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Supporting Information for

Long-term Baseline Ozone Changes in the Western US: A Synthesis of Analyses

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Introduction

This supporting information presents additional discussion of the northern mid-latitude ozone distribution with illustrative figures and their explanations, which support the analysis and interpretation of results in the main text. Figure S1 is an estimation of the important time scales influencing ozone concentrations in the northern mid-latitude troposphere and their dependence on altitude. Figure S2 is a plot derived from the multi-model ensemble of troposphere ozone budgets compiled in Table 5 from Stevenson et al. (2006). Figure S3 illustrates the autocorrelation functions from two de-seasonalized ozone time series used in this work (Pacific MBL and Lassen NP.)

Text S1. Vertical Dependence of Major Tropospheric O_3 Timescales

In order to compare relevant time scales of vertical convective mixing, horizontal advection, dry deposition, and photochemical destruction as a function of height we estimated them in the following manner and present them in Figure S1. We use the NCEP Reanalysis Seasonal Climate composites page (https://psl.noaa.gov/cgi-bin/data/composites/printpage.pl) to derive annual mean values of air temperature, specific humidity, and zonal wind speeds from 30°N to 60°N at each of eight altitudes from 1–8 km to establish mean conditions for chemical reaction rates and horizontal advection rates. To estimate the vertical mixing due to convection we use the ERA-40 reanalysis data of convective mass flux as reported in Doherty et al. (2005) for the zonal band from 30-60N. The mass fluxes are converted to vertical velocities by the air density and these are added in series to get the progressive time scales for mixing up/down into the free troposphere. To derive time scales for dry deposition we link these convective rates with an average deposition velocity of 2.1 mm/s with the understanding that at midlatitudes in the Northern Hemisphere the surface is about half ocean (v_d ~ 0.25 mm/s) and half land (v_d ~ 4.0 mm/s). The photolysis frequencies for generating excited atomic oxygen, $O(^1D)$, as a function of height are taken from observations over the North Pacific presented in Hall et al. (2018) from the ATom-1 mission and scaled for diurnal and annual averaging. Reaction rates for OH + O_3 and HO_2 + O_3 and $O(^1D)$ + H_2O, N_2, and O_2 are calculated from the coefficients provided in the JPL publication 15-10 (Burkholder et al., 2015). Representative daytime/spring tropospheric profiles of OH and HO_2 were estimated based on Tan et al. (2001).

