Supporting Information for

Enhanced Aerosol Mass in the Tropical Tropopause Layer Linked to Ozone Abundance

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1. Model calculation of ozone profile in the TTL

The natural ozone chemical cycle is described by the Chapman reactions as follows:

$$O_2 \xrightarrow{h\nu} O + O \quad \text{(R1)}$$

$$O + O_2 \xrightarrow{M} O_3 \quad \text{(R2)}$$

$$O_3 \xrightarrow{h\nu} O + O_2 \quad \text{(R3)}$$

$$O + O_3 \rightarrow O_2 + O_2 \quad \text{(R4)}$$

The rate equations for [O] and [O_3] are

$$\frac{d[O]}{dt} = 2j_{O_2} - k_2[O][O_2][M] + j_{O_3}[O_3] - k_4[O][O_3] \quad (1)$$

$$\frac{d[O_3]}{dt} = k_2[O][O_2][M] - j_{O_3}[O_3] - k_4[O][O_3] \quad (2)$$

Combining (1) and (2) we obtain

$$\frac{d[O + O_3]}{dt} = 2j_{O_2}[O_2] - 2k_4[O][O_3] \quad (3)$$

Since [O] $\ll$ [O_3], equation (3) can be written as

$$\frac{d[O_3]}{dt} = 2j_{O_2}[O_2] - 2k_4[O][O_3] \quad (4)$$

The fast interconversion between O and O_3 (R2 and R3) leads to the following relationship between O and O_3 concentrations (Seinfeld and Pandis 2016):

$$\frac{[O]}{[O_3]} = \frac{j_{O_3}}{k_2[O_2][M]} \quad (5)$$

Therefore the production rate of O_3 is expressed as

$$\frac{d[O_3]}{dt} = 2j_{O_2}[O_2] - \frac{2k_4 j_{O_3}[O_3]^2}{k_2[O_2][M]} \quad (6)$$

Where

- $k_2 = 6.0 \times 10^{-34}(T/300)^{-2.4}$, with an average of 1.7 x 10^{-33} cm^6 $molec^{-2}$ s^{-1} in the TTL.
- $k_4 = 8.0 \times 10^{-12}\, exp(-2060/T)$, with an average of 2.0 x 10^{-16} cm^3 $molec^{-1}$ s^{-1} in the TTL.
- j_{O_3} ranges from 3 x 10^{-4} s^{-1} (SZA=85°) to 6.5 x 10^{-4} s^{-1} at SZA = 0° in the TTL (Seinfeld and Pandis, 2016, Fig. 4.13 on p. 112).
- j_{O_2} ranges with increasing altitude from 2.0 x 10^{-15} s^{-1} to 7 x 10^{-14} s^{-1} at SZA = 0° in the TTL (2016, Fig. 4.12 on p.111).

From the observations we have the following average concentrations:

[M] = 1.5 x 10^{18} molecules cm^{-3}
$[O_2]$ = 0.21 x [M] = 3.2 x 10^{17} molecules cm^{-3}
$[O_3]$ = 117 ppb = 1.9 x 10^{11} molecules cm^{-3}

Using the these values, we find that the first term of equation (6) is $2j_{O_2}[O_2]$ = 1.2 x 10^3–4.4 x 10^4 molecules $cm^{-3}s^{-1}$, and the second term of equation (6) is $\frac{2k_4 j_{O_3}[O_3]^2}{k_2[O_2][M]}$ = 5.3–11.5 molecules $cm^{-3}s^{-1}$, which can be neglected as it is about 1000 times smaller than the first term. Therefore the O_3 formation rate becomes

$$\frac{d[O_3]}{dt} = 2j_{O_2}[O_2] \quad (7)$$

We used the vertical profile from Seinfeld and Pandis (2016, Fig. 4.12 on p.111) and the vertical profile of $[O_2]$ calculated from the measurements to derive the ozone production rate. The calculated vertical profile of the ozone production rate is shown in Fig. S7. The O_3 concentration in the TTL is calculated as

$$[O_3]_i = [O_3]_{i-1} + \left(\frac{d[O_3]}{dt}\right)_i \cdot \Delta t_i = [O_3]_{i-1} + \left(2j_{O_2}[O_2]\right)_i \cdot \Delta t_i$$

