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

Anonymous Referee #1

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GENERAL COMMENTS:

Irradiance measurements exist in widespread networks in a long historical database. Actinic flux measurements, on the other hand, require relatively expensive, complex equipment and carefully calibrated detectors. Actinic flux measurements consider photons from all directions equally and is used to calculate molecular photolysis frequencies. Irradiance measurements, on the other hand, rely on a cosine response optic. Hence photons at the horizon are lost and a correction must be applied to calculate an actinic flux approximation. This paper bypasses a conversion of global irradiance

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(direct plus diffuse irradiance) to actinic flux. Instead, it explores an algorithm to calculate photolysis frequencies of jNO2 and jHCHO by comparing ground-based irradiance measurements directly with photolysis frequencies calculated from co-located actinic flux measurements.

SPECIFIC COMMENTS:

Introduction: The paper would be improved by a short description of the difference between global irradiance and actinic flux. Confusion between the two remains common in the broader scientific community.

Section 3.3: The average values of Jcalc/J(X) ratios are certainly useful in a climatological sense. However, the readers would be well served by a discussion of the limitations of the study. How well does the calculation track with actinic flux on a partly cloudy day? For instance, the error on individual points exceeds 75% in some instances. While these are extremes and due in part to the matching of different scan times (as discussed in section 3.3), the large overall errors, regularly exceeding +/-12%, indicate that the real-time variations in photolysis frequencies cannot be measured sufficiently by this method. Clouds and aerosols have a substantial effect on the local light environment, and cosine response instruments simply cannot measure this sufficiently. This effect is amplified at large SZA. Consider for example a light environment with the sun at $>$75 degrees SZA in variable clouds. The cosine head cannot properly detect whether or not the instrument is being shaded by clouds. This is perhaps the largest contributor to the errors in the ratios. The effect of this on the mean is noted on P1629, L12-24.

Thus, in situ chemical studies are not supported well by global irradiance measurements because the real-time spherical light environment (the actinic flux as seen by a molecule at a point in space at a particular time) is not measured. The method described in this paper is certainly an important contribution to the literature. However, it is best used by those studying longer time scale data sets and looking at climatological conditions and changes.

Additionally, the angular response of various cosine heads can be quite variable and this can have a significant impact on both real-time and climatological measurements as a function of SZA.

P1628, L6-7: See the discussion above. The ratio at high SZA (>85 deg) provides a satisfactory average, but the ˜12% (2 sigma) values are not useful for real time events "Satisfactorily" depends on the needs of the data user. (see also P1630, L7-9 and P1631, L5-6).

P1629, L21-24: This is an important note about the errors, but the reader should be aware that this does not significantly affect the analysis in this paper. The cross-sections and quantum yields are used consistently throughout the paper.

Figures 1 and 3: These figures would be improved by the addition of the HCHO data.

Figures 2, 4-8: The authors should explain the visible artifacts introduced by the binning method.

Figures 4-8 and discussion: I would like to hear any comments on the presentation of one standard deviation (STD) errors in this paper. One STD represents the range of 68% of the data (e.g. jNO2 would have +/- ˜6% error), whereas, two STDs represents 95% of the data (e.g. jNO2 would have +/- ˜12% error). Two STDs is commonly for this reason and would more closely characterize the range in photolysis frequency error..

TECHNICAL CORRECTIONS:

P1620, L22-23: Perhaps "several species" underrepresents the "numerous important species" affected by atmospheric photolysis.

P1622, L19: Typo "O3 catalytic"

P1628, L8: Typo "expected"

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