We would like to thank reviewer #1 for reading and re-reading our manuscript and providing additional, conscientious feedback. Below are our point-by-point responses.

**General comments**

- The paper is excessively wordy and there are grammar errors. I urge the authors to use less words whenever possible and en dashes in their compound adjectives to enhance readability and check their grammar.
- There needs to be more consistent use of terms and abbreviations. For example, sometimes the authors use "RL" and sometimes "residual layer"
- The abstract should be treated as separate from the paper and the abbreviations and terms should be re-defined.

We have attempted to reduce the wordiness of the manuscript where possible, and utilized all acronyms consistently.

- "pairs of flights" needs to be introduced as early as the abstract. It's not a given that pairs of flights means night and following morning.

Done.

- More information on the regressions should be given. The authors regress ozone on x, y, and z, and then calculate the partial derivatives? What is the error and amount of variability explained by the regression? How many data points go into the regression?

Separate regressions were performed for every flight. We have clarified this in the text and summarized the key parameters ($r^2$, n, slope errors, etc.).

- Again, I urge the authors to shorten and clarify their discussion of nitrate, as it is hard to follow.

We have accepted most of the reviewer's suggested edits for this section. However, these key processes of nitrate loss have not been explicitly stated in other literature, so we feel that it is necessary to go through them in a thorough, step-by-step format. This justifies the importance of nitrate loss for the nocturnal ozone budget as one of our key conclusions of this study.

We made one additional minor change where we state that the VOC pathway of nitrate loss can consume either 1 or 2 $O_x$ molecules.

- It would be very useful for the reader if section names were a bit more detailed (e.g., articulated findings, or objectives).

Done.

- I still find it challenging to interpret Figure 9 with the topography on the map. I urge the authors to reconsider including the topography on this figure.

We have removed the topography for this particular figure and colorized the contours.

**Line-by-line comments**

Line 82: Insert “, which is ” before known more generally

Done.

Line 102-130: This introductory paragraph on the Fresno Eddy is extremely long and still seems out of context. Please better contextualize this discussion.

We have more clearly stated up front (in the introduction, abstract, and conclusions) our aim in discussing the Fresno Eddy. Namely, we point out that the LLJ is a branch of the Fresno Eddy, which induces nocturnal vertical mixing. This mixing may counteract the effect of the eddy recirculating ozone and its precursors.

Additionally, In accordance with the reviewer’s suggestion we have chosen to move much of the detailed discussion of the Fresno Eddy formation from the introduction section to the section on the Fresno Eddy and LLJ.

Line 115: Many readers may not know what a Froude number is. Please briefly define
Line 114-5: “act as a barrier to the jet” is not clear; please rephrase

After further consideration, we have removed the specific Froude number threshold since the Lin and Jao (1995) model did not initialize the flow parallel to the Tehachapi mountains. Changed to “The Tehachapi Mountains will topographically block the flow of the LLJ (Lin and Jao, 1995).” And this is now in section 3.3.

Line 115: By “eddy feature” do the authors mean the eddy? Please clarify in text

Removed “feature”.

Line 140-2: This is helpful to the reader, but it seems quite strange to have this description without a prior introduction of the study in the introduction

We moved this statement to the last paragraph of the introduction where the general scientific layout and objectives of this study are outlined.

Line 148: typo

Cut “currently made”.

Line 149: “ozone problems” is too colloquial

This sentence was removed in order to reduce wordiness of the paper.

Line 150-5: This paragraph would benefit from a sentence introducing that the authors are going to start talking about modeling. The authors need to more directly state that models don’t capture the nocturnal circulation motivates their study in the text.

Added “Owing to the complex topography and stable stratification overnight, the dynamics of the NBL and RL in California are difficult to model.”

Line 151: “—“ should be “-“; please check elsewhere that the authors use of “—“ vs. “-“ is correct.

Done.

**Line 157-69: This is too long and the motivation from daytime studies is a bit convoluted. I brought this up previously but I don't feel like the authors sufficiently addressed my concern (or convinced me that the discussion is necessary). Can the authors simply say that most studies focus on the day, and thus our understanding of the nocturnal ozone budget and mixing on ozone air pollution more generally is limited?**

We have removed the detail about the role of horizontal advection in past daytime budget studies, to improve the flow of this paragraph. We do, however, believe that the references to past daytime budget studies is appropriate in the introduction to give readers the ability to investigate the different uses of this technique. Because the nitrate chemistry is so central to the interpretation of this study's results we believe it is important to maintain the general outline of the major chemical pathways in the introduction.

**Line 171: Why are there quotes on depletes?**

Removed quotations.

**Line 175: Please give the audience context for "broader dataset" - what dataset are the authors using? Also, please say the goal of this analysis here.**

Changed to "Second, to determine whether our findings can be generalized to climatological timescales we analyze synoptic conditions around the LLJ, and look at a broader dataset of LLJ strength and the following afternoon's ozone concentrations using Radio Acoustic Sounding System (RASS) and California Air Resources Board (CARB) ground network data (sections 3.3 and 3.4)"

**Line 177: "bolster" has a negative connotation in my opinion**

Changed to "further support"

**Line 198: "lab" -> "laboratory"**

Done.

**Line 200: I'm not sure that it's ok to cite papers in preparation**
**Line 231: I'm not sure that it's to cite papers that have been submitted**

Citations removed.

**Line 233-4: "If time permitted on … , we typically completed … or flew …"**

Done.

**Line 236: "Residual Layer ozone project" has not been defined or acknowledged previously, please revise; "ground tracks" seems colloquial; please give acronyms for the sites that are used on the plot in the caption (as well as which network a given site is a part of). Why are only some of them labeled on the figure? Please label them all.**

**Additionally, please move the label closer to the "x" - not always easy to tell which "x" goes with which label**

**"ground tracks" changed to "flight paths". Airports were labeled with ICAO identifiers, and ground sites were marked with an "x". We recognize that this may have been confusing, so we adjusted the figure and caption to more clearly differentiate the airports from the ground sites.**

**Line 250: please cut "aforementioned"**
**Line 252: the objective aims to use? "to address this objective, we use a method …"**

**Done.**

**Line 263: "the flight volume" is a bit colloquial - please rephrase**

**Removed "within the flight volume" as we feel the description is adequate without that information.**

**Line 269: where is the storage term in equation 1?**

**Clarified as "The storage (left hand side) term"**

**Line 272: it would be helpful if the authors had a line here saying something like "in the following sections, we detail the methods for estimating the terms in equation 1"**
**Line 276-298: Why isn't this paragraph its own section (to estimate h)?**
**Line 290: I think it would be clearer to state "late night and morning flight pairs"**

**Done.**

**Line 303: I think it is confusing to say that O3, NO2 and NO3 are grouped together for Ox here. The authors clarify that their definition of Ox is different from that conventionally used in the following lines but I think some general restructuring of this part would help with clarity.**

**Below is the modified paragraph:**

**The chemical loss term in Equation 1 is expected to be an important component of the NBL $O_x$ budget. Both $NO_2$ and $NO_3$ are able to regenerate ozone in the presence of sunlight and participate in the same sequence of reactions, which are normally grouped together into a family of species referred to as odd oxygen ($O_x = O_3+NO_2+2NO_3+3N_2O_5$) (Brown et al., 2006; Wood et al., 2004); however, since we did not measure $NO_3$ and $N_2O_5$, in this study we estimate $O_x$ as merely the sum of $O_3+NO_2$ because these are expected to exceed to concentrations of the other $O_x$ species by 1-2 orders of magnitude (Brown et al., 2003; Smith et al.,1995). Considering $O_x$ is useful for our study because the family is conserved in the rapid oxidation of NO by $O_3$ (R1 below) yielding $NO_2$, which is quickly photolyzed to regenerate $O_3$ once the sun rises as part of the standard daytime photostationary state.**

**Line 335: are 30 ppb of O3 and 20 ppt of NO3 hypothetical values for SSJV? Please clarify in the text**

They are typical values observed in the SSJV. Clarified in the text.

Line 338: which surface air quality network? I asked this previously; please specify in the text.

Specified CARB network in text.

Line 343: Will the authors directly link this nitrate lifetime with the implications for ozone here?
Added "Hence, we conclude that (R6) should not be ignored in general as it may ultimately reduce the chemical loss rate of $O_x$."

Line 373: cut "obvious"
Line 376: cut "and best accounts …. dominant."

Done.

Line 378: cut "very"
Line 379: cut "highly"

"Very important" changed to "critical". "Highly" cut.

Line 283: ampersand should not be used here after Table 2
Line 392: give acronyms used in figure in figure caption
Line 395: "2nd" -> "second"
Line 403: "would be" -> "are"
Line 410: "the 1-second Ox data"

Done.

Line 414: this is not a sentence

Changed to "Per convention, u is the mean x-component (zonal) wind and v is the mean y-component (meridional) wind."

Line 420: the authors' field campaign or that of Padro? Please clarify in the text
Line 422: does Padro conclude this or do the authors infer this? Please clarify in the text

Changed to "There are reports of ozone deposition in the area of our field campaign from a 1994 study using the eddy covariance technique (Padro, 1996). The findings of their study suggest nocturnal ozone deposition velocities are several times smaller than their daytime counterparts, but we infer that the overall process is still important for the budget in the NBL because of the smaller mixed layer depth (Eq. 1)."

Line 426: cut "purposefully"
Line 436: cut "on any given night"
Line 436-7: "likely accounts … in Ox"

Done.

**Line 461: Why is this worth noting? Is this observed in a figure? Otherwise seems extraneous to include this.**

**Moved to section 3.4 where this is better contextualized.**

**Line 481: Why is uncertainty in deposition computed in this way? It would only make sense to me if the authors are considering a deposition flux here. Do the authors mean the deposition flux (rather than the deposition velocity) here? If so, please specify.**

**Yes, we meant deposition flux, which we have now stated in the text.**

**Line 489: can the authors refer the reader to where they did this previously (e.g., the section)?**
**Line 501: In the level? Cut level?**
**Line 504: Zhong et al. (2004)**
**Line 508: Cut "It is noted that"**

**Done.**

**Lines 512-4: Can the authors more closely link with line with the previous finding (i.e., that this is additional evidence supporting a minimal influence of advection)**

**Added "which further supports the idea that the influence of advection on our scalar budget analysis is minimal."**

**Line 520: "is"-> "are"**
**Line 524: Cut "that is"**

**Done.**

**Line 525: Define acronym**

**Changed standard deviation acronym to σ**

**Line 528: "To analyze variability of the jet strength" does not give me much insight as to what the authors are trying to do here. Please more clearly lay out the goal. Also, in the following paragraph, will the authors please refer to the figures that they are referencing more.**

**Changed to "To analyze possible synoptic influences of the jet strength" and included more references to figures.**

**Line 535: "where"-> "that showed that"**
**Line 539: "were" -> "was"**
**Line 542: Cut "thing"**

**Done.**

**Line 543: Please clarify in the text what the authors mean by essentially**
**Line 541-552: This entire paragraph needs to be re-worked for clarity**
**Line 550: By optimal, do the authors mean the best for good air quality? Please revise**

The updated paragraph is pasted below:

Although the LLJ and Fresno Eddy are not synonymous, we propose that the northwesterly LLJ can be the dominant feature of the eddy's northerly flow component. This leads to an important question about the role of the Fresno Eddy in modulating the daily ozone peak. Beaver and Palazoglu (2009) purport that ozone levels in the central SJV are particularly high on days when the morning southerly wind at Parlier, a site about midway between Fresno and Visalia, is strong, concluding that recirculation from the downslope branch of the Fresno Eddy significantly controls the day's buildup of ozone. However, mixing induced by LLJs in other parts of the world has been shown to decrease ozone levels the following day (Hu et al., 2013; Neu et al., 1995). Thus, it may be the case that a Fresno Eddy associated with a particularly strong LLJ may decrease ozone the following day if the recirculation of ozone and its precursors does not overcompensate for overnight losses due to vertical mixing down to the surface. We suggest that the Fresno Eddy, when present, will act to recirculate pollutants regardless of the strength of the LLJ. That is, a stronger eddy will not recirculate pollutants any more than a weaker one will. Thus, the nighttime dynamical conditions that will lead to the greatest ozone levels the following day may consist of a Fresno Eddy just coherent enough to effectively recirculate pollutants, but without an associated LLJ so strong as to deplete the RL ozone by vertical mixing. There is currently no established link in the literature between the Fresno Eddy and LLJ strength. Thus, future research should investigate which of these two nocturnal mechanisms (recirculation from the eddy or RL depletion by vertical mixing) will dominate the ozone budget on any given night, taking into consideration the different possible structures and timing of the Fresno Eddy as well as the synoptic conditions that engender them.

**Line 555: Refer to Figure 9?**

Done.

**Line 560-2: Why is this worth noting? What is the implication of this finding? Please include in text**

We have removed this brief discussion in the interest of simplifying this section.

**Line 575: "50% of daytime values during convective conditions"?**
**Line 576: "TKE increases"**

Done.

**Line 578: "air pollution problem" is too colloquial**

Removed "problem".

**Line 580: Again, what is higher ozone pollution potential?**

Removed "potential".

**Line 583-5: Suggestion to break this into two sentences. "relative validity" doesn't make much sense**

Text now reads “On the other hand, greater coupling between the NBL and RL, induced by turbulence generated by the LLJ, could reduce the amount of ozone stored in the RL reservoir rendering cleaner air the following day. To test this hypothesis, the relationship between the eddy diffusivity values found in our study and regional mean surface ozone from the CARB network is analyzed.”

Line 590: Is the growth entraining into the RL? Suggest re-phrasing

Changed to “after the bulk of the fumigation has occurred”.

Line 592: Instead of saying “were in the predicted direction” can the authors just say the direction of the relationship?
Line 596: “we explored”
Line 600: “is”-> “are”

Done.

Line 604: “This” is confusing here, because the authors were just talking about the outlier

Clarified as “This overall relationship supports our hypothesis that the LLJ leads to stronger mixing, which in turn leads to more RL ozone depletion.”

Line 614: “is neglected”, “combining an estimate of aerodynamic resistance”
Line 618: “the”
Lines 619-20: “The difference in U10 … assuming an average U10 of …”
Line 626: “will need to”-> “should”

Done.

Line 635: “for oceans and the free troposphere”

Clayson and Kantha (2008) applied a method that has previously been used in the oceans *to* the free troposphere, so the original wording is more correct. Clarified this in the text as “Clayson and Kantha (2008) applied a technique that has been *previously* used in oceans to the free troposphere, where turbulence is sparse and intermittent, much like the NBL.”

Line 642: cut “where”

Done.

Line 643-4: So do the authors use the median or the average…?

Median – specified this in text.

Line 648: “is”=>”are”

Done.