Where *i* indicates the parameters at altitude *i*, and Δt_i (5 s) represents the time it takes the air to rise from altitude *i*-1 to altitude *i*, using a constant ascent rate of 0.25 mm s^{-1} (Park et al 2010; Avallone and Prather 1996; Seinfeld and Pandis 2016). The calculation is performed for the

altitude range of 14.5–18.9 km, with a prescribed [O_3] at 14.5 km of 28.8 ppb, which represents the average observed O_3 concentration at that altitude.

References

Park, S., Atlas, E. L., Jimenez, R., Daube, B. C., Gottlieb, E. W., Nan, J., Jones, D. B. A., Pfister, L., Conway, T. J., Bui, T. P., Gao, R. S. and Wofsy, S. C.: Vertical transport rates and concentrations of OH and Cl radicals in the Tropical Tropopause Layer from observations of CO 2 and halocarbons: implications for distributions of long- and short-lived chemical species, Atmos. Chem. Phys., 10, 6669–6684, doi:10.5194/acp-10-6669-2010, 2010.

Seinfeld, J. and Pandis, S.: Atmospheric chemistry and physics: from air pollution to climate change, Wiley, Hoboken, N. J., 2016.

Supporting Figures

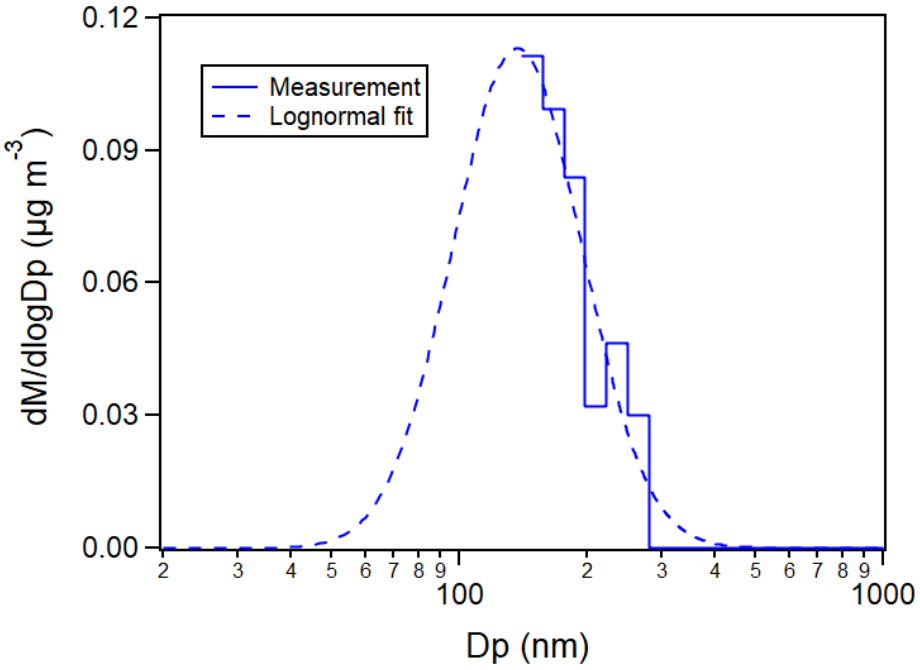

Figure S1. Lognormal fit of the average mass size distribution for the TTL measurements.

