quality of the fit did not increase significantly as measured by the ~~reduced~~ adjusted R^2.

1 Introduction

It is widely recognised that the chemistry of the clean troposphere is driven by a few key oxidizing species, with a major contributor being the hydroxyl radical (OH) (Crutzen, 1974). The hydroxyl radical reacts rapidly with a wide range of compounds, including methane, CO, and hydrocarbons. The concentration of OH present in the atmosphere is always small, but

because of its high reactivity it can still play a dominant role in determining the atmospheric fate of organics. It has also long been realised that changes in the amount of OH in the atmosphere could have a profound effect on global air quality and there has been a long-term effort to develop techniques to measure the key chemical species (Heard and Pilling, 2003). The most direct measure is the concentration of OH itself. There are several techniques now in use for such measurements, including fluorescence, UV absorption and mass spectrometry (Heard and Pilling, 2003) although ~~none have been operated for long periods of time at a single site~~only one long term measurement set has been reported to our knowledge (Rohrer and Berresheim, 2006) .

The primary source of OH is through the photolysis of ozone to produce ~~O^{1}D~~ O(^{1}D) through the reactions:

$$O_3 + h\nu \xrightarrow{J(O^1D)} O(^1D) + O_2\left(^1\Delta_g, ^3\Sigma_g^-\right) \quad \text{(R1)}$$

$$O(^1D) + M \xrightarrow{k_2} O(^3P) \quad \text{(R2)}$$

$$O(^1D) + H_2O \xrightarrow{k_3} 2OH \quad \text{(R3)}$$

The ~~branching ratio between Reactions (R2) and (R3~~fraction of O(^{1}D) reacting with water (and hence producing OH) (Q) is given by:

$$Q = k_3[H_2O]/(k_3[H_2O] + \sum_i k_i[M_i]) \quad (1)$$

Here the summation is over the collision partners M_i, primarily O_2 and N_2. Q depends on the amount of water vapour, but typically around 10 % of O(^{1}D) produced reacts to form OH ($Q \approx 0.1$). This can be calculated provided atmospheric pressure and the water vapour concentration is known, since the rate constants have been measured (Sander et al., 2006).

The rate of ozone photolysis in Reaction (R1), $J(O^1D)$, can be described by:

$$J(O^1D) = \int \sigma(\lambda,T)\phi(\lambda,T)F(\lambda)d\lambda \quad (2)$$

which is the wavelength integration of $\sigma(\lambda,T)$, the (temperature dependent) absorption cross-section of ozone, $\phi(\lambda,T)$, the quantum yield of $O(^1D)$ production, and $F(\lambda)$, the "~~actinic flux~~spectral actinic flux density", which is the spherically integrated ~~solar flux~~spectral radiance. There are a number of measurements of $J(O^1D)$ via chemical actinometers (Hofzumahaus et al., 2004), although due to their nature they are difficult to deploy for long periods of time, making either filter radiometers or spectral radiometers an attractive alternative (Bohn et al., 2008).

1.1 Techniques for the measurement of actinic flux density (F)

There are a range of radiometric techniques used for the determination of actinic flux, and the strengths of various detectors has been assessed by a field comparison experiment (Bohn et al., 2008). All these techniques relied on calibrations using reference light sources.

1.1.1 ~~Angular response~~Estimating actinic flux density from irradiance measurements

The ideal viewing geometry for the determination of $F(\lambda)$ detects photons from all directions equally (all 4π steradian). For locations not over reflective surfaces like snow the upwelling radiation is relatively small, and so most measurements of $F(\lambda)$ are made viewing downwelling radiation only (e.g., Junkermann et al., 1989).

Most quantitative UV observations measure global irradiance (E) (the energy striking a horizontal plane), and so there have been a number of attempts to convert global irradiance into actinic flux (Kazadzis et al., 2004; Kylling et al., 2003; McKenzie et al., 2002; Schallhart et al., 2004; Webb et al., 2002).

If it is assumed that there is no upwelling radiation (surface albedo $= 0$), the actinic flux is given by

$$F = F_0 + F_{\downarrow} \tag{3}$$

where F_0 is the direct actinic flux and $F_\downarrow$ is the diffuse flux. Similarly, the global irradiance (E) is given by

$$E = \mu E_0 + E_\downarrow \tag{4}$$

where E_0 is now the direct beam irradiance, $\mu = \cos\theta$ where θ is the solar zenith angle and $E_\downarrow$ is the diffuse irradiance. As $E_0 = F_0$, it is now possible to simply write

$$F = \alpha E_\downarrow + E_0 = \alpha(E - E_0) + E_0 \tag{5}$$

where α is the ratio of the diffuse actinic flux to diffuse irradiance. If the diffuse irradiance is not measured, this ~~is recast in the form (Kazadzis et al., 2004)~~ can be rearranged into the following relationship suggested by Kazadzis et al. (2004) .

$$\frac{F}{E} = \alpha + (1 - \alpha\mu)\frac{E_0}{E} \tag{6}$$

The ratio α ~~is reasonably well behaved, especially~~ needs to be determined at the wavelengths relevant for the ~~O(^{1}D) photolysis (McKenzie et al., 2002; Webb et al., 2002)~~ ***latexdiff fail*** photolysis (McKenzie et al., 2002; Webb et al., 2002) , and this will be discussed in Section 3.1.