**Line 664-5: sentence is too colloquial**

**Changed to "The weak correlation is probably the result of the limited data set coupled with the challenging nature of both the eddy diffusivity and BRN measurements."**

**Line 693: cut "a lot"**
**Line 693-4: "the observations of elevated mixed layers may be"**
**Line 695: "to confirm that this is not the case, we examine"**
**Line 698: "they"**

**Done.**

**Line 700: What are the implications of this finding?**

**Added "Even in the two month averages, some nocturnal unstable layers are detectable between 500 and 1500 m, which further supports the existence of persistent elevated mixed layers that may contribute to overnight mixing of pollutants in the lower troposphere over the valley."**

**Line 704: Mention ozone?**

**Mentioned $O_x$.**

**Line 705: again, please change "air quality problems"**

**Changed sentence to "We have demonstrated a method for performing a nocturnal Ox budget analysis using aircraft data, and applied it to estimate the effects of turbulent mixing in the NBL, which can be used to help understand many air quality issues in the SJV."**

**Line 707: correlations between what and both Richardson number and ozone? Specify**

**Specified eddy diffusivities.**

**Line 713: the context of high ozone episodes is hardly discussed in the text**

**Changed to, "… and highlights the significant influence that synoptic and mesoscale meteorological conditions can have on the overnight destruction of ozone, thereby impacting the following day's peak concentrations."**

**Line 717: "next-day ozone"?**
**Line 719: "11 out of 12 days WHEN ozone concentration exceeded 100 ppm over Visala were preceded"**

**Done.**

**Line 722: the ozone reservoir where? Please specify in text**

**Specified RL.**

**Line 723-4: suggestion to separate this into two sentences**

**Text now reads "There it is subject to dry deposition at the surface, wherein the deposition velocity itself may be modulated by the strength of the LLJ. Because the near-surface winds are accelerated by an overlying jet, a stronger LLJ reduces the aerodynamic resistance resulting in more efficient transport to surfaces and stomata where ozone can be taken up."**

**Below I copied and pasted some of my initial reviews (black), along with the authors' response (green), and my response (black, bold). I ask that the authors also respond to these comments.**

Line 157: Do the authors average over a large area? The limitations would only be overcome if so, right?
Response: The scalar budget technique we present covers a large swath of the SSJV, and thus the terms in the budget equation can be taken as averages of the entire region for which the budget is performed.
**Will the authors more clearly articulate in the text, somewhere close to the beginning, that they are examining a large area of the SSJV? This should be closely linked with the authors' introduction of the Fresno Eddy.**

**Done (see line 119/120).**

Line 259: Please specify the field site and time examined in Padro 1996.
Response: changed to "Combining those measurements with an estimated 0.2 cm s-1 nighttime dry deposition velocity of ozone at night in the SSJV (Padro, 1996), we can indirectly estimate *Kz*."
**My interpretation of Padro 1996 is that they examine several field sites in the SSJV - which one do the authors examine? Please specify in the text**

**Changed to "Combining those measurements with an estimated 0.2 cm $s^{-1}$ nighttime dry deposition velocity of ozone in the SSJV (an average from a study over cotton, grass, mixed deciduous forest, and vineyard field sites by Padro, 1996), we can indirectly estimate Kz. In the following sections, we detail the methods for estimating the terms in Equation 1"**

Line 271: "A blend of these three methods" is too vague. Please specify the method
Response: Changed to "all three of these methods were used in tandem."
**A "blend" / "in tandem" is too vague. How do the authors combine them? Please specify in the text**

**Changed paragraph pasted below that attempts to clarify how these methods are combined:**

**Profiles of wind speed, potential temperature, $NO_2$, and $O_3$ from each night and morning flight were analyzed to make a best guess of the NBL height, h. Figure 4 shows the average scalar profiles from all 15 late night flights to illustrate the typical gradients in the lower portion of the atmosphere. One method of determining h is to observe the lowest elevation where $\partial\theta/\partial z$ becomes close to adiabatic, as the layer below that physically represents air that is in thermodynamic communication with the radiatively cooled surface (Stull, 1988). Another method is to use the level of wind maximum, or LLJ height, when one is present. We found that both of these estimates typically yielded similar values of h. On nights where**

**there was significant disagreement between the two different estimates, the vertical jump (or sharpest gradient) of $O_x$ in the height region of the NBL-RL interface was considered, as this likely points to a region of maximum mixing. In such cases, we averaged the height where the steepest gradient was observed with the estimates obtained from the other two methods. It should be noted that some subjectivity was involved for determining a final value of h for each night because wind maxima and thermal gradients were not always clearly defined in the profiles. All of the aforementioned factors lead to an estimated uncertainty of ±100 m for all of the NBL heights obtained. The average conditions from the late night and morning flights are presented in Table 1.**

Table 2: What do the authors mean that values may not match literature values? How is the extrapolation and valley average done? It seems like this info should be somewhere in the paper or supplementary material.
Response: We found that often, the measurements in the studies were taken in specific areas such as crop fields. Since the aim of this analysis was merely to get a reasonable estimate, we used our meteorological knowledge to estimate whether a valley-averaged concentration may be slightly higher or lower than what was reported in the study.
Changes made:
The measurements in some of the studies above were taken in specific crop fields. Since the aim of this analysis was merely to obtain an order of magnitude estimate, we predicted whether a valley-averaged concentration may be slightly higher or lower than what was reported in the study. Thus, values here may not exactly match literature.

**I think back-of-the-envelope calculations are fine here, but the authors need to describe the method. Their description is too hand wavy. Somewhere in the text the authors should describe the land use characterization of the SSJV to give context to the several references to agriculture (e.g., is only a little of the SSJV agriculture?)**

**Table 2 has been updated to specify the methods behind the (rough) estimates with footnotes. Also specified that the SJV contains about 5 million acres (~20,000 km$^2$) of irrigated land.**

Line 403: What is the similar environment? Please specify
Response: Specified that this study was done in a flat grass field.
**Now it needs to be more clear that this is a land use type (or climate?) representative of the SSJV.**

**Changed to "Based on an abundance of observations of nocturnal ozone dry deposition velocities reported in the literature over a broad variety of grassland and agricultural surfaces similar to those found in the SSJV (Pederson et al., 1995; Pio et al., 2000; Meszaros et al., 2009; Neirynck et al., 2012; Lin et al., 2010), all ranging between about 0.1 – 0.3 cm s$^{-1}$, we estimate a dry deposition velocity of 0.2 cm s$^{-1}$ (± 0.1 cm s$^{-1}$) for our purposes."**

Lines 423-4: By surplus of Ox do the authors mean where Ox indicated by the purple line is greater than Ox indicated by the black line? Please specify this. Also please specify in the caption which of the terms have been inferred (and refer to section on calculation) and which have been observed.
Changes made:
The dashed profiles show the expected profile that would have been observed on the morning flight if only advection (blue), chemical loss (green), or both advection and chemical loss (red)

processes were occurring. The observed morning Ox (magenta) is inferred to exceed the predicted morning Ox (red) due to the vertical mixing term in the scalar budget equation. **Figure 6.** Ox profiles from 2016-06-04 overnight analysis, NBL height (green line), and lower bound to vertical mixing gradient (yellow line). The solid lines are observations and the dashed lines are inferred.

**Ok, but now it is not exactly clear why Figure 6 is included in the paper. What should the reader be taking away from this snapshot figure? Please better integrate this figure and the discussion of it into the text.**

**Added "The contribution of vertical mixing to the budget can be visualized as an inferred difference between $O_x$ profiles that are observed and $O_x$ profiles that are predicted from other terms in Equation 1. Figure 6 shows an example of [this]…" and we moved this figure and its associated discussion to section 2.2.5, as we feel it is more appropriate there after considering the reviewer's comment.**

Line 445: There should be an introductory sentence here, instead of starting with a specific component's error calculation.
Response: Added "Here we estimate the uncertainty for each term in the budget equation, as well as the ultimately calculated eddy diffusivities." as an introductory sentence.
**In my opinion "ultimately calculated" leaves room for confusion. Please rephrase**

**Removed "ultimately calculated".**

Section 3.3: This section is confusing because the authors say that the presence of Fresno Eddy could be problematic for their analysis. Then, they say that the predominant circulation during their flights is similar to Fresno Eddy, but then they say any recirculation has a minimal impact on their results (lines 492-3). A lot of the analysis on Fresno Eddy could be cut, especially because it's found to be irrelevant. This would help with clarity and flow. Additionally, can the authors split Section 3.3 in two? One section on Fresno Eddy, and one on the low-level jet?
Response: As addressed in some of the following comments, we have attempted to clarify our discussion of the Fresno Eddy and where it fits in to this work. We firmly believe that a clear discussion of the Fresno Eddy is absolutely necessary to retain because it is constantly referred to in air quality discussions of the SJV, but not clearly understood. It is a major conclusion of the paper that we sample and describe the Fresno Eddy in a new and better way, which we believe can help illuminate future studies. We have tried to clarify the discussion where possible, but maintain that the low-level jet is *part and parcel* of the Fresno Eddy, therefore separating the two into distinct sections in the manuscript only perpetuates the misleading distinction.

**I still think the discussion of the Fresno Eddy feels tangential. I urge the authors to better articulate "It is a major conclusion of the paper that we sample and describe the Fresno Eddy in a new and better way, which we believe can help illuminate future studies" in their paper (upfront, and in the conclusions).**

**See earlier response to lines 102-130.**

Lines 480-2: I don't really know what the takeaway here is.
Response: Here we are stating that Zhong et al. (2004) was presenting a climatological analysis of typical summertime conditions, while our flights were targeting periods of higher ozone, thus

the synoptic and mesoscale conditions during our flights might be systematically different from climatological norms.

**Ok, so can the authors more clearly state this rather than what they currently have (which feels tangential)?**

**Now stated directly in the text.**

Lines 516-526: It seems like this should be a paragraph on it's own, and better linked with the mention around Line 512 of Fresno Eddy. Referring to "LLJ" generally in this paragraph here is particularly confusing because in the preceding lines the authors were talking about weak vs. strong LLJ.

Response: We have made this a separate paragraph.

**Again, it seems like the authors have only responded to half of my concern.**

**In the new manuscript, we have attempted to clarify the linkage between the LLJ and Fresno Eddy, and why they are both being discussed as a single entity.**

Lines 593-5: Why would Rb be 0 at night? This doesn't make much sense to me. Is this stated in the Padro 1996? Rb is not included in Padro 1996 Figure 4. In Massman [1994] Rb is estimated to be nonzero for the CODE vineyard. I recommend specifying that not only Ra is modeled in Massman [1994] but Rc is too (it's not a residual of observed vd and estimated Ra and Rb). Then I might just say here that modeled Ra and Rc are similar at night and Rb is unknown, rather than zero. It's also important to note that this is only one way of estimating Ra (u/u_*ˆ2) and estimates at night are likely highly uncertain.

Lines 600-3: How would taking changes in Ra into account in the budget calculation change the eddy diffusivity estimate?

Response: Added suggested literature and stated that rb is unknown and thus not included in this approximation. The average error of Kz due to the uncertainty of Vd is calculated to be ~0.50 m2 s-1, which is included in the original error propagation analysis.

Changes made:

Where *ra* is the aerodynamic resistance, *rb* is the viscous sub-layer resistance, and *rc* is the surface (canopy) resistance. Figure 4 in Padro (1996) suggests that for ozone at night, *ra* ~ *rc* ~ 250 s m-1. *rb* is likely non-zero (Massman et al., 1994) but will be neglected here because it is unknown.

**Seems to me like it is important to spell out "The average error of Kz due to the uncertainty of vd is calculated to be ~0.50 m2 s-1, which is included in the original error propagation analysis" in the text close to this discussion**

**Done (lines 644/645).**

Line 607: Why should the authors values be comparable to Banta et al. 2006 and Lenschow et al. 1988? Please specify. Line 610: Did Banta et al. try to remove buoyancy waves? Line 610-1: Why? What is the implication of this finding?

Response: Specified that these are studies of NBL turbulence. Banta et al. (2006) is a meta analysis of other studies. To the best of my knowledge, buoyancy waves were not removed. While we were hoping that our TKE would have a relationship with ozone the following day, it is a very noisy measurement and we were also using many approximations to estimate it, as outlined in the paper.

Changes made:

Here we attempt to build confidence in the eddy diffusivity estimates by analyzing additional metrics of turbulence. We find that nocturnally and spatially averaged TKE in the NBL ranges from 0.35 and 1.02 m2 s-2, which is very comparable to values obtained in other NBL studies (Banta et al., 2006; Lenschow et al., 1988).

**Can the authors please clarify in the text why they are mentioning that they did not remove buoyancy waves? I would suggest saying something like "differences between the studies may reflect Banta et al. 2006 removing buoyancy waves" if this is what the authors are implying**

**Please answer my question about the implication of the finding (now Lines 632-3)**

**After contacting the lead author we have verified that Banta et al. (2006) did not remove buoyancy waves.**

**Text now reads "The average value of $\sigma_u/U_x$ in this study is 0.11, approximately double what was reported in Banta et al. (2006). There is no detectable relationship between our calculated NBL TKE and eddy diffusivities, LLJ speed, or MDA8 the following day, which implies that the eddy diffusivities calculated from the scalar budget analysis may be a better measure of nocturnal mixing strength than TKE."**

Line 659-60: Why is this more likely? What's the implication of this?

Response: We are stating that although unstable layers are observed more frequently in urban areas compared to rural areas, we may have simply detected them more often there because the aircraft spends more time in urban areas. Hence, the apparent pattern of more unstable layers in urban areas could be insignificant.

Lines 663-4: Briefly, how would they contribute to overnight mixing?

Response: Absolutely unstable layers in the atmosphere promote the production of turbulence and thus vertical mixing.

**Please incorporate the authors' response into the main text**

**Done (lines 698/699).**

Line 675-6: How does this fit into the above discussion? What are the implications of this finding?

Response: This fits into the above discussion because we are showing the unstable layers appearing in the climatological averages of the 915 MHz profiler. The implications of this are that it lends some additional credibility to their existence.

**Please incorporate the authors' response into the main text**

**Done (lines 728/729).**

Line 691: Seems strange to mention that the authors demonstrate something "within the context of high ozone episodes" when ozone hasn't been mentioned yet in the conclusion. On a similar note, the authors haven't noted in the conclusion that there was a particular focus strategy of the flights, so it's strange to mention it. It's helpful for the reader if the conclusion can really stand alone from the rest of the text. Line 692: Specify where the soundings and surface monitoring data are from (locations, networks) here

Line 692-3: Specify the implication of this finding (tie back to hypothesis) Line 694: What do the authors mean "although in the former analysis"? In the analysis of soundings and surface network data? This could be more clearly articulated, and it should be directly stated that this is not found in the airborne measurements. Line 695-6: "is an important link that may have consequential implications for modeling studies and policy making" is vague and verbose. I think the authors' findings are important for modeling and policy, but this sentence doesn't do much to convince me of it. Line 697: Introduce Visalia Line 698: "infer" -> "determine" Line 701: Spell out

that reduced aerodynamic resistance means more efficient transport to surfaces where ozone can deposit Line 704: It would be good to articulate that this may be why the correlation between night turbulence + next day ozone may not always be high. Line 704:
“Airborne measurements from flights over Bakersfield, CA showed ...”
Response: Focus strategy of the flight restated in conclusion. The other requested changes have been made.
Changes:
A limitation of our study is the lack of sample size, with only 12 pairs of overnight and morning flights. However, we believe this study demonstrates the importance of synoptic and mesoscale features at night within the context of high ozone episodes, and the utility of this type of focused flight strategy where terms in the scalar budget equation are measured.
The larger set of RASS and ARB surface network data from Visalia, CA establishes a correlation between low level jet speed and the maximum 1-hour ozone the following afternoon for summertime months, further suggesting the link between nocturnal mixing and the following days ozone. Similarly, the correlations between the aircraft-estimated eddy diffusivities and MDA8 the following day also suggest that vertical mixing in the NBL plays an important role in determining ozone concentrations. In particular, we note that 11 of 12 days where the Visalia, CA ozone concentration exceeded 100 ppb was preceded by a low-level jet speed < 9 m/s. While we cannot determine a causal relationship between a strong low-level jet, stronger mixing, and reduced ozone pollution, we propose that a stronger LLJ leads to greater mixing, which helps deplete the ozone reservoir by bringing it into the stable boundary layer overnight. There it is subject to deposition to the surface, and that dry deposition rate may itself be partially modulated by the strength of the LLJ through reduced aerodynamic resistance resulting in more efficient transport to surfaces where ozone can deposit. Subsequently, when thermals begin to form after sunrise the following morning, there is less ozone to fumigate downward. While the correlation between nocturnal mixing and ozone the following day is not always strong, it is an important link that may have consequential implications for modeling studies and policy making. For example, our findings highlight the crucial need of models to capture the LLJ and Fresno Eddy with sufficient resolution. Policy makers may consider putting more stringent emission limitations on days where synoptic and mesoscale patterns appear to favor a lack of overnight mixing. Of course, in addition to nocturnal mixing, photochemical production of ozone as well as advection will play a major role in the ultimate daytime peak ozone levels observed, which may be why the correlation between nighttime turbulence and afternoon ozone is not always high. Airborne measurements from flights over Bakersfield, CA showed an average photochemical production as high as 6.8 ppb h-1, with an average advection of -0.8 ppb h-1, though on any given day advection tended to be more comparable in magnitude to photochemical production (Trousdell et al., 2016).
Lines 704-6: Spell out the implication of this finding.
Response: We were mainly pointing this out to remind the reader that even though the advection term on average tends to be near zero, it can be large for any particular data point.
**Changing “within the context of” —> “for”, “establishes”-> “shows”, “the following days” -> “next-day”, “a lack of overnight”-> “weak nocturnal” would be helpful**

**Done.**

Line 706: In what study? Trousdell et al. 2016? If so, the subject should not be “we”, it should be “they” or better, Trousdell et al. (2016) Lines 704-10: I’m not quite following why the discussion of Trousdell et al. 2016 is relevant for the conclusions of this paper. Lines 711-2: “illustrated”-> “suggested”; “which consequently has impacts for”-> “and thus likely impacts”

Response: Here we are reminding the reader that there is more to the picture than just vertical mixing of ozone at night, since afternoon ozone concentrations are influenced by advection and photochemical production.
Changes made:
In that study they have demonstrated that on days with very high ozone that pose hazards to human and agricultural health, the ozone abundance is dependent on elevated ozone in the mornings that serve to catalyze photochemical production through the afternoon. Future modeling studies may directly investigate these factors, which may help elucidate the causal mechanisms of high ozone events. We have also suggested that the fate of the NO3 plays an important role in the nocturnal Ox budget chemical loss term, and thus likely impacts the following day's maximum ozone concentration.
**I find the discussion of Trousdell et al. 2016 tangential (and thus confusing for the reader). I agree that it is important to point out that photochemical production may lead to the weak correlation. This is could be spelled out concisely after "While the correlation between nocturnal mixing and ozone the following day is not always strong, …". On a similar note (in terms of re-structuring this section), I recommend cutting "it is an important link that may have consequential implications for modeling studies and policy making" because it is vague and wordy and the following sentences illustrate this point well.**