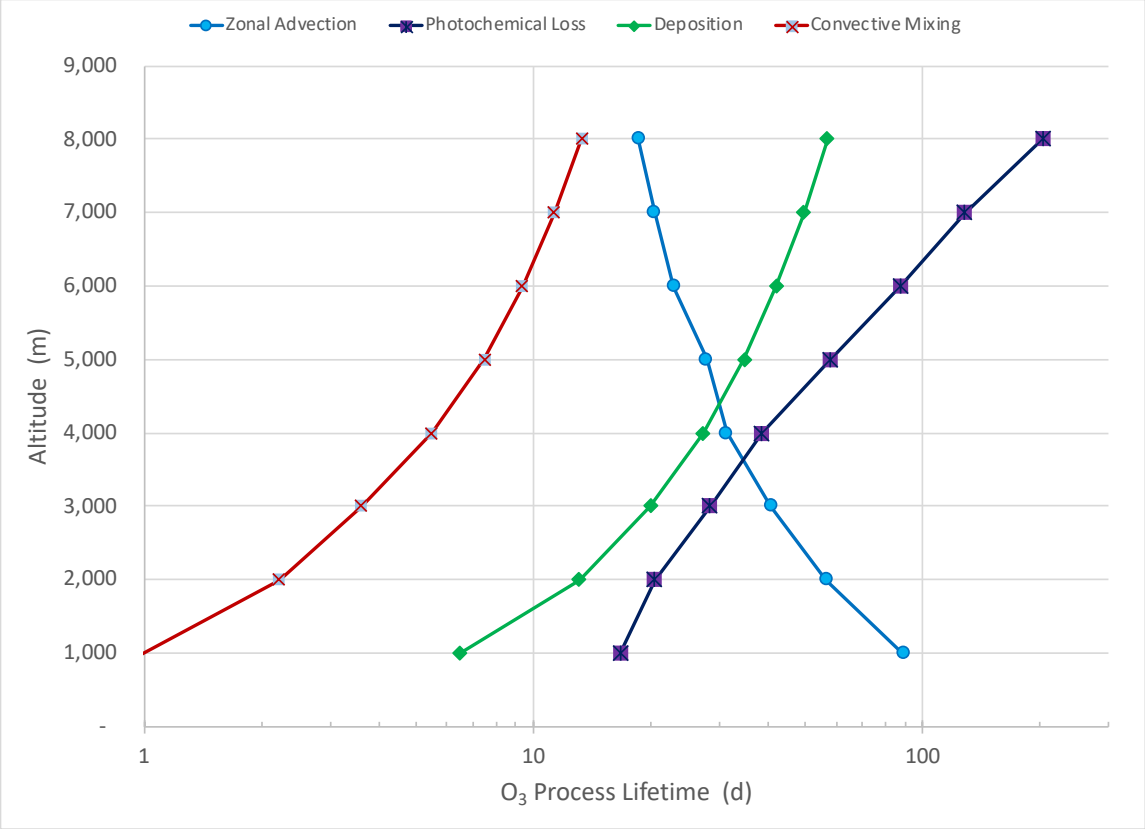

Figure S1: Vertical Dependence of Major Tropospheric O_3 Timescales in the Zonal Band from 30°N – 60°N.

Text S2. Correlation Among 26 Global Chemical Transport Models' Gross Production and Loss of Tropospheric Ozone

A common relationship found in global chemical transport models with respect to the tropospheric ozone budget is that the gross photochemical loss rates are typically about 5-10% smaller than the gross production rates, regardless of their absolute magnitude. Figure S2 plots the 21 loss and production values from the models surveyed in Stevenson et al. (2006), and also includes the background tropospheric run of Crutzen et al. (1999). Aside from the difference in absolute values in all the models spanning about a factor of two, the production and loss terms tend to compensate to a great degree due to the related photochemical cycles of O_3, HO_x, RO_2, and NO_x. The one counter-example is the run without anthropogenic sources reported by Crutzen et al. (1999) where the high loss rate is sustained by an extremely large stratospheric source in that model, which was two and a half times larger than the model mean in Stevenson et al. (2006).