Estimating the ratio of the direct beam to global irradiance (E_0/E) has been more difficult. Schallhart et al. (2004) have therefore used a semi-empirical method which parameterized the relationship (F/E) based on the ratio of observed irradiance to clear sky irradiance, where the clear sky irradiance is calculated. Using data from four locations they found their results gave better agreement between measured and calculated F (7 %, 2σ) than that reported using Eq. (6) and no knowledge of the direct to global irradiance ratio (Kylling et al., 2003; Webb et al., 2002). Using global irradiance measurements combined with direct irradiance every 10 nm, Kazadzis et al. (2004) estimate an overall uncertainty of around 10 % (1σ).

1.1.2 ~~Wavelength response~~Strategies for spectral measurements

Three types of measurement detector have typically been used; a filter radiometer, a scanning spectrometer or a diode array/CCD detector equipped spectrometer system (Bohn et al., 2008; Hofzumahaus et al., 2004). Each approach has limitations. The filter radiometer measures at a fixed wavelength range, which needs then to be calibrated using the actual atmospheric ozone column and solar zenith angle factors (Bohn et al., 2004). The scanning spectrometer takes time to scan through the spectrum, rather than measuring at a fixed time, leading to measures that are "time-smeared" rather than "time-averaged". For the production of a short-lived species like $O(^1D)$ this can lead to difficulties in comparing with other measurements. Finally, the diode array/CCD system needs to have well characterized stray-light corrections applied (Bohn et al., 2008; Hofzumahaus et al., 2004; Edwards and Monks, 2003).

1.2 ~~Measurements~~ Estimates of ~~production~~ $J(O^1D)$ at Cape Grim

The Cape Grim Baseline Air Pollution Station ("Cape Grim"), (40°40′56″ S, 144°41′18″ E) is a site near the northwest tip of Tasmania that experiences periods of clean maritime air from the southern ocean. During two intensive measurement campaigns SOAPEX-1 (1995) (Monks et al., 1998) and SOAPEX-2 (1999) (Creasey et al., 2003) filter radiometers have been deployed to measure $J(O^1D)$. During SOAPEX-2 the OH concentration was also measured. The measurements during the second campaign clearly demonstrated a simple link between $O(^1D)$ production and OH concentrations in clean atmosphere conditions (Creasey et al., 2003).

As part of the Cape Grim measurement program spectral UV-B irradiance (both global and diffuse) has been measured routinely. The purpose of this work is to use the spectral UV-B measurements to estimate $J(O^1D)$ for the period ~~of SOAPEX-2 and~~ 2000–2005, to assess estimates of the photolysis rates and to then develop a climatology. In particular, the impact of clouds and ozone will be assessed.

2 Experimental Setup

All UV-B irradiance measurements reported here have been made in the radiation enclosure at the Cape Grim Baseline Air Pollution Station. This is located some 300 m north of the main building (Cainey et al., 2007). The location avoids the shadow of the telecommunication tower that is situated just to the north of the main building. The experimental details of the UV-B measurements and in-situ calibration technique have been reported elsewhere (Wilson and Forgan, 1995; Wilson, 2006, 2007). In brief, the system alternately measures global and diffuse irradiance with a scanning double monochromator (Optronics Laboratories OL752) known as SRAD. Diffuse irradiance is measured by ~~shading the global diffuser~~the the global diffuser with a small shading disk mounted on the elevation arm of a sun tracker (Wilson, 2006) . The spectral scans are spaced at 5–10 min intervals, depending upon the time of day. The instrument is calibrated at 342 nm using well characterized sunphotometer measurements of direct beam irradiance, and the other wavelengths calibrated using the Ratio-Langley technique ~~(Forgan, 1988)~~ (Wilson and Forgan, 1995) . All this is referenced to a top of the atmosphere spectrum (Chance and Kurucz, 2010) which serves as the primary calibration of both wavelength and intensity. The optical input for the system was modified in October 1999, resulting in higher optical throughput (and hence better signal/noise ratios) and a diffuser with a better cosine response. ~~Hence the period of operation during SOAPEX-2 (February 1999) is distinct from the period following the modification, although the measurement and calibration strategies are the same.~~ The focus of this work is therefore on the period after the change in diffuser.

It is worth noting that the cosine error of the diffuser is determined from the solar zenith angle dependence of the ratio of the SRAD direct beam irradiance to the sunphotometer. A correction for this variation can then be applied during the calibration.

The resulting database of measurements includes ~~alternative~~ alternating estimates of global and diffuse irradiance at each wavelength and time. The determination of the components of the irradiance at a single time is based on interpolation of the (e.g. diffuse) measurements before and after the (e.g. global) measurement in question (Wilson and For-

gan, 1995), and so the derived signals are an approximation of the value for the 10–20 min period around the nominal measurement time.

The input diffuser was constructed from PTFE but was not temperature controlled. The phase change reported for this material at around 292 K (Ylianttila and Schreder, 2005) is therefore a source of uncertainty in these measurements. This will also impact upon the calibration, so that this will be at least partially captured in the variability of the calibrations.

