Reviewer #1 Response

Although I do think this paper merits publication in ACP, I would like to see substantial revisions before publication. However, these revisions for the most part have to do with improving structure and clarity of the manuscript. As is, the paper pretty severely lacks cohesion. I found it challenging to understand the goals, results, and implications of most sections. The abstract, introduction, and conclusion focus on the relationship between nocturnal turbulence and next day ozone, but there is quite a lot of supplemental analysis investigating the assumptions going into the Ox budget calculation, the uncertainties with respect to the inferred eddy diffusivity, etc. These parts could be much better integrated with the rest of the text. A clear articulation of the goals of each section at the beginning of the section, and a more detailed roadmap of the investigation in the introduction could be helpful. I like that the results and discussion are combined, but in many sections there is no discussion of the implications of the results, and they are not discussed in the conclusions. There are several figures that are barely discussed and I urge the authors to reconsider whether they should be included in the paper. The paper would strongly benefit from a streamlining of the analysis

Response: We would like to thank reviewer #1 for providing insightful comments on our submission to ACP. As stated in our response to reviewer #2, we have attempted to better partition the methodology and results. We have also made some revisions such that the goals of the study are articulated towards the beginning.

Most of the figures have been adjusted to improve quality and legibility. In particular, we changed the terrain to be greyscale, higher resolution, and less distracting. However, we believe the terrain in each figure is important because flow characteristics in California are highly influenced by it. Larger text for fonts has been used, as requested.

We presented a new analysis of the MDA8 vs. LLJ correlation that removes the outlier point where LLJ > 25 m s^{-1}.

Line-by-line comments:

Lines 56-57: Will the authors please include the point about dry deposition in a separate sentence? Also, the way the part about deposition is phrased too much does not really suggest that there is much uncertainty to this estimate, but there it is quite uncertain (see comments below)

Response: changed to “Here we investigate the hypothesis that on nights with a strong low-level jet (LLJ) ozone in the residual layer is more effectively mixed down into the stable boundary layer. There 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”

Line 58: Would “more” be better than “stronger” here?
Line 63: “infer” instead of “measure”
Line 73: I find “occasion” as a verb to be non-intuitive

Lines 96-99: Will the authors refer to the stable layer as the NBL for consistency? This part is quite dense, especially for readers not fluent in boundary layer meteorology
Lines 101-104: I'm not seeing why the last two sentences are needed here. I would urge the authors to be as concise as possible here, again for readers not as fluent in BL meteorology
Line 110: Replace the "is" in "is important" to "is likely important". Also, both is plural, so "is" should be "are"

Response: Changed "occasion" to "are associated with" in line 73. All other semantic changes have been made. The two sentences from lines 101-104 have been removed and the stable layer is now referred to as the NBL.

Lines 112- 128: I struggled with this paragraph, which feels out of place. It's not clear why the authors start to talk about the Fresno Eddy. One option would be to move this paragraph to Section 3.3. Another option would be to more clearly direct the reader as to why they are introducing it (i.e. that it challenges their analysis). Also, will the authors please briefly introduce ozone production potential?

Response: Added "The complex nocturnal wind patterns in the SSJV contribute to the challenges of understanding and forecasting ozone pollution in our study region" to the beginning of the paragraph. Also changed "ozone pollution potential" to simply "ozone pollution".

Lines 129-140: I find this paragraph a bit awkward, especially the first sentence with the term "acknowledge". It seems like this sentence should be followed by a discussion of assumptions made, but this does not seem to be the case. The authors then proceed to mostly talk about daytime conditions, then say nitrate chemistry and dry deposition cannot be ignored. Why even talk about daytime? I would suggest saying that the focus of this work is nighttime and previous work has focused on daytime. The discussion of daytime doesn't feel meaningful, and it's confusing for the reader. Also, I'm confused about the point of mentioning nitrate chemistry and dry deposition here in this way. Do the authors examine these processes in detail later on? Perhaps framing it like that would help.

Response: Here we are discussing the context of the scalar budget equation in general, although I do understand why discussing daytime studies in detail might be confusing. The discussion about advection is relevant for both daytime and nighttime scalar budgets, but we changed the sentence regarding daytime photochemical production to "Studies performing daytime scalar budgets of ozone (Conley et al., 2011; Lehning et al., 1998; Lenschow et al., 1981; Trousdell et al., 2016) have shown that chemical production is important, and similarly, we expect the chemical loss of ozone to be important at night."

Line 152: Does "this ozone difference" refer to the day-to-day difference in ozone concentration? Please specify

Response: Yes, changed to "the aforementioned ozone difference".

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.

Line 161: Does "in this area" refer to Taiwan, or SSJV?

Response: Changed to "ozone problems in southern Taiwan"

Lines 194-196: Do the authors think that their "somewhat arbitrary" cutoff has a substantial Influence on their results?

Response: Changing the cutoff will result in different TKE values, but the night to night variability should not be affected by this. The TKE analysis is mostly supplemental to the main thesis and would not change our conclusions. This is an issue that arises in any stable boundary layer study.

Lines 199-204: Again, do the authors think that this assumption has a substantial influence on results?

Response: The similarity relationships are employed as a best approximation and we acknowledge that the uncertainty in our TKE estimates are high. Again, we do not use the TKE estimates for anything critical to our conclusions.

Lines 241-242: Seems like this sentence is unnecessary

Response: Removed.

Line 247: Please cut "tracked by", it's confusing. The ultimate fate of nitrate? Please specify.

Response: Changed to "then computed by the reaction …, and the ultimate fate of nitrate will affect…"

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 K_z."
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."

Line 290: Do the authors mean that NO2 and O3 are by far the dominant species of Ox? Please specify

Response: Changed to "as these are by far the dominant species of O_x."

Lines 319-386: This is a lot of information. I found this section very confusing and long-winded. Will the authors please break this paragraph up? It would be helpful if the authors stated the goal of this analysis upfront and more clearly stated what the assumptions are, the bases for making them, and how they feed into calculating the net reaction of R1-R6 as a constant multiple of R2.

Response: To clarify the aim of this paragraph, we added "Thus, determining the dominant loss of nitrate is crucial for our analysis" to the end of the previous paragraph (line 318). We started a new paragraph on line 327 ("There is a further question), 347 ("With longer lifetimes"), and 355 ("Given the obvious").

Lines 323-234: But the authors just said that their airborne measurements are supported by the ground-level measurement network? What is the measurement network used? Do the authors not trust that it provides values that should be regionally representative?

Response: Changed to "However, both the ground network and aircraft observations may be biased high to the regional average because of their proximity to…"

Lines 327: This "channel of NO3" meaning R6?

Response: Yes.

Line 330: What are the "VOC reactions in our analysis"? So does this finding mean that the authors ignore R6?

Response: Changed "our analysis" to "Table 2". For these calculations, we are only considering the VOC channel of nitrate loss (R5) in order to answer the question of whether or not R5 is important.

Lines 319-330: So what's the conclusion here? It looks like the authors are finding a basis for including R6, but also a basis for not including R6.

Response: R6 should be included. We have separated the paragraph that addresses R6 from the paragraph that addresses VOCs to avoid confusion.

Changes made:

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); however, at 30 ppb of O3 and 20 ppt of NO3 the lifetimes of NO to (R1) and (R6) are nearly equivalent (~80s). Our measurements indicate ground-level NO of about 0.6 ppb at midnight (SD = 1 ppb), corroborated by the surface air quality network, increasing in the early morning 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 cm3 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, results in an NO3 lifetime of only 25 seconds. Hence, we conclude that (R6) should not be ignored.

There is then a further question as to whether any VOCs would be able to compete with this channel of NO3 consumption. An investigation into the faster VOC reactions with NO3 per Atkinson et al. (2006) and Gentner et al. (2014a) is presented in Table 2. The estimated lifetime of NO3 due to the VOC reactions in Table 2 is 9.5 seconds, about four times the lifetime of NO3 with respect to the presence of 0.6 ppb of NO (2.5 seconds)

Line 344: “Out of respect for” should be “Based on”
Line 348: Can “channel” be “reaction”? I find “channel” confusing and a bit colloquial
Line 352: Why is temperature shown in Figure 5 if it is not discussed? Also, in the caption of Figure 5 the acronyms of the airports should be spelled out.

Response: Semantic changes have been made. The temperatures of Figure 5 are later referenced in lines 480-482.

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.

Lines 390: Will the authors better explain what the linear regression here is for, and how it is done?

Response: It is our opinion that the linear regression was concisely summarized here.

Line 403: What is the similar environment? Please specify

Response: Specified that this study was done in a flat grass field.

Line 404: I don’t think the authors have specified yet that the SSJV is an agricultural region.

Response: Replaced “these agricultural regions” with “the SSJV”.

Line 405: What's the basis of using these papers, over other ozone deposition papers? Half of these papers are not listed in the references list. There are also additional papers on CODE (California Ozone Deposition Experiment) that the authors may find helpful - for example, Massman 1994, Padro et al. 1994, Grantz et al. 1997. The authors should specify whether they are looking at an average of the CODE sites, or one in particular (there is a vineyard, cotton field, …)

Line 409: Will the authors at least spell out that 2.5 cm/s is likely much higher than the deposition velocity for NO2 should be, and perhaps cite some previous work here?

Response: Corrected the reference list to include Meszaros et al. (2009) and Pederson et al. (1995). We found the Lin et al. (2010) reference to be the most helpful in that it summarized past estimates in Table 3, and it specifically focused on nocturnal dry deposition values.

Changes made:

Results from a European field study in a flat grass field 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 based on these, as well as other (Pederson et al., 1995; Meszaros et al., 2009; Neirynck et al., 2012; Lin et al., 2010), literature values.
We purposefully ignore NO_2 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 $|v_{d\ NO2}|$ < ~ 2.5 cm s^{-1}, an assumption supported by the literature (Pilegaard et al., 1998; Walton et al., 1997).

Line 410: Is the vertical flux divergence used in the last term or the last two terms?

Response: Yes, it refers to the last two terms.

Lines 412-3: Will the authors better explain what the linear regression here is for, and how it is done?

Response: Changed to "A linear regression through the 20 m resolution vertical O_x profile is used to determine dOx/dz (for the last term in equation 1) in the upper…"

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 O_x (magenta) is inferred to exceed the predicted morning O_x (red) due to the vertical mixing term in the scalar budget equation.
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.