**We have followed these suggestions.**

Lines 712-5: But what exactly is so uncertain about nitrate, and why will it affect ozone? There should be a line stating that the authors haven't measured nitrate on their flights, and how/why this leads to uncertainty in their analysis. The authors should re-introduce alpha, and why it's important. I really like how the authors have spelled out that nitrate measurements (specifically the lifetime) are needed in future nocturnal airborne measurement campaigns. Are there any other measurements or techniques that their analysis suggests doing or developing would reduce uncertainty?
Response: We have followed these suggestions and are also stating that deposition velocity measurements of ozone using eddy covariance on future campaigns would be helpful.
Changes made:
We have also suggested that the fate of the NO3 plays an important role in the nocturnal Ox budget chemical loss term, and thus likely impacts the following day's maximum ozone concentration. The loss of the nitrate radical at night can occur from N2O5 hydrolysis, reaction with VOCs, or a very rapid reaction with small NO concentrations, and there is considerable uncertainty regarding which reactions dominate without direct measurements of NO3. Thus, the lifetime of NO3 can range from seconds to several minutes, which affects the chemical loss term in the scalar budget equation. It is thus crucial to measure the lifetime of NO3 in future studies that analyze the NBL ozone or Ox budget. We also suggest more direct measurements of aerodynamic resistance and ozone deposition at the surface by eddy covariance in conjunction with future airborne studies.
**Direct measurements of aerodynamic resistance are not really feasible at this point so I would recommend slightly rephrasing. Additionally, it's not really clear whether the authors want airborne ozone eddy covariance fluxes, or ground-based ozone eddy covariance fluxes.**

**Specified that these are suggestions for future field campaigns. Text now reads "We also suggest more direct estimates of aerodynamic resistance and ozone deposition at the surface by ground-based eddy covariance flux measurements in conjunction with future airborne studies."**

# Residual Layer Ozone, Mixing, and the Nocturnal Jet in California's San Joaquin Valley

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**Abstract:** The San Joaquin ~~valley~~ Valley of California is known for excessive ~~secondary~~ ozone air pollution owing to local production combined with terrain-induced flow patterns that channel air in from the ~~highly populated~~highly-populated San Francisco Bay area and stagnate it against the surrounding mountains. During the summer, ozone violations of the National Ambient Air Quality Standards (NAAQS) are notoriously common, with the San Joaquin Valley having an average of 115 violations of the ~~recent~~ current 70 ppb standard each year between 2012 and 2016. Because regional photochemical production peaks with actinic radiation, most studies focus on the daytime, and consequently t~~T~~he nocturnal chemistry and dynamics that contribute to these summertime high ozone events ~~have yet to be fully~~are not as well elucidated. Here we investigate the hypothesis that on nights with a strong low-level jet (LLJ), ozone in the residual layer (RL) is more effectively mixed down into the ~~stable boundary layer~~nocturnal boundary layer (NBL) w~~. T~~here it is subject to dry deposition to the surface, the rate of which is itself enhanced by the strength of the LLJ, resulting in lower ozone levels the following day. Conversely, nights with a weaker ~~jet~~ LLJ will sustain ~~residual layers~~RLs that are more decoupled from the surface, retaining more ozone overnight, and thus lead to more fumigation of ozone ~~in~~ the following mornings, giving rise to higher ozone concentrations the following afternoon. The relative importance of this effect, however, is strongly dependent on the net chemical overnight loss of $O_x$ (here $[O_x] \equiv [O_3] + [NO_2]$) which we show is highly uncertain without knowing the ultimate chemical fate of the nitrate radical ($NO_3$). We analyse aircraft data from a study sponsored by the California Air Resources Board (CARB) aimed at quantifying the role of ~~residual layer~~RL ozone in the high ozone episode events in this area. By formulating nocturnal scalar budgets based on pairs of consecutive flights: the first ~~-~~around midnight and the second just after sunrise the following day~~s (henceforth referred to as "flight pairs")~~, we estimate the rate of vertical mixing between the RL~~residual layer (RL)~~ and the NBL~~nocturnal boundary layer (NBL)~~, and thereby infer eddy diffusion coefficients in the top half of the NBL. The average depth of the NBL observed on the 12 pairs of flights of this study was 210 (± 50) m. Of the average -1.3 ppb $h^{-1}$ loss of ~~the~~ $O_x$ ~~family (here $[O_x] = [O_3] + [NO_2]$)~~ in the NBL during the overnight hours from midnight to 06:00 PST, -0.2 ppb $h^{-1}$ was found to be due to horizontal advection, -1.2 ppb $h^{-1}$ due to dry deposition, -2.7 ppb $h^{-1}$ to chemical loss via nitrate production, and +2.8 ppb $h^{-1}$ from mixing into the NBL from the ~~residual layer~~RL ~~overnight~~. Based on the observed gradients of $O_x$ in the top half of the NBL, these mixing rates yield eddy diffusivity estimates ranging from 1.1 ~~–~~- 3.5 $m^2\ s^{-1}$~~-~~, which ~~that~~ are found to inversely correlate with the following afternoon's ozone levels, ~~and~~ providinge support for our hypothesis. The diffusivity values are approximately an order of magnitude larger than the few others reported in the extant literature for the NBL, which further suggests that the vigorous nature of nocturnal mixing in this region, due to the LLJ, ~~has~~ may have an important control on daytime ozone levels. Additionally, we propose that the LLJ is a branch of what is colloquially referred to as the ~~Fresno Eddy~~Fresno Eddy, which has been previously proposed to recirculate pollutants. However, vertical mixing from the LLJ may counteract this effect, which highlights the importance of studying the LLJ and ~~Fresno Eddy~~Fresno Eddy as a single interactive system. T~~investigate t~~he synoptic conditions that are associated with strong ~~nocturnal jets~~LLJs ~~and find that on average,~~are found to contain deeper troughs along the California coastline ~~are associated with stronger jets~~. The LLJs observed during this study had an average centreline height of 340 m, ~~an~~ average speed of 9.9 m $s^{-1}$ ($\sigma$~~SD~~ = 3.1 m $s^{-1}$), and a typical peak timing around 23:00 PST. Seven years of 915 MHz radio-acoustic sounding system and surface air quality network data show an inverse correlation between the jet strength and ozone the following day, further suggesting that air quality models need to forecast the strength of ~~this nocturnal dynamical feature~~the LLJ in order to more accurately predict ozone violations.

## 1. Introduction

The main source of air for California's Southern San Joaquin Valley (SSJV) is incoming maritime flow from the San Francisco Bay area, which gets accelerated toward the southern end of the valley as a consequence of the valley-mountain circulation (Rampanelli et al., 2004; Schmidli and Rottuno, 2010). The local sources of ozone precursors are scattered along this primary inflow path to the SSJV. The ozone ~~buildup~~build-up in the SSJV results from both the large amount of local upwind sources and the Tehachapi Mountains to the south which block the flow, preventing advection out of the region (Dabdub et al., 1999; Pun et al., 2000). Because of this tendency for the air to stagnate, both daytime and nocturnal ~~vertical mixing~~mesoscale dynamics are likely important in the phenomenology of ozone pollution in this area.

Under typical fair weather conditions over the continents, thermals are generated near the surface beginning shortly after sunrise, buoyantly forcing a convectively mixed layer, which is known more generally as the ~~convective~~ daytime atmospheric boundary layer (ABL). As solar heating increases ~~of~~ the Earth's surface temperature ~~increases~~ throughout the day, this layer reaches its maximum height by late afternoon, typically between 700 and 900 m in ~~California's central valley~~the SJV during summer months (Bianco et al., 2011~~; Trousdell et al., in preparation~~). Around sunset, when the solar heating ~~of the surface ends~~abates, the convective thermals ~~are cut~~shut off and ~~can~~ no longer power turbulent mixing in the boundary layer. The result of the subsequent radiative cooling of the ground throughout the night forms a stable, nocturnal boundary layer (NBL)~~ near the surface~~, typically extending between 100 and 500 m (Stull, 1988) above the surface. The erstwhile convective layer from the daytime, after spinning down and no longer actively mixing, functions as a residual reservoir for pollutants and other trace gases from daytime emissions and photochemical production. This layer overlying the NBL is known as the residual layer (RL).

During both daytime and nighttime, mixing can occur between the boundary layer and the layer of air above. In the daytime over land in clear sky conditions, this process of entrainment is ~~-~~driven by convective thermals that penetrate into the laminar free troposphere above, ~~which~~ and then sink back into the convective layer, and may be augmented by wind shear near the top of the boundary layer (Conzemius and Fedorovich, 2006). Entrainment has been shown to be a significant factor for near-~~-~~surface air quality~~pollution~~, and more generally for scalar budgets, as the two interacting layers ~~usually~~ often have different trace gas concentrations (Lehning et al., 1998; Trousdell et al., 2016; Vilà-Guerau de Arellano et al., 2011). At night, another type of gas exchange can occur between the aforementioned ~~stable boundary layer~~NBL and the ~~residual layer~~RL by shear-induced mixing. Extensive observations of the structure of the NBL indicate that a localized wind maximum near the top of the NBL, known as a ~~low~~ low-level jet (LLJ), is often present (Banta et al., 2002; Garratt, 1985; Kraus et al., 1985). This ~~low level jet~~LLJ is able to drive sheer production of turbulence, ~~in an intermittent, cyclical manner,~~thereby ~~powering~~ promoting the mixing between these layers despite the stable stratification. In this study, we ~~put forth a hypothesis~~suggest that the LLJ in the SSJV is part of the northerly flow component~~dominant~~ of what is colloquially referred to as the ~~Fresno eddy~~Fresno Eddy. As we attempt to show,

~~The complex nocturnal wind patterns in the SSJV contribute to the challenges of understanding and forecasting ozone pollution in our study region. The LLJ in the SSJV is known to contribute to the formation of a commonly observed late night and early morning mesoscale wind feature known as the Fresno Eddy, which~~The ~~Fresno eddy~~Fresno Eddy can drive both vertical mixing and regional horizontal advection. ~~The aforementioned daytime northwesterly valley wind continues into the late evening, decoupling from the surface and forming a LLJ (Davies 2000). The Tehachapi Mountains act as a barrier to the jet if the Froude number equal to the square root of the kinetic to gravitational potential energy of flow encountering a barrieris lower than about 0.2 (Lin and Jao, 1995). The eddy feature is formed during the hours before dawn when this northwesterly flow interacts with southeasterly nocturnal downslope flow coming from the high southern Sierra Nevada Mountains, although there is some question as to the extent to which the southeasterly flow observed in the morning hours is merely the result of a topographic deflection and recirculation of the nocturnal jet. The Coriolis force helps to circulate this flow; however, a mesoscale low is not thought to develop (Bao et al. 2007, Lin and Jao, 1995). It is worth noting that the valley flow peaks shortly after~~

sunset, while the katabatic drainage flow peaks shortly before dawn, so these two components of the Fresno eddy are (Bianco et al., 2011), suggesting that shear-induced downward mixing of RL ozone in this region may be particularly strong. Beaver and Palazoglu (2009) found that ozone pollution in the central San Joaquin Valley is particularly high following day (Aneja et al. 2000; Zhang and Rao, 1999). Using SODAR data from the Swiss plateau, Neu et al. (1995) estimated that about 75 % of the contribution to the differencefollowing day's early afternoon ozone was due to vertical the NBL depletion. This study was done in complex terrain of Switzerland and primarily used SODAR data. They of time the wind maximaum at night were observedas below 150 m, and the aforementioned early afternoon ozone Coupling of the RL and NBL via intermittent turbulence has also been shown to correlate with overnight ozone spikes at ground-level monitoring stations (Salmond and McKendry, 2005). Because of the complexity of intermittent nocturnal turbulence, the spatial and temporal distributions of these spikes are unknown, and thus it is not known the extent to which these ozone spikes help to deplete the residual layerRL ozone or contribute to the following day's from Southern Taiwan also found that residual layerRL ozone plays an important role in the following day's ozone with fumigation of this ozone into the developing daytime boundary layer accounting for 19 48% of the variance daily maximum (Lin 20122008). As the ozone problems in Southern Taiwan are not heavily driven by local sources, a

Owing to the complex topography and stable stratification overnight, the dynamics of the NBL and RL in California are difficult to model. Bao et al. (2008) reports that while the Weather Research and Forecasting (WRF) model is able to qualitatively capture the LLJ, systematic errors up to 2 m -s$^{-1}$ are observed, with root mean square errors of 4 – 5 m -s$^{-1}$. Above 2000 m, a similar magnitude of errors in the model's ability to forecast wind is observed, and since the LLJ is influenced by this upper level synoptic forcing, there is a need for more systematic study of the background synoptic conditions associated with strong and weak LLJs. The authors also note that apart from the 915 MHz Radio Acoustic Sounding Systems (RASS), observations of the LLJ in the SSJV are lacking in spatial coverage. This further highlights the need for an observational-based study of low level winds in the SSJV during high ozone episodes.

At the core of our observational method, we acknowledge recognize that most scalar budgets are driven by horizontal advection, vertical mixing (primarily entrainment), and local emissions/uptake, and net chemical production (including chemical gains and/or losses). Conley et al. (2011) and Faloona et al. (2009) have shown that on any given day, advection can be a relatively large and significant term in the daytime scalar budget. However, when averaged over numerous flight days, the advection is often close to zero. While many previous sStudiesstudies performing of daytime scalar ozone budgets of ozone (Kleinman et al., 1994; Conley et al., 2011; Lehning et al., 1998; Lenschow et al., 1981; Trousdell et al., 2016) have shown that photochemical production is important, and similarly, wea few nocturnal studies have highlighted significant losses of ozone in the dark (Brown et al., 2006; Stutz et al., 2010), we present here the first complete budget to include the mixing and chemistry overnight. expect the chemical loss of ozone to be important at night.. The nocturnal ozone chemistry is driven primarily by its well-known reaction radical. The nitrate radical has many different loss pathways including can combining with $NO_2$ to equilibrate with (which can undergo hydrolysis on surfaces),s, reacting with VOCshydrocarbons, and or rapidly reacting with NO to $NO_2$ (Brown et al., 2006, 2007; Wood et al., 2004). As we will attempt to show, the chemical fate of the nitrate radical is highly uncertain and this plays an important critical role in the net overnight chemical loss of ozone, and the following day's ozone level. Additionally, dry deposition of the chemical species of interest cannot be ignored for scalar budgets (Conley et al., 2011; Faloona et al., 2009). While the aforementioned studies focused on daytime scalar budgets, to our knowledge, no attempts have been made at nocturnal scalar budgets using aircraft data. Our goal is to test whether more nocturnal mixing between the ~~residual layer~~RL and ~~stable boundary layer~~NBL, induced by wind-shear turbulence beneath a strong ~~low level jet~~LLJ, will ~~effectively~~ "deplete" ozone in the ~~residual layer~~RL, making less available to fumigate the following morning and seed further photochemical production. One advantage of the present study is that we use airborne data to sample a large area, which overcomes the limitations of studies using ground monitoring stations that may be influenced by the intermittent bursts of turbulence and confounds of~~ed by~~ uncertain horizontal advection. We will proceed with this in three ways: first, we introduce a method for analysing nocturnal scalar budgets of flight data, which is similar to that of the daytime scalar budgets, and attempt to estimate the eddy diffusivity of $O_x$ in the NBL on each night of the field campaign (sections 3.1 and 3.2). Second, to determine whether our findings can be generalized to climatological timescales we ~~analyse~~ analyze synoptic conditions around the LLJ, and look at a broader dataset of LLJ strength and the following afternoon's ozone concentrations using Radio Acoustic Sounding System (RASS) and California Air Resources Board (CARB) ground network data (sections 3.3 and 3.4). Lastly, we look at other metrics of NBL turbulence in our campaign data such as Turbulent Kinetic Energy (TKE), Bulk Richardson Number (BRN), and elevated mixed layers in order to further support ~~bolster confidence in~~ our findings (sections 3.5 and 3.6).

## 2. Nocturnal $O_x$ Budgeting Methodology

### 2.1. Airborne Data Collection

Aircraft data was collected by a Mooney Bravo and Mooney Ovation, which are fixed-wing single engine airplanes operated by Scientific Aviation Inc. The wings are modified to sample air through inlets, which flow to the on-board analyzers. Temperature and relative humidity data were collected by a Visalia HMP60 Humidity and Temperature Probe, ozone was measured with a dual beam ozone absorption monitor (2B Technologies Model 205), and NO was measured by chemiluminescence (ECO PHYSICS Model CLD 88). $NO_x$ was measured by utilizing a photolytic converter (model 42i BLC2-395 manufactured by Air Quality Design, Inc.). For flights performed in 2016, a pre-reaction chamber was also installed to monitor and subtract the changing background signal, reducing the detection threshold to < 50 ppt. Frequent calibrations were performed in the field, generally once per deployment, with zero and span checks daily. Calibrations for NO measurements were performed with a NIST-traceable standard by Scott-Marrin, Inc. Calibrations for $NO_x$ measurements were performed by titrating the NO standard with an ozone generator (2B Technologies, Model 206 Ozone Calibration Source.) During routine operation on the aircraft, the lamp of the photolytic converter was toggled on and off at 20-second intervals during the flights (corresponding to approximately 1.5 km horizontal and 50 m vertical displacements by the aircraft), requiring linear interpolation for continuous NO and $NO_2$ data. The pre-reaction chamber was toggled on for a 40 second period every 10 minutes in order to measure the background signals of NO and $NO_x$, and the background signals were subtracted from the measurement. The interpolated $NO_2$ signal was noted to decay approximately exponentially after powering up, which sometimes affected the first 15-30 minutes of flight. The presumed artifact was successfully replicated in the ~~lab~~laboratory with a constant $NO_2$ concentration, and was removed by exponential detrending ~~(see Trousdell et al., in preparation for a detailed discussion.)~~.