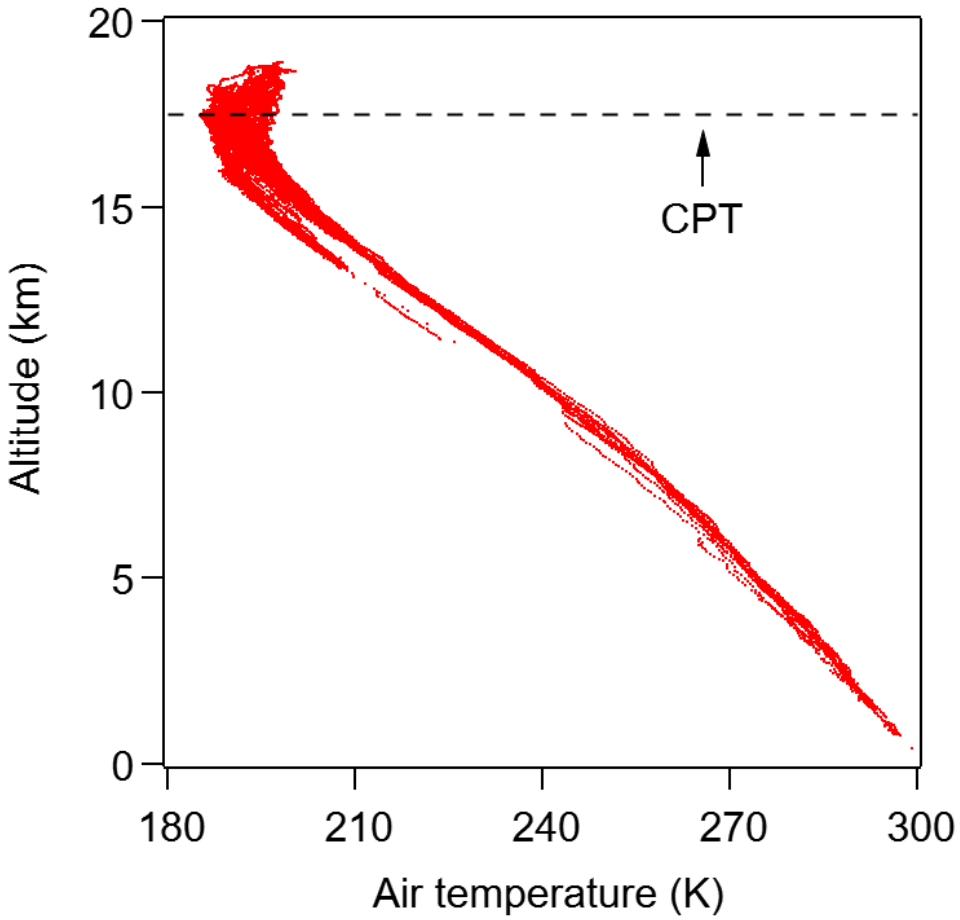

Figure S2. Vertical profile of air temperature measured from all flights.