Line 429: How is the error propagation calculated? At least refer to Section 3.2
Table 3: What exactly is the error estimate? At least refer to Section 3.2
Line 433: Please cut "Another way to frame … NBL"
Line 434: Please cut "Further". (In my opinion, doing this and the above suggestion would make this part more digestible).

Response: References to Section 3.2 have been made and the requested cuts have been completed.

Changes made:

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 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.)

Line 438: Do the authors mean NO2 is less than O3 by 10-20 ppb here?
Response: Yes. Changed to "O_3 is less than NO_2 by…"

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.

Line 455-6: I would cut the term "conservative". What basis do the authors have for this value judgement? It seems little, especially in terms of the ozone deposition velocity

Response: Done.

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.

Lines 468-72: Are Zhong et al. 2004 describing the Fresno Eddy conditions, or other prevailing conditions? Please specify.

Response: Changed to "Zhong et al. (2004) uses a series of 915 MHz radio acoustic sounding systems to analyze low-level winds in the SSJV. Their Figure 4 shows that at night, …"

Line 473: The authors need to more clearly specify that they are suggesting there are Fresno Eddy conditions during their flights.

Response: Changed to "…observations, suggesting the presence of a Fresno eddy during our flights."

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.

Figure 7: What is shown in the background of the plots? It's hard to see the yellow and light blue colors on top of the grey. I recommend using a different color scheme and/or thicker lines.
Response: The color scheme used was the best one we could find in terms of readability. However, we have increased the resolution so that the arrows stand out better.

Line 494: I would repeat the hypothesis more in full here (i.e., the effects of the nocturnal jet on the next day's ozone levels; "contribute to the variability of ozone" is a bit vague).

Line 494-5: Again, "explored some of the meteorological factors that are absent from the current literature" is vague. Further, why would the authors only explore unexplored factors?

Response: changed to "…variability of maximum daytime ozone concentration, we explored the synoptic patterns that are associated with differing strengths of the LLJ".

Line 498: "in 100m bin space" is too colloquial

Response: Changed to "averaged in 100 m vertical bins,…"

Lines 506-525: This paragraph is confusing. The authors should state up front what they are investigating here.

Response: Moved "To analyze variability … (N=165 nights)" to the first sentence of the following paragraph (line 506) for better flow.

Line 506: Explicitly say which thresholds correspond to strong and weak jets
Line 506: What is "it" here? The trough? Please specify
Line 512: Why the mention of Fresno Eddy here? Are the authors trying to attribute eastward trough to Fresno Eddy not happening? Please clarify
Line 516: What are "those" conditions?

Changes made:

To analyze variability of 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 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. 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 southerly geostrophic wind aloft, which directly opposes the up-valley northwesterly thermally driven flow. We also note the positive correlation found between the LLJ strength and the upwelling index ($r^2 = 0.3018$, $p < 10^{-5}$), which is primarily driven by the North Pacific High, which when strong, acts to push the trough farther eastward as seen in Figure 8. These findings are consistent with the Lin and Jao (1995) modeling study where the Fresno Eddy (and thus 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 present, consistent with Figure 8 (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.

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.

Lines 522-527: I'm not exactly sure why the authors feel the need to compromise here.

Response: Changed to "As a provisional synthesis of these seemingly conflicting findings"

Lines 523-524: Previously the authors had said the Fresno Eddy and the LLJ are not the same thing, but here the authors seem to be referring to them interchangeably.
Lines 527: What is in addition to synoptic forcing?
Lines 532: High temperature could also decrease deposition through stomatal pores
Line 534: -> With the NARR climatology.

Response: We are suggesting that the LLJ is the strongest branch of a Fresno eddy, thus a strong eddy will produce a strong LLJ. We have attempted to clarify this in the text and we have added the discussion of stomatal pores.

Changes made:

Future research may attempt to further establish the degree to which the LLJ and Fresno Eddy are linked, as well as which of these two nocturnal mechanisms will dominate the ozone budget under different synoptic conditions. As a provisional synthesis of these seemingly conflicting findings, we suggest that the Fresno Eddy, when present, will act to recirculate pollutants regardless of the strength of the LLJ (the strongest branch of the eddy). That is, a stronger eddy will not recirculate pollutants any more than a weaker eddy will. Thus, the optimal nighttime dynamics for ozone pollution the following day may consist of a Fresno Eddy just coherent enough to effectively recirculate pollutants, but without its strongest branch too strong as to deplete the RL ozone by vertical mixing.
In addition to the synoptic patters discussed above, slightly lower surface temperatures across the entire region during stronger low-level jets are observed. This could either be a consequence of the synoptic flow (southerly geostrophic flow will generally result in warmer temperatures) or itself be an underlying precursor to the LLJ (a colder delta region 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 jet 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 9: A map showing the difference in 2m air temperature for stronger vs. weaker LLJ may be more effective. Hard to see the contours. Or maybe just cut the elevation map, and color by temperature contours.

Response: Figure 9 has been changed as suggested

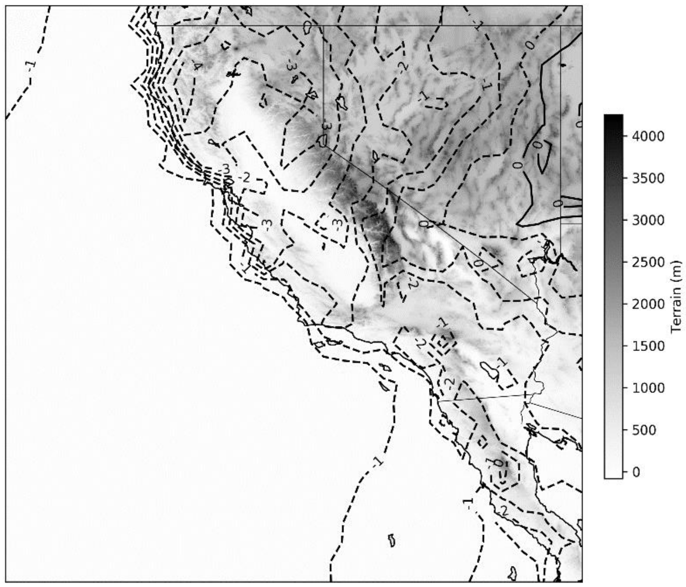


Figure 11 is never referenced, but I think it should be on Line 545. Figure 11 is interesting, but very tangential, and I think the figure and the short discussion of it should be cut.

Response: Figure 11 removed along with the discussion of it.

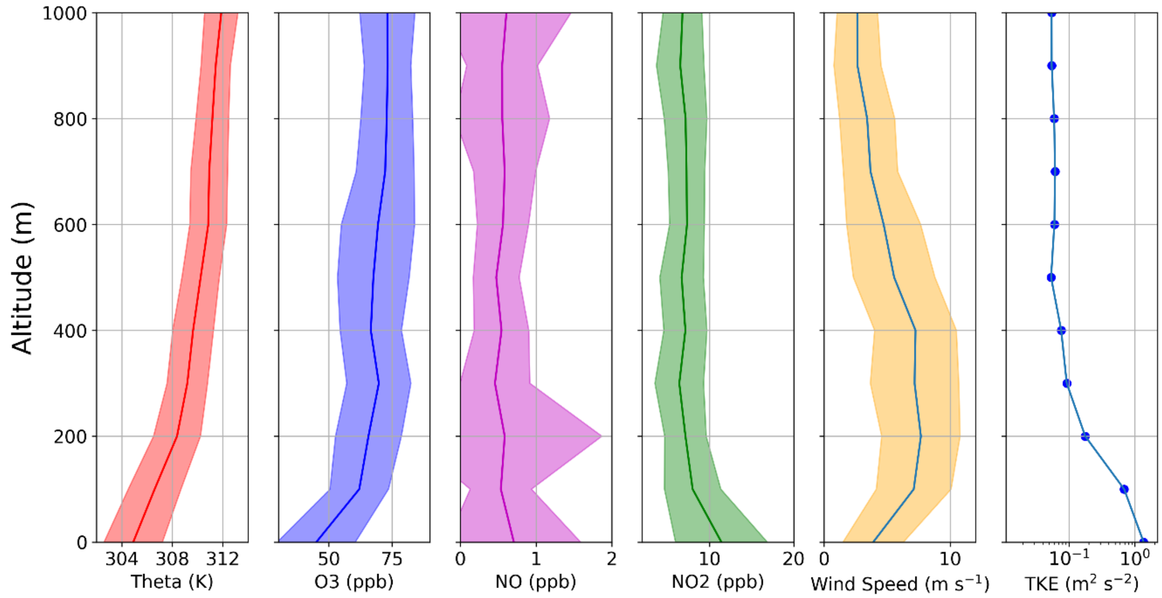
Line 551: “Another look at … ” is not a very helpful way of introducing what the authors are doing here. What are the authors trying to investigate here? Also, what is overnight layering?

Section 3.4 What’s the rationale for including the discussion of Figure 12 in the previous section, as opposed to at the beginning of this one? Seems like it would flow better in Section 3.4.

Response: Section 3.4 now starts here. We removed figure 12 and instead added the TKE profile to figure 4, and reference that here.

Changes made:

As seen in Figure 4, an average low-level jet height between 200-400 m is seen, which corresponds approximately with the average observed stable NBL depth.



Line 562: "several previous studies examining different parts of the world"

Line 567: Will the author please make it more clear that their hypothesis is stated on lines 564-5? Line 566: Specify regional mean ozone from monitoring stations in a certain network
Lines 568: Here are the authors examining ozone at the monitoring stations or measured on the aircraft? Please specify

Changes made:

On the other hand, several previous studies examining different parts of the world have proposed that mixing induced by nocturnal jets may decrease ozone levels the following day (Hu et al., 2013; Neu et al., 1995). Greater coupling between the NBL and RL could reduce the amount stored in the RL reservoir rendering cleaner air the following day. This relationship between the eddy diffusivity values found in our study and regional mean surface ozone from the CARB network is analyzed, and serves as both an additional check on the relative validity of the calculated K_z values as well as a test of this proposed hypothesis.

Line 574: Why would the relationship be strongest for MDA8? How much stronger is the relationship for MDA8 vs. max hourly, 24 hour average? If it's a lot stronger, is MDA8 roughly representing ozone at the same hours each day? Examining this could be insightful. Also, why is this relationship stronger for MDA8 than that observed during the fumigation period?

Response: Jin et al., JGR, 2013 suggests that the MDA8 occurs fairly consistently between 13 and 14 PST. For the 24 hour average ozone correlation with eddy diffusivity, $r^2 = 0.40$. I believe that the relationship is notably weaker for the fumigation periods due to slight variations in timing of the peak boundary layer growth rate.