Winds are measured using a Duel-Hemisphere Global Positioning System combined with direct airspeed measurements, as described in Conley et al. (2014). The winds are measured at 1 Hz, and the power spectra is observed to fit the Kolmogorov Scaling Law within the inertial subrange (approximately from 0.12 - 0.5 Hz in the daytime convective boundary layer corresponding to roughly 150 ~~–~~- 600 m spatial scales). At night, the -5/3 slope is observed from 0.02 ~~–~~- 0.5 Hz (Fig. 1), corresponding to length scales of 150 ~~–~~- 3700 m, the largest of which are likely contributions from buoyancy waves. This is evident by the calculated Brunt~~–~~-Väisälä frequencies (Fig. 2), which have an average value of 0.023 Hz in the NBL. For simplicity sake, we consider anything smaller than this buoyancy frequency to be "turbulence", and use $1/N_{BV}$ ~ 50 seconds to be the sampling time to observe wind variances, though we recognize that this cutoff is somewhat arbitrary. The turbulent kinetic energy (TKE) is estimated by correcting the observed wind variance of a given detrended 50-second signal with the integrated nocturnal power spectra beyond the Nyquist frequency (0.5 Hz) using a -5/3 extrapolation, which indicates that approximately 11 % of the total variance is not directly captured by the system. Only horizontal winds are measured, thus similarity assumptions are required to estimate vertical wind variance ($\sigma_w^2$). While some similarity relationships have been reported for the ~~stable boundary layer~~NBL (Nieuwstadt, 1984), we were not able to measure the governing parameters. However, Banta et al. (2006) reported a meta-analysis of ~~stable boundary layer~~NBL studies with an average $\sigma_w^2/\sigma_u^2$ of 0.39, where $\sigma_u^2$ is the streamwise variance. We applied this correction to our TKE measurements to account for the missing vertical wind variance.

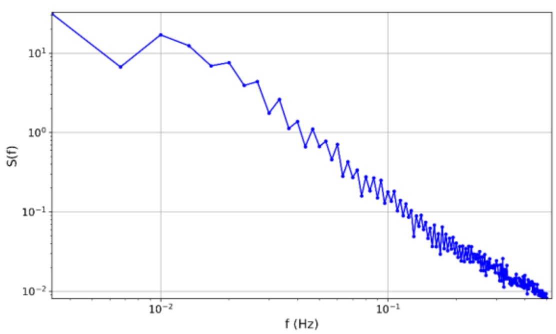


**Figure 1.** Power spectra for nighttime winds averaged over 309 5-minute samples. The average airspeed was 76.6 m $s^{-1}$.

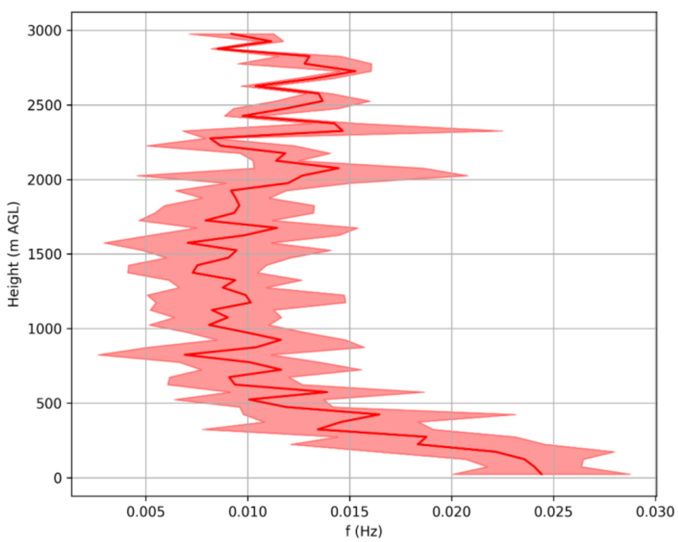


**Figure 2.** Mean and standard deviation profile of Brunt~~-~~–Väisälä frequencies for all ~~late night~~late-night flights. The mean value within the stable boundary layers is 0.023 $s^{-1}$.

Data was collected on 5 separate deployments (10-12 September 2015, 2-4 June 2016, 28-29 June 2016, 24-26 July 2016, 12-18 August 2016). During a given deployment, 4 flights per day were conducted (7, 11, 15, and 22 PST). Each deployment consisted of stationing the airplane at Fresno Yosemite International Airport (FAT), with each flight comprising a transect to Bakersfield Meadows Field Airport (BFL) and back spanning approximately 2 hours and 15 minutes (Fig. 3). Profiles of the full boundary layer and above were taken at Fresno and Bakersfield. Along the Fresno-Bakersfield transect, altitude legs of 500, 1000, and 1500 m AGL were conducted in a randomized order. Low passes were also flown over the Tulare (TLR), Delano (DLO), and Bakersfield airports, but in 2016 we replaced the low approaches at Tulare with Visalia (VIS) to coincide with the NOAA LIDAR deployment ~~(Langford et al., submitted)~~. All of these airports are within a few hundred meters of California Highway 99, or in the case of Fresno and Bakersfield within an urban center. If time ~~was remaining~~permitted on any given flight, we typically ~~utilized it by either completing~~completed an extra profile at Visalia, or ~~flying~~ flew west toward Hanson to better sample the nocturnal LLJ.

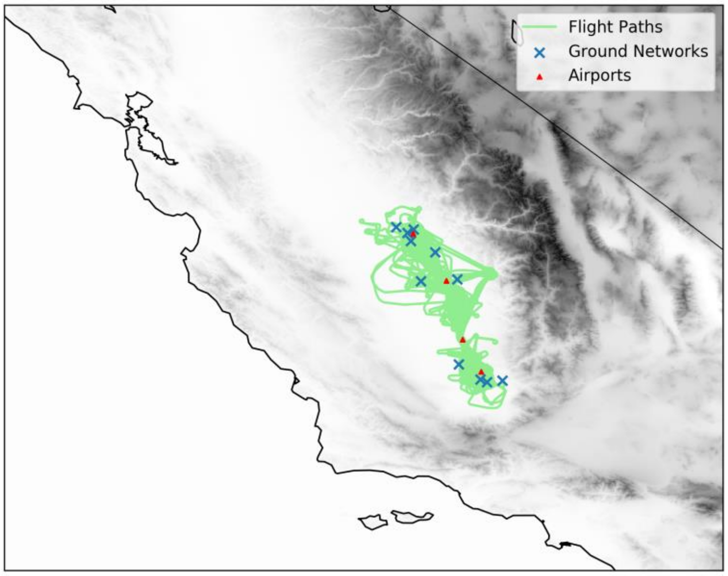


**Figure 3.** Ground tracksFlight paths of all flights of the Residual Layer Ozone projectall aircraft deployments in this field campaign (green). Airports with where low approaches were conducted (red triangles) and ground ozone monitors are shown(blue crosses) are shown. From north to south, the airports are Fresno Yosemite International Airport (FAT), Visalia Municipal Airport (VIS), Delano Municipal Airport (DLO), and Bakersfield Meadows Field Airport (BFL). From north to south, the CARB The ground ozone network stations stations are(blue crosses) used were Fresno-Sierra Skypark #2, Clovis-N Villa Avenue, Fresno-Garland, Fresno-Drummond Street, Parlier, Visalia-N Church Street, Hanford-S Irwin Street, Shafter-Walker Street, Bakersfield-5558 California Avenue, Edison, Bakersfield Municipal Airport. Bakersfield-5558 California Avenue, Bakersfield-Municipal Airport, Clovis-N Villa Avenue, Edison, Fresno-Drummond Street, Fresno-Garland, Fresno-Sierra Skypark #2, Hanford-S Irwin Street, Parlier, Shafter-Walker Street, and Visalia-N Church Street.

The nocturnal scalar budget analyses presented here utilizes all late night (~ 21:45 – 00:00 PST) flights in which a subsequent flight was conducted the following morning (~ 06:15 – 08:30 PST). The dates (before midnight PST) of the late nightlate-night flights for the 12 overnight periods are shown in Table 1. Additionally, late night flights without a subsequent morning flight were flown on 12 September 2015 and 26 July 2016, and morning flights without a preceding late night flight were flown on 10 September 2015, 24 July 2016, 12 August 2016, and 14 August 2016. These additional flights are included in the analyses here that refer exclusively to either the late night or morning flights, but were not used for the scalar budgets.

### 2.2. Scalar Budget Conceptual FrameworkAnalysis

Here we aim to test the importance of the aforementioned nocturnal mixing on the ozone budget in this region by applying a scalar budgeting technique to the aircraft data in order to estimate an eddy diffusivity between the stable

~~boundary layer~~NBL and the ~~residual layer~~RL. ~~This objective aims to use a~~To address this objective, we use a similar method that has been presented with daytime scalar budgets (Conley et al., 2011; Faloona et al., 2009; Trousdell et al., 2016) to further demonstrate the overall practicality of this methodology.

The nocturnal budget equation is formulated by the Reynolds-averaged conservation equation for a scalar – in this case $O_x$ – in a turbulent medium. $O_x$ is defined here as $NO_2$+$O_3$ in order to avoid the effects of titration of $O_3$ by NO. If not depleted by chemical oxidation to $NO_3$ and further reaction products, $NO_2$ will photolyze the following day to reproduce ozone in photostationary state, so it can act as an overnight reservoir of ozone. The chemical loss of $O_x$ is then computed by the reaction between $O_3$ and $NO_2$ to form nitrate, and the ultimate fate of nitrate will affect the overall $O_x$ loss. In the stable nighttime environment we will treat the mixing between the RL and NBL by using an eddy diffusivity. The NBL $O_x$ budget can thus be represented as:

$$\frac{\partial[O_x]}{\partial t} = -\alpha k_{O3+NO2}[O_3][NO_2] - \bar{u}\frac{\overline{\Delta[O_x]}}{\Delta x} - \bar{v}\frac{\overline{\Delta[O_x]}}{\Delta y} + \frac{-[O_3]_{SFC^*}|v_d|}{h} + \frac{K_z\frac{\Delta[O_x]}{\Delta z}}{h} \qquad \textbf{(1)}$$

Where the term on the left represents the change in concentration with respect to time ~~within the flight volume~~. The leftmost term on the right side of Eq. 1 represents the net loss of $O_x$ due to chemical reaction of the resultant $NO_3$ and contains an unknown constant of proportionality, α, which depends on the subsequent reaction pathway of $NO_3$, and can range from 0 ~~–~~– 3. For reasons later discussed, α is assumed to be ~ 1.5 for this analysis. The next two terms represent changes due to advection by the horizontal wind, followed by terms representing the dry deposition of ozone to the surface, and finally the vertical turbulent mixing term that uses the vertical gradient and the eddy diffusivity, $K_z$ – a number that encapsulates the strength of the overnight mixing. The storage (left hand side) term, chemical loss, advection, surface ozone, and ~~stable boundary layer~~NBL height can be calculated using the aircraft data. Combining those measurements with an estimated 0.2 cm s$^{-1}$ nighttime dry deposition velocity of ozone ~~at night~~ in the SSJV (an average from a study over cotton, grass, mixed deciduous forest, and vineyard field sites by ~~(~~Padro, 1996), we can indirectly estimate $K_z$. In the following sections, we detail the methods for estimating the terms in Equation 1.

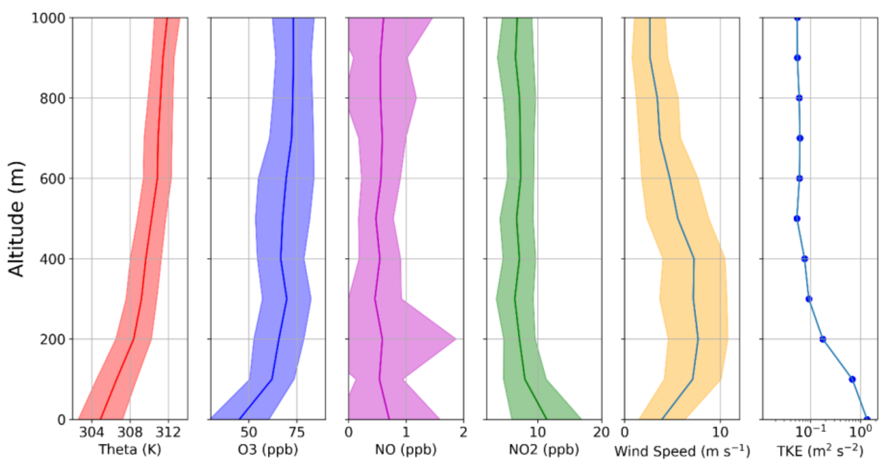

**Figure 4.** Mean and ±1 standard deviation (~~swatches~~swathes) of potential temperature, ozone, NO, $NO_2$, ~~and~~ wind speed, and turbulent kinetic energy (mean only) from all ~~late night~~late-night flights.

### 2.2.1. NBL Height

Profiles of wind speed, potential temperature, $NO_2$, and $O_3$ from each night and morning flight were analyzed to make a best guess of the NBL height, *h*. Figure 4 shows the average scalar profiles from all 15 late night flights to illustrate the typical gradients in the lower portion of the atmosphere. One method of determining *h* is to observe the lowest ~~point~~ elevation where $\partial\theta/\partial z$ becomes close to adiabatic, as the layer below that physically represents air that is in thermodynamic communication with the radiatively cooled surface (Stull, 1988). Another method is to use the level of wind maximum, or LLJ height, when one is present. We found that both of these estimates typically yielded similar values of *h*. On nights where there was significant disagreement between the two different estimates, the vertical jump (or sharpest gradient) of $O_x$ in the height region of the NBL-RL interface was considered, as this likely points to a region of maximum mixing~~The drop in momentum above the jet is similar to the jump in other scalars (humidity, methane, etc) often observed at the top of either the NBL or daytime atmospheric boundary layer~~. ~~In our case, the vertical jump (or sharp gradient) of $O_x$ in this height region should be considered, as this likely points to a region of maximum mixing. All three of these methods were used in tandem for both the late night and corresponding morning flight to determine an average *h* for each night~~In such cases, we averaged the height where the steepest gradient was observed with the estimates obtained from the other two methods. It should be noted that some subjectivity was involved for determining a final value of *h* for each night~~, since~~because wind maxima and thermal gradients were not clearly defined in the profiles. All of the aforementioned factors lead to an estimated uncertainty of ±~~-~~100 m for all of the NBL heights obtained. The average conditions from the late night and morning flights are presented in Table 1.

| Flight Date | NBL Height h (m) | NBL $O_3$ (ppbv) | NBL $NO_2$ (ppbv) | MDA8 (ppbv) | BV Frequency N ($s^{-1}$) | BRN | TKE ($m^2\ s^{-2}$) | LLJ Max $U_x$ ($m\ s^{-1}$) | $\sigma_u/U_x$ |
|---|---|---|---|---|---|---|---|---|---|
| 9 Sep 2015 | 250 | 45.4 | 16.5 | 82.7 | 0.025 | 0.68 | 0.35 | 8.1 | 0.09 |
| 12 Sep 2015 | 130 | 31.2 | 18.5 | 67.2 | 0.018 | 0.89 | 0.70 | 4.0 | 0.22 |
| 3 Jun 2016 | 260 | 52.7 | 6.0 | 87.8 | 0.021 | 0.23 | 0.35 | 12.0 | 0.05 |
| 4 Jun 2016 | 220 | 59.0 | 6.1 | 92.3 | 0.026 | 0.80 | 0.50 | 5.9 | 0.12 |
| 29 Jun 2016 | 150 | 43.0 | 9.9 | 91.9 | 0.022 | 0.28 | 0.41 | 10.0 | 0.08 |
| 25 Jul 2016 | 190 | 44.2 | 12.0 | 85.5 | 0.022 | 0.71 | 0.43 | 6.4 | 0.10 |
| 26 Jul 2016 | 320 | 51.6 | 8.7 | 94.8 | 0.023 | 0.99 | 0.56 | 8.0 | 0.08 |
| 13 Aug 2016 | 150 | 49.8 | 13.9 | 92.1 | 0.017 | 0.41 | 0.61 | 9.1 | 0.08 |
| 15 Aug 2016 | 250 | 42.5 | 11.6 | 74.3 | 0.023 | 0.37 | 1.02 | 10.3 | 0.08 |
| 16 Aug 2016 | 210 | 44.8 | 14.1 | 86.8 | 0.025 | 0.52 | 0.71 | 9.4 | 0.10 |
| 17 Aug 2016 | 170 | 48.3 | 15.9 | 91.5 | 0.024 | 1.35 | 0.74 | 6.2 | 0.12 |
| 18 Aug 2016 | 190 | 48.8 | 12.6 | 92.2 | 0.025 | 1.00 | 0.71 | 5.6 | 0.17 |
| **Average** | **208** | **46.8** | **12.1** | **86.6** | **0.023** | **0.69** | **0.59** | **7.9** | **0.11** |
| **Stdev.** | **53** | **6.5** | **3.8** | **7.9** | **0.003** | **0.32** | **0.19** | **2.2** | **0.04** |

**Table 1.** NBL heights, ozone, $NO_2$, Brunt~~–~~-Väisälä (BV) frequencies, Bulk Richardson Number (BRN), Turbulent Kinetic Energy (TKE), and LLJ maximum wind speeds observed during the late night ~~/~~and morning flight pairs. Maximum daily 8-hour average ozone (MDA8) values are from the following day and are an average of the 11 ground networks in our flight region.

