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Atmospheric Measurement Techniques Discussions

Interactive comment on "Relationship between the NO_2 photolysis frequency and the solar global irradiance" *by* I. Trebs et al.

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Sasha Madronich: The authors present a detailed analysis of the correlations between global irradiance G, which is commonly measured as part of standard met observations, and the NO_2 photolysis coefficient j, which is only measured with specialized equipment actinometers, or spherically integrating filter radiometers and spectroradiometers). Both quantities are dependent on the available incident solar radiation so that a correlation is certainly expected. But there are also differences, primarily due to different contributing wavelengths and different angular responses, which could lead to substantial scatter and bias in the correlations. Clouds, aerosols, water vapor, ground elevation and reflections all induce slightly different angular and/or wavelength dependencies. The presentation of the empirical correlations is interesting and is based on

an impressive collection of data from several field campaigns at different locations. These data alone justify publication.

However, the discussion of how different factors affect G and j could be improved, possibly along the lines suggested below. This could be done mostly by editing the text, rather than needing any significant reanalysis of the data. A distinction should be made between getting j correct in an average sense, i.e. averaged over many different locations, days, and sky conditions, vs. getting it correct for any given episode (e.g. a single high pollution event). The latter is obviously more important for use in field experiments, such as surface-atmosphere exchange studies. For this reason, it is important to identify and discuss the effects of individual factors and how they may cause the correlation to deviate from the bulk averages during any specific episode.

Reply: The authors thank Sasha Madronich for the thorough assessment of the manuscript. We will carefully consider his suggestions in the revised version. Moreover, we will emphasize more strongly the empirical character of the derived parameterization which of course cannot completely replace measurements of $j(NO_2)$ under all conditions and at all locations. However, it is believed that in the absence of direct measurements of $j(NO_2)$ the method is more reliable than radiation transfer calculations with poorly known input parameters, in particular in the presence of clouds. The factors which may lead to deviations from the empirical correlation will be addressed in more detail as recommended.

Sasha Madronich: 1. Water vapor: The global irradiance G is sensitive to absorption by H_2O vapor at near-infrared wavelengths. Roughly 1/4 to 1/3 of the incident solar radiation can be absorbed by H_2O, the exact value depending on the local atmospheric water column (e.g. Figure 6.1 of Peixoto and Oort (1992), Fig. 4.6 of Brasseur and Solomon (1986), or similar textbooks). On the other hand, H_2O absorption is negligible over the wavelengths (ca. 300-420 nm) where NO_2 photolyzes. Therefore atmospheric variability in H_2O will induce variability in G but not j. The authors mention this issue only very briefly (page 1549/line 23), and only to say that H_2O absorption is not

included in the TUV model which therefore is not used to calculate G. Some more discussion of this issue is desirable. How much difference in G would be expected between a dry and a humid environment? What was the range of H_2O values observed at the various locations? Is this a major contributor to the observed scatter in the G vs. j correlations? Are there indirect effects of H_2O on j, e.g. via the hygroscopic growth of aerosols?

Reply: The issue of water vapor absorption is indeed interesting and will be addressed in more detail in the revised version of the paper. The attenuation of solar irradiance by water vapor is strongly non-linear (e.g., Iqbal, 1983). At normal incidence, water columns of 1 cm and 10 cm lead to attenuations of about 150 W m^{-2} and 250 W m^{-2}, respectively (Fig. 11.3 in Houghton, 1986). Thus, the natural variability of water vapor is expected to influence the data in Fig. 2 but overall the scatter is probably dominated by other effects, most importantly clouds. Direct water vapor column measurements are not available for the different measurement sites. Ground based measurements of relative humidity exist but these are only representative for the boundary layer and cannot be converted to total water columns. On the other hand, at least for model atmospheres, there is a correlation between water vapor concentration at the ground and total water (e.g. Tomasi et al. 1998). This relation was used to estimate the water columns at the sites Guangzhou and Jülich. The results are consistent with satellite data (e.g. MODIS) which indicate typical ranges of water vapor of about 1-4 cm for Europe and 4-7 cm for the tropics. However, no water dependence was evident in the $j(NO_2)$-G correlations for the estimated ranges (4-6 cm for Guangzhou, 1.5-4.5 cm for Jülich). Nevertheless we will state that there may be deviations under extremely dry conditions (e.g., polar regions) which were not covered by our measurements.