Line 578: It would help the reader to briefly restate the hypothesis.

Response: Changed to “Because this analysis consisted of only 12 flights, we decided to explore a larger data set that might support the hypothesis that a stronger LLJ reduces ozone the following day.”

Lines 580-3: Wait, why not MDA8 here?

Response: For consistency, we changed the analysis to look at MDA8. The new figure is reported below, and the outlier point is removed.

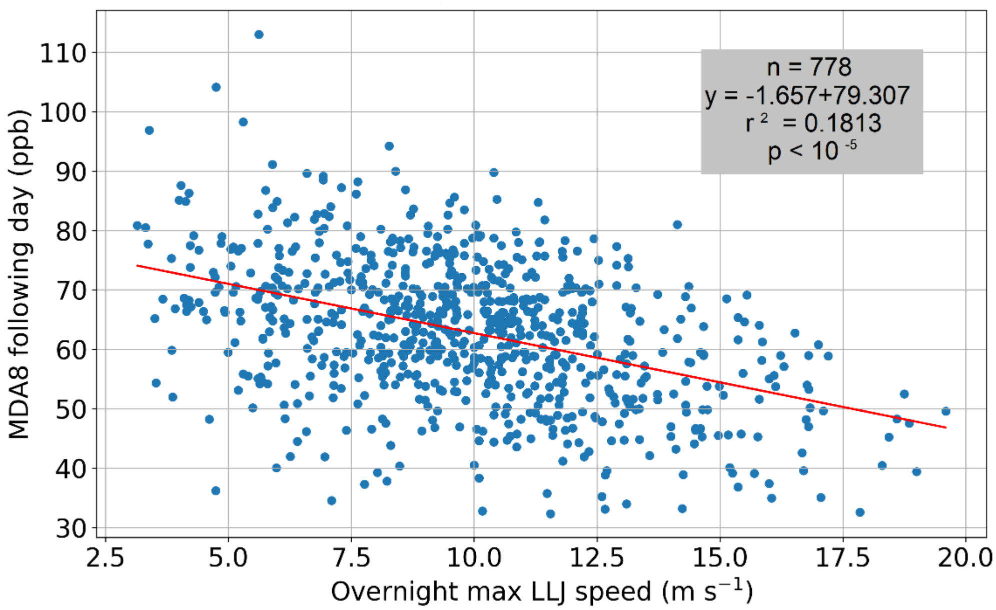
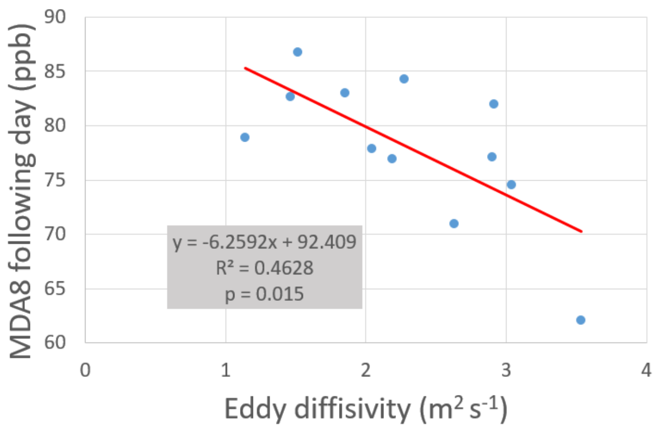


Figure 13 and 14: Please be consistent in terms of ozone on the y vs. x axis.

Response:

Figure 13 (now figure 10) has been adjusted to meet this request.



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_*^2) 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 r_b is unknown and thus not included in this approximation. The average error of K_z due to the uncertainty of V_d is calculated to be ~0.50 $m^2\ s^{-1}$, which is included in the original error propagation analysis.

Changes made:

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

Section 3.5: It would be helpful if the authors introduced the goal of their analysis in this section upfront.

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 $m^2 s^{-2}$, which is very comparable to values obtained in other NBL studies (Banta et al., 2006; Lenschow et al., 1988).

Line 624: “lower end of the range inferred from the Ox budget”. It would be helpful here if the authors re-stated the range of eddy diffusivities that they infer from the Ox budget. Line 626: “our estimates inferred from the Ox budget” Line 631: “similar turbulent environment to ours”? Line 634: Specify here that the Lenschow et al. 1988 eddy diffusivity from the lower half of the NBL is the most comparable. Line 636: “variability in the reported values”

Response: All changes have been made as requested.

Changes made:

Using the average NBL Brunt–Väisälä frequency of 0.023 Hz and a mixing efficiency of 0.6 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 boundary by Kondo et al. (2014) estimated 7-day average overnight diffusivities of 0.05 – 0.13 $m^2 s^{-1}$, which is 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 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.

Lines 640-4: What’s the point of this analysis? Because this relationship is expected, does this build confidence in the authors’ estimate of eddy diffusivity (at least the variability in eddy diffusivity)? If so, it should be explicitly stated.

Response: Yes, the point of this analysis was to build confidence of our eddy diffusivity measurements. We have clarified this in the first sentence of this section: “Here we attempt to build confidence in the eddy diffusivity estimates by analyzing additional metrics of turbulence."

Lines 645-9: To me flow is better if the order of these two sentences is flipped

Response: Disagree with reviewer here because subjective turbulence should be mentioned before delving into it.

Lines 658-9: Briefly, why would the unstable layers have to extend upward beyond the NBL depth?

Response: changed to "as the unstable layers appear to be above the NBL where there is communication with the surface."

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

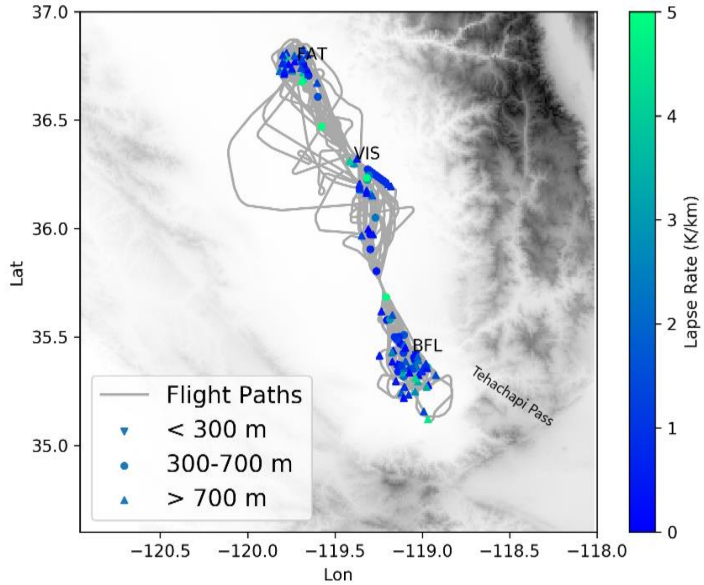
Response: We are stating that although unstable layers are observed more frequently in urban areas compared to rural areas, we may have simply detected them more often there because the aircraft spends more time in urban areas. Hence, the apparent pattern of more unstable layers in urban areas could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

Figure 16: Why is only 50 m shown? The authors say they examine thickness of 50m and 100m. It is challenging to interpret this plot. Another color scheme, and a zoomed in map would be better. Also, the font size should be increased. It would be helpful to indicate the location of the Tehachapi pass on the map.

Response: We have made the requested adjustments to the figure. Only 50 m is shown in order to reduce the number of figures in this submission, and we did not believe the 100 m thickness plot added anything particularly useful.



Lines 668-9: Where is this shown? Also, "seen"-> "observed" Line 669: What finding?
Line 674-5: It might be more clear to state that the figure does not support the hypothesis that the authors outlined on lines 671-2. Also where is this figure? It would be helpful if the authors specified that it is not shown.

Response: We did not include this figure for sake of brevity. We are referring to the finding stated in the previous sentence. "Finding" has been removed for better flow.

Changes made:

However, this is consistent with the study by Cho et al. (2003) which found no relationship between turbulence and static stability in the free troposphere. Since the aircraft is moving horizontally a lot faster than it is vertically, one may be concerned that our observations of elevated mixed layers are an artifact of localized temperature gradients that are more prominent in the horizontal dimension.

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.

Line 687: Cut "slightly"
Line 689: "A limitation of our study"
Line 690: Cut "being conducted". Also what do the authors mean by pairs? Do they mean morning and evening flights? I would specify this. "pairs" is non-intuitive.

Response: These changes have been made.

Changes made:

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.

Line 690: What demonstrates? Specify what "it" is.

Response: Changed to "the study demonstrates".

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.

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.

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 NO_3 plays an important role in the nocturnal O_x 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 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 direct measurements of NO_3. 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 thus 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 of aerodynamic resistance and ozone deposition at the surface by eddy covariance in conjunction with future airborne studies.

Reviewer #2 Response

Reviewer comment: The authors hypothesize that a strong low-level nighttime jet more effectively mixes down ozone into the stable nighttime boundary layer where it deposits, resulting in lower ozone the next day. On nights with a weaker jet, the residual layer remains decoupled and results in higher ozone the next day. This paper introduces methods for developing nocturnal scalar budgets from aircraft observations. This hypothesis and support from aircraft contributions is a useful contribution to our understanding of the effect of weather patterns on ozone. One general comment is that the authors could better motivate their statement that air quality models need to better forecast this feature with a brief overview of the current ability of models to simulate the nocturnal low-level jet. Generally the paper would also benefit from clearer presentation of the methodology and results including checking for consistent use of terms and figure referencing. The authors seem to discuss methodology and results intermixed in multiple locations, and a more coherent progression of methodology and results would both shorten and clarify the author's hypothesis and findings. This paper should be published in ACP after addressing these revisions and the comments below.

Response: We would like to thank the reviewer for the useful feedback regarding our submission to ACP, and their recommendation for publication. We have attempted to better partition the methodology and results in the revised manuscript by outlining the plan for the paper in the introduction. We have also included a brief discussion of modeling in the literature review.

Excerpt of changes:

Our goal is to test whether more nocturnal mixing between the residual layer and stable boundary layer, induced by wind-shear turbulence beneath a strong low level jet, will effectively "deplete" ozone in the residual layer, making less available to fumigate the following morning and seed further photochemical production. 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 Ox in the NBL on each night of the field campaign (sections 3.1 and 3.2). Second, we analyse synoptic conditions around the LLJ, and look at a broader dataset of LLJ strength and the following afternoon's ozone concentrations (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 bolster confidence in our findings (sections 3.5 and 3.6).