3 Methodology

3.1 Derivation of $J(O^1D)$ production from UV-B measurements

As the Cape Grim UV data set includes both the diffuse and global irradiance, Eq. (5) can be used, as the direct beam irradiance can be derived from the difference between the global and diffuse (see Eq. 4). This leaves the determination of the ratio (α). For the wavelength region of interest (300–330 nm), a value of 2.0 could be used, which is the value appropriate for isotropic radiation (McKenzie et al., 2002). However, as the optical depth at Cape Grim is typically low (Wilson and Forgan, 2002) , the calculated Rayleigh scattering values reported by Kylling et al. (2003) and clear skies. In cloudy conditions α decreases to values typically around 1.7 - 1.8. The calculations have been carried out using both the clear sky estimate of α and a value of 1.73, typical of cloudy conditions (Kylling et al., 2003) . For the analysis here the values using the lower value for α have been used to give a relationship: ***latexdiff fail*** In practice the difference between this and the isotropic assumption is small. unless otherwise noted.

For the ozone absorption cross section (σ (λ, T), Eq. 2) the measurements of Malicet et al. (1995) at 22 °C have been used, in conjunction with the temperature dependent O^1D quantum yield (Sander et al., 2006), derived using the hourly average air temperature measured at Cape Grim (as part of the meteorology program) (Cainey et al., 2007).

The UV-B measurements span the region 298–335 nm, and this can lead to an underestimate of the photolysis rate. A study by Jäkel et al. (2006) found that cut-offs below

298 nm did not perturb the estimate of $J(O^1D)$ by more than 5 %, with the maximum error at times of low column ozone and high sun. Test measurements using spectra measuring out to 340 nm found that including the region between 335–340 nm altered $J(O^1D)$ by less than 1 %. There is no recommended quantum yield for O^1D above 340 nm (Sander et al., 2006). The estimates presented here will therefore be biased low by the limited wavelength coverage by typically less than 5 %.

The ~~calibration uncertainty of the measurements is estimated to be 5~~uncertainty in these derived $J(O^1D)$ values have been estimated, with details given in the supplementary information. In brief, the irradiance measures are estimated to have an uncertainty (1σ) of 9 – 12 %~~based on the uncertainties in the top of the atmosphere spectrum used as the calibration (Chance and Kurucz, 2010) , and the variability in the calibration observed from the multiple calibrations carried out during the 6, implying a total uncertainty of around 8~~. The combined uncertainty of all terms is found to be around 25 %~~in $F(\lambda)$~~. This does not include the impact of model assumptions including the assumption of isotropic diffuse irradiance.

3.2 Modeling $J(O^1D)$

In the analysis of data the model TUV version 5.0 has been used (Madronich and Flocke, 1997). One of the changes in this version of the model is the use of the same solar spectrum (Chance and Kurucz, 2010) as that used for the calibration of SRAD. The calculations have been run at a range of solar zenith angles using an aerosol optical depth of 0.05 at 550 nm, a value typical of conditions at Cape Grim (Wilson and Forgan, 2002). Because the model uses the same spectral data (top of the atmosphere spectrum, ozone cross section, quantum yield) the agreement between measurements and model should be close to the uncertainty in F, which is estimated to be around 12 % (Supplementary material).

4 Results and discussion

4.1 ~~Comparison of measured $J(O^1D)$ with other measurements~~

4.1 Comparison of measured $J(O^1D)$ with model estimates

~~During SOAPEX-2 there were two sets of filter radiometer measurements made covering a period of around 1 month (18 January 1999–17 February 1999). The filter radiometers were operated by a group from the University of Leicester and the University of Leeds (Sommariva et al., 2004) . The radiometers are quoted as having an uncertainty of 20–30(Creasey et al., 2003; Monks et al., 1998; Sommariva et al., 2004) at solar zenith angles less than 60. The filter radiometer values have been corrected for total ozone column and solar zenith angle dependence. A comparison of measurements as reported from SOAPEX-2 and SRAD are shown in Fig. 1. It can be seen that there is very good agreement between these two instruments under these conditions. It shows that the two estimation approaches, based on very different instruments and calibration strategies produce estimates of $J(O^1D)$ that are very similar.~~

~~A second comparison is the measurements~~ The measurements can be compared with the clear sky calculations performed using TUV 5.0, where the experimentally derived values have been estimated using both a clear sky and cloudy estimate of α. The results of this are shown in Fig. ~~2.~~ 1. It can be seen that for the data from both February 2000 (low column ozone) and October 2003 (high column ozone) there is good agreement between model and measurement (average deviation 2 %) if the appropriate value (clear sky) of α is used. Differences at high sun are around 3 %. Several days exist where the irradiance appears to vary smoothly but with differences of up to 10 % at solar noon. This could be due in part to the limited measurement range (Sect. 3.2), a calibration issue that occurs at these solar zenith angles, aerosol, ozone column estimate errors or due to ~~cloud. The~~ clouds. The aerosol optical depth does not appear large (based on the sun photometer) and the ozone retrieved using the midday calibration are not substantially different from the satellite. The smooth change in $J(O^1D)$ implies no ~~cloud~~ clouds near the sun, but there can be ~~cloud~~

clouds well away from the sun that is ~~reducing~~ altering the observed photolysis rate. Without a measure of the cloud field it is hard to distinguish between these possibilities.

4.2 Annual cycle in $J(O^1D)$

The data collected for the period 2000–2005 are shown in Fig. ~~3.~~ 2. The dataset comprises ~~of~~ over 108 000 measurements. The gaps in the dataset represent times when the equipment failed.