For the domain of interest, all measured $NO_2$ and $O_3$ data was averaged for each 20 m altitude bin in order to generate mean vertical profiles of $O_x$. Separate profiles were created for the late night flight and the subsequent morning flight. The height of the ~~stable boundary layer~~NBL for each night (*h*) was used as the upper altitude limit observations to obtain advection, chemical loss, and time rate of change (storage) terms for the budget equation, since the budget equation is meant to be applied to the NBL. The overnight average $O_x$ profile was subtracted from the Sunrise profile and divided by the time difference between the midpoints of each flight to compute the storage term.

### 2.2.~~1~~2. Nocturnal ~~Ozone and $NO_x$ Chemistry~~Chemical Loss of $O_x$

~~As previously mentioned, t~~The chemical loss term in Equation 1 is expected to be an important component of the NBL $O_x$ budget. Both $NO_2$ and $NO_3$ are able to regenerate ozone in the presence of sunlight and participate in the same sequence of reactions, ~~which~~ therefore the species are normally grouped together into a family ~~of species~~ referred to as odd oxygen ($O_x$~~). $O_x$ is usually defined as~~ = $O_3+NO_2+2NO_3+3N_2O_5$) (Brown et al., 2006; Wood et al., 2004); however, since we ~~were unable to~~did not measure ~~the higher oxidation state~~ $NO_3$ and $N_2O_5$~~$NO_y$ species~~, in this study we ~~will define~~estimate $O_x$ as merely the sum of $O_3+NO_2$~~,~~ ~~as~~ because these are ~~by far the dominant species of $O_x$~~expected to exceed to concentrations of ~~$NO_3$ and $N_2O_5$~~the other $O_x$ species by 1-2 orders of magnitude (Brown et al.,1995). Considering $O_x$ is useful ~~in this case~~for our study because the family is conserved in the rapid oxidation of (R1 below)~~,~~ yielding $NO_2$~~.~~, which ~~that~~ may be~~is~~ quickly photolyzed ~~back~~ to regenerate ~~to~~ $O_3$ once the sun rises as part daytime photostationary state.

Aside from dry deposition to the Earth's surface, $NO_x$ chemistry is the main loss of ozone at night, counteracting its role in production during the daytime (Brown et al., 2006, 2007). The chemical loss of ozone at night begins with the production of the nitrate radical (R2):

**(R1)** $NO + O_3 \rightarrow NO_2 + O_2$
**(R2)** $NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_3$ photolyzes rapidly once the sun rises, so the ultimate net loss of ozone depends on the loss of nitrate in the dark. The loss occurs mainly via three general channels. In one channel, dinitrogen pentoxide is formed (R3), which has a backwards reaction and can be a source of $NO_2$ if not deposited onto moist surfaces or aerosols to form nitric acid via hydrolysis (R4):

**(R3)** $NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M$
**(R4)** $N_2O_5 + H_2O \rightarrow 2HNO_3$
**Net (R1-R4)**: $NO + 2O_3 + NO_2 \rightarrow 2NO_z$

where $NO_z = NO_y - NO_x$ to represent the family of products of $NO_x$ oxidation. In another channel, nitrate is lost by reaction with a wide array of organic compounds. This process can typically be represented by (R5), but in some cases, organic compounds can re-arrange to produce an $NO_2$ molecule (R5a) (Brown et al., 2006):~~:~~

**(R5)** $NO_3$ + (VOC, etc.) $\rightarrow$ organic nitrates

**(R5a)** $NO_3$ + (VOC, etc.) $\rightarrow$ organic nitrates + $NO_2$

**Net (R1, R2, R5)**: $NO + 2O_3 \rightarrow NO_z$

**Net (R1, R2, R5a)**: $NO + 2O_3 \rightarrow NO_z + NO_2$

However, in urban environments with nocturnal sources of NO, nitrate is reduced back to $NO_2$ by the very rapid reaction:

**(R6)** $NO + NO_3 \rightarrow 2NO_2$

**Net (R1, R2, R6)**: $2NO + 2O_3 \rightarrow 2NO_2$

If the hydrolysis of $N_2O_5$ (R4) is the dominant $NO_3$ sink, then the net reaction leads to a loss of 3 $O_x$ molecules per nitrate produced (R2). However, if the dominant loss is reaction with VOC~~'~~s ~~(R5)~~ then the net reaction leads to ~~2~~ between 1 (R5a) and 2 (R5) $O_x$ molecules lost per R2. And if there is sufficient NO, R6 will dominate the nitrate loss leading to no net $O_x$ loss per R2. Thus, determining the dominant loss of nitrate is crucial for ~~ours or, in fact,~~ any analysis of the diurnal budget of ozone.

Reaction (R6) has often been ignored at night under the presumption that local sources of NO are sparse and reaction (R1) will outcompete reaction (R6) (Brown et al., 2007; Stutz et al., 2010).~~;~~ H~~h~~owever, at observed values of 30 ppb of $O_3$ and an estimated 20 ppt of $NO_3$ (Smith et al., 1995), the lifetimes of NO (~80s) ~~to~~ with respect to (R1) ~~and (R6) are~~ would be nearly equivalent ~~(~80s)~~to that of (R6). Our measurements indicate ground-level NO of about 0.6 ppb at midnight (σ~~SD~~ = 1 ppb), corroborated by the CARB surface air quality network, increasing in the early hours to 2-4 ppb. However, both the ground network and aircraft observations may be biased high to the regional average because of their proximity to California Highway 99 and other urban centers (Fig. 3). Nevertheless, the rate of reaction (R6) is 2.6 x $10^{-11}$ $cm^3$ $s^{-1}$ $molec^{-1}$ (Sander et al., 2006), extremely rapid relative to the others, such that even 60 ppt of NO~~,~~ (an order of magnitude lower than what our measurements indicate~~,~~) would result~~s~~ in an $NO_3$ of only 25 seconds. Hence, we conclude that (R6) should not be ignored in general~~,~~ as it may ultimately reduce the chemical loss rate of $O_x$~~.~~ overnight.

There is then a further question as to whether any VOCs would be able to compete with this channel of $NO_3$ consumption. An investigation into the ~~faster~~ most rapid VOC reactions with $NO_3$ per Atkinson et al. (2006) and Gentner et al. (2014a) is presented in Table 2. In this analysis, concentrations of VOCs are estimated from available reports in the SJV, which given its roughly 5 million acres of irrigated land (Li et al., 2016), may vary widely from one location to another due to the presence of diverse crop canopies. The estimated lifetime of $NO_3$ due to the VOC reactions in Table 2 is ~~9.5~~12.2 seconds, about ~~four~~ five times the lifetime of $NO_3$ with respect to the presence of 0.6 ppb of NO (2.5 seconds). We note that although there are few direct observations of $NO_3$ in the SSJV, the CALNEX campaign conducted one flight that measured concentrations of about 10-40 ppt shortly after sunset on 24 May 2010 (https://esrl.noaa.gov/csd/groups/csd7/measurements/2010calnex/P3/DataDownload/index.php). Smith et al. (1995) present DOAS measurements from 15 nights in July and August 1990 (their Figure 6a) from a site 32 km southeast of Bakersfield suggesting that $NO_3$ concentrations in the SSJV peak around 30 pptv within an hour or two after sunset and plateau in the middle of the night around 10 ppt, then decline to zero by sunrise. The variability of $NO_3$ reported in that study is high, with nocturnal values ranging from near zero to over 50 ppt. Under a simplified, steady-state model, the expected lifetime of $NO_3$ can be estimated using the second-order reaction rate for (R2) for the formation of the nitrate radical, and combining all of the loss channels into a single lifetime ($\tau_{NO3}$):

$$\tau_{NO3} = \frac{[NO_3]}{k_2[NO_2][O_3]} \quad \textbf{(2)}$$

Using the average NBL ozone and $NO_2$ from Table 1, a $NO_3$ concentration of 10 ppt would imply its lifetime to be about 25 seconds, which is about twice as large as our estimate from Table 2. Based on these direct measurements of $NO_3$, our lifetime calculations likely represent a lower bound and further illustrate the uncertainty given the sensitivity to the unconstrained VOCs and our NO measurements, which have an envelope of error that spans a large range of possible nitrate loss lifetimes.

With longer lifetimes of nitrate loss with respect to the VOC and NO reactions, we are faced with the possibility that hydrolysis of $N_2O_5$ is also an important loss channel, increasing the amount of $O_x$ molecules lost per nitrate molecule formation in (R2). Smith et al. (1995) report that the lifetime of $NO_3$ was found to be highly dependent on relative humidity, with lifetimes ranging from seconds to 10 minutes when the relative humidity is above 45 % (presumably due to $N_2O_5$ hydrolysis), but between 10 and 60 minutes when below the 45 % threshold. Figure 5 shows the diurnal cycle of temperature and relative humidity observed at the airports in our flight region during the days of our campaign, compared with the 2015-2016 1 June – 30 September averages. The > 45 % relative humilities observed at FAT and VIS imply that the hydrolysis of $N_2O_5$ is an important sink for $NO_3$.

Given the ~~obvious~~ importance of the nitrate loss to VOCs and NO, but some importance of the $N_2O_5$ hydrolysis, we use a best estimate that each effective collision of $NO_2$ and $O_3$ will lead to the net loss of approximately 1.5 (±0.5) molecules of $O_x$ from the net effects of the entire series of reactions outlined above. This is a "center of the envelope" estimate for the possible range of 0 – 3~~, and best accounts for the lack of certainty as to which (if any) nitrate loss channel is dominant~~. Although our measurements are unable to constrain this coefficient, the ultimate fate of the nitrate radical can be seen to have a ~~very important~~critical role in quantifying the net loss of $O_x$ overnight, and without a greater understanding of the nitrate budget, predicting this loss rate is ~~highly~~ uncertain.

| VOC | k (cm$^3$/mlc*s) cm$^3$ mlc$^{-1}$ s$^{-1}$ | Best Guess ppt | $\tau_{NO3}$ s | Source |
|---|---|---|---|---|
| o-Cresol | 3.33 (10$^{-11}$) | 10 | 120 | Estimate[1] |
| linalool | 2.22 (10$^{-11}$) | 50 | 36 | Arey et al. 1990[3] |
| 3-methylfuran | 1.90 (10$^{-11}$) | 9 | 235 | Steiner et al. 2008 |
| b-caryophyllene | 1.67 (10$^{-11}$) | 13 | 190 | Gentner et al. 2014b |
| 6-Methyl-5-hepten-2-one | 1.67 (10$^{-11}$) | 10 | 241 | Estimate[2] |
| limonene | 1.33 (10$^{-11}$) | 26 | 117 | CalNex |
| myrcene | 1.11 (10$^{-11}$) | 29 | 124 | Gentner et al. 2014b |
| sabinene | 9.52 (10$^{-12}$) | 3 | 1284 | CalNex |
| b-phellandrene | 8.33 (10$^{-12}$) | 10 | 482 | Estimate[2] |
| Phenol | 7.41 (10$^{-12}$) | 10 | 542 | Estimate[2] |
| a-pinene | 6.06 (10$^{-12}$) | 47 | 142 | CalNex |
| b-pinene | 2.67 (10$^{-12}$) | 3 | 4654 | CalNex |
| Trans 2-butene | 7.94 (10$^{-13}$) | 130 | 389 | Steiner et al. 2008 |
| isoprene | 6.94 (10$^{-13}$) | 68 | 853 | CalNex |
| camphene | 6.54 (10$^{-13}$) | 7 | 8502 | CalNex |
| **NET** | | | **12.2** | |

[1] Drew Gentner of Yale University, personal communication.

[2] No measurements reported in the SSJV, an order of magnitude estimate is made based on typical aerosol concentrations.

[3] Arey et al. (1990) reported 70 ppt in an orange grove. We estimate 50 ppt as a SJV average.

**Table 2.** Estimations of VOC reactions with nitrate in the summertime nocturnal boundary layer for the SSJV. Reaction rates from Atkinson & Arey (1998), Table 2 ~~&~~ and Atkinson (2006). ~~The measurements in some of the studies above were taken in specific crop fields. Since the aim of this analysis was merely to obtain an order of magnitude estimate, we predicted whether a valley-averaged concentration may be slightly higher or lower than what was reported in the study. Thus, values here may not exactly match literature.~~

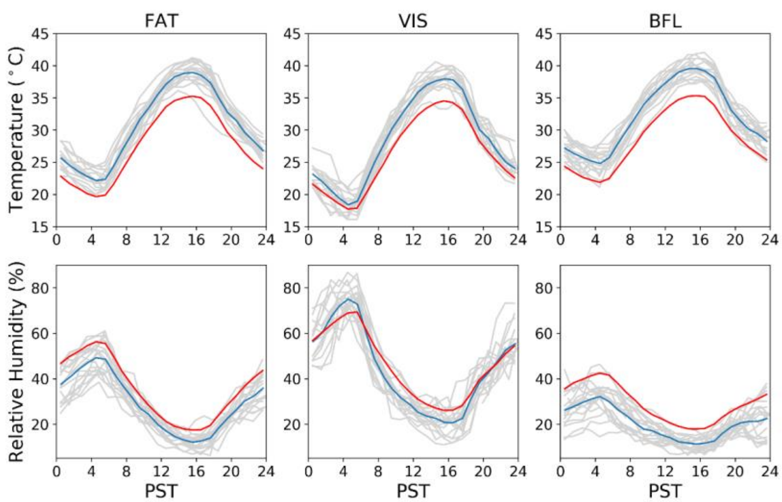

**Figure 5.** Diurnal plots of temperature and relative humidity during flight days of the Residual Layer Ozone campaign (individual days = grey lines, campaign average = blue lines), compared to 1 June –– 30 September 2015 and 2016 averages (red lines) at the Fresno (FAT), Visalia (VIS), and Bakersfield (BFL) airports Automated Weather Observing System (AWOS) network. Hours are in Pacific Standard Time (PST).

Consequently, we calculate the net reaction (R1-R6) for the nocturnal chemical loss rate of $O_x$ as a constant multiple of (R2). The 2nd second order rate equation for the net chemical loss of $O_x$ is calculated by:

$$\left.\frac{dO_x}{dt}\right|_{chemical\ loss} = -\alpha k_{O3+NO2}[O_3][NO_2] \qquad \textbf{(3)}$$

Where α can range from 0 –– 3, and per the discussion above, is estimated to be 1.5 ± 0.5 (uncertainty discussed in section 3.2). To estimate a value for the second order rate constant ($k_{O3+NO2}$), we start with the temperature dependent function for this reaction (Sander et al., 2006):

$$k_{O3+NO2} = 1.2(10^{-13}) * e^{\frac{-2450}{T}} \qquad \textbf{(4)}$$

Where T is the temperature in Kelvin. For the domain being analyzed, an instantaneous value of $k_{O3+NO2}$ is determined at each data point. These values of $k_{O3+NO2}$ are then averaged to obtain a constant value for the given night. It should be noted that small errors in the value of $k$ that would beare within the order of our temperature fluctuations were found to not have a measurable impact on the chemical loss term. To estimate the chemical loss of $O_x$, the initial 20 m altitude bins for $NO_2$ and $O_3$ are taken from the late night and morning profiles. In each bin, the concentrations are linearly interpolated between the late night and morning values, so that there is an estimation of the current average concentration within that bin at every time during the night.