Specific comments:

1. Page 3, line 125. I don't understand whether the authors are using the Beaver and Palazoglu (2009) paper to support their hypothesis. They initially say that a strong nighttime LLJ reduces ozone the next day, so how does this reconcile with strong nighttime ventilation resulting in high ozone the next day?

Response: Beaver and Palazoglu (2009) point to the recirculation effects of the Fresno eddy, which as we state later, may appear to conflict with our hypothesis rather than support it. Changes made:

Beaver and Palazoglu (2009) found that ozone pollution in the central San Joaquin Valley is particularly high on days where the preceding nocturnal Fresno Eddy is strong, even when strong ventilation is occurring. They also found that the early morning downslope flow through the Tehachapi pass is a strong predictor of ozone pollution in the SSJV. However, mixing induced by nocturnal jets has been shown to decrease ozone levels the following day in other parts of the world (Hu et al., 2013; Neu et al., 1995), so one might suspect that a Fresno eddy that creates a particularly strong LLJ on a given night may decrease ozone the following day if the recirculation of ozone does not compensate for the loss due to vertical mixing.

2. Page 8, line 259. Can you comment on the validity of using 0.2 cm/s for the ozone dry deposition velocity when you argue that deposition will be enhanced when the nighttime LLJ is strong?

Response: We estimate that 0.2 cm s^{-1} is an average value of ozone dry deposition at night in our region, and our stated error is 50%. Thus, the estimated variation due to changes in jet strength (~40%) is within our envelope of uncertainty.

3. Page 14, line 376. Please discuss where the uncertainty on the 1.5 value comes from/ this is unclear from the previous discussion.

Response: The uncertainty of this coefficient is discussed in section 3.2 (lines 450-457). Manuscript now refers readers to this section when the value of alpha is first introduced.

4. Page 15, line 410. Do you mean the last term (not the last two)?

Response: While the last term represents the flux at the top of the NBL, the second to last term represents the surface flux. Thus, the flux divergence in the vertical direction is represented by the last 2 terms in equation 1.

5. Page 15, line 423. Please use consistent language to avoid confusion. Do you mean the surplus of Ox observed on the morning flight is inferred to be driven by the "advection" term?

Response: The surplus of O_x refers to the difference between the projected O_x if there were only chemistry and advection at play, and the actual observed morning O_x. Since chemistry and advection has been modeled in this figure, we assume the difference between projected and observed is due to vertical mixing.

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.

6. Page 16, Table 3. You haven't actually explicitly described yet as far as I can tell the procedure for calculating the storage term.

Response: dO_x/dt is calculated from the aircraft profile difference between the late night and sunrise flights.

Additions made:

The overnight average Ox profile was subtracted from the Sunrise profile and divided by the time difference between the midpoints of each flight to compute the storage term.

7. Page 16, line 435. Please clarify which term refers to the observed time rate of change, since no term appears to be double the sum of chemical loss and deposition.

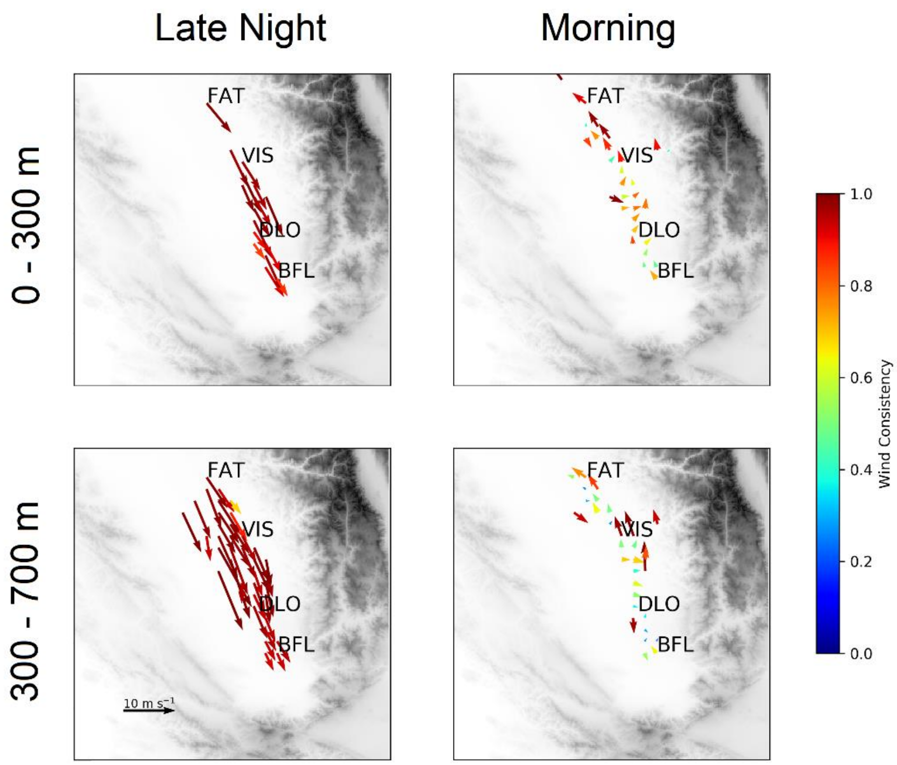
Response: Thank you for catching this – this was misstated. We have changed the text to "Further, both losses of Ox added together are about triple the observed time rate of change, and thus the physical and chemical losses are largely (2/3rds) compensated by vertical mixing."

8. Page 17, line 445. How is the error in the nocturnal PBL height included in the error analysis?

Response: The error in the NBL height is included in the error propagation analysis for the eddy diffusivities.

9. Page 17, line 477. It would be useful to show on the figure the extent of the SSJV and point out the nocturnal low-level jet.

Response: We have extended the image further to the south to show the full SSJV. However, as the figure mainly focuses on observations, we avoid adding cartoon schematics of the mesoscale features, which are not fully known.



10. Page 18, line 501. Give the corresponding PST, since that is what is stated in the abstract.

Response: Done.

11. Page 18, line 504. I assume you are referring to Figures 8-9 here for the daily average synoptic charts? If so, please add this to the text.

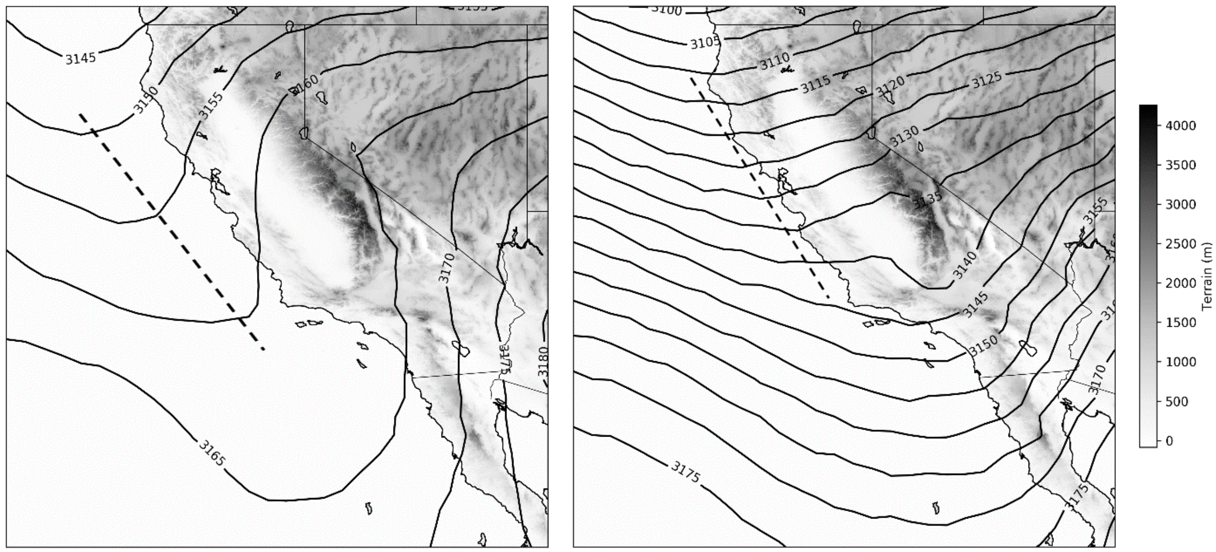
Response: Done.

Changes made:

To analyze variability of 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 strength was less than 7 m s^{-1} (N=147 nights), and greater than 12 m s^{-1} (N=165 nights).

12. Page 19, line 506. Could you again highlight this offset of the figures so that the reader can easily pick out this 100 km difference?

Response: We have drawn a dotted dashed line in the figures to indicate the mean trough axis.



13. Page 19, line 510. You don't need Figure 10, just tell us the correlation coefficient and p-value.

Response: Figure 10 removed.

14. Page 19, line 531. Why would higher temperatures increase photochemical production at night? What about higher temperatures increasing soil NOx? Also, you haven't mentioned PAN at all – wouldn't higher temperatures result in more PAN decomposition to increase Ox?

Response: Here we are arguing that greater daytime photochemical rates (including those due to increased PAN dissociation) during warmer synoptic periods might be an additional factor that increases surface ozone. This would act in addition to less nocturnal mixing (due to the synoptic conditions favoring high temperatures making a weaker LLJ).

15. Figure 11 – please explain the legend in the figure caption.

Response: We have removed this figure from the manuscript in response to another reviewer, as it is not central to our thesis.

16. Page 22, line 555. Is there an explanation for the different behavior of TKE here?

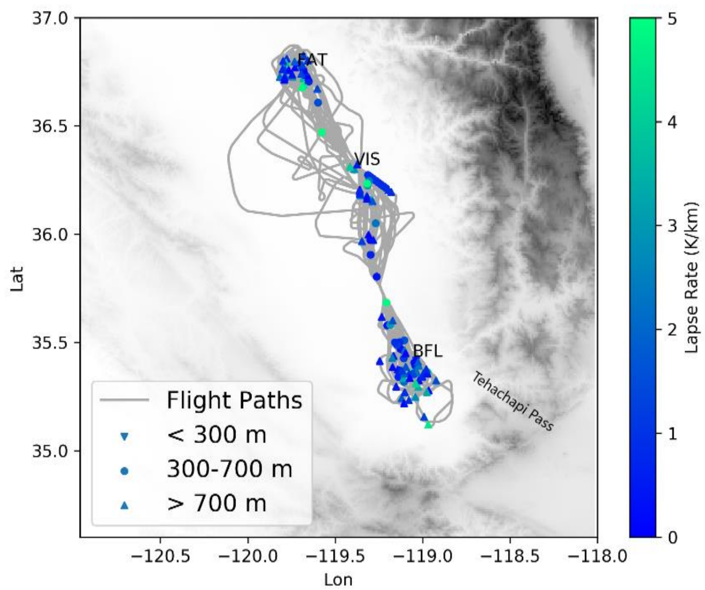
Response: This is likely due to there being less shear immediately under the jet compared to the amount of shear in the surface layer.