The annual cycle is the dominant feature in this plot. To quantify this, monthly mean values have been calculated by sorting all data from a month into 24 hourly bins, and from these bins producing an average daily cycle for each month. It is assumed that if no measurement is made in one of the 24 hourly bins during the month that the average is zero~~, except where the hour before and after have non-zero values. In this case the average of those two values is used. This is only necessary where instrument failures have severely limited data collection in a particular month.~~. The average of the 24 hourly averages is then calculated for each month in the 6 years. This method has been used to limit the impact of possible biases from collecting spectra at varying time intervals.

Despite the variability seen in the individual measurements (see ~~Figs. 1 and 3~~Fig. 2), the monthly averages are relatively stable (Fig. ~~4~~3, top panel). The lower panel of Fig. ~~4~~ 3 shows that for mid-summer and mid-winter the interannual variability in the monthly averages is 3–4 %, with the increases in-between presumably driven by the rate of change of the solar zenith angle at midday, the factor also driving much of the observed annual cycle. The resultant average monthly $J(O^1D)$ for Cape Grim is also presented in Table 1 along with the standard deviations.

~~Previous measurements of~~ Measurements of $J(O^1D)$ have been reported for 2002 – 2006 in the eastern Mediterranean (Gerasopoulus et al., 2012) . The interannual variability in the monthly mean maximum clear sky irradiance is of the order of 7 – 8 %. This is comparable to the monthly relative standard deviation in all measurements at Cape Grim (9.2 %). The two locations are very different, both in terms of aerosol loadings and cloudiness, so the similarity is not expected.

Earlier measurements of interannual variability of UV-B have been reported for Ushuaia in Argentina (Frederick et al., 2001). For global irradiance at 305 nm they found an interannual variability (standard deviation) of around 25 %. The variability in global irradiance could be expected to be bigger than that for $J(O^1D)$ with the different dependence on the angle of incidence of radiation. The mean of the monthly relative standard deviation (9.2 %) is indeed slightly lower than that observed for global UV-B irradiance (10.8 %) as determined from the Cape Grim data. However, both are significantly less than reported from Argentina. This is presumably a reflection of the difference in climate, with Cape Grim routinely experiencing cloudy conditions.

To investigate any trend in the data both monthly trends for each month and trends as a function of season have been calculated. The most significant linear trend is in summer (December–February) (-1.7 ± 1.1 (std. dev.) % year^{-1}), but this is not significant at the 90 % level. Satellite estimates of changes in irradiance at 305 nm due to stratospheric ozone and ~~cloud~~ clouds at this latitude are 0.3–0.4 % year^{-1} (averaged over 1979–2008) (Herman, 2010). For the shorter period measured here it is not possible to detect changes of that magnitude, and local effects on ~~cloud~~ cloudiness could determine the magnitude (and sign) of the observed trend.

4.3 Ozone column dependence

The dependence of $J(O^1D)$ on solar zenith angle has been determined by sorting all data into 5° bins, and the results are summarized in Fig. ~~5.~~ 4. For this plot, zenith angles up to 82.5° have been included. All measurements have been adjusted to 1 a.u. (correction for the annual variation in the earth-sun distance; Iqbal, 1983). A few measurements made at solar zenith angles below 17.5° have been excluded as they represent a brief period in mid-summer. Included in the plot are $J(O^1D)$ estimates calculated using the TUV model for cloud free conditions and an aerosol optical depth of 0.05. Calculations for two ozone column amounts are shown, 250 and 350 DU, which are typical seasonal maximum and minimum values observed in this location as derived from satellite measurements (TOMS) (http://disc.sci.gsfc.nasa.gov/acdisc/TOMS).

A significant fraction of the variability can be due to the differences in the ozone column during the year. To characterize the dependence, ~~the measured $J(O^1D)$ values~~ functions of the following form were fitted to ~~a function of the form~~the measured $J(O^1D)$:

$$J(O^1D) = \left(\sum_i A_i \exp(-B_i/\cos\theta) \right) \cdot \left(O_3^{sat}/300\right)^{-RAF} \quad (7)$$

where θ is the solar zenith angle, O_3^{sat} is the total ozone column retrieved from satellite for the measurement day, and A_i, B_i and RAF are fitted. RAF is the Radiation Amplification Factor to be determined (Micheletti et al., 2003). The results for the fit to the entire dataset using either one or two exponential terms ($i = 1$ or 2) are shown in Table 2 and for one exponential term in Fig. ~~5.~~ 4. Using two exponentials produces a slightly better fit, and both fits produce an RAF estimate in excellent agreement with calculations of 1.4–1.5 (McKenzie et al., 2011).

Using this derived ozone RAF the dataset was normalized to both 300 DU and 1 a.u. as shown in Fig. ~~6.~~ 5. Given the large difference between the median and average values for the bins, a second fit was performed to the median of the binned values of Fig. ~~6~~5, and the fits are also included in Table 2. For reference, the fits with two exponential terms, using all data and the medians is included in Fig. ~~6.~~ 5. It should be noted that the increase in R^2 is due to the change in the nature of the data being fitted.