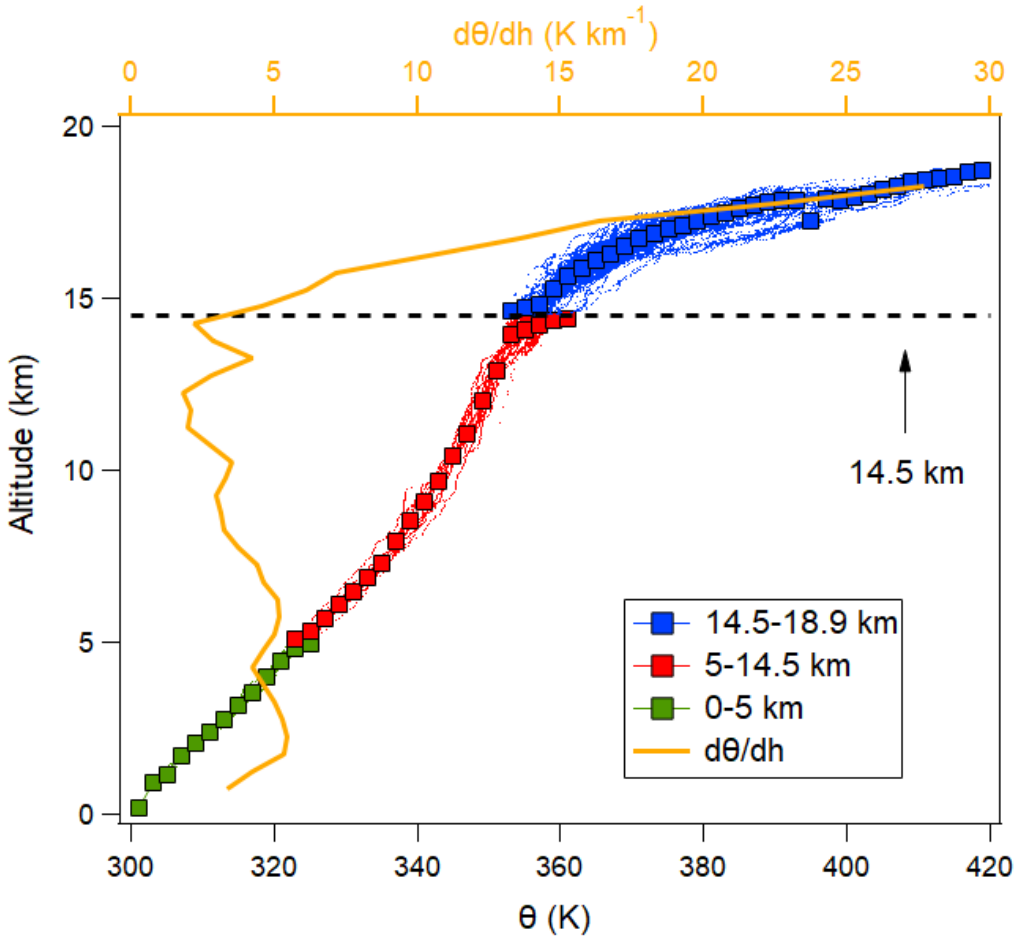

Figure S3. Vertical profiles of potential temperature (θ) and the lapse rate of θ. In the altitude-θ profile, individual data points (5-s averages) are shown by the dots and the averages (by θ of 2K) are shown by the solid squares.

