

Response to Referee #2 comments on "Photochemical Production of Ozone and Emissions of NO_x and CH₄ in the San Joaquin Valley" published 19-Feb-19
Review Received and published: 8 March 2019

We thank the referee for their thorough reading of the manuscript, and address the individual comments below:

Trousdell et al. present data from flights over the San Joaquin Valley in California. They calculate NO_x and CH₄ emission rates for this region, as well as photochemical ozone production rates. This could be a good paper, however it is currently lacking in several ways. First, the authors should describe the steps taken to determine the different terms in equation 1. Show a vertical profile of NO_x, show how you determine z_i, etc. This will make it easier for the reader to follow the authors' conclusions.

Because these methods have been repeated in several previous papers from our group [Trousdell et al., 2016; Conley et al., 2009; Faloon et al., 2009; Conley et al., 2011] and the scope of this work is already expansive, we have chosen to minimize the step by step elaboration of the scalar budgeting method. On p.8, l.10 we state, "For a more in-depth discussion of the airborne budgeting technique and specifics for the budgets of methane and ozone in the SJV see Trousdell et al. (2016)." But we have added an example profile in the supplementary materials (new Figure S1) and a more explicitly methodological review in the text stating, "Boundary layer heights were determined from each profile (approximately 8-12 per flight) based on the abrupt increase in potential temperature and drop in water vapor. The locations and time of each of these observations were then fit by a multilinear regression in time and the horizontal dimension to determine the ABL growth rates and gradients which go into the budget to determine the entrainment velocity (Trousdell et al., 2016). Taking all the airborne data observed below the derived (linear) time-dependent ABL depth we then perform the same multi-linear regression for all the scalars including potential temperature, water vapor, O₃, NO_x, and CH₄. Aligning the x-axis with the mean wind direction, U, the advection and temporal trend terms of Equation 1 are derived from the coefficients of the linear regression fit to the ABL NO_x concentration field in time and horizontal direction (Conley et al., 2011)."

The writing style should be improved as well. This paper would be better if the authors **introduced each section** with some background information about **what they are doing and why**. There are numerous grammatical mistakes throughout the paper. I have tried to correct some, listed below. Commas should separate introductory clauses in sentences. Often there are missing spaces between words and parentheses. Subscripts are sometimes missing. Until these changes are made, I find it difficult to properly review it. Therefore, I recommend that major revisions are necessary.

Because Section 4 is very detailed and has many subsections, we have introduced the introductory paragraph below to help guide the reader through the reasoning of this reticulate section:

"4 Results and Discussion

In the following section we present a variety of inferences gleaned from the three scalar budgets performed for NO_x to derive regional surface emissions (4.1.1), and for O_3 to derive afternoon photochemical production rates (4.1.2) and see how that fits in to the overall diurnal budget of ozone (4.1.2.1), and for CH_4 to derive regional emissions (4.1.3). Because of the large discrepancy between our estimates of NO_x emissions and that of the state inventory, we further explore possible reasons to explain the difference. The first is the hypothesis put forward by Almaraz et al. (2018) that there is a substantial source of NO from fertilized agricultural soils that is not accounted for in current state inventories (4.1.1.1). The second is the possibility that the Soberanes Fire in the mountains of the Coast Range approximately 200 km to the west may have influenced our NO_x budget in the ABL around Fresno (4.1.1.2). The third explores the bias introduced by measuring only during the afternoon when NO_x emissions are thought to be highest (4.1.1.3), and the fourth discusses the possibility of a chemical interference in the measurement of NO_2 , which in our system relies on photolysis followed by the chemiluminescence measurement of NO (4.1.1.4). The interference hypothesis is further explored by calculating Leighton ratios (4.1.1.5) in order to determine if the observed $\text{NO}_2:\text{NO}$ ratios appear consistent with the theoretical photostationary state between O_3 , NO, and NO_2 expressed in the Leighton ratios. This latter point leads naturally to the discussion of our estimates of ozone photochemical production (4.1.2) because it, in principle, is related to deviations in the observed Leighton ratios. Next, we present the observed spatial patterns of these scalars in the ABL calculating their horizontal autocorrelation lengths (4.2) to potentially infer emissions heterogeneity, and then finally we discuss the way we estimate the errors (4.3) in all the derived values of this budgeting study."