The removal of the variation due to changes in stratospheric ozone, as described by the satellite ozone measurements, reduces the interquartile variability by up to 20 % as shown in Fig. ~~7.~~ 6. The effect on high sun (~~low~~ small solar zenith angle) measurements is smaller, as this is only collected in mid-summer and so the ozone variability is small. At ~~higher~~ larger solar zenith angles ($> 50°$) the percentage reduction diminishes also, presumably because, as the absolute intensity decreases, other effects, including the impact of measurement uncertainty, become larger.

4.4 Cloud impact

Clouds can both reduce and enhance solar radiation at the ground level. Figure ~~6~~ 5 shows that the ~~90~~99th percentile value closely follows the clear-sky calculated value at solar zenith angles less than 50°. This ~~implies that approximately 10~~suggests that approximately 1 % of these measurements show an enhancement of radiation due to ~~cloud~~clouds, a phenomenon often observed (Calbó et al., 2005). The likelihood of this cloud enhancement appears to increase with increasing solar zenith angle with up to 25 % of measurements showing an enhancement by 65°, presumably as a result of the changes in scattering geometry in the atmosphere.This could also be due to errors in the model or unidentified cosine errors. However, the question does arise as to whether such behaviour is consistent with known cloud impacts on radiation.

To assess the overall impact of ~~cloud~~clouds, the ratio of the median value to the calculated clear – sky value was determined (Fig. ~~8~~7). This shows that for solar zenith angles ~~greater~~ less than 70° the median is approximately ~~85~~75 % of the calculated clear sky value. From 20–70° the calculated impact of ~~cloud~~ clouds on $J(\mathrm{O}^1\mathrm{D})$ increases by 5–6 %, a trend also predicted in models of the cloud impact on UV irradiance (Lindfors and Arola, 2008).

The results for solar zenith angles greater than 70° show that clouds have a diminishing impact as the sun approaches the horizon, as noted at other locations (Mateos et al., 2014). This can be a result of the increasing importance of scattered light under these conditions due to the longer atmospheric path for the direct beam. As scattered radiation has become more significant, it could be expected that clouds more readily enhance the observed radiation (Fig. ~~6~~5) to the point that their overall impact is small (Fig. ~~8~~). ~~7~~). It can be concluded that the behaviour shown in Figure 6 is consistent with other measures of cloud properties.However, both measurement uncertainties (smaller signals and variations in detector angular response) and modelling limitations could be playing a significant role. The enhancement in inter-quartile range, also shown in Fig. ~~8~~7, could also be due to a combination of cloud impact or measurement uncertainty.

Attempts to capture the cloud variability through independent observations have not been very successful. Measures such as visual observations and automatic sky cameras have not been implemented at Cape Grim. While sunphotometers make measurements during this period, they do not make measurements of cloud optical depth as has been used elsewhere (Anton et al., 2012). Longwave downward radiation (LDR) measurements have been used to estimate cloudiness (Marty and Philipona, 2000; Dürr and Philipona, 2004). The attraction of this measure is that LDR is relatively insensitive to the solar position, and so should be independent of the other factors influencing $J(\mathrm{O^1D})$. An attempt at using LDR has been made using half-hourly long-wave radiation averaged values measured at Cape Grim (Wilson and Shinkfield, 2007) to derive the Clear-Sky Index (Marty and Philipona, 2000). In this case it was possible to produce a fit extending Eq. (8) with an additional term (Clear-Sky Index)$^{\alpha}$, where α is a fitted parameter. Fitting the entire dataset where LDR values were available returned a significant value for the exponent (-0.19 ± 0.01). However, the fit did not improve significantly, as measured by the ~~reduced~~ adjusted R^2 (increases of ~ 0.0005), implying that this is not a useful approach. This could be due to the insensitivity of long-wave radiation measures to higher-level clouds (Schade et al., 2009; Boers et al., 2010). However, cloud bases are often low at Cape Grim ~~, as highlighted~~ (800 - 1000m, as observed by LIDAR measurements, (Young, 2007) and so LDR should be a reasonable measure. It is more likely that the features of clouds that cause changes in the observed LDR are not simply related to those features which result in a significant reduction (or enhancement) of $J(\mathrm{O^1D})$.

A dependence of $J(\mathrm{O^1D})$ on aerosols has been identified in measurements in the eastern Mediterranean, (**?**) which could in principle be part of the variation identified here as a cloud impact. However, the low aerosol optical depth (mean of 0.07 at 500 nm compared with 0.23 in the Mediterranean (Gerasopoulus et al., 2011) makes this a small effect, especially when compared to the very common cloud cover at Cape Grim.

4.5 Wider relevance of the observations

The atmospheric composition at Cape Grim is dependent on wind direction and clean or "baseline" conditions are defined by standard measures (Downey, 2007). The ~~chemical outcome~~ impact on atmospheric chemistry of the photolysis measured here will depend on whether the local atmosphere is clean or polluted. However, an analysis of the data presented here filtered for only those measurements collected under "baseline" conditions gives results not statistically different from those observed for the entire dataset. As the baseline selection process eliminates a significant fraction of the data, the variability does increase.