17. Page 24, line 602. Can you clarify whether you are still considering a high canopy resistance in the vd calculation?

Response: We are assuming that the canopy resistance does not change.

18. Figure 16 – The font size here is difficult to read.

Response: See adjusted figure below



19. One general comment – the use of eddy diffusivity to evaluate turbulent mixing is most generally applicable to the daytime convective mixed layer. The authors could better support why this framework is applicable to the stable nocturnal boundary layer. This is better done in 3.5, so possibly referencing this section earlier on would be useful.

Response: Eddy diffusivities were the most practical way of estimating the NBL mixing due to the logistics of our study. We have highlighted other literature where eddy diffusivity is estimated in stable, non-convective environments.

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

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Abstract: The San Joaquin valley is known for excessive secondary air pollution owing to local production combined with terrain-induced flow patterns that channel air in from the 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 70 ppb standard each year between 2012 and 2016. The nocturnal dynamics that contribute to these summertime high ozone events have yet to be fully elucidated. Here we investigate the hypothesis that on nights with a strong low-level jet (LLJ) ozone in the residual layer is more effectively mixed down into the stable boundary layer. There ~~where~~ 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 will sustain residual layers that are more decoupled from the surface and thus lead to ~~stronger~~ more fumigation of ozone in the mornings giving rise to higher ozone concentrations the following afternoon. We analyse aircraft data from a study sponsored by the California Air Resources Board (CARB) aimed at quantifying the role of residual layer ozone in the high ozone episode events in this area. By formulating nocturnal scalar budgets based on flights around midnight and just after sunrise the following days, we estimate the rate of vertical mixing between the residual layer (RL) and the nocturnal boundary layer (NBL), and thereby ~~measure~~ infer eddy diffusion coefficients in the top half of the NBL. The average depth of the NBL observed on the 12 pairs of flights was 210 (± 50) m. Of the average -1.3 ppb h^{-1} loss of the O_x family (here $[O_x] \equiv [O_3] + [NO_2]$) 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 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 $m^2\ s^{-1}$ that are found to inversely correlate with the following afternoon's ozone levels, and provide 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 an important control on ozone. Additionally, we investigate the synoptic conditions that ~~occasion~~ are associated with strong nocturnal jets and find that on average, deeper troughs along the California coastline are associated with stronger jets. The LLJ had an average height of 340 m, an average speed of 9.9 m s^{-1} (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, suggesting that air quality models need to forecast the strength of this nocturnal feature in order to more accurately predict ozone violations.

1. Introduction

Under typical fair weather conditions over the continents, thermals are generated near the surface beginning shortly after sunrise, forcing a convectively mixed layer, known more generally as the convective atmospheric boundary layer. As solar heating of the Earth's surface increases throughout the day, this layer reaches its maximum height by late afternoon, typically between 700 and 900 m in California's central valley during summer months (Bianco et al., 2011; Trousdell et al., in preparation). Around sunset, when the solar heating of the surface ends, the convective thermals are cut off and can no longer power turbulent mixing in the boundary layer. The result of the 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). The 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, this process of entrainment is driven by convective thermals that penetrate into the laminar free troposphere, which 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 surface pollution, and more generally scalar budgets, as the two interacting layers usually 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 and the residual layer by shear-induced mixing. Extensive observations of the structure of the NBL indicate that a localized wind maximum near the top of the ~~stable layer~~NBL, known as a low level jet (LLJ), is often present (Banta et al., 2002; Garratt, 1985; Kraus et al., 1985). This low level jet is able to drive sheer production of turbulence in an intermittent, cyclical manner, powering the mixing between these layers. ~~In stable air, wind sheers are able to build in the presence of dynamic forcing due to a lack of vertical momentum transport. Once the wind shear is great enough to produce turbulence, the momentum is mixed out vertically, which reduces the shear, and the cycle restarts (Van de Wiel et al., 2002).~~

California's complex terrain amplifies the challenge of both studying and managing air pollution in this area. 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 ~~et al.~~and Rottuno, 2010). The local sources of ozone are scattered along this primary inflow path to the SSJV. The ozone buildup 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 ~~is~~ are likely important in the phenomenology of ozone pollution in this area.

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 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 ~~nocturnal jet~~LLJ (Davies 2000). The Tehachapi Mountains act as a barrier to the jet if the Froude number is 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 not time-coherent. The initial northwesterly wind and a low Froude number are both critical for determining whether or not the eddy will form on a given night (Lin and Jao, 1995). Monthly averaged wind speeds from June through August of the low level jet near the Fresno eddy up to 12 m s^{-1} have been reported (Bianco et al., 2011). Beaver and Palazoglu (2009) found that ozone pollution ~~potential~~ in the central San Joaquin Valley is particularly high on days where the preceding nocturnal Fresno Eddy is strong, even when strong ventilation is occurring. They also found that the early morning downslope flow through the Tehachapi pass is a strong predictor of ozone pollution ~~potential~~ in the SSJV. However, mixing induced by nocturnal jets has been shown to decrease ozone levels the following day in other parts of the world (Hu et al., 2013; Neu et al., 1995), so one might suspect that a Fresno eddy that creates a particularly strong LLJ on a given night may decrease ozone the following day if the recirculation of ozone does not compensate for its loss due to vertical mixing.

It has been previously shown that residual layer ozone can have a substantial correlation with ground-level ozone the following day (Aneja et al. 2000; Zhang and Rao, 1999). Neu et al. (1995) estimated that about 75 % of the contribution to the difference in afternoon ozone concentrations from one day to the next is from residual layer depletion. This study was done in complex terrain of Switzerland and primarily used SODAR data. They also found a strong correlation ($r^2 = 0.74$) between weaker turbulence in the RL, inferred from the amount of time the wind maximum at night was below 150 m, and the aforementioned ozone difference. Coupling of the RL and NBL via intermittent turbulence has also been shown to correlate with 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 layer ozone or contribute to the following day's ozone. One advantage of our study is that we are using 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 confounded by uncertain horizontal advection.

A study from Southern Taiwan also found that residual layer ozone plays an important role in the following day's ozone concentrations, with fumigation of this ozone into the developing daytime boundary layer accounting for 19 % of the variance (Lin 2012). As the ozone problems in Southern Taiwan are not heavily driven by local sources, a more extensively mixed daytime boundary layer can in fact contribute to a buildup, rather than ventilation, of ozone, because the daytime intrusion into the formal residual layer outcompetes the local production. This, and the fact that many ozone forecasts currently made only take into account local daytime boundary layer dynamics, highlights the need for studying the effects of residual layer ozone in more areas that have ozone problems.

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 LLJ. 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.

It has been previously shown that residual layer ozone can have a substantial correlation with ground-level ozone the following day (Aneja et al. 2000; Zhang and Rao, 1999). Neu et al. (1995) estimated that about 75 % of the contribution to the difference in afternoon ozone concentrations from one day to the next is from residual layer depletion. This study was done in complex terrain of Switzerland and primarily used SODAR data. They also found a strong correlation ($r^2 = 0.74$) between weaker turbulence in the RL, inferred from the amount of time the wind maximum at night was below 150 m, and this ozone difference. Coupling of the RL and NBL via intermittent turbulence has also been shown to correlate with 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 layer ozone~~

2.1. 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 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 (σ_w^2). While some similarity relationships have been reported for the stable boundary layer (Nieuwstadt, 1984), we were not able to measure the governing parameters. However, Banta et al. (2006) reported a meta-analysis of stable boundary layer studies with an average σ_w^2/σ_u^2 of 0.39, where σ_u^2 is the streamwise variance. We applied this correction to our TKE measurements to account for the missing vertical wind variance.

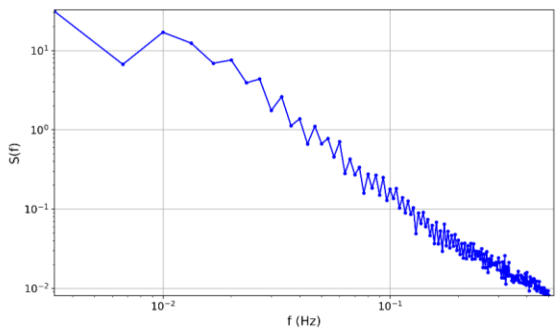

Figure 1. Power spectra for nighttime winds averaged over 309 5-minute samples. The average airspeed was 76.6 m s^{-1}.

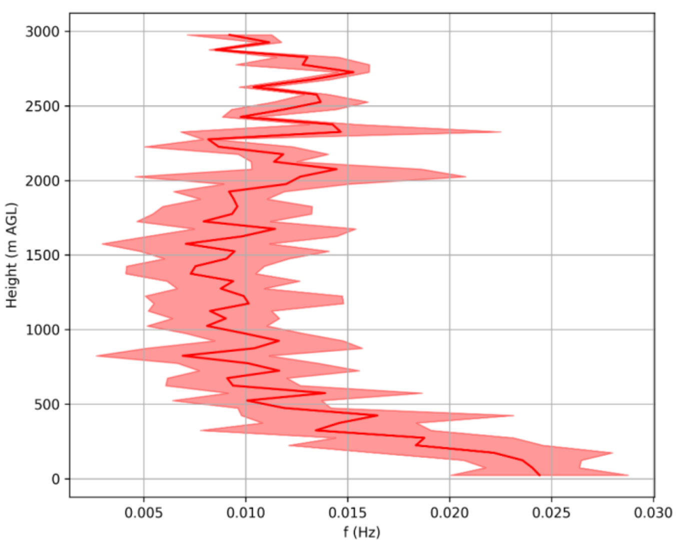

Figure 2. Mean and standard deviation profile of Brunt–Väisälä frequencies for all late night flights. The mean value within the stable boundary layers is 0.023 s^{-1}.

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 on any given flight, we typically utilized it by either completing an extra profile at Visalia, or flying west toward Hanson to better sample the nocturnal LLJ.

