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Interactive Comment

Interactive comment on "NO_2 and HCHO photolysis frequencies from irradiance measurements in Thessaloniki, Greece" *by* C. Topaloglou et al.

C. Topaloglou et al.

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Response to Referee 2

MS-NR: acpd-2005-0046 Title: NO2 and HCHO photolysis frequencies from irradiance measurements in Thessaloniki, Greece. Author(s): C. Topaloglou, S. Kazadzis, A. Bais, M. Blumthaler, B. Schallhart, and D. Balis

Introduction: A paragraph was added to the introduction giving the definitions of the actinic flux and the global irradiance as recommended. "The actinic flux is defined as the total number of photons [e.g. Madronich, 1987] incident on a spherical surface. The actinic flux describes the radiation incident on a spherical surface such as the molecules of the atmospheric species and is the suitable radiation quantity for photolysis frequencies determination. On the other hand, the global irradiance describes the radiance on a horizontal surface integrated over the whole upper hemisphere, weighted with the cosine of the incidence angle." The reference was added to the ref. list.

Section 3.3: In the conclusion section it was added that the mean and standard deviations serve long-term series and climatological data users (see comment below).

The whole method is based in the fact that the variability of the actinic flux to global irradiance, at the wavelength region of interest, for a given solar zenith angle and a given irradiance level, is very small. That's why the polynomials can be used at least satisfactorily, with the reported uncertainty. There are about 20 cases that deviate more than 20% for the ratio Jcalc / J(NO2). There are mostly broken cloud sky cases. The reasons for these deviations are:

Mainly, the fact that the independent variable (irradiance integral from 375-400nm) represents a given time period in the scanning process. There are extreme cases, where a part of the scan is performed under cloudy (sun covered) conditions and another part with direct sun irradiance contribution. So there are few cases that the overall scan could be attributed to a certain irradiance level (in the polynomial analysis) but in reality, this level could be lower or higher. Our opinion is that these cases are just a small fraction of the overall picture.

Even in the case where J are plotted versus actinic flux, there is some variability, caused by the fact that the integrated Js use the whole spectrum instead of just the 375-400 part. This variability is transported to the relationship between Js and the irradiance integral and is a main reason for extreme cases of variability.

It is true that the cosine (and the actinic diffuser) can not detect if there is a direct contribution to the measurement quantities or not. Using the integral of the irradiance at a given range we use an overall picture of the situation of the sky which seems to simulate the real J measurement with the given limitations. Even for the polynomial for

ACPD

5, S457–S461, 2005

the sza bins with the greatest variability (60-70 degrees), the correlation coefficient R2 is very high (0.96).

(Minor reason). In partly cloudy cases, a scan that lasts about 6-7 minutes is just an average picture of the given atmospheric irradiance situation. The spectrometer itself is measuring at each wavelength actinic flux and global irradiance simultaneously. Even if the instrument was measuring two actinic flux scans (instead of one global and one actinic scan) in a situation like this, these two scans could have a difference due to the small time difference (1-2 seconds) in combination with the extreme variable radiation field.

With the detailed analysis (Table 2) we tried to distinguish clear, broken clouds and overcast conditions that could help the reader understand the limitations of the method and their dependence on cloud effects.

P1629, L12-24: It has to be taken into consideration that ratios that contain Brewer versus Bentham data include not only the limitations of the method but also instrumental differences between the two spectroradiometers. A sentence was added: “Finally, regarding the analysis presented including Brewer to Bentham instrument ratios, one has to take into account the two instruments’ differences. The global spectral irradiance data comparison from the two instruments in the UVB and UVA, showed a ratio of 0.971ś0.086 (2σ) and 0.973ś0.084 respectively (Bentham measuring higher) for the reported period.”

Discussion of the limitations of the method and P1628, L6-7: A paragraph was added at the conclusion section: “The method could be best used by scientists studying longer time scale datasets and looking at climatological conditions and changes. For individual cases one has to take into consideration the statistical analysis and results that are presented and also the uncertainties resulting from instrumental errors.”

Cosine heads: The analysis and the polynomial retrieval have been made using an instrument with no (<1%) cosine error. It is evident that if the polynomials will be implemented to an instrument with non-ideal angular response the results will be affected by this error. Generally the errors that are analyzed in this paper are linked with the method itself and not with possible instrumental errors of the spectroradiometers that could use it.

The cross section and quantum yield uncertainty: For both two the above comments A sentence was corrected: “It should also be noted that all σ values presented in this study are related to the uncertainty of the method itself and not with uncertainties of the cross section and quantum yield functions or instrumental (measurement) uncertainties.”

Figures 1 and 3: HCHO analysis was added concerning figures 1 and 3 as recommended.

Figures 2 and 4-8 artefacts - bins: The visible artefacts that are mentioned for the figures 2, and 4-8 are not the results of the binning method but of the measuring schedule of the instrument. The instrument was measuring at fixed time (every whole and half hour) and this resulted to an unbalanced data set in terms of solar zenith angle coverage (in terms of 1 degree solar zenith angle set). A frequency (1 degree solar zenith angle) distribution analysis showed a systematic feature: 30-40% of the measurements at each 5 solar angle bin are measured to a fixed angle and then the number of measurements are decreasing systematically for the rest 4 angles of the bin.

This effect (which to our opinion is not so crucial for the whole analysis) shown in figure two where the actual measurements are presented is transferred also to the other plots as reported.

Standard deviation: Since two STD’s are most commonly used for the characterization of the dataset, all standard deviations (1 sigma) where changed to 2 sigma in both text and figures.

Technical corrections: All typos were corrected as suggested.

General comment: A paragraph was added in the text to explain the choice of the J(NO2) instead of J(NO2)/J(pseudo) parameterization as a function of Irradiance and solar zenith angle.

“Alternatively, using global irradiance instead of actinic flux in formula (8), a series of pseudo NO2 photolysis frequencies (Jpseudo) were produced and the ratio J(NO2) / Jpseudo as a function of the global irradiance integral (E375-400) was examined. 3rd degree polynomials J(NO2)/Jpseudo = f(E375-400) were retrieved, and their application showed similar results to those derived from the first method described. (Their average ratio was 1.002ś0.100 (2σ) including all solar zenith angles). This technique is similar to the J(O1D) analysis presented in Kazadzis et al., 2004, (using J(O1D)/Jpseudo ratio and irradiance at 325nm) so the implementation of this method for J(NO2) data using the integral of the irradiance (E375-400) and solar zenith angle is also described. The advantage of using the first method described, directly retrieving J(NO2) from global irradiance, is that input optic spectroradiometers having upper wavelength limits lower than 420nm, (e.g. Brewer single and double spectroradiometers) can be used, as it is described in section 3.3. “

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 1619, 2005.

ACPD

5, S457–S461, 2005

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