Sasha Madronich: 2. Clouds: While clear sky correlations show curvature, in the presence of clouds the correlations are approximately linear with zero intercept (see Eq.11 of Madronich, 1987a). The same decrease of G could be obtained either by lowering the solar elevation under clear skies (along the curved correlation), or by the presence

of clouds under constant solar elevation (linear correlation). Thus two different values of j could be associated with the same value of G. How big is this difference? Also, for broken clouds there can be some complex effects due to the spectral shifts that occur when the direct solar beam is blocked by clouds (see Crawford et al., 2003, esp. their Fig. 2). Such spectral shifts will obviously affect G differently than j. Some assessment of these cloud effects would be helpful (as was also recommended by Referee 1).

Reply: The curvature of clear sky correlations between $j(NO_2)$and G is apparent only at G exceeding approximately 400 W m^{-2}. At lower G the relationship between $j(NO_2)$ and G is linear also under clear sky conditions. This behavior was reproduced qualitatively by TUV model calculations and is accidental because diffuse and direct contributions to $j(NO_2)$ rise oppositely at low G (parabolic for direct and hyperbolic for diffuse). Under overcast conditions the relationship is also linear and G usually remains below 400 W m^{-2}. The actual slope will depend on the distribution of sky radiance and the fraction of UV-A and shortwave radiation absorbed by the clouds, but within experimental error the slope appears to be similar to that under clear sky conditions. This similarity is again considered accidental and cannot be rationalized by simple assumptions. Broken cloud conditions with occasional sunshine and reflections on cloud sides are expected to induce significant deviations from the simple relationship. However, as already mentioned in the answer to the first reviewer these deviations are expected to be temporary and are partly eliminated by the 30 min averaging periods. A data set with higher time resolution (not considered in this work) indeed shows increased scatter which gradually decreases upon extending the averaging period. A quantitative assessment of these short term fluctuations is beyond the scope of this work. On the other hand, we will show in an additional figure for two sites that measured sunshine durations as a proxy for cloud cover have no apparent effect on the empirical relationship.

Sasha Madronich: 3. Aerosols: The optical properties of aerosols at UV wavelengths are not well known, but most probably depend on size-dependent composition. Spec-

trally different effects on G and j may be expected at different locations, depending on the prevailing type of aerosols (soot, sulfate, organics, dust, etc.). Indeed, Table 3 shows j/G ratios at Guangzhou 20% higher than at Jarú which could well be due to differences in aerosol composition (although the text on p. 1553, lines 5-7 claims no significant dependence). These differences should not be dismissed because they can have a significant effect on local photochemistry (for high NO_x conditions, O_3 production scales linearly with j).

Reply: The paragraph about the impact of aerosols and atmospheric pollution will be revised. The authors realized that only choosing AOT data for selected times at different sites will not give a complete picture of the aerosol effect. Thus, we decided to remove Table 3 and introduce an additional Figure 7, showing the effect of AOT on the ratio j/G for different pollution episodes at the Guangzhou site. These results and also AOT measurements from Jarú during wet and dry (biomass burning) season show that the effect of AOT on j/G is not substantial. The ratio j/G and its diurnal variation can vary for different sites, but this also depends on other effects, such as ozone columns.

Sasha Madronich: 4. Surface elevation: On p. 1554/lines 15-26, it is said that the effect of altitude was calculated with the TUV model, but the vertical gradient (1.5% km^{-1}) was much smaller than measured at Marondera, or reported by Pfeifer et al. and by Schmucki and Philipona for other locations. I have several concerns with this topic: a) The measurements at Marondera were made at a single location and therefore do not give the altitude gradient. I don't think you can estimate the altitude gradient by comparing different locations (aerosols, clouds, albedo could all be different). b) The two cited studies are for irradiance not actinic flux. The altitude effects on actinic flux are typically much smaller than for irradiance (for high sun, because diffuse radiation is relatively more important for actinic flux than for irradiance). For example, a quick calculation with TUV, using the default Elterman aerosol profile, gives a vertical gradient of 1.1% km^{-1} for actinic flux and 2.5% km^{-1} for irradiance. c) The vertical gradient of j is sensitive to aerosol optical depth and single scattering albedo at UV wavelengths. As

already mentioned above, these optical properties are not well known, so it is unclear how they were used as input in the TUV model in the reported calculations. Obviously, larger amounts of absorbing aerosols will cause a stronger vertical gradient of j.