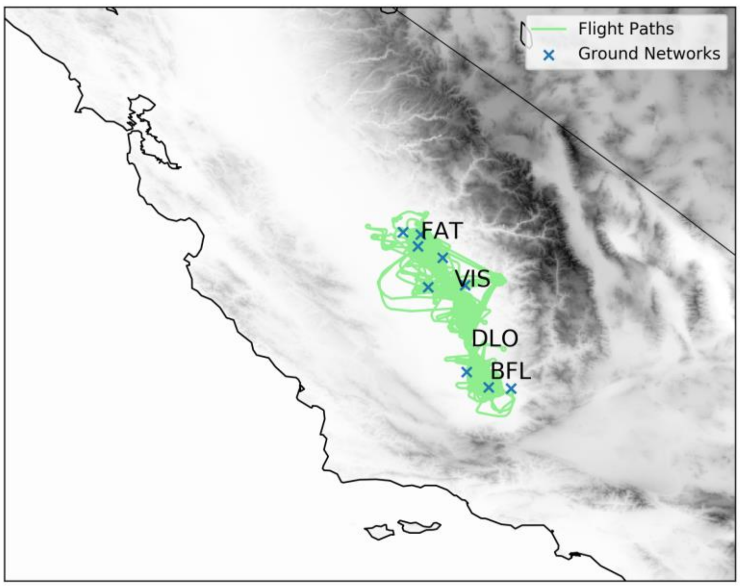

Figure 3. Ground tracks of all flights of the Residual Layer Ozone project. Airports with low approaches and ground ozone monitors are shown. The ground network stations (blue crosses) used were Bakersfield-5558 California Avenue, Bakersfield-Municipal Airport, Clovis-N Villa Avenue, Edison, Fresno-Drummond 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 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. Budget Conceptual Framework

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 and the residual layer. This objective aims to 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. ~~Analyzing such budgets allows one to answer the critical questions regarding what is ultimately giving rise to the observed pollutant levels in a fixed area.~~

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 ~~tracked~~ computed by the reaction between O_3 and NO_2 to form nitrate, ~~but~~ and ~~its~~ 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 term, chemical loss, advection, surface ozone, and stable boundary layer 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 (Padro, 1996), we can indirectly estimate K_z.

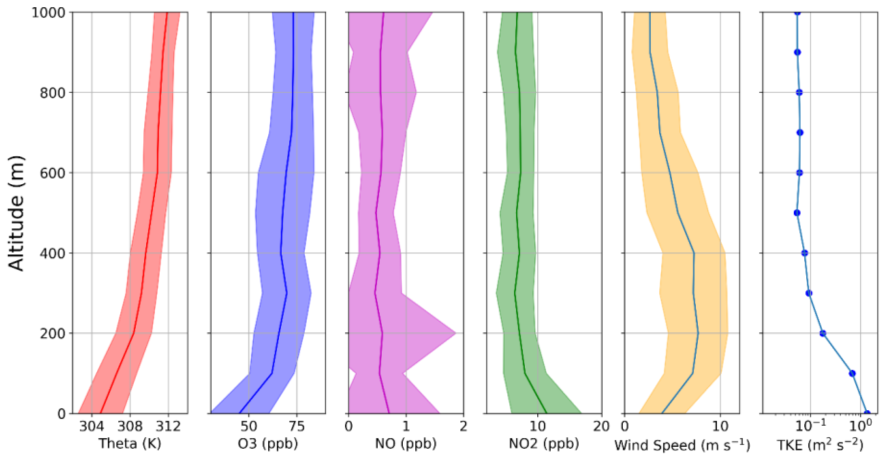

Figure 4. Mean and ±1 standard deviation (swatches) of potential temperature, ozone, NO, NO_2, and wind speed from all late night flights.

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 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. 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. ~~A blend of these three methods was ultimately used~~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. 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 ($m\ s^{-1}$)	σ_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 / 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 for each night (*h*) was used as the upper altitude limit when averaging 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. Ozone and NO_x Chemistry

As previously mentioned, 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 grouped together into a family 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 measure the higher oxidation state NO_y species, we will define O_x as O_3+NO_2, as these are by far the dominant species of O_x. Considering O_x is useful in this case because the family is conserved in the rapid oxidation of NO by O_3 (R1), yielding NO_2 that is quickly photolyzed back to O_3 once the sun rises as part of the standard 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:

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

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

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 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. Thus, determining the dominant loss of nitrate is crucial for our analysis.

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); however, at 30 ppb of O_3 and 20 ppt of NO_3 the lifetimes of NO to (R1) and (R6) are nearly equivalent (~80s). Our measurements indicate ground-level NO of about 0.6 ppb at midnight (SD = 1 ppb), corroborated by the surface air quality network, increasing in the early morning 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 ~~However, these values may be biased high relative to the regional average because the aircraft flew low approaches near~~ 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, results in an NO_3 lifetime of only 25 seconds. Hence, we conclude that (R6) should not be ignored.

There is then a further question as to whether any VOCs would be able to compete with this channel of NO_3 consumption ~~making reaction (R6) negligible for our study~~. An investigation into the faster VOC reactions with NO_3 per Atkinson et al. (2006) and Gentner et al. (2014a) is presented in Table 2. The estimated lifetime of NO_3 due to the VOC reactions in ~~our analysis~~ Table 2 is 9.5 seconds, about four 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 (τ_{NO3}):

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

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. ~~Out of respect for~~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 ~~channels~~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 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 ppb	τ_{NO3} s	Source
o-Cresol	3.33 (10^{-11})	0.01	12.0	Estimate
linalool	2.22 (10^{-11})	0.05	36.1	Arey et al. 1990
3-methylfuran	1.90 (10^{-11})	0.009	234.9	Steiner et al. 2008
b-caryophyllene	1.67 (10^{-11})	0.005	4.8	Gentner et al. 2014b
6-Methyl-5-hepten-2-one	1.67 (10^{-11})	0.05	48.2	Estimate
limonene	1.33 (10^{-11})	0.026	116.6	CalNex
myrcene	1.11 (10^{-11})	0.01	378.8	Gentner et al. 2014b
sabinene	9.52 (10^{-12})	0.003	1284.2	CalNex
b-phellandrene	8.33 (10^{-12})	0.05	96.4	Estimate
Phenol	7.41 (10^{-12})	0.05	108.4	Estimate
a-pinene	6.06 (10^{-12})	0.047	142.3	CalNex
b-pinene	2.67 (10^{-12})	0.003	4653.8	CalNex
Trans 2-butene	7.94 (10^{-13})	0.13	389.3	Steiner et al. 2008
isoprene	6.94 (10^{-13})	0.068	853.2	CalNex
camphene	6.54 (10^{-13})	0.007	8502.4	CalNex
NET			9.5	

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 & 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~~Valley-averaged concentrations are extrapolated from information in references indicated so~~. Thus, values here may not exactly match literature.

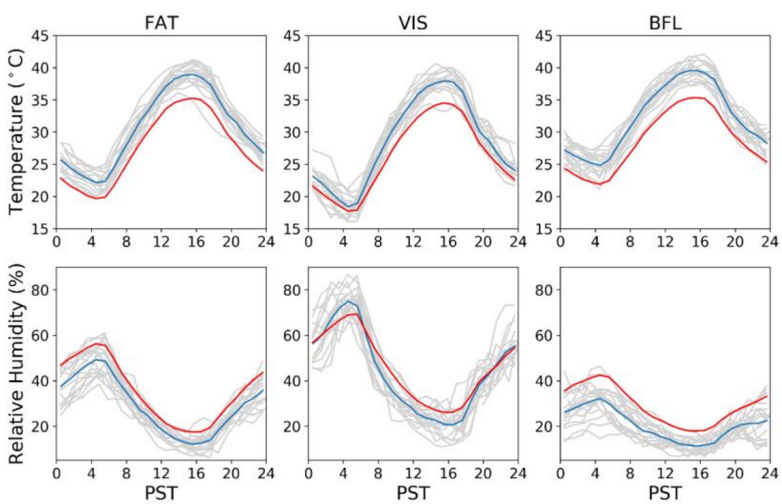

Figure 5. Diurnal plots of temperature and relative humidity during flight days of the Residual Layer Ozone campaign (individual days = grey lines, campaign average = blue lines), compared to 1 June – 30 September 2015 and 2016 averages (red lines) at the Fresno, Visalia, and Bakersfield airports Automated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

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 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 be 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.

2.2.2. Horizontal Advection by Mean Wind

The ~~A~~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. A multiple linear regression is fit through the O_x data for latitude (*y*), longitude (*x*), and altitude (*z*), allowing estimations for $\partial[O_x]/\partial x$ and $\partial[O_x]/\partial y$ in the horizontal advection terms. The total advection term within the NBL on a given flight is:

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

Where *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.

2.2.3. Dry deposition of O_x

Deposition of ozone is presumed to be the main 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 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 few times smaller than the daytime counterpart, but still important for the budgeting technique presented here. Results from a European field study in a ~~similar environment~~flat grass field 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 ~~these agricultural regions~~the SSJV based on these, as well as other (Pederson et al., 1995; Meszaros et al., 2009; Neirynck et al., 2012; Lin et al., 2010), literature values.

We purposefully ignore NO_2 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).

2.2.4. 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 ~~in Equation 1~~. For the top part of the stable boundary layer, 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 linear regression through the 20 m resolution vertical O_x profile is used to determine ~~the O_x gradient (~~$\partial[O_x]/\partial z$ (for the last term in Equation 1)~~)~~ in the upper portion appeared to contain the strongest gradient. 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 is likely to account for the vertical gradient (Fig. 6). The eddy diffusivity can now be solved for with all of the other terms estimated.

3. Results and Discussion

3.1. Overnight Mixing and the O_x Budget

Figure 6 shows an example of the observed profiles of O_x on the late night and morning flights, for the series performed on 2016-06-04. The height of the NBL is shown (green), and the lower bound of the layer used in the vertical gradient fit is shown (yellow). 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 ~~surplus of~~morning O_x (magenta) ~~observed on the morning flight~~ is inferred to ~~be driven~~ mixing term in the ~~budget~~scalar budget equation.