Another important question is how reliably the climatology measured here is representative of a larger region. Cape Grim, sitting on the coast could have a cloud environment different to locations out to sea and inland. A study of the global irradiance at a number of locations concluded that Cape Grim experienced cloud conditions similar to the southern ocean in this area (Bishop et al., 1997)~~, and a~~. While the station is some 90m above sea level, the observations remain well below the cloud base height of 800 – 100m (Young, 2007) . A study of rainfall has shown that while rainfall varies when moving inland it is reasonably constant along the coast (Jasper and Downey, 1991). The ISCCP dataset (http://isccp.giss.nasa.gov/index.html) shows that cloud amount at this latitude band over the oceans is 80–90 %, with little dependence on longitude and without an obvious trend over the period 1984–2008. Therefore, the cloud impacts observed at Cape Grim should be representative of the marine environment at these latitudes.

Modelling studies (Liu et al., 2006) calculated that the impact of ~~cloud~~ clouds on $J(O^1D)$ is around 8 % averaged throughout the troposphere, but that ground level impacts are larger, of the order of -20 %. The data presented here shows ~~a slightly smaller impact of cloud~~ an impact of clouds on $J(O^1D)$ ~~when using the median estimate, but close to identical to that calculated using the mean values for the individual sza bins~~consistent with the calculation. The reduction is half that often observed for global UV irradiance at ~~the average cloud factor of 0.8 to 0.9~~50 % cloud cover (Calbó et al., 2005) , underlining the relative insensitivity of

actinic flux ~~to cloud (Calbó et al., 2005)~~ density to clouds. This is a result of the relative importance of diffuse radiation to the photolysis rate, and the limited impact of ~~cloud~~ clouds on total diffuse irradiance (Blumthaler et al., 1994).

The results of this study permit the prediction of $J(O^1D)$ in the current climate. The impact of stratospheric ozone recovery should be well described by our current understanding. However, it would be useful to estimate the likely impact of future changes in clouds properties on $J(O^1D)$. With the reasonable agreement between models and observations seen at Cape Grim there can be some confidence in their predictions. For the maritime environment investigated here the overall impact of ~~cloud~~ clouds is relatively small (~~15–20~~20 %) given the 80–90 % cloud cover. Any future climate changes would need to change the frequency of clouds significantly to alter $J(O^1D)$ greatly. Other changes, such as a change in cloud optical depth may be more significant. Verifying any such changes in $J(O^1D)$ will require ongoing observations.

5 Conclusions

Six years of estimates of $J(O^1D)$ are presented for a clean Southern Hemisphere marine site. The impact of solar zenith angle and total column ozone can be clearly seen and quantified and the stratospheric ozone dependence is in good agreement with radiation model estimates. The impact of ~~cloud~~ clouds can also be characterized, with bounds on the impact of clouds determined as a function of solar zenith angle. However, attempts at modelling the impact of clouds using independent radiation measurements (Longwave Downward Radiation) produced ~~significant~~ fits that did not significantly improve the quality of the model. So while the impact of ~~cloud~~ clouds can be quantified, a good proxy for this has proven elusive.

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Table 1. Monthly mean photolysis rate $J(O^1D)$. This is calculated using hourly averages for each of the 24 h in the day.

Month	Mean (std. deviation) $s^{-1} \times 10^{-6}$
1	~~11.77 (0.45~~10.59 (0.42)
2	~~10.02 (0.80~~9.02 (0.74)
3	~~6.27 (0.71~~5.69 (0.67)
4	~~3.34 (0.28~~3.06 (0.23)
5	~~1.86 (0.27~~1.72 (0.24)
6	~~0.95 (0.07~~0.90 (0.08)
7	~~1.02~~ 0.09 (0.03)
8	~~1.77~~ 1.65 (0.14)
9	~~3.49 (0.72~~3.18 (0.64)
10	~~5.60 (0.77~~5.12 (0.70)
11	~~9.01 (0.45~~8.03 (0.35)
12	~~11.54 (0.80~~10.40 (0.78)

Table 2. Results for fitting $J(O^1D)$ with the form shown in Eq. (8). Brackets [...] surround values that have been assumed in the fit. Uncertainties (in brackets) are standard errors in the last quoted figure of the fitted parameters. Units for A_1 and A_2 are s^{-1}. The "median fit" is a fit to the medians as shown in Fig. ~~6~~ 5.

Fit	$A_1/10^{-4}$	B_1	$A_2/10^{-5}$	B_2	RAF
All data	~~1.869(8)~~ 1.608(7)	~~1.626(3)~~ 1.592(3)			~~1.454(9)~~ 1.403(9
	~~5.2(2)~~ 4.6(1)	~~2.94(4)~~ 2.92(4)	~~2.8(1)~~ 2.4(1)	~~0.77(2)~~ 0.74(2)	~~1.477(9)~~ 1.426(9
Medians	~~2.4(2)~~ 2.2(2)	~~1.78(8)~~ 1.77(8)			~~[1.454]~~ [1.43]
	~~4.5(3)~~ 4.4(5)	~~2.59(10)~~ 2.7(1)	~~1.8(4)~~ 1.8(5)	~~0.62(7)~~ 0.64(9)	~~[1.454]~~ [1.43]

~~Comparison of SOAPEX-2 data (Creasey et al., 2003) and data derived from SRAD.~~