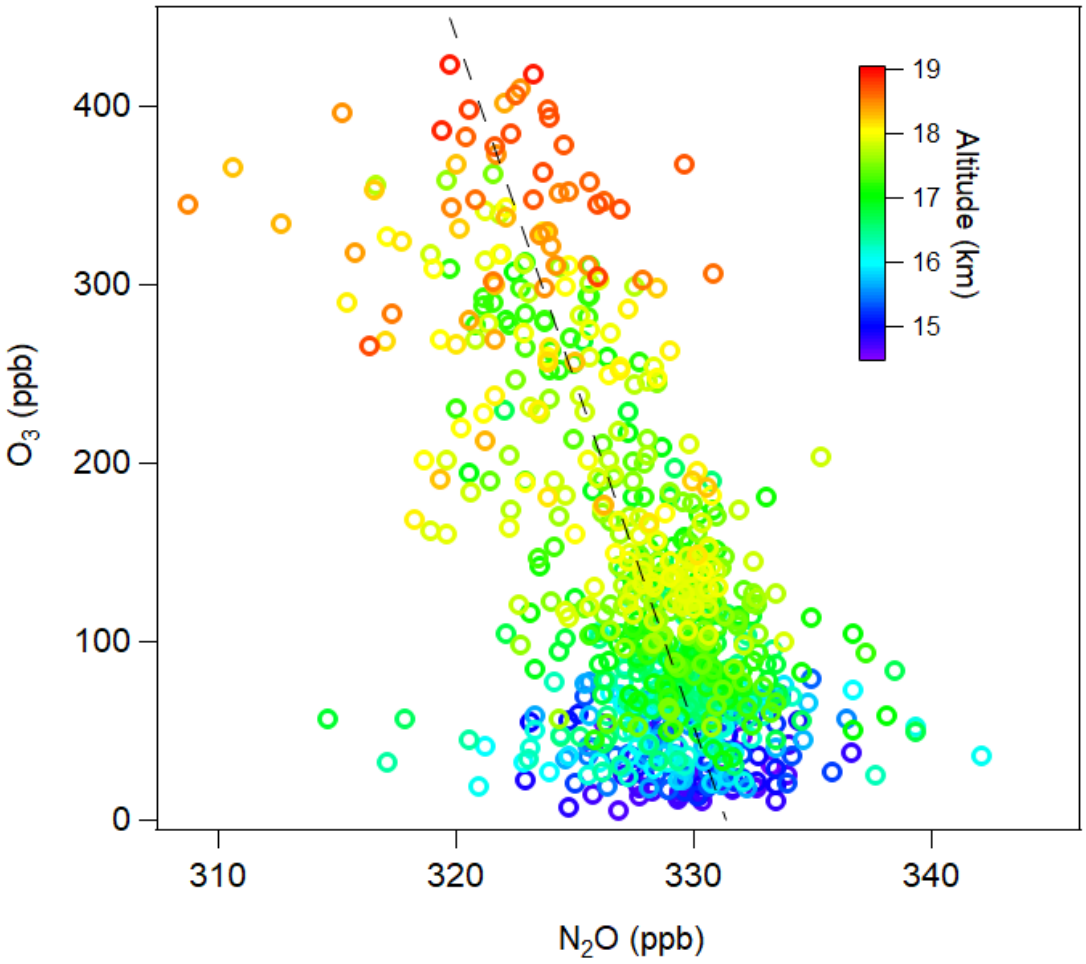

Figure S4. Scatter plot of O_3 versus N_2O in the TTL. The dashed line indicates linear fit.