Reply: The authors did not intend to compare measured and modeled altitude gradients. The wording 'altitude gradient' calculated using the TUV model was chosen to reproduce our measurements at higher surface elevations. This was probably misleading and will be revised accordingly. The references about the altitude gradient will be removed since they do not refer to actinic fluxes. As mentioned in the paper, for sites below 800 m, TUV (using $AOT_{550\,nm}$ = 0.235 and ω_0 = 0.99) was able to reproduce the measurements. Our attempt was to calculate scenarios using TUV trying to reproduce our measured values at higher elevations. For the Marondera site at 1630 m a.g.l., a change of ω_0 to 0.85 (more absorbing aerosols) or to AOT = 0.135 only slightly changes j and does not reproduce the measured values. We will revise the paragraph, also pointing out the limitations of the application of TUV due to unknown input parameters.

Sasha Madronich: 5. Surface albedo (α): Multiplication by (1+α) is ok for irradiance, and is also ok for isotropically diffuse radiation (including that below clouds). But the Lambertian reflection factor for the direct beam actinic flux depends also on the solar zenith angle: 2(α)cos(sza) - see Eq. 3 of Madronich (1987b). The simple multiplication by 1+α is not theoretically justified, and since it was not actually measured in this work, it should be used with caution. Large errors could occur if the albedo is large (e.g., snow). The authors limited the validity of their correlation to small albedo values where the errors are of course smaller. But some cautionary statement about the proper use of the albedo would be useful.

Reply: This will be clarified and a cautionary statement will be added. The contribution of direct sun to $j(NO_2)$ rarely exceeds 50% under clear sky conditions. At SZA=0 this would lead to a factor (1+1.5α). At low sun (SZA>60°) the contribution of direct sun diminishes and the factor will be close to (1+α). The same is true for overcast

conditions. The actual increase will thus vary between (1+α) and (1+1.5α) and the potential absolute error of this correction will increase accordingly with α.

Sasha Madronich: 6) Behavior at low sun: Fig. 4 shows a non-zero value of j (calculated from TUV) for zero G (estimated from Schmetz and Raschke). It would be useful to discuss this in more detail, since large relative errors in j could result. It is indeed true (the authors cite van der Hage 1993) that j decreases more gradually than G as the sun sets. However, I think another reason may be at play here. TUV has a pseudo-spherical correction for atmospheric curvature, so it calculates j values even for sza > 90 degrees. Specifically, if the top of the model atmosphere is set to 80 km, it will calculate non-zero j values up to sza = 96 degrees. On the other hand, the value of G was estimated from a parameterization by Schmetz and Raschke (this citation is not readily available to me). How does their parameterization work at sza = 90 degrees? Does it allow for twilight, or is it simply set to zero because cos(90) = 0? Forcing G = 0 at 90 degrees would explain the non-zero intercept of Figure 4. Finally, the use of linear j vs. G correlations is overstated (abstract, conclusions, Figure 6). To my knowledge very few people, if any, actually use such linear correlations (e.g. from Bahe et al., 1980). Much more common is to use a theoretical calculation of clear sky j, followed by an adjustment for local conditions (e.g. clouds) based on irradiance measurements (global as in this study, or UV-A with the Eppley radiometer). I suggest de-emphasizing this argument, and removing the associated Figure 6.

Reply: The parameterization of Schmetz Raschke (1978) indeed forces G through zero at SZA=90° and therefore does not allow for twilight. The top of the TUV model atmosphere was set to 120 km. This issue will be added to the discussion of Figure 4. The authors do not fully agree with the latter statement. The linear function of Bahe et al., 1980 was used in surface-atmosphere exchange studies by some European scientists (e.g., Walton et al., 1997). Obviously, it was not commonly used by the international community. Figure 6 will be removed and some statements will be revised.

Minor comments:

1538/2: delete parentheses (or commas) around j(NO_2)

1538/27: The statement that 'our function can be applied to estimate chemical life times of the NO_2 molecule with respect to photolysis' seems a very roundabout way of saying that this lifetime is simply 1/j.

1539/13: Wavelengths for NO_2 photolysis should include some visible, up to 420 nm.

1539/14: Careful with the definition of a 'unit sphere'. The actinic flux is the radiant energy incident on a sphere having unity cross sectional area (not unity radius nor unity surface area).

1539/17: NO_2 can also be an important absorber in some areas, e.g. polluted urban.

1541/6: Not sure why the word 'implied' is being used here. Madronich (1987a) explained direct observations of the curvature between UV-A and j.

1542/1-4: why is the wet season defined as Oct to Jan, but 80

Reply: These minor comments will be incorporated into the revised version.

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