Some other questions I had are as follows:

More explanation is needed for the boundary layer height (ABL). For these flights, what were the ABL heights determined from aircraft and from the model. What were they used in Equation 1?

We did not include these details in this manuscript because we are preparing another, companion paper that focuses strictly on the entrainment and ABL dynamics of the valley. That work will present boundary layer heights as well as the observed growth and advection rates, and ultimately the inferred entrainment velocities used in the scalar budgeting in this work. We have included the average boundary layer heights for each flight in Table 1, and where we mention this companion work we have added the average values:

"In a future companion paper, along with the boundary layer heights, z_i , (650 ± 50 m) and entrainment velocities, w_e , (3.0 ± 1.8 cm s^{-1}), we present the surface sensible heat fluxes for our flight region via two independent methods."

p. 5, line 5, and Figure 2, define in what time period is this probability calculated?

The data interval of 2006-2015 is now mentioned in the text and in the figure caption.

p. 5, line 21, before using WRF for vertical mixing, how does the model compare with ABL heights?

The WRF model predicts ABL depths that are approximately 30% larger than our observations. However, we plan to discuss and explain this in the aforementioned companion work to be submitted to "Boundary Layer Meteorology" soon. The WRF results central to this study are the vertical velocities at the top of the observed ABL heights, which should not be directly linked to the ABL results of the model.

p. 9, line 7, add units to 6×10^6 . Table 1 needs more information/description. Are the authors solving for F_0 ? What are the estimates of z_i on these days? Also, you should use the same notation for average scalar as in Equation (1).

Done.

p. 13, line 24, Please explain where this 59% number comes from

Upon reviewing the weekend/weekday bias, we found that we had overestimated its effect. We have rewritten the section to make it more clear, and the conclusion is that our sampling bias (due to hour of day and day of week combined) may be 45% higher than a long-term average inventory value as explained in the text:

" Assuming an average decrease of NO_x emissions on weekends to 0.73 the weekday rate, our average daily emission rate would be a factor of 1.04 ($= (5.73/6.46) \times (7/6)$) higher than inventories, which average over 5 weekdays and 2 weekend days. Taken together, the timing of the flights relative to the inventory's average summer emission rate could lead to a positive bias in our measurements of 45% ($= 1.4 \times 1.04$)."

Section 4.1.1.5., explain what the Leighton ratio is before discussing the deviation of it and presenting a modified ratio

Done.

Supplemental Information, Figure 1: It appears the conversion had some formatting errors

Apologies, the supplement has been reproduced (with an additional figure requested above) and resubmitted.

Grammar:

p. 2, line 2, add comma after “scalars” p. 3, line 9, change to “data tend to be” p. 9, line 1, add comma after “budgets” p. 9, line 22, change “%50” to “50%” p. 10, line 2, change to “data were” p. 11, line 22, add a comma after “In their model for soil NO_x” p. 12, line 13, start sentence with “It is . . .” p. 12, line 14, add comma after “satellite” p. 12, line 21, add comma after “urban air” p. 13, line 6, subscript the 2 in “NO₂” p. 14, line 20, change “try and” to “try to”, and subscript “NO₂” p. 14, line 25, change “lose” to “loss”, and subscript “NO₂”. p. 15, line 12, I’m confused by “14-6” p. 16, line 3, end sentence after “temperature” p. 16, line 16, the sentence beginning with “Marr” needs to be re-written. p. 16, line 23, change “where” to “were” p. 18, lines 11 and 12, subscript the 3 in “O₃” p. 20, line 16, change comma between “CH₄” and “NO_x” to “and” p. 21, line 9, subscripts for NO_x and CH₄ Figure 6 caption, there is something missing between “2.” and “10.7”

Ok, these changes were made.