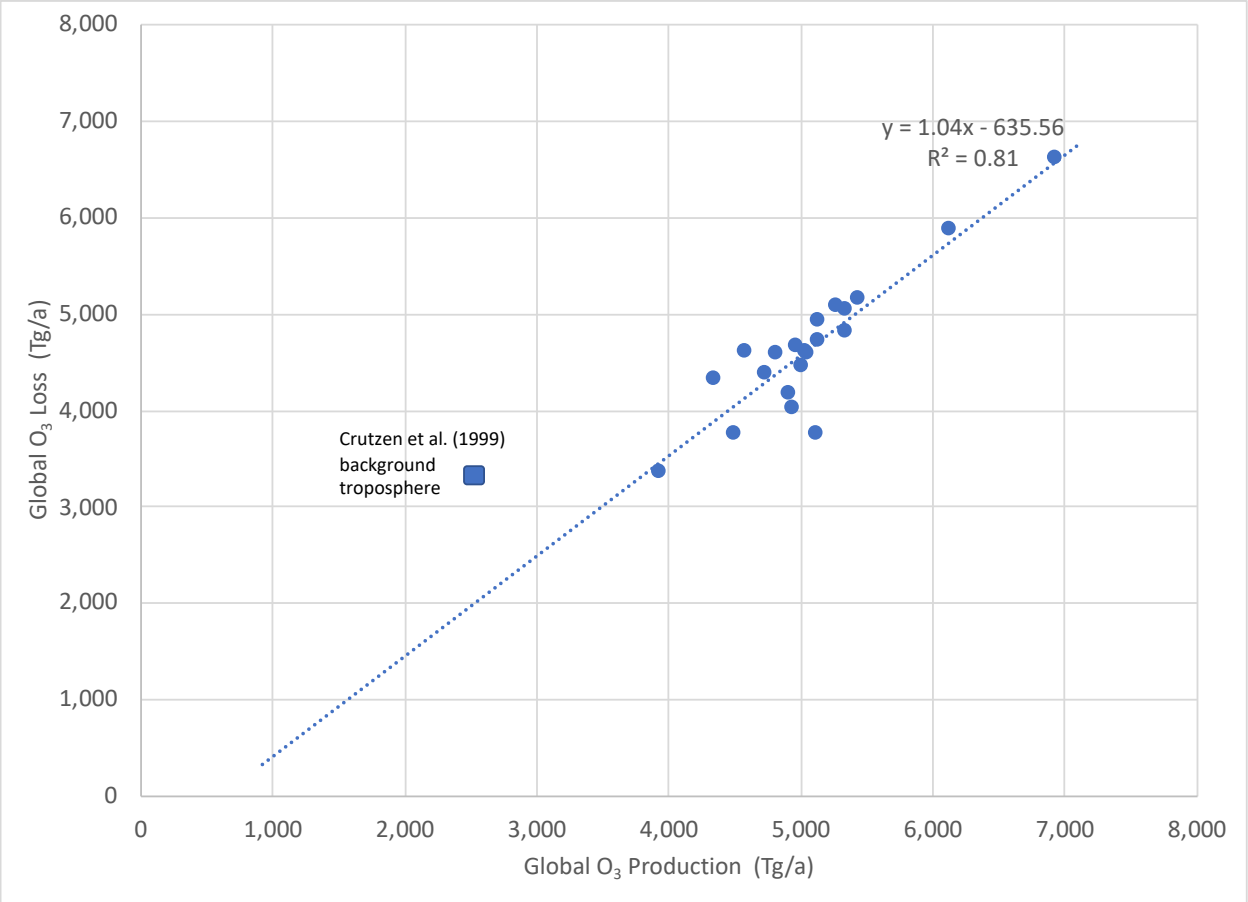

Figure S2: Correlation of gross photochemical production and loss rates among 21 chemical transport models tabulated in Stevenson et al. (2006).

Text S3. Similarity of zonal mean ozone at northern mid latitudes

The conceptual picture for understanding the long-term changes of ozone at northern mid-latitudes recognizes that the circum-global transport time is significantly shorter than the net lifetime of ozone, which implies that a relatively constant zonal mean ozone concentration exists. The circum-global transport time is about 25 to 30 days, as indicated by a simple tracer experiment of a surface release using a global Lagrangian chemistry-transport model (STOCHEM-CRI; Derwent et al., 2018) driven by 1998 meteorological fields from the UK Meteorological Office Unified Model archive (Collins et al., 1997). The STOCHEM-CRI model finds that the northern mid-latitude ozone lifetime is about 50 to 60 days, when only loss processes are considered. However, in situ ozone production from photochemical oxidation of precursor compounds proceeds simultaneously with the photochemical and dry deposition loss processes to partially balance the loss; consequaently the mean net lifetime of ozone in an isolated air parcel at northern mid-latitudes is several months or longer. Meridional eddy fluxes of ozone can lead to perturbations of local concentrations, but on average the meridional gradients of ozone are small at 30 and 60 N (e.g., Figure 2 of Crutzen et al., 1999), as are the mean meridional winds (e.g., Figure 7.17 of Peixoto & Oort, 1992); thus meridional advection does not, on average, significantly affect the mid-latitude budget of tropospheric ozone.

