**Atmospheric
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# *Interactive comment on* "Relationship between the NO$_2$ photolysis frequency and the solar global irradiance" *by* I. Trebs et al.

**S. Madronich (Referee)**

sasha@ucar.edu

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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 NO2 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

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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.

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?

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

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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).

3. Aerosols: The optical properties of aerosols at UV wavelengths are not well known, but most probably depend on size-dependent composition. Spectrally 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 $\sim$20% higher than at Jaru 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 NOx conditions, O3 production scales linearly with j).

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) 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 for actinic flux and 2.5%/km 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.

5. Surface albedo (alpha): Multiplication by (1+alpha) 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(alpha)cos(sza) - see Eq. 3 of Madronich (1987b). The simple multiplication by 1+alpha 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.

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 $\sim$ 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

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de-emphasizing this argument, and removing the associated Figure 6.

Minor comments:

1538/2: delete parentheses (or commas) around j(NO2)

1538/27: The statement that 'our function can be applied to estimate chemical life times of the NO2 molecule with respect to photolysis' seems a very roundabout way of saying that this lifetime is simply 1/j.

1539/13: Wavelengths for NO2 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: NO2 can also be an important absorber in some areas, e.g. polluted urban.

1542/6: 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% of annual rainfall is between Nov and March? Seems inconsistent.

References:

Crawford, J., R. E. Shetter, B. Lefer, C. Cantrell, W. Junkermann, S. Madronich, and J. Calvert, Cloud impacts on UV spectral actinic flux observed during the International Photolysis Frequency Measurement and Model Intercomparison (IPMMI), J. Geophys. Res., 108(D16), 8545, doi:10.1029/2002JD002731, 2003.

Peixoto, J. P. and A. H. Oort, Physics of Climate, American Institute of Physics, New York, 1992.

Brasseur G. P. and S. Solomon, Aeronomy of the Middle Atmosphere, D. Reidel Publ., Dordrecht, 1986.

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