### 2.2.23. Horizontal Advection by Mean Wind

The advection term in Equation 1 is calculated by first collecting all 1-second $O_x$ data points for the late night and morning flights separately. For each flight, Aa multiple linear regression is fit through the 1-second $O_x$ data for latitude ($y$), longitude ($x$), and altitude ($z$), allowing estimations for the horizontal gradients of $O_x$ ($\partial[O_x]/\partial x$ and $\partial[O_x]/\partial y$) in the horizontal advection terms. The $r^2$ values of the regressions ranged from 0.25 to 0.69, and the number of data that they contained ranged from 2813 to 5323. Typical values of the horizontal $O_x$ gradients were of order 0.1 ± 0.02 ppb km$^{-1}$. To compute theThe total advection term within the NBL on a given flight, these gradients are combined the mean wind speeds is:

$$Advection_{Ox} == -\left[\left(\frac{\partial[O_x]}{\partial x} * \bar{u}\right) + \left(\frac{\partial[O_x]}{\partial y} * \bar{v}\right)\right] \qquad \textbf{(5)}$$

Where Per convention, $u$ is the mean $x$-component (zonal) wind and $v$ is the mean $y$-component (meridional) wind. The same procedure is repeated for the morning flights, and the advection terms from the late night and morning flights are averaged together.

**2.2.34. Dry deposition of $O_x$**

Dry dDeposition of ozone is presumed to be the mainan important sink of $O_x$ at the surface, the flux of which can be parameterized as the product of the surface ozone values (measured directly from the aircraft) and the deposition velocity for ozone. There are reports of ozone deposition in the area of this our field campaign from a 1994 study using the eddy covariance technique (Padro, 1996). The findings of their study suggest nocturnal ozone deposition velocities are a fewseveral times smaller than their daytime counterparts, but we infer that the overall process is still important for the budgeting technique presented herein the NBL because of the smaller mixed layer depth (Eq. 1). Results from a European field study in a flat grass field, largely representative of the SSJV, corroborates this finding (Pio et al., 2000). We thus estimate a dry deposition velocity of 0.2 cm $s^{-1}$ ± 0.1 cm $s^{-1}$ for ozone at night in the SSJV bBased on thesean abundance of , as well as otherobservations of nocturnal ozone dry deposition velocities reported in the literature over a broad variety of grassland and agricultural surfaces similar to those found in the SSJV (Pederson et al., 1995; Pio et al., 2000; Meszaros et al., 2009; Neirynck et al., 2012; Lin et al., 2010), all ranging between about 0.1 – 0.3 cm $s^{-1}$, we estimate a dry deposition velocity of 0.2 cm $s^{-1}$ (± 0.1 cm $s^{-1}$) for our purposes, literature values. deposition on the basis that crop canopies can be either a small source or sink of $NO_2$ at the surface (Walton et al., 1997)). The amount of $O_x$ lost overnight due to deposition would be within our stated uncertainty (± 0.86 ppb $h^{-1}$) as long as $|v_{d\ NO2}| < \sim 2.5$ cm $s^{-1}$, an assumption supported by the literature (Pilegaard et al., 1998; Walton et al., 1997).

**2.2.45. Vertical Turbulent Mixing between the NBL and the RL**

Finally, a vertical flux divergence for $O_x$ must be estimated for Equation 1, which is represented by the last two terms. For the top part of the stable boundary layerNBL, the flux of $O_x$ can be interpreted as an eddy diffusivity ($K_z$) multiplied by the vertical gradient of $O_x$ between the NBL and RL. A For each flight, a linear regression through the 20 m resolution verticalthe 1-second $O_x$ profile data within the NBL-RL interface is used to determine $\partial[O_x]/\partial z$ (for the last term in Equation 1) in the upper portion of the NBL that appeared to contain the strongest $O_x$ gradient. The average $r^2$ value of the 24 regressions was 0.11, and the number of data points that they contained ranged from 116 to 2166. Typical values of the vertical $O_x$ gradients were ~0.07 ± 0.04 ppb $m^{-1}$. The layers used for the regression fit were 100 - 200 m thick and did not extend below 70 m AGL on any given night to avoid capturing the region where the $O_x$ sink due to surface deposition and/or reaction with freshly emitted NO is likely to accountlikely accounts for the vertical gradient in $O_x$ (Fig. 6). The eddy diffusivity can now be solved for with all of the other terms estimated.

**3. Results and Discussion**

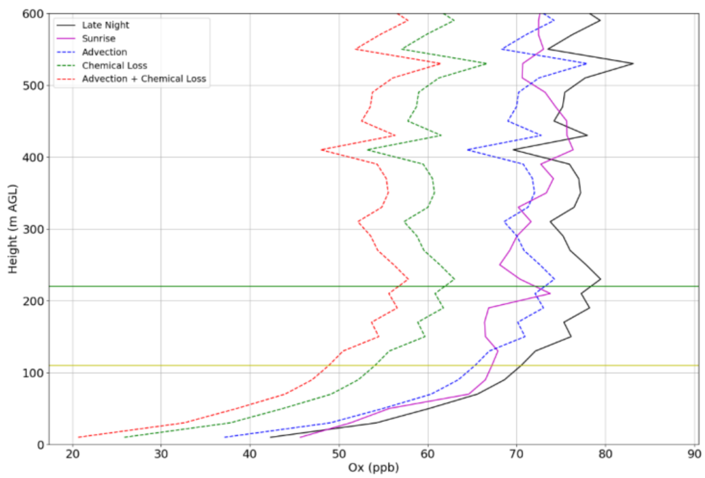


**Figure 6.** $O_x$ profiles from 2016-06-04 overnight analysis, NBL height (green line), and lower bound to vertical mixing gradient (yellow line). The solid lines are observations and the dashed lines are ~~inferred~~calculated based on expected changes due to horizontal advection (blue), chemical loss (green), and the sum of the two (red).

## 3. Results and Discussion

### 3.1. ~~Overnight Mixing and the $O_x$~~ Scalar Budget Results

Results of the scalar budget analysis for all 12 paired late night and morning flights are presented in Table 3. An error propagation analysis (discussed in section 3.2) is presented for each term in the budget, as well as for the ~~*ultimately*~~

| Flight Date | Storage ppb $h^{-1}$ | Advection ppb $h^{-1}$ | Chemical Loss ppb $h^{-1}$ | Vertical Mixing ppb $h^{-1}$ | Deposition ppb $h^{-1}$ | Eddy Diffusivity $m^2$ $s^{-1}$ |
|---|---|---|---|---|---|---|
| 9 Sep 2015 | -2.3(0.2) | -3.2(0.2) | -3.6(1.3) | 5.1(3.1) | -0.6(0.4) | 3.0(1.3) |
| 12 Sep 2015 | -0.2(0.2) | -0.0(0.1) | -2.9(0.9) | 4.0(5.2) | -1.4(1.3) | 3.5(3.0) |
| 3 Jun 2016 | -0.7(0.1) | 0.3(0.2) | -1.5(0.4) | 1.5(0.9) | -1.0(0.6) | 2.9(1.4) |
| 4 Jun 2016 | -0.5(0.2) | -0.6(0.1) | -1.9(0.6) | 3.2(2.0) | -1.2(0.8) | 2.9(1.2) |
| 29 Jun 2016 | -1.3(0.2) | -1.0(0.1) | -2.2(0.6) | 3.4(3.1) | -1.6(1.3) | 2.0(1.1) |
| 25 Jul 2016 | -1.2(0.2) | 0.6(0.2) | -2.7(0.8) | 2.0(1.5) | -1.2(0.9) | 1.1(0.6) |
| 26 Jul 2016 | -1.4(0.2) | 0.2(0.2) | -2.2(0.8) | 1.3(1.0) | -0.7(0.4) | 1.5(1.1) |
| 13 Aug 2016 | -1.4(0.2) | -0.3(0.2) | -3.4(1.1) | 4.1(3.6) | -1.8(1.5) | 2.3(1.2) |
| 15 Aug 2016 | -1.1(0.1) | 0.6(0.2) | -2.5(0.9) | 1.8(1.3) | -0.9(0.6) | 2.6(1.6) |
| 16 Aug 2016 | -1.9(0.2) | -0.1(0.1) | -3.0(1.1) | 2.3(1.9) | -1.0(0.7) | 2.2(1.4) |
| 17 Aug 2016 | -2.0(0.2) | 0.1(0.1) | -3.7(1.4) | 2.8(2.5) | -1.2(0.9) | 1.5(1.0) |
| 18 Aug 2016 | -1.6(0.2) | 0.5(0.2) | -3.1(1.2) | 2.2(2.0) | -1.2(0.9) | 1.9(1.3) |
| **Average** | **-1.30 (0.18)** | **-0.24 (0.16)** | **-2.73 (0.93)** | **2.81 (2.34)** | **-1.15 (0.86)** | **2.28 (1.35)** |
| **Standard Dev.** | **0.59** | **1.00** | **0.66** | **1.12** | **0.33** | **0.69** |

**Table 3.** Results from the nocturnal scalar budget for all terms. Estimated error (see section 3.2) in parenthesis.

Of note is the fact that on average, the chemical loss is expected to be a little more than twice as large as the physical loss from dry deposition. For dry ~~deposition~~deposition, the average lifetime of ozone is 28 h (200 m / 0.002 m $s^{-1}$), and for chemical loss it is 12 h. Both losses of $O_x$ added together are about triple the observed time rate of change, and thus the physical and chemical losses are largely (~ 2/3) compensated by vertical mixing. Because the RL consistently contains more ozone than the stable NBL, turbulent mixing will result in a transfer of ozone into the NBL. While $NO_2$ is observed to be higher in the NBL than in the RL (by about 3-5 ppbv), it is a much smaller contribution to the $O_x$ ($O_3$ is less than $NO_2$ by anywhere from 10-20 ppbv.) Thus, vertical mixing at the top of the ~~stable boundary layer~~NBL, influenced by the strength of the LLJ, is inherently a source term of $O_x$ to the lower NBL. ~~It is also worth noting that the chemical loss of $O_x$ does not vary significantly between the RL and NBL because the increase of $NO_2$ in the NBL is compensated by the decrease of $O_3$, although this assumes that there are not other chemical differences that alter the ultimate reaction fate of nitrate (altering the coefficient α in Eq. 1.)~~

**3.2. Error Analysis**

Here we estimate the uncertaint~~y~~ies for each term in the budget equation, as well as those for the resultant ~~ultimately calculated~~ eddy diffusivities. The storage term error is computed by first taking the standard deviation of 1-second ozone measurements divided by the square root of the number of samples, then the standard error of the means for both the late night and morning profiles are combined. This analysis is carried out in 20 m altitude bins separately and then averaged together because there is more uncertainty at lower altitudes due to fewer measurements. The advection term error is computed from the standard error of the slopes of the regression fit, with errors propagating for each of the 4 advection components for both the *u* and *v* components of wind. To compute the chemical loss error, the large uncertainty of the α coefficient must be taken into consideration. Based on our analysis concluding that all channels of nitrate loss are probably non-negligible, we infer that α is between 0.5 and 2.5 with a 95 % confidence interval. Thus, one standard error for the α coefficient is about 0.5. An error propagation is then carried out for each 20 m altitude bin, using the standard deviations of the $O_3$ and $NO_2$ measurements divided by the square root of the sample size. As previously stated, the estimated standard errors of the ~~stable boundary layer~~NBL height and surface deposition of ozone are taken to be 100 m and 0.1 cm $s^{-1}$, respectively. The surface ozone standard error is computed as the standard deviation of the aircraft measurements divided by the square root of the sample size, and the vertical $O_x$ gradient uncertainty is computed by the standard error of the regression slope. The uncertainties in the vertical mixing, deposition flux, and diffusivity values can then be computed by standard error propagation. The resultant relative error estimates of the nighttime diffusivities are about 50 %, and errors of this order seem reasonable based on a technique that assumes the closure of 4 independently measured terms. Past studies using similar airborne budgeting methods have estimated relative uncertainties ranging from 15-75 % (Conley et al., 2011; Faloona et al., 2009; Kawa & Pearson, 1989; Trousdell et al., 2016).

**3.3 The ~~Fresno Eddy~~Fresno Eddy and ~~Low-Level Jet~~LLJ**

The formation of the ~~Fresno eddy~~Fresno Eddy begins when the daytime northwesterly ~~mountain-~~valley wind continues into the late evening, decoupling from the surface and forming a LLJ (Davies 2000). The Tehachapi Mountains will typically topographically block the flow of the LLJ (Lin and Jao, 1995). The eddy is formed during the hours before dawn when this northwesterly flow interacts with southeasterly nocturnal downslope flow coming from the high southern Sierra Nevada Mountains, although there is some question as to the extent to which the southeasterly flow observed in the morning hours is merely the result of a topographic deflection and recirculation of the nocturnal jet. The Coriolis force helps to circulate this flow; however, a mesoscale low is not thought to develop (Bao et al. 2007, Lin and Jao, 1995). We note that the valley flow peaks around midnight, while the katabatic drainage flow peaks ~~shortly before~~near dawn, so these two components of the ~~Fresno eddy~~Fresno Eddy are not time-coherent. The initial northwesterly wind and a topographic blockage are both critical for determining whether or not the eddy will form on a given night (Lin and Jao, 1995).

One complicating factor ~~that remains~~ for ~~this particular~~our scalar budget analysis is the ~~presence of the Fresno eddy and its~~ influence that this eddy will have on our measurements of advection. If an eddy is recirculating a scalar quantity, using a simple linear fit model as we did in section 2.2.3 to estimate advection would be questionable, especially if the flight area only covered a small portion of the larger mesoscale circulation. Zhong et al. (2004) uses a series of 915 MHz RASS to analyze low-level winds in the SSJV. Their Figure 4 shows that at night, the northwesterly ~~low level jet~~LLJ is formed in the ~~San Joaquin Valley~~SJV, and a weak katabatic southerly flow is observed in the foothills to the east at the Trimmer site. As the night progresses, the eddy becomes more coherent as the northwesterly jet relaxes while the southerly flow strengthens and expands westward. After daybreak, the eddy appears to deform and disintegrate with much of the SSJV experiencing a strong southerly wind.

This pattern is roughly consistent with our aircraft observations, suggesting the presence of a ~~Fresno eddy~~Fresno Eddy during our flights. An analysis of the average wind vectors and their consistency for all nocturnal and morning flights in the approximate ~~stable boundary layer~~NBL (0-300 m AGL) and ~~residual layer~~RL (300-700 m AGL) are shown in Figure 7. The wind consistency is defined as the ratio of the vector-averaged wind speed to the magnitude-averaged wind speed, with values close to 1 indicating a consistent wind direction (Stewart et al., 2002; Zhong et al., 2004). The nocturnal ~~low-level jet~~LLJ can be seen clearly to fill most of the SSJV in both the NBL and RL. In the morning ~~residual layer~~RL ~~level~~, there is localized consistent southerly flow closest to the foothills, some of which may be regarded as surprisingly strong. The lower level winds in the morning are consistent with the deformed eddy. We note that caution should be exercised in directly comparing our flight data to the analysis from Zhong et al. (2004) as our flights specifically targeted high ozone episode events, which we based primarily on high temperature stagnation conditions~~, so they may be subject to a meteorological bias~~ (see Fig. 5). Thus, the synoptic and mesoscale conditions during our flights may be systematically different from the climatological norms presented in Zhong et al. (2004).

From this ~~analysis~~analysis, we conclude that it is likely that our dataset captures the bulk of the dominant flow (and thus advection) on both the late night and morning flights, which are averaged and interpolated. ~~It is noted that the~~The average advection term for the 12 nights presented is -0.24 ppb $h^{-1}$, which is nearly an order of magnitude smaller than the chemical loss and storage terms. The small average contribution from advection is consistent with previous findings from daytime scalar budgets performed over the oceans (Conley et al., 2011; Faloona et al., 2009) and in the SJV (Trousdell et al., 2016) and what might be expected in the presence of a recirculating eddy. Lastly, it is noted that individually adjusting each flight to have an advection term of zero (to assume full eddy recirculation) results in only a 3 % change to the average of the diffusivity values, which further supports the idea that the influence of advection on our scalar budget analysis is minimal.

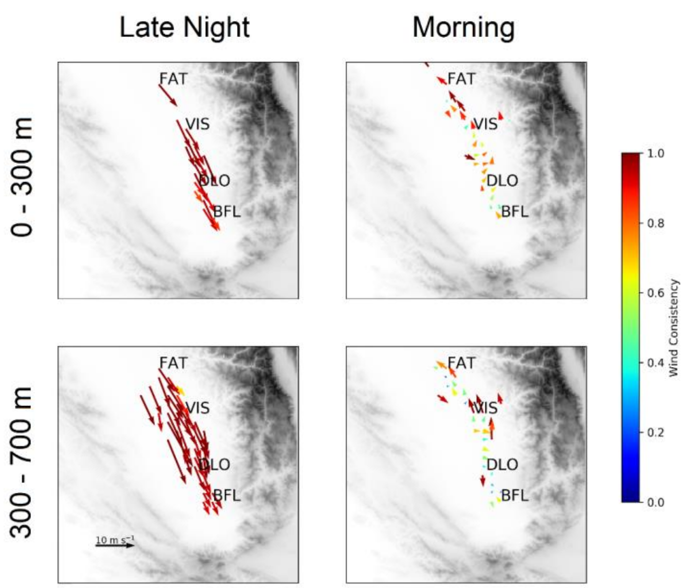


**Figure 7.** Wind consistency for late night flights and morning flights in the NBL (0 ~~-~~– 300 m) and the RL (300 ~~-~~– 700 m).