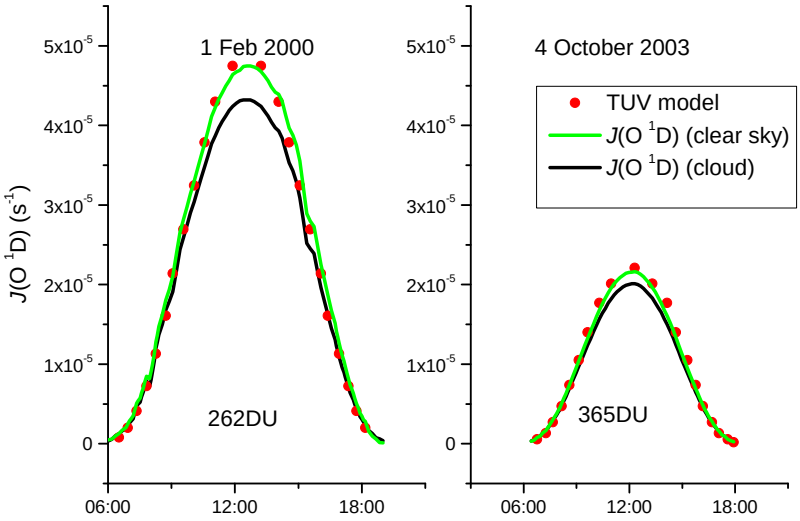

Figure 1. Comparison of clear sky calculation values to measurements. Calculations have been performed with the column ozone amount reported by satellite. $J(O^1D)$ has been calculated using an α of 1.96 relevant to clear skies (green line) and 1.73 (cloudy - black line).

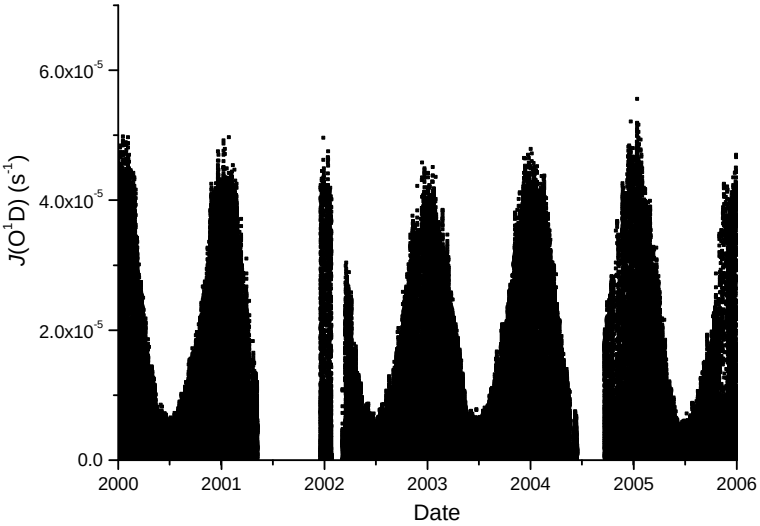

Figure 2. Photolysis rate $J(\mathrm{O}^1\mathrm{D})$ observed at Cape Grim 2000–2005. Gaps in the data are due to instrument failure.

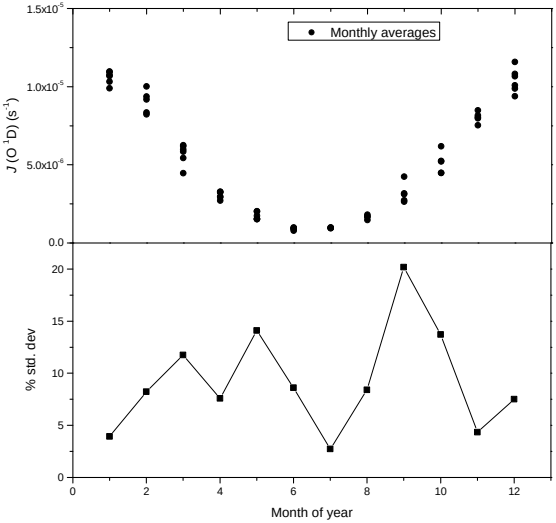

Figure 3. Annual cycle of $J(\mathrm{O}^1\mathrm{D})$. The bottom panel shows the scatter in the monthly values as a percentage of the monthly mean.

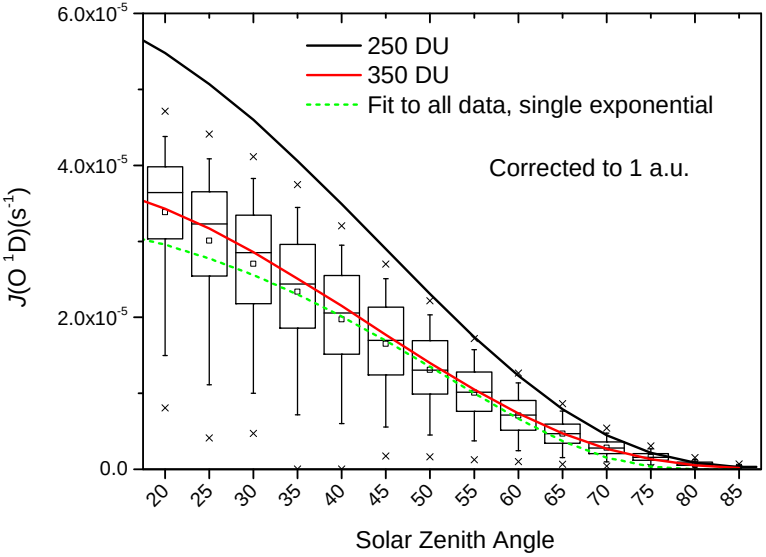

Figure 4. Solar zenith angle dependence of $J(O^1D)$. Crosses mark the 1 and 99 percentile. The boxes span $25/75$ %, the whiskers mark 10 and 90 %, the central line indicates the median and the square the average value. The x axis value is the central value of the 5° bin used. The two solid lines were calculated using TUV (V 5.0) for ozone column amounts of 250 DU (February) (black solid line) and 350 DU (September)(red dashed line). The ~~dashed~~ short-dashed green line is the fit to a single exponential term to all data.