Within the midlatitude troposphere the rate of photochemical ozone loss decreases, while the speed of advection increases with altitude. Writ large, vertical gradients in baseline ozone arise due to the elevated source in the stratosphere coupled to the surface sink of dry deposition. Modeling of background ozone by Crutzen et al. (1999) indicates that net photochemical production above about 800 hPa in the northern midlatitudes ranges from -1.0 ppb/day in the lower troposphere to +0.2 ppb/day in the upper troposphere, further reinforcing the overall positive vertical gradient in baseline ozone, and suggesting a lifetime of ~100 days with respect to net photochemistry throughout the bulk of the troposphere. However, typical convective mass flux schemes suggest that the overturning time scale is less than ~ 20 days at northern mid-latitudes (Figure S1), which tends to minimize the vertical ozone gradient (e.g., Fig 1B, Lelieveld & Crutzen, 1994). Overall, the long net ozone lifetime, zonal transport, and relatively rapid vertical overturning implies that a mean ozone concentration is established on a time scale of weeks to months, and that this mean concentration must be similar throughout northern mid-latitudes. This picture also implies a relatively smooth and systematic seasonal cycle of ozone in baseline air masses.

Text S4. Ozone variability at northern mid latitudes

Ozone varies about the zonally similar mean ozone concentration on a wide spectrum of shorter and longer time scales. The mean ozone concentration varies seasonally, due to seasonal changes in sources and sinks. An air parcel within the circulating river of air receives sporadic injections of ozone and its photochemical precursors from European, Asian and North American anthropogenic sources and from the natural stratospheric source. Ozone injected from the extremely arid stratosphere maintains an anti-correlation with water vapor across vast expanses of the troposphere (Newell et al., 1999) extending its photochemical lifetime with respect to OH production. The infusions of anthropogenic NO_x and VOC precursors into the general tropospheric flow, accelerate photochemical ozone production, but also concomitantly enhance photochemical losses as well due to increases in HO_x abundance and production of NO_3 radicals in the dark. Consequently, significant deviations from the circulating mean ozone are brought about in the environment of prolonged net photochemical lifetimes. In addition, air parcels with different ozone production and loss histories are entrained from and exported to

higher and lower latitudes. The overall result is local and regional, quasi-chaotic ozone variability superimposed on the mean concentration.

Text S5. Quadratic fits vs. Linear trend analysis

Cooper et al. (2020) discuss two particular problems with the use of polynomial fits to characterize long-term ozone changes. The first is the inability of polynomials to describe multi-year ozone fluctuations that can be fit by other techniques. For our purposes, this inability is an advantage rather than a problem, because we aim to avoid the influence of multi-year ozone fluctuations, i.e., interannual variability, which obscure the systematic decadal scale changes that are our focus. The second identified problem is that the long-term change determination over the entire time span of the measurements, including at the beginning of the data record, is impacted by additional data added to the end of a time series as new measurements are made. The results of polynomial fits do change in this manner, because the parameter values are more precisely determined by longer time series, but these more precise parameter values generally fall within the confidence limits of the earlier derived, less precise parameters. Moreover, fits to progressively longer time series allow for the inclusion of additional terms in the polynomial fits, allowing flexibility in fitting the later data, and minimizing changes of the fit to the earliest measurements. Notably, this second problem also characterizes linear trend analysis, as the derived trend generally changes as a time series of measurements is extended; however linear trend analysis does not provide a means for the functional form to evolve as non-linear changes become apparent. Parrish et al. (2019) show that the polynomial fits, as used in this work, provide an effective approach for quantifying non-linear, long-term changes of atmospheric concentrations. The ability of polynomial fits to effectively quantify non-linear, long-term changes in the presence of substantial interannual variability is more important for our purposes, than are any problems.