Since the ~~low-level jet~~LLJ is hypothesized to contribute to the variability of maximum daytime ozone concentration, we explored the synoptic patterns that are associated with differing strengths of the LLJ. Seven years of data (2010-2016) from the 915 MHz sounder located in Visalia, CA, ~~is~~ are compiled to obtain the ~~low-level jet~~LLJ speed and the height at which it was observed. For this ~~analysis~~analysis, we define the nocturnal ~~low-level jet~~LLJ speed as the maximum hourly-averaged wind speed observed below 1000 m averaged in 100 m vertical bins from 23 PST to 7 PST, specifically during the summer months (defined here as 1 June ~~-~~– 30 September). The 1000 m cutoff is used to ensure that the wind maximum ~~that is~~ captured is related to the LLJ at the top of the NBL rather than free-tropospheric wind. Using this definition, the ~~low-level jet~~LLJ had an average height of 340 m, an average speed of 9.9 m $s^{-1}$ ($\sigma$~~SD~~ = 3.1 m $s^{-1}$) and a typical peak timing around 23 PST. The 700 mb level corresponds to approximately 3000 m, well above the Pacific Coast Range but approximately in line with the top of the Southern Sierras.

To analyze ~~variability~~ possible synoptic influences o~~f~~n the jet strength, daily average synoptic charts from the North American Regional Reanalysis (NARR) are created in Figures 8 and 9 for days when the ~~low-level jet~~LLJ strength was less than 7 m $s^{-1}$ (N=147 nights), and greater than 12 m $s^{-1}$ (N=165 nights). Both the strong and weak low-level jets show a climatological trough pattern, but the mean trough axis is situated about 100 km to the east for the strong cases (Fig. 8b). We also note that the pressure gradient is at least twice as strong for the stronger low-level jets, and that the synoptic pattern of the weak jets favors a southerly geostrophic wind aloft, which directly opposes the up-valley northwesterly thermally driven flow. We also note find the a positive correlation found between the LLJ strength and the upwelling index ($r^2 = 0.3018$, $p < 10^{-5}$), calculated by NOAA's Pacific Fisheries Environmental Lab at 33N, 119W (https://www.pfeg.noaa.gov/products/PFEL/modeled/indices/upwelling/NA/upwell_menu_NA.html). The indiceswhich is are primarily driven by the strength and position of the North Pacific High, which, when strong, acts to push the 700 mb trough farther eastward as seen in Figure 8b, and is associated with lower sea surface temperatures and thus enhanced thermal forcing of the coupled sea breeze and valley wind. These findings are consistent with the Lin and Jao (1995) modeling study where that showed that the Fresno EddyFresno Eddy (and thus associated LLJ) did not form when the synoptic flow over the coastal range was westerly. Beaver and Palazoglu (2009) found that maximum daily 8-hour average ozone (MDA8) exceedances were more frequent in the central and southern San Joaquin Valley when an offshore ridge or onshore high were was present, consistent with Figure 8a8 (right). The results of our study suggest that this may be at least partially explained by the presence of a weaker LLJ under those synoptic conditions.

It is important to note that the Although the LLJ and Fresno Eddy are not synonymous, they are related inwe propose that the northwesterly LLJ iscan be the strongest branch dominant feature of the of the eddy's northerly flow component. This leads to an important question about the role of the Fresno Eddy in modulating the daily ozone peak. Beaver and Palazoglu (2009) purport that ozone levels in the central SJV are particularly high on days when the morning southerly wind at Parlier, a site about midway between Fresno and Visalia, is strong, concluding that recirculation from the downslope branch of the Fresno Eddy significantly controls the day's buildup of ozone. However, mixing induced by LLJs in other parts of the world has been shown to decrease ozone levels the following day (Hu et al., 2013; Neu et al., 1995). Thus, it may be the case that a Fresno Eddy associated with a particularly strong LLJ may decrease ozone the following day if the recirculation of ozone and its precursors does not overcompensate for overnight losses due to vertical mixing down to the surface. We suggest that the Fresno Eddy, when present, will act to recirculate pollutants regardless of the strength of the LLJ, which is the strongest branch of the eddy. That is, a stronger eddy will not recirculate pollutants any more than a weaker one will. Thus, the nighttime dynamical conditions that will lead to the greatest ozone levels the following day may consist of a Fresno Eddy just coherent enough to effectively recirculate pollutants, but without an associated LLJ so strong as to deplete the RL ozone by vertical mixing. There is currently no established link in the literature between the Fresno Eddy and LLJ strength. FThus, future research should investigate which of these two nocturnal mechanisms (recirculation from the eddy or RL depletion by vertical mixing) will dominate the ozone budget on any given night, taking into consideration the different possible structures and timing of the Fresno Eddy as well as the synoptic conditions that engender them.Although the LLJ and Fresno Eddy are not exactly the same thing, rathersynonymous, the LLJ is part of the northwesterly flow that is an important precursor to the Fresno Eddy. When the eddy is presentwhen the Fresno Eddy is present, the northwesterly LLJ is essentially typically the strongest branch of the eddy. This leads to an important question about the role of the Fresno Eddy in modulating the next-day ozone. Beaver and Palazoglu (2009) found that ozone pollution in the central SJV is particularly high on days where the preceding nocturnal Fresno Eddy is strong, concluding that recirculation from the Fresno Eddy contributes to a buildup of ozone. However, mixing induced by

LLJs has been shown to decrease ozone levels the following day in other parts of the world (Hu et al., 2013; Neu et

In addition to the synoptic patterns discussed above, slightly lower surface temperatures across the entire region are observed during stronger low-level jetsLLJs are observed (Fig. 9). This could either be a consequence of the synoptic flow (southerly geostrophic flow will generally result in bring warm air advection warmer temperatures) or itself be an underlying precursor to the LLJ. In the latter, (a ~2 K colder greater temperature difference between the delta region and the SSJV for strong LLJs (seen in Fig. 9) will lead to more up-valley thermal forcing resulting in stronger winds that decouple from the surface at night). The higher temperatures associated with the weak nocturnal jets may make for a twofold mechanism for high ozone: the high temperatures either causing increased photochemical production or resulting from increased meteorological stagnation, and a lack of mixing overnight induced by the low level jetLLJ causing less depletion of the RL ozone. Warmer nights may also result in less dry deposition of $O_x$ through stomatal pores. It is worth noting that this relationship with temperature is only apparent with the NARR climatology, as ambient overnight low temperature at Visalia yields only a very weak relationship with the jet strength ($r^2 = 0.035$, $p < 10^{-5}$).

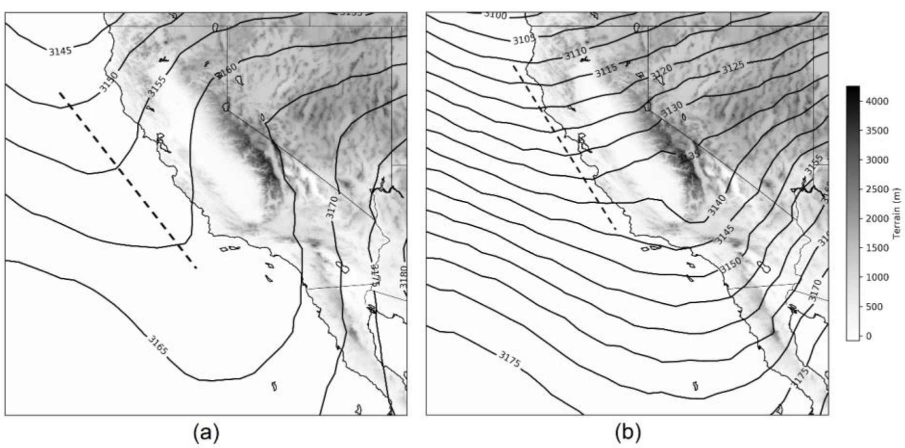


**Figure 8.** North American Regional Reanalysis 700 mb Geopotential Height (m) for low-level jet speeds exceeding 12 m $s^{-1}$ (left) and below less than 7 m $s^{-1}$ (righta) and greater than 12 m $s^{-1}$ (b).

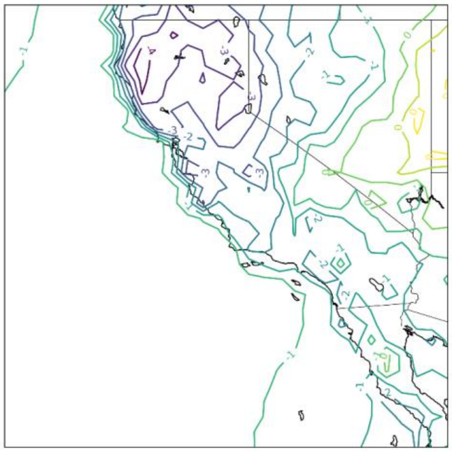

**Figure 9.** North American Regional Reanalysis 2 m air temperature (°C) difference between cases where low-level jet speeds exceeding 12 m $s^{-1}$ and cases where it is below 7 m $s^{-1}$ at 01 PST. Positive values indicate warmer surface temperatures for strong jets.

### 3.4. Vertical Turbulent Mixing and and Next-Day Ozonethe LLJ

As seen in Figure 4, an average low-level jetLLJ height between of 200-400 m is seen, which corresponds approximately with the average observed stable NBL depth. Likely due to the shear induced by the LLJ, turbulence is seen to be vigorous at night with TKE values about 50 % of what is observed during the daytimedaytime values during convective conditions. HoweverFurther, TKE is seen to increaseincreases toward the surface, contrary to what would be expected in the presence of an elevated jet.a condition that Banta et al. (2006) refers to this as a “traditional” stable TKE profileboundary layer.

The thermals generated by solar heating after sunrise initiate a fumigation process whereby as the daytime boundary layer develops, the ozone that was in the RL will beis mixed downward. The change in surface ozone concentration (d[$O_3$]/dt) due to fumigation peaks at around 08:00 am PST and continues until about 10:00 am PST. The relationship of between our estimated eddy diffusivities with and ozone during the fumigation period is strongest at 10:00 am PST, after the bulk of the vertical mixing due to the boundary layer growth growing and entraining into the RLfumigation has occurred ($r^2$=0.291, p=0.070). The relationshipsA negative correlation between eddy diffusivities and the maximum 1-hour ozone, 24 hour24-hour average ozone, and MDA8 were also in the predicted directionfound, with the strongest relationship found for the MDA8 ($r^2$=0.463, p=0.015), as shown in Figure 10. This supports our hypothesis that stronger NBL turbulence is associated with lower ozone the following day.

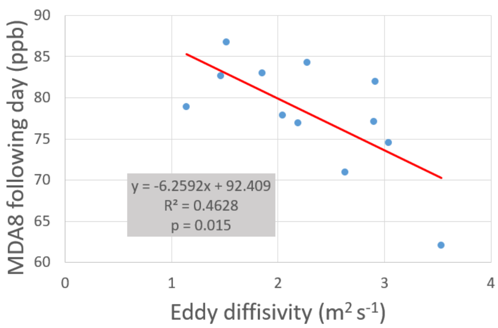


**Figure 10.** Correlation between overnight eddy diffusivity and maximum daily ~~8 hour~~8-hour average ozone (MDA8) the following day. All values are averages of 11 CARB surface network stations that are within the flight region.

Because this analysis consisted of only 12 flights, we ~~decided to explore~~explored a larger data set that might support the hypothesis that a stronger LLJ reduces ozone the following day. 7 years of ~~low-level jet~~LLJ speeds obtained from the Visalia sounder from 2010 ~~–~~- 2016 is combined with the CARB surface network ozone monitoring site at Visalia N Church St (36.3325° N, 119.2908° W, 30 m elevation) for analysis. Only calendar days 152 through 273 (June ~~–~~- September) ~~is~~ are included. The ~~low-level jet~~LLJ, hypothesized to be the main contribution to the variability in overnight mixing between the RL and NBL, is compared with MDA8 observed the following day, shown in Figure 11. It can be seen that a stronger nocturnal ~~low-level jet~~LLJ is correlated, albeit weakly, with lower ozone the following day ($r^2$=0.181, $p < 10^{-5}$). A single outlier was removed where the LLJ exceeded 25 m $s^{-1}$. ~~This is in line with~~Thise overall relationship ~~found~~ supports our hypothesis that the ~~low-level jet~~LLJ ~~will~~ leads to stronger mixing, which in turn leads to more ~~residual layer~~RL ozone depletion.

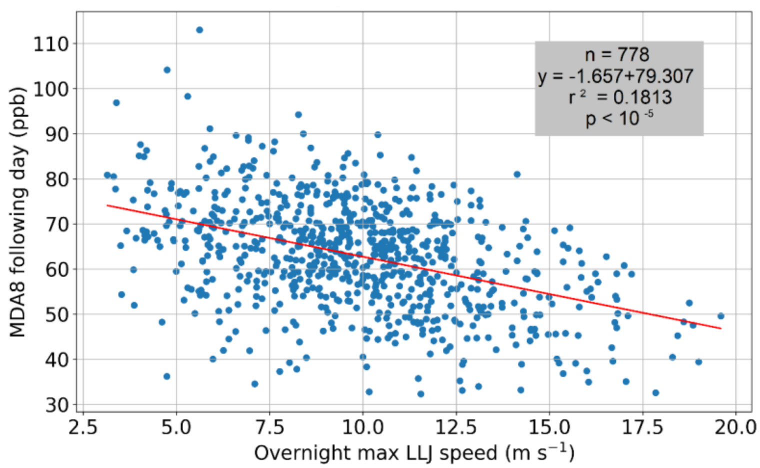

**Figure 11.** Correlation between nocturnal low level jet speed and the following day's MDA8 in Visalia, CA, for Calendar days 152-273 from 2010-2016.

The physical processes of RL $O_x$ depletion once it mixes down into the NBL is a further question. The main destruction processes of $O_x$ in the NBL are chemical loss and dry deposition. One possibility is that surface sources of $NO_2$ contribute to the excess nocturnal chemical depletion of $O_x$ in the NBL. However, the chemical loss of $O_x$ is not thought to vary significantly between the RL and NBL because the increase of $NO_2$ in the NBL is compensated by the decrease of $O_3$ (see Fig. 4), although this assumes that there are no other chemical differences that alter the reaction fate of nitrate (i.e. $\alpha$ in Eq. 1). ~~In addition to a stronger LLJ mixing down more ozone, a further~~Another possibility is that the deposition velocity of ozone may be enhanced by a reduction of aerodynamic resistance under a stronger LLJ. The dry deposition of any gas may be characterized by a series of resistances (Wesely, 1989):

$$v_d = \frac{1}{r_a + r_b + r_c} \quad \textbf{(6)}$$

~~Where~~ where $r_a$ is the aerodynamic resistance, $r_b$ is the viscous sub-layer resistance, and $r_c$ is the surface (or canopy) resistance. Figure 4 in Padro (1996) suggests that for ozone at night, $r_a \sim r_c \sim 250$ s m$^{-1}$. $r_b$ is likely non-zero (Massman et al., 1994) but ~~will be~~is ~~neglected here because it is unknown~~typically several times smaller than the other resistances (Georgiadis et al., 1995; Pilegaard et al., 1998), so we assume that $r_a = r_b + r_c = 250$ s m$^{-1}$ to yield our ~~assumed~~estimated deposition velocity of 0.2 cm s$^{-1}$. Combining ~~the~~ an estimate of aerodynamic resistance due to mass transfer ($r_a$ = U~~u~~ where $u_*^2$ is the momentum flux) and parameterizing the momentum flux as a function of 10-meter wind speed, $U_{10}$~~,~~, and ~~the bulk transfer~~a drag coefficient ~~for heat~~ $C_{D\not{H}}$ ($u_*^2 = C_{D\not{H}} U_{10}^2$) we roughly approximate $r_a$ as:

$$r_a \sim \frac{1}{C_{D\not{H}}\, U_{10}} \quad \textbf{(7)}$$

In the 7 years of LLJ data at Visalia, ~~The~~ the 10-meter wind speed is correlated with the jet strength ($r^2 = 0.309$, $p < 10^{-5}$). On average, $U_{10}$ was 1 m s$^{-1}$ for 5 m s$^{-1}$ jets, and 2.5 m s$^{-1}$ for 15 m s$^{-1}$ jets. ~~An~~ Assuming an average $U_{10}$ of 1.75 m s$^{-1}$ and $r_a$ =of 250 s m$^{-1}$, this would imply that $C_{D\not{H}} \sim 2.3 \times 10^{-3}$. A sensitivity analysis indicates that ~~this~~ the difference $U_{10}$ between strong and weak jets would result in an approximate 40~~-~~% change in $v_d$. We thus conclude that the LLJ likely plays a significant role in modulating the dry deposition rate, where a strong jet decreases $r_a$ and thus increases $v_d$, further contributing to a loss of ozone overnight. It is important to note that what we have presented is only a rough estimate of the variability of $r_a$, and thus future studies ~~will need to~~should measure these parameters with more precision in order to better estimate the degree to which the LLJ can modulate dry deposition in the SJV. The average error of $K_z$ due to the uncertainty in $v_d$ is calculated to be ~0.50 m$^2$ s$^{-1}$, ~~which~~and is included in ~~the~~our ~~original~~ error

**3.5. Eddy Diffusivity and other estimates of Turbulence**

Here we attempt to build confidence in the eddy diffusivity estimates by analyzing additional metrics of turbulence. We find that nocturnally and spatially averaged TKE in the NBL ranges from 0.35 and 1.02 m$^2$ s$^{-2}$, which is very comparable to values obtained in other NBL studies (Banta et al., 2006; Lenschow et al., 1988). Table 1 shows the TKE, LLJ speed, as well as the ratio of the streamwise variance to LLJ speed ($\sigma_u/U_x$) for each night. The average value of $\sigma_u/U_x$ in this study is 0.11, approximately double what was reported in Banta et al. (2006)~~, although we did not attempt to remove buoyancy waves from our data~~. There is no detectable relationship between our calculated NBL

TKE and eddy diffusivities, LLJ speed, or MDA8 the following day, which implies that the eddy diffusivities calculated from the scalar budget analysis may be a better measure of nocturnal mixing strength than TKE.