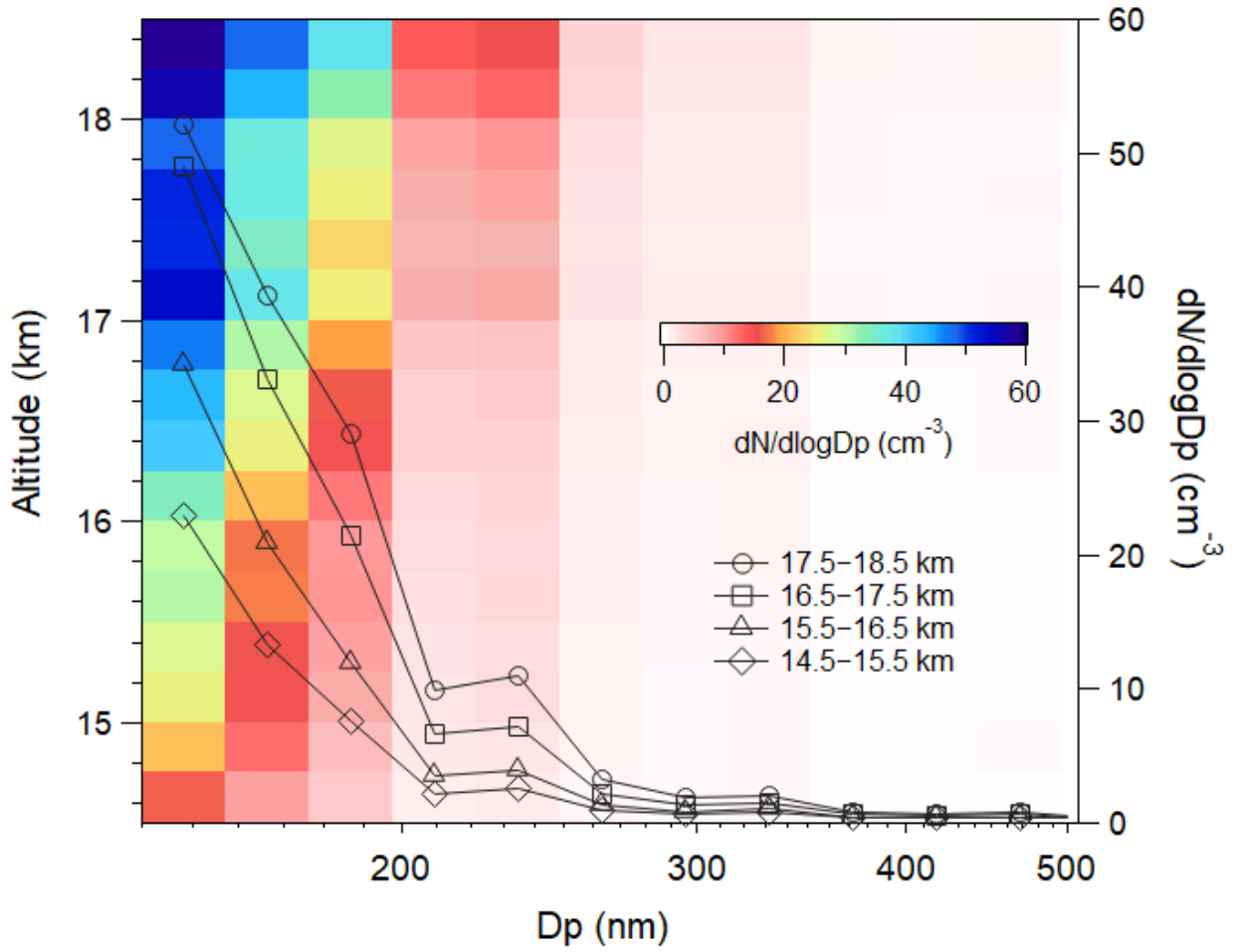

Figure S5. Image plot illustrating aerosol number size distribution with altitude in the TTL. The line and markers represent averages at various altitudinal intervals.