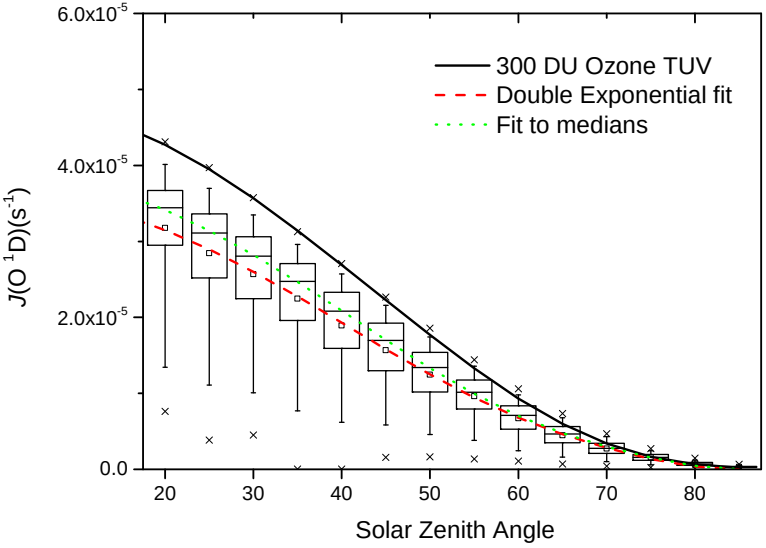

Figure 5. Cape Grim measurements of $J(O^1D)$ adjusted to a nominal 300 DU and 1 AU. The solid line is the calculated $J(O^1D)$ for clear skies and 300 DU ozone column and an aerosol optical depth of 0.05 using TUV 5.0 (Madronich and Flocke, 1997). The two broken lines are the results of the fits to two exponential terms to either all data or the median value of each bin (see also Table 2).

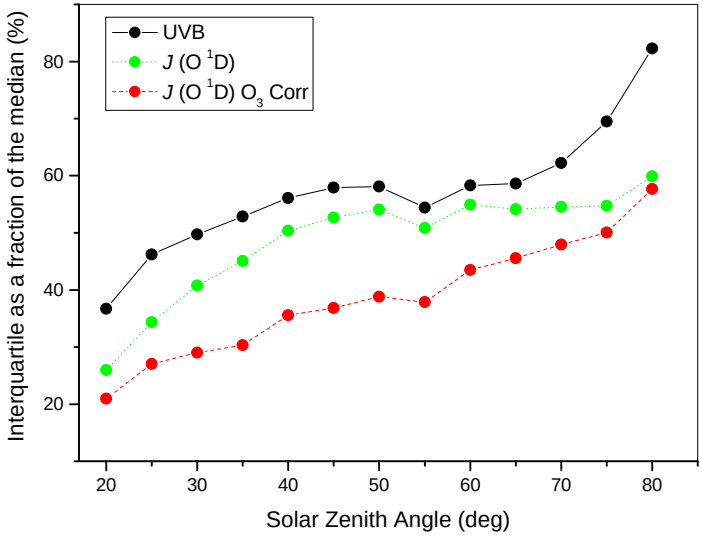

Figure 6. The interquartile (75–25 %) difference as a percentage of the median value as a function of solar zenith angle. UVB is the global irradiance, and the other two terms are the derived photolysis rates, with the red curve measurements have been corrected to a constant column ozone amount.

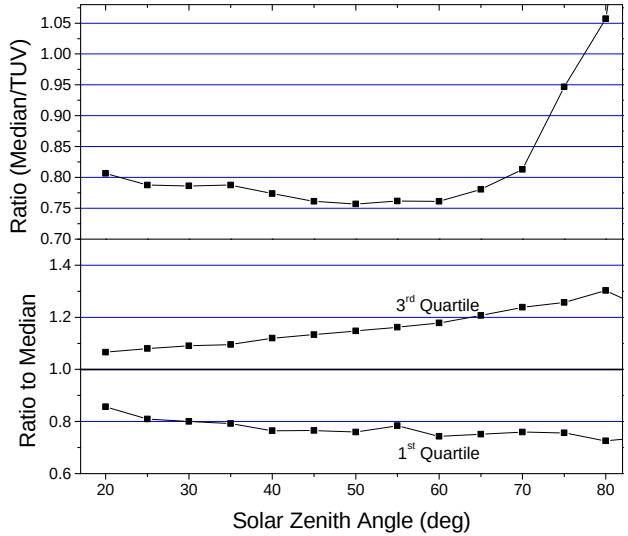

Figure 7. Top panel shows the ratio of the median measured $J(\mathrm{O}^1\mathrm{D})$ to that from a calculation for clear skies. The bottom panel shows the spread in quartile values as a ratio to the median.