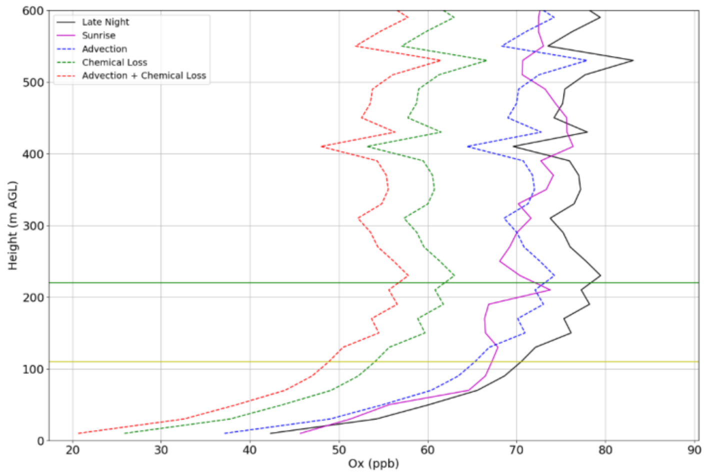

Figure 6. O_x profiles from 2016-06-04 overnight analysis, NBL height (green line), and lower bound to vertical mixing gradient (yellow line). The solid lines are observations and the dashed lines are inferred.

Results of the scalar budget analysis for all 12 paired 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 calculated K_z values.

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. ~~Another way to frame that is as competing timescales of ozone loss in the NBL: f~~For dry deposition the average lifetime of ozone is 28 h (200 m / 0.002 m s^{-1}), and for chemical loss it is 12 h. ~~Further, b~~Both losses of O_x added together are about ~~double~~ triple the observed time rate of change, and thus the physical and chemical losses are largely (~ 2/3)~~partially~~ 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, 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 uncertainty for each term in the budget equation, as well as the 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 height and surface deposition of ozone are ~~conservatively~~ 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, 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 and Low-Level Jet

One complicating factor that remains for this particular analysis is the presence of the Fresno eddy and its influence on our measurements of advection. If an eddy is recirculating a scalar quantity, using a simple linear fit model as we did to estimate advection would be questionable, especially if the flight area only covered a small portion of the larger mesoscale circulation. ~~Figure 4 of~~ 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 is formed in the San Joaquin Valley, 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 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 (0-300 m AGL) and residual layer (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 can be seen clearly to fill most of the SSJV in both the NBL and RL. In the morning residual layer 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. 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).

From this 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 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.

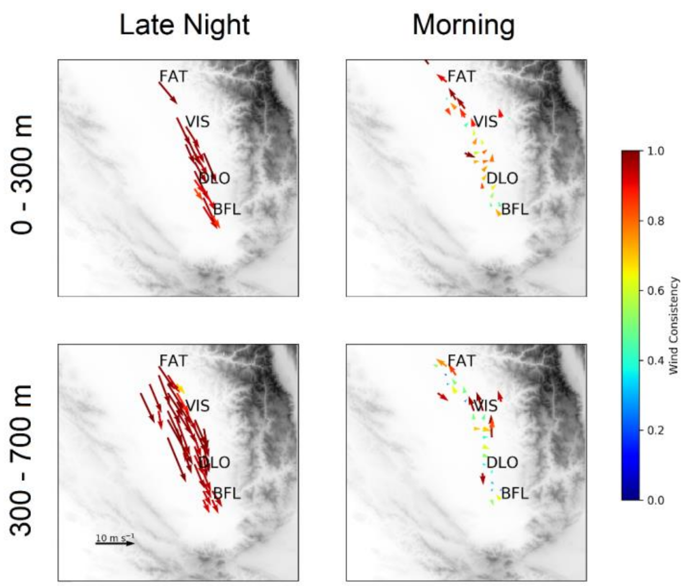

Figure 7. Wind consistency for late night flights and morning flights in the NBL (0 – 300 m) and the RL (300 – 700 m).

Since the low-level jet is hypothesized to contribute to the variability of maximum daytime ozone concentration, we explored ~~some of the possible contributing meteorological factors that are absent in the current literature~~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 compiled to obtain the low-level jet speed and the height at which it was observed. For this analysis we define the nocturnal low-level jet speed as the maximum hourly-averaged wind speed observed below 1000 m ~~in 100 m bin space~~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 had an average height of 340 m, an average speed of 9.9 m s^{-1} (SD = 3.1 m s^{-1}) and a typical peak timing around ~~07 UTC~~23 PST.

To analyze variability of 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 strength was less than 7 m s^{-1} (N=147 nights), and greater than 12 m s^{-1} (N=165 nights).

It is important to note that the LLJ and Fresno Eddy are not exactly the same thing, rather, the LLJ is part of the northwesterly flow that is an important precursor to the Fresno Eddy. When the eddy is present, the LLJ is essentially the strongest branch. Nevertheless, Beaver and Palazoglu (2009) conclude that recirculation from the Fresno Eddy contributes to a buildup of ozone, while we conclude that a strong jet may lead to lower ozone. Future research may attempt to further establish the degree to which the LLJ and Fresno Eddy are linked, as well as which of these two nocturnal mechanisms will dominate the ozone budget under different synoptic conditions. As a provisional ~~compromise~~synthesis of these seemingly conflicting findings, we suggest that the Fresno Eddy, when present, will act to recirculate pollutants regardless of the strength of the LLJ (the strongest branch of the eddy). That is, a stronger eddy will not recirculate pollutants any more than a weaker eddy will. Thus, the optimal nighttime dynamics for ozone pollution the following day may consist of a Fresno Eddy just coherent enough to effectively recirculate pollutants, but without its strongest branch too strong as to deplete the RL ozone by vertical mixing.

In addition to ~~synoptic forcing~~the synoptic patters discussed above, slightly lower surface temperatures across the entire region during stronger low-level jets are observed. This could either be a consequence of the synoptic flow (southerly geostrophic flow will generally result in warmer temperatures) or itself be an underlying precursor to the LLJ (a colder delta region 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 jet 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 ($r^2 = 0.035$, $p < 10^{-5}$).

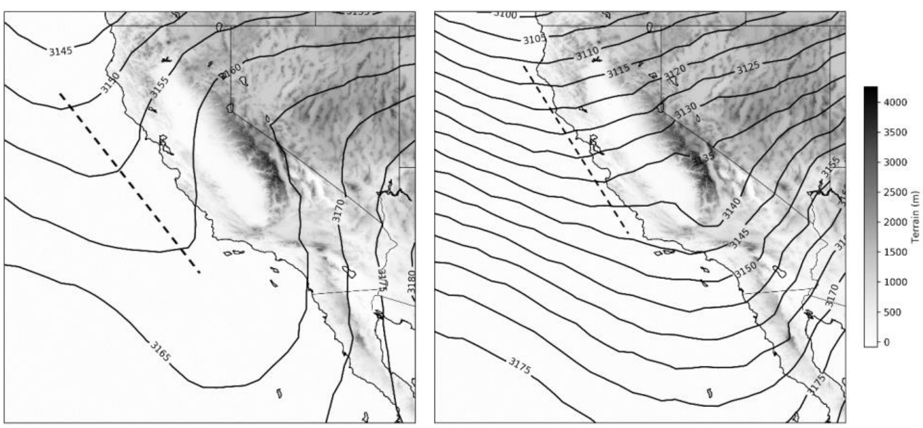

Figure 8. North American Regional Reanalysis 700 mb Geopotential Height (m) for low-level jet speeds exceeding 12 m s^{-1} (left) and below 7 m s^{-1} (right).

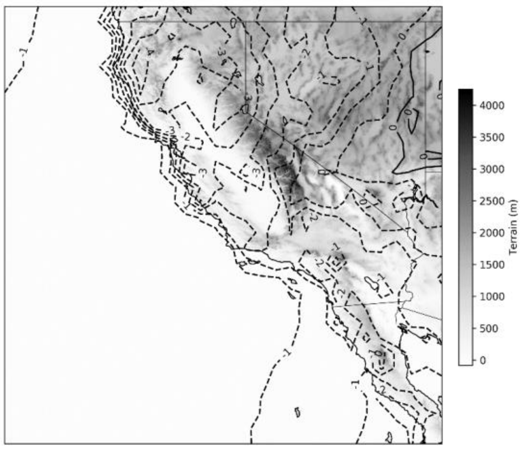

Figure 9. North American Regional Reanalysis 2 m air temperature (°C) ~~for~~ difference between cases where low-level jet speeds exceeding 12 m s^{-1} ~~(left)~~ and cases where it is below 7 m s^{-1} ~~(right)~~. Positive values indicate warmer surface temperatures for strong jets.

~~**Figure 10.** Upwelling index at 33° N as a function of low-level jet speed.~~

~~**Figure 11.** Seasonal variation of LLJ height in comparison with the previous daytime boundary layer height at Chowchilla.~~

~~Another look at the overnight layering, including the low level jet, is presented in the average scalar profiles for all late night flights of Figure 12. An~~ As seen in Figure 4, an average low-level jet height between 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 daytime during convective conditions. However, TKE is seen to increase toward the surface, contrary to what would be expected in the presence of an elevated jet. Banta et al. (2006) refers to this as a "traditional" TKE profile.

~~**Figure 12.** Select scalar profiles and ±1 standard deviation from all late night flights.~~

The thermals generated by solar heating after sunrise initiate a fumigation process where as the daytime boundary layer develops, the ozone that was in the RL will be mixed downward. The change in surface ozone concentration ($d[O_3]/dt$) due to fumigation peaks at around 8 am PST and continues until about 10 am PST. The relationship of our estimated eddy diffusivities with ozone during the fumigation period is strongest at 10 am PST, after the bulk of the vertical mixing due to the boundary layer growth entraining into the RL has occurred (r^2=0.291, p=0.070). The relationships between eddy diffusivities and the maximum 1-hour ozone, 24 hour average ozone, and MDA8 were also in the predicted direction, with the strongest relationship found for the MDA8 (r^2=0.463, p=0.015).

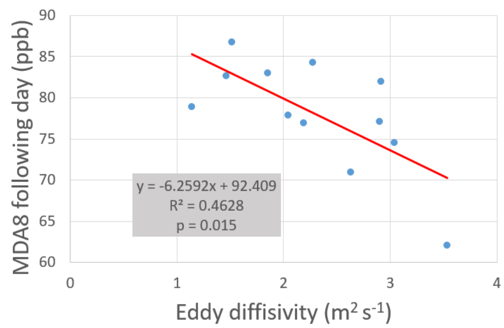

Figure 10~~3~~. Correlation between overnight eddy diffusivity and maximum daily 8 hour average ozone (MDA8) the following day. All values are averages of 11 CARB surface network stations that are within the flight region.