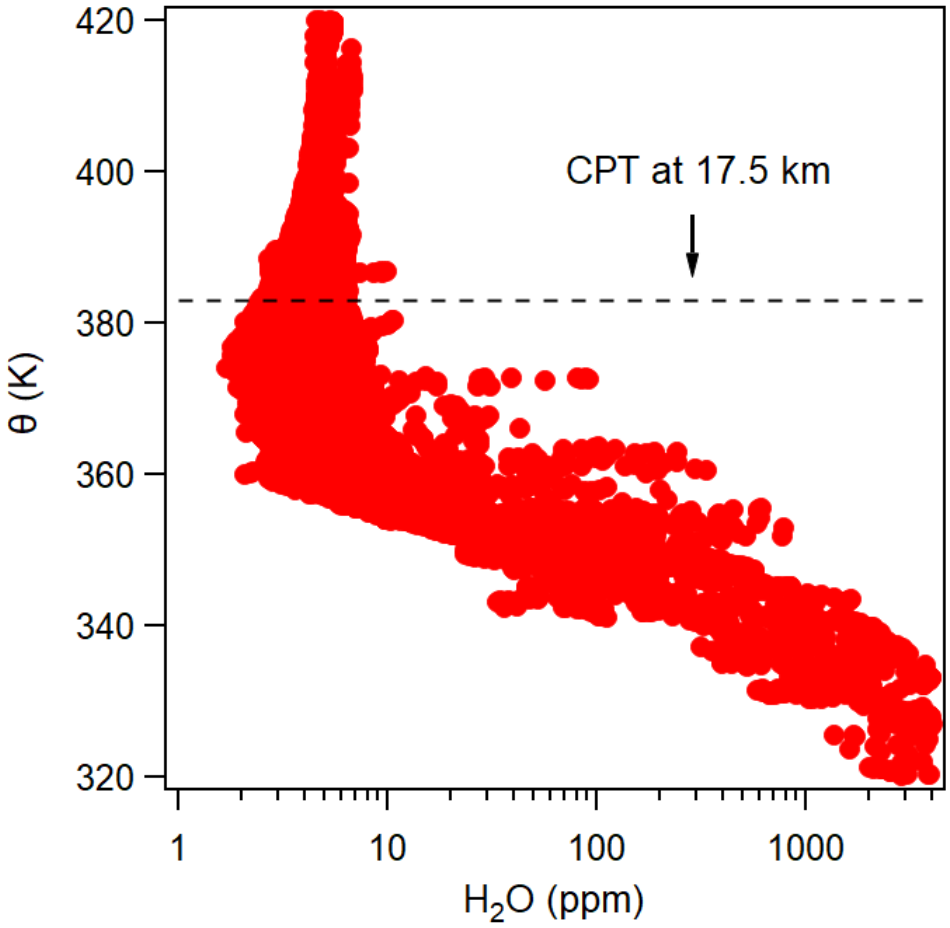

Figure S6. θ versus water vapor mixing ratio.

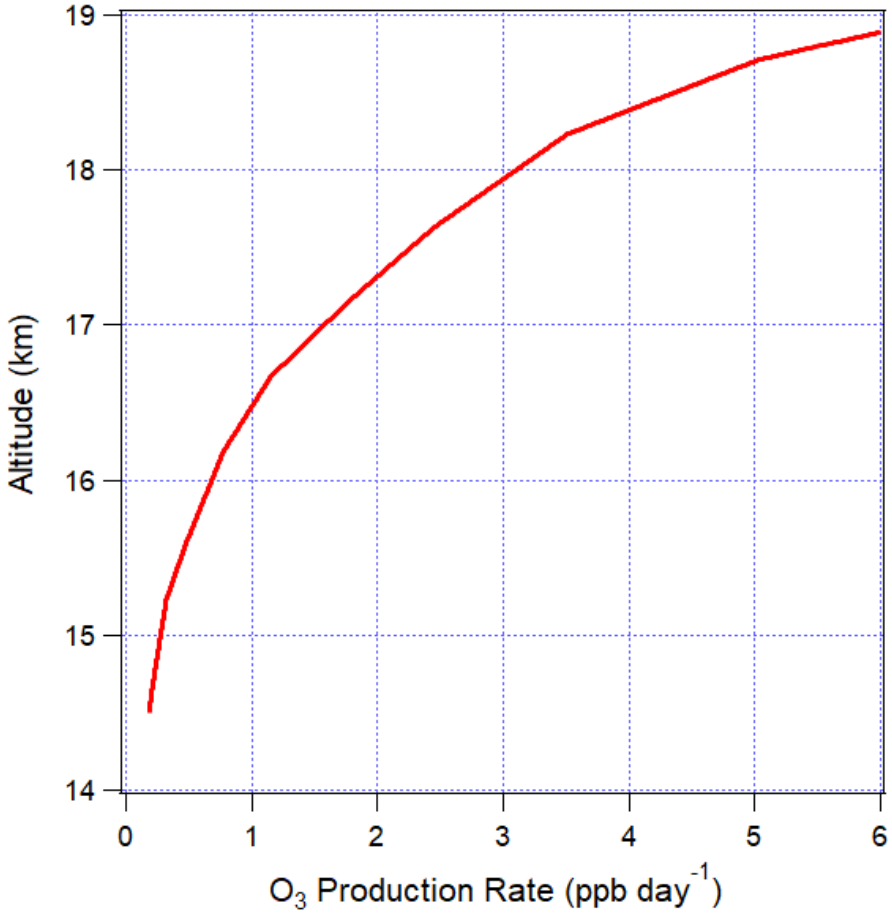

Figure S7. Calculated vertical profile of ozone production rate in the TTL.