Our budget method of estimating turbulent dispersion differs from some other attempts that have been made for stably stratified environments. Clayson and Kantha (2008) applied a technique that hads been previously used in oceans to the free troposphere, where turbulence is sparse and intermittent, much like in the NBL. Their method involves using high-resolution soundings to estimate a length scale of overturning eddies, known as the Thorpe scale (Thorpe, 2005), which is then used to obtain estimates of turbulent dissipation rate, and subsequently eddy diffusivity. This is done by relating the Thorpe scale to the Ozmidov scale, where if the Brunt-Vaisala frequency ($N_{BV}$) is known, TKE dissipation rate ($\varepsilon$) can be estimated. Eddy diffusivity can then be estimated as a product of the TKE dissipation and $N^{-2}$:

$$K_z = \gamma \varepsilon N_{BV}^{-2} \quad \textbf{(8)}$$

Where γ is the mixing efficiency, which can vary between 0.2 and 1 (Fukao et al., 1994). From the nocturnal power spectra (Fig. 1) we use a Kolmogorov fit to estimate ε, which is determined to be approximately 4.8 x $10^{-6}$ $m^2$ $s^{-3}$ for the overall altitude range of our nighttime flights (surface to ~3000 m), but a median of 3.0 x $10^{-4}$ $m^2$ $s^{-3}$ is observed in the NBL. Using the average NBL Brunt–-Väisälä frequency of 0.023 Hz, and a mixing efficiency of 0.6, and the median NBL ε results in an eddy diffusivity of 0.34 $m^2$ $s^{-1}$, which is about three times smaller than the lower end of our range (1.1 –- 3.5 $m^2$ $s^{-1}$). A recent study of vertical mixing based on scalar budgeting of Radon-222 in the stable boundaryNBL by Kondo et al. (2014) estimated 7-day average overnight diffusivities of 0.05 – 0.13 $m^2$ $s^{-1}$, which is are an order of magnitude below our estimates inferred from the $O_x$ budget. However, Wilson (2004) conducted a meta-analysis of radar-based estimates of eddy diffusivity in the free troposphere, which is also a generally stable environment, and found a general range of from 0.3 –- 3 $m^2$ $s^{-1}$. Pisso and Legras (2008) estimated diffusivities of about 0.5 in the lower stratosphere during Rossby wave-induced intrusions of mid-latitude air into the subtropical region. A modeling study by Hegglin et al. (2005) reports diffusivities of 0.45 –- 1.1 $m^2$ $s^{-1}$ in the lower stratosphere with an average Brunt–-Väisälä frequency of 0.021 Hz, indicating a similar turbulent environment to ours. Finally, Lenschow et al. (1988) analyzed flight data in the NBL over rolling terrain in Oklahoma, and found eddy diffusivities for heat ($K_h$) of ~0.25 $m^2$ $s^{-1}$ for the upper half of the NBL, and ~1 $m^2$ $s^{-1}$ for the lower half. To our knowledge, the latter is the most comparable observational finding within the NBL to our range of diffusivities. Nevertheless, the variability in the reported values leads to the inevitable conclusion that vertical diffusivity in very stable environments is poorly understood, and further research is necessary to illuminate its phenomenology. More specifically, while it is possible that the diffusivity measurements in this study are slightly largebiased high (e.g., due to overestimates of the chemical loss parameter α), it is also possible that the LLJ and other mesoscale wind features of the complex terrain account for stronger nocturnal mixing in the SSJV compared to that of other stable environments.

Lastly, we estimate the Bulk Richardson number (BRN) on each late nightlate-night flight within the NBL, using 100 meter bins to estimate wind shear. A range of Richardson numbers between 0.23 and 1.34 is obtained, and the estimates are seen to have a slight negative relationship with eddy diffusivities, as expected (illustrated in Fig. 12). The weak correlation is probably the result of the limited data set coupled with the challenging nature of the measurements of bothWhile the relationship is not strong, it is important to remember that both parameters are noisy estimatesBoth the eddy diffusivity and BRN measurements are challenging measurements, thus we did not anticipate

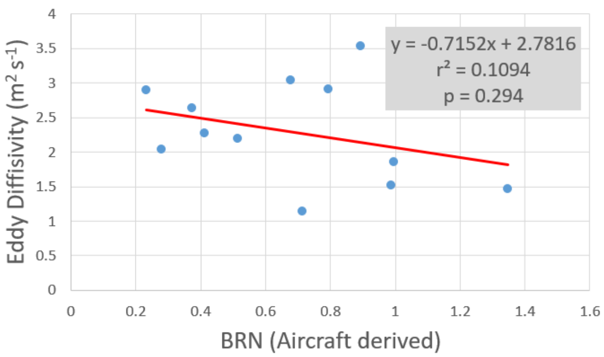


**Figure 12.** Eddy diffusivities and Bulk Richardson Numbers (BRN) derived from aircraft observations.

### 3.6. Nocturnal Elevated Mixed Layers

During the late nightlate-night flights in stable environments, the flight crew reported many patches of turbulence. While most of these subjective reports were during low approaches and thus likely attributable to wind shear between the LLJ and the surface, they noted that some patches corresponded with what appeared to be elevated mixed layers, i.e. layers of air where virtual potential temperature was observed to decrease with height. These layers may be of special interest to our analysis of overnight mixing, since absolutely unstable layers of air promotegenerate turbulence and thus vertical mixing. Understanding these anomalies may guide future research toward a deeper phenomenological understanding of overnight mixing and turbulence in the SSJV.

The locations of the layers detectedgreater than 50 m thickness, along with their elevation and magnitudelapse rate, areis shown in Figure 13. One feature of note is that the layers appear to be more prominent over urban areas, such as Fresno, Visalia, and Bakersfield. This may lead one to suspect that some of these layers are driven by an urban heating effect, however, this seems unlikely as the unstable layers appear to bemostly above the NBL wherein there is communication with the surface is relatively rapid. We may have simply detectedTRather, the appearance of these layers more oftenclustering around in urban areas because moremay be the result of a flight time is spent in those locations. Hence, the apparent pattern of more unstable layers in urban areas could sampling bias and thus may not be insignificant. It is perhaps more likely that this is an artifact of more flight time in those areas. Another feature worth noting is that more unstable layers are observed closer to the Tehachapi pass. One possible explanation for this is that the katabatic flow down the mountain slopes detrain along the way and are carried over the valley by local advection before mixing with surrounding air. Given that these layers are found from near the bottom of the residual layerRL all the way up to 2.5 km, it is possible that they contribute to the overnight mixing of $O_x$ from the RL to the NBL and generally maintainby maintaining a fairly well-mixed lower atmosphere over the valley. Further research, both observational and modeling-based, is needed to explore this possibility.

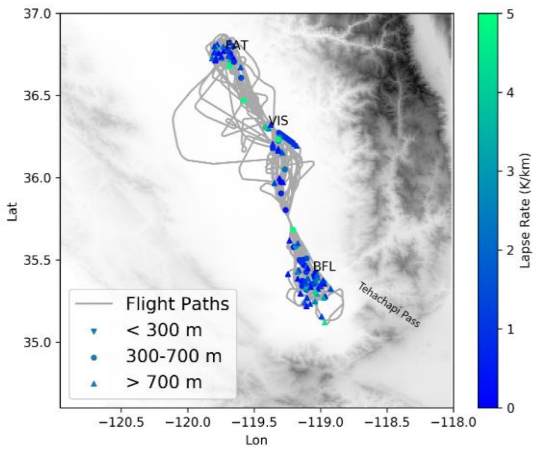


**Figure 13.** Detected nocturnal elevated mixed layers with at least 50 meters thickness, with elevations shown.

The unstable layers are not ~~seen~~ found to have more TKE than the rest of the atmosphere. While~~, and~~ this may reflect the limitations of the method used to estimate turbulence from this low-cost wind measurement system~~.~~ ~~However, this~~, it is consistent with the study by Cho et al. (2003) ~~which~~ that found no relationship between turbulence and static stability in the free troposphere. Interestingly, their analysis of aircraft data collected over the Pacific Ocean up to 8 km altitude found unstable layers in 6 to 25% (depending on the layer thickness definition of 100 m to 10 m) of their profiles above the boundary layer (Cho et al., 2003). ~~Since~~ Because the aircraft ~~is~~ moves more than ten times ~~ing~~ ~~horizontally a lot~~ faster horizontally than ~~it is~~ vertically during profiling, ~~one may be concerned that our observations of elevated mixed layers~~the observations of the elevated mixed layers may be ~~are~~ an artifact of localized temperature gradients that are more prominent in the horizontal dimension. To ~~check this~~confirm that this is not the case, we ~~plotted~~ examined the wind quivers in the unstable layers along with the direction of the colder air. The cooler air was not systematically detected in any one direction, which supports the hypothesis that ~~these~~ they are true vertical temperature gradients.

To analyze the stability, wind shear, and turbulence from a climatological standpoint, a July-August 2016 composite of the 915 MHz Visalia sounder data is presented in Figure 14. Even in the ~~climatological~~ two month averages, some nocturnal unstable layers are detectable between 500 and 1500 m, which further supports the existence of ~~these~~persistent elevated mixed layers ~~which~~that may contribute to overnight mixing of pollutants in the lower troposphere over the valley.

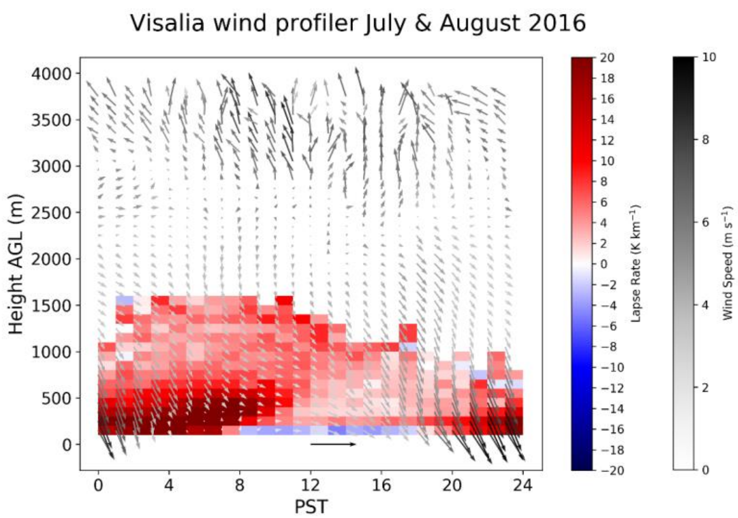


**Figure 14.** Stability and wind quivers for the Visalia 915 MHz sounder, 1 Jul 2016 – 31 Aug 2016.

**4. Conclusions**

We have demonstrated a method for performing a nocturnal $O_x$ scalar budget analysis using aircraft data, and applying estimate the effects of turbulent mixingce in the stable boundary layerNBL, which can be related used to help the SSJV. Inherently, eddy diffusivity estimates for any given night will have a large uncertainty due to the indirect nature of the measurement and the limited flight durations. However, the overall between-flight consistency and the correlations of the eddy diffusivities with both the Richardson number and surface ozone suggest that this method is informative. We obtain eddy diffusivity values between 1.1 and 3.5 $m^2 s^{-1}$, which are larger but approximately within the same order of magnitude of values that have been obtained from other studies in the free troposphere, lower stratosphere, and nocturnal boundary layerNBL. A One limitation of our study is the lack of sample size, with only morning flights. HoweverNevertheless, we believe this study demonstrates the importance of focused flight strategies measure the individual terms of the scalar budget equation, and highlights the significant influence that synoptic and mesoscale features atmeteorological conditions can have on the over-night within the context offor high ozone day's peak concentrationsf focused flight strategy where terms in the scalar budget equation are measured.

The larger set of RASS and ARB surface network data from Visalia, CA establishes shows a correlation between low level jetLLJ speed and the maximum 1-hour ozoneMDA8 the following afternoon for summertime months, further suggesting the a link between nocturnal mixing and the following daysnext-dayensuing day's ozone levels. In particular, we note that 5 out of 6 days when the Visalia, CA ozone MDA8 exceeded 90 ppb wereas preceded by a weak LLJ (< 7 m $s^{-1}$). Similarly, the correlations between the aircraft-estimated eddy diffusivities and MDA8 the following day also suggest that vertical mixing in the NBL plays an important role in determining controlling ozone concentrations. In particular, we note that 11 of 12 days where the Visalia, CA ozone concentration exceeded 100

~~ppb was preceded by a low-level jet speed < 9 m/s.~~ While we cannot unequivocally ~~determine~~ infer a causal reduced ozone ~~pollution~~levels, we propose a feasible process link between ~~that~~ a stronger LLJ leadings~~s~~ to greater helps deplete the ozone reservoir in the RL by bringing it into the ~~stable boundary layer~~NBL overnight. There it is at~~to~~ the surface, wherein~~and~~ th~~eat~~ ~~dry~~ deposition ~~rate~~ velocity itself may ~~itself~~ be ~~partially~~ modulated by the strength of the LLJ.~~. This may occur through~~ Because the near-~~-~~surface winds are accelerated by an overlying jet, a stronger LLJ ~~-~~reduces~~d~~ the aerodynamic resistance resulting in more efficient transport to surfaces and stomata where ozone can ~~deposit~~be taken up. Subsequently, when thermals begin to form after sunrise the following morning, there is less ozone to fumigate downward. We propose that the LLJ is a branch of the ~~Fresno eddy~~Fresno Eddy, and the vertical mixing it induces may offset some of the next-day ozone enhancement that results from the eddy recirculating pollutants. ~~While the correlation between nocturnal mixing and ozone the following day is not always strong, it is an important link that may have consequential implications for modeling studies and policy making. For example, o~~Our findings highlight the crucial need of models to capture the LLJ and ~~Fresno eddy~~Fresno Eddy with sufficient resolution, and p~~. P~~olicy makers may consider putting more stringent emission limitations on days where synoptic and mesoscale patterns appear to favor ~~a lack of overnight~~weak nocturnal mixing.

~~Of course, the~~The relative importance of these dynamical effects depends on the exact magnitude of the chemical overnight. We ~~have also~~ suggest~~ed~~ that the ultimate fate of the $NO_3$ radical plays a very~~n~~ important role in the ~~nocturnal~~ loss term, and thus likely impacts the following day's maximum ozone concentration. The loss of the nitrate radical at night can occur from $N_2O_5$ hydrolysis, reaction with VOCs, or a very rapid reaction with small NO concentrations, and there is considerable uncertainty regarding which reactions dominate without concurrent ~~direct~~ measurements of $N_2O_5$,~~.~~ and VOCs. Thus, the lifetime of $NO_3$ can range from seconds to several minutes, which affects the chemical loss term in the scalar budget equation. It is therefore~~us~~ crucial to measure the lifetime of $NO_3$ in future studies that analyze the NBL ozone or $O_x$ budget. We also suggest more direct ~~measurements~~ estimates of aerodynamic resistance ozone deposition at the surface by ground-based eddy covariance flux measurements in conjunction with future airborne studies.

**Data Availability**

All of the aircraft data used in this analysis can be found at https://www.esrl.noaa.gov/csd/groups/csd3/measurements/cabots/

**Author Contribution**

IF designed the research study and DC, JS, and SC carried it out. DC and SC designed the scalar budget code and DC carried out the analysis. Other analyses were performed by DC, IF, JS, NF, and JT. DC prepared and submitted the manuscript.

**Competing Interests**

The authors declare that they have no conflicts of interest.

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