Text S6. Autocorrelation functions for two of the time series used in this analysis (Pacific MBL and Lassen Volcanic NP)

The de-seasonalized monthly ozone residuals for two of the time series in the analysis of Parrish et al. (2020) are used to calculate their autocorrelation functions shown in Figures S3. The decorrelation times indicated in the annotations are used to correct the confidence limits of uncertainties of the parameters derived in the long-term change fits. While the majority of the autocorrelation fades after 1-2 months, lingering autocorrelation out to 3 years can be seen in the Pacific MBL data, and from 2-4 years in the Lassen NP data. Failure to adequately account for autocorrelation of data over the full spectrum of significant time scales results in an overestimation of the accuracy of parameter values (i.e., underestimations of their confidence limits) derived from any linear or non-linear regression analyses such as the literature results discussed in our manuscript and included in Table 1. This lingering autocorrelation issue is at least partially overcome by the 2 year means used in deriving the Figure 1.

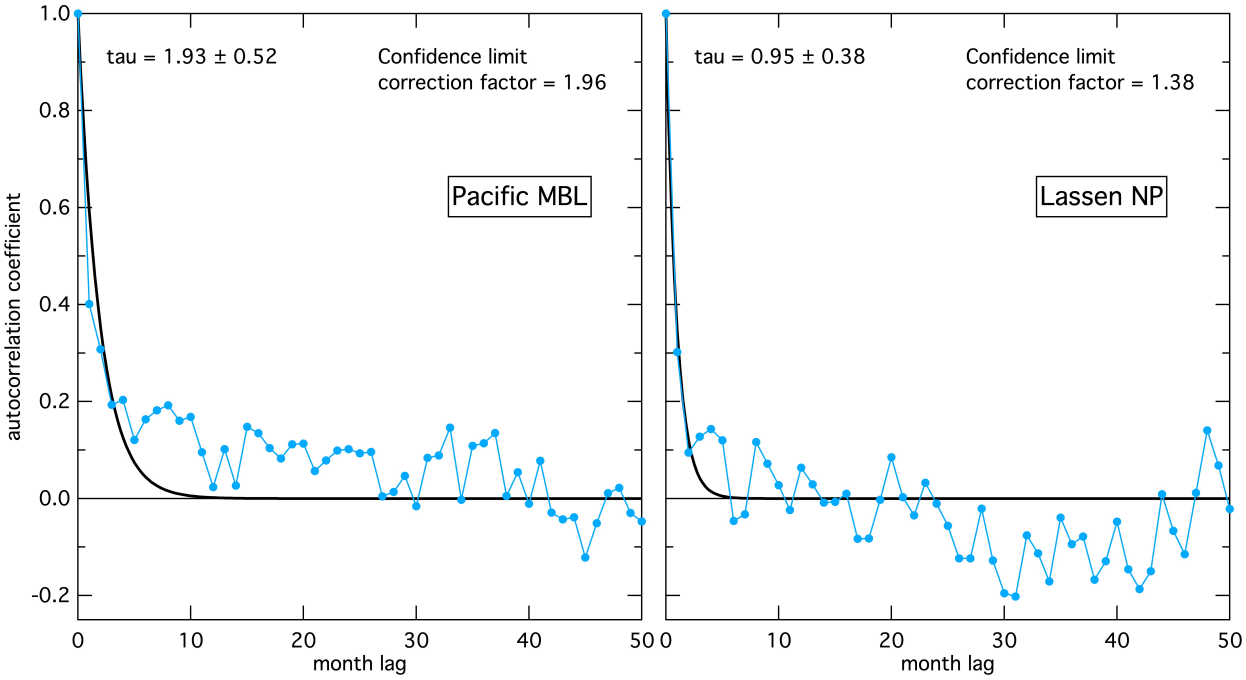

Figure S3: Autocorrelation functions for the (left) the 21 year time series in the Pacific MBL and (right) the 15 year time series from Lassen Volcanic NP. An exponential function is fit to the near-term function to estimate the correction to confidence limits of the decadal trends reported in the literature.

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