~~In an effort to increase the sample size to better test this hypothesis~~Because this analysis consisted of only 12 flights, we decided to explore a larger data set that might support the hypothesis that a stronger LLJ reduces ozone the following day.~~,~~ 7 years of low-level jet 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 included. The low level jet, hypothesized to be the main contribution to the variability in overnight mixing between the RL and NBL, is compared with ~~the maximum 1-hour ozone~~MDA8 observed the following day, shown in Figure 11~~4~~.~~–~~ It can be seen that a stronger nocturnal low-level jet is correlated, albeit weakly, with lower ozone the following day (r^2=0.~~168~~181, $p < 10^{-5}$). A single outlier was removed where the LLJ exceeded 25 m s^{-1}. This is in line with our hypothesis that the low level jet will lead to stronger mixing, which leads to more residual layer ozone depletion.

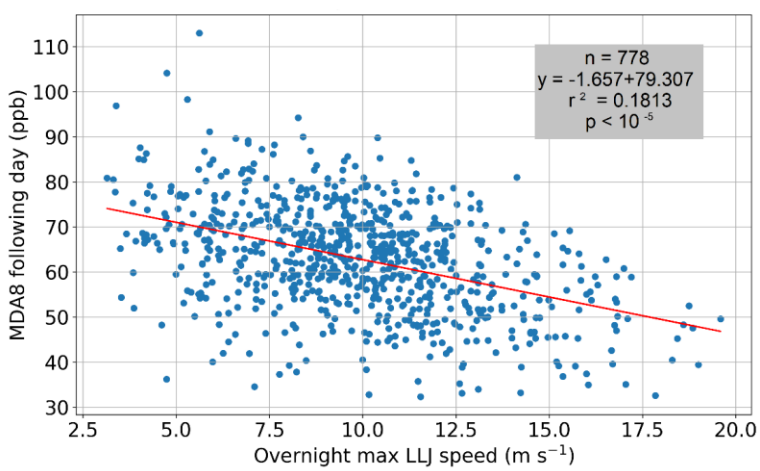

Figure 11~~4~~. Correlation between nocturnal low level jet speed and the following day's ~~maximum ozone~~MDA8 in Visalia, CA, for Calendar days 152-273 from 2010-2016.~~.~~

In addition to a stronger LLJ mixing down more ozone, a further 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 r_a is the aerodynamic resistance, r_b is the viscous sub-layer resistance, and r_c is the surface (canopy) resistance. Figure 4 in Padro (1996) suggests that for ozone at night, $r_a \sim r_c \sim 250$ s m^{-1}~~, and~~. r_b is likely non-zero~~negligible~~ (Massman et al., 1994) but will be neglected here because it is unknown. Combining the aerodynamic resistance due to mass transfer ($r_a = u\, u_*^{-2}$, 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 coefficient for heat C_H ($u_*^2 = C_H U_{10}^2$) we roughly approximate r_a as:

$$r_a \sim \frac{1}{C_H\, U_{10}} \quad \textbf{(7)}$$

In the 7 years of LLJ data at Visalia, 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 average U_{10} of 1.75 m s^{-1} would imply that $C_H \sim 2.3 \times 10^{-3}$. A sensitivity analysis indicates that this difference in U_{10} between strong and weak jets would result in a 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 measure these parameters with more precision in order to better estimate the degree to which the LLJ can modulate dry deposition in the SJV.

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. ~~While eddy diffusivity is one way to estimate mixing strength in the NBL, estimates of TKE within the NBL on each night may be a useful additional metric.~~ 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~~;) and~~ Lenschow et al., ~~(~~1988). Table 1 shows the TKE, LLJ speed, as well as the ratio of the streamwise variance to LLJ speed (σ_u/U_x) for each night. The average value of σ_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.

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 has been used in oceans to the free troposphere, where turbulence is sparse and intermittent, much like 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 (ε) 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 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 boundary by Kondo et al. (2014) estimated 7-day average overnight diffusivities of 0.05 – 0.13 m^2 s^{-1}, which is 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 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, ~~this~~ the latter is the most comparable observational finding within the NBL to our range of diffusivities. Nevertheless, the variability ~~of these reports~~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 large, 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 other stable environments.

Lastly, we estimate the Bulk Richardson number (BRN) on each late 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 negative relationship with eddy diffusivities, as expected (Fig. ~~15~~12). While the relationship is not strong, it is important to remember that both parameters are noisy estimates.

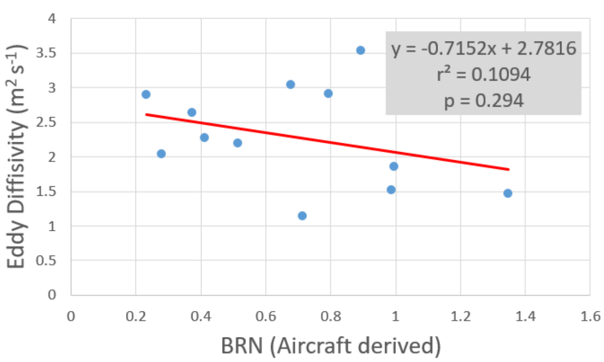

Figure 12~~5~~. Eddy diffusivities and Bulk Richardson Numbers (BRN) derived from aircraft observations.

3.6. Nocturnal Elevated Mixed Layers

During the late 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. Understanding these anomalies may guide future research toward a deeper phenomenological understanding of overnight mixing and turbulence in the SSJV.

The time series of all late night flights was scanned for any period where 1) the aircraft maintained an ascent (or descent) rate of at least 1.4 m s^{-1}, and 2) during a given elevation span of 100 m, a virtual potential temperature decrease with height was observed. The process was repeated for a thickness of 50 m.

The locations of the layers detected, along with their elevation and magnitude, is shown in Figure 13~~6~~. 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 ~~would have to extend upward beyond the NBL depth~~appear to be above the NBL where there is communication with the surface. 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 layer 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. Further research, both observational and modeling-based, is needed to explore this possibility.

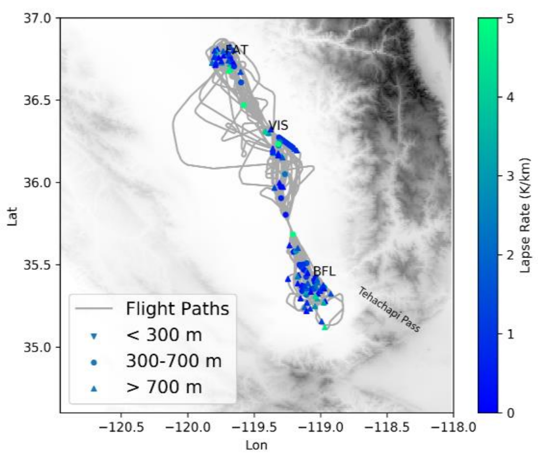

Figure 13~~6~~. Detected nocturnal elevated mixed layers with at least 50 meters thickness, with elevations shown.

The unstable layers are not seen to have more TKE than the rest of the atmosphere, and this may reflect the limitations of the method used to estimate turbulence from this low-cost wind measurement system. However, this ~~finding~~ is consistent with the study by Cho et al. (2003) which found no relationship between turbulence and static stability in the free troposphere. Since the aircraft is moving horizontally a lot faster than it is vertically, ~~it is possible~~one may be concerned that our observations of elevated mixed layers ~~reflect~~ are an artifact of localized temperature gradients that are more prominent in the horizontal dimension. To check this, we plotted 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 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~~7~~. Even in the climatological averages, some nocturnal unstable layers are detectable between 500 and 1500 m.

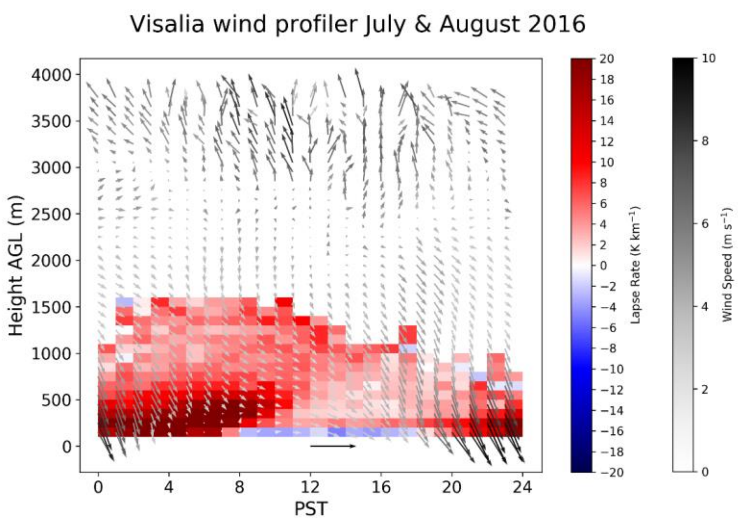

Figure 1~~7~~4. Stability and wind quivers for Visalia 915 MHz sounder, 1 Jul 2016 – 31 Aug 2016.

4. Conclusions

We have demonstrated a method for performing a nocturnal scalar budget analysis using aircraft data, and applying it to estimate the effects of turbulence in the stable boundary layer which can be related to air quality problems. 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 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 ~~slightly~~ 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 layer. ~~The obvious limitation in~~A limitation of our study is the lack of sample size, with only 12 pairs of overnight and morning flights~~overnight flight pairs being conducted~~. However, we believe ~~it~~ 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 ~~soundings~~ 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. ~~Our limited aircraft dataset suggests a similar relationship, although in the former analysis, the low level jet is presumed to be predictive of mixing strength. While the correlation is not very strong, explaining only about 17 % of the variance, it is an important link that may have consequential implications for modeling studies and policy making.~~ 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 ~~infer~~ 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~~s~~ the ozone reservoir by bringing it into the stable boundary layer overnight.~~,~~ ~~where~~ 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 ~~very~~always strong~~, explaining only about 17 % of the variance~~, 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. ~~Other flights we performed in the Bakersfield area~~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). In that study ~~we also~~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 ~~illustrated~~ suggested that the fate of the NO_3 plays an important role in the nocturnal ~~ozone~~ O_x budget ~~which consequently has impacts for~~and thus likely impacts the following ~~days~~day's maximum ozone concentration. 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 direct measurements of NO_3. ~~The~~ Thus, the of NO_3 can range from seconds to several minutes~~ depending on the dominant loss pathway~~, which affects the chemical It is thus 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 of aerodynamic resistance and ozone deposition at the surface by eddy covariance in conjunction with future airborne studies.

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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