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Atmospheric Chemistry and Physics
Discussions

# *Interactive comment on* "Carbon Dioxide and Methane Measurements from the Los Angeles Megacity Carbon Project: 1. Calibration, Urban Enhancements, and Uncertainty Estimates" *by* K. R. Verhulst et al.

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Response to Referee #2 Comments

1. Overview

We would like to thank the reviewer for their valuable comments, many of which we incorporated into a revised version of the manuscript. Below we provide responses to the specific comments and a summary of changes to the manuscript, where applicable.

2. Technical/minor comments



Abstract:

Author Response (Comment 1): The extra "to" was removed.

Author Response (Comment 2): We have clarified the sentence as follows: "The USC site near Downtown LA exhibits median hourly enhancements of ∼20 ppm CO2 and ∼150 ppb CH4 during 2015, and ∼15 ppm CO2 and ∼80 ppb CH4 during midday hours (12-16:00 LT, local time), which is the typical period of focus for flux inversions."

Author Response (Comment 3): We reworded the sentence as follows: "The largest component of the measurement uncertainty is due to the single-point calibration method; however, the uncertainty in the background mole fraction is much larger than the measurement uncertainty."

Section 2.3:

Author Response (Comment 1): The G2201-i and G1101-i analyzers are not mentioned in the main text because results from these analyzers are not included as part of this study. We list them in Table 1 because they are relevant as prior measurement sites. The footnotes in Table 1 were reorganized and reworded throughout for clarity. No additional changes were made to the text.

Author Response (Comment 2): Correct. As we discuss in the text, it was not possible to calibrate all the instruments in a laboratory prior to field deployment. As the reviewer comment notes, this is not ideal, which is why we dedicate a significant part of our analysis to investigating the error in single-point calibration method and the slope (epsilon) estimates for various Picarro analyzers with similar model numbers. As stated in the text on page 22, lines 25-26: "Our approach relies on independent estimates of $\varepsilon$ (epsilon), the slope parameter, to determine the magnitude of the systematic and random components of the (extrapolation) error in our calibration method." For more details, see Section 6.1.1 Extrapolation uncertainty, and results in Tables S2 and S3 and Figures S5 and S6). No additional changes were made to the text.

Section 2.4:

Author Response (Comment 1): The repeated sentence was removed.

Author Response (Comment 2): Yes, all tanks used in the LA network are calibrated to the same NOAA/WMO scales (X2007 for $CO_2$ and X2004A for $CH_4$). The text on page 9, lines 17-19 was edited as follows: "The SIO standards are filled using a similar procedure, except tanks are filled with natural coastal air from Scripps Pier in La Jolla, California, and the tanks are also calibrated against standards on the same WMO-scales."

Author Response (Comment 3): The missing period in the second paragraph was added.

Author Response (Comment 4): In response to this comment, we moved up the first reference to the high mole fraction tanks to the first paragraph in Section 2.4: "In addition to the ambient-level calibration and target tanks, the VIC and LJO sites had high mole-fraction standard tanks installed at the time of this study. These tanks were prepared by NOAA/ESRL and calibration assignments were provided prior to deployment (roughly 500 ppm $CO_2$ and 2600 ppb $CH_4$)."

Section 3.1:

Author Response: This sentence was also pointed out by another reviewer. We decided that the content was not critical to this paper, we removed the first sentence of Section 3.1.

Tables 2 and 3:

Author Response: Tables 2 and 3 provide the statistics of the $CO_2$ and $CH_4$ measurements. We feel this quantitative information would be lost in figures and is more appropriately presented in table format. No changes were made to the manuscript.

Section 4.1:



Author Response: For the purposes of this study, there was an effort to ascertain criteria for selecting background both $CO_2$ and $CH_4$ observations. The $CO_2$ background selection criteria for S.D. within 1 hour (0.3 ppm $CO_2$) is based selection criteria used by Thoning et al., (1989, JGR) to select background $CO_2$ observations at Mauna Loa, HI. There are no similar criteria published for $CH_4$, so we came up with our own based on the observed variability at our sites. In general, $CH_4$ exhibits more hour-to-hour variability (relative to its baseline) compared to $CO_2$. Therefore, different filtering parameters were needed to limit the variability while not excluding too much data. Since we are using an hour-to-hour criteria for $CO_2$, the hour-to-hour variability is already somewhat restricted, so imposing an additional hour-to-hour criteria for $CH_4$ did not seem appropriate. In response to this comment – and another similar comment from reviewer #3 – we performed additional tests on the data filter criteria used for each site. To summarize those changes, we included a new figure in the supplement (Figure S4, see below), showing histograms of the 1 hour S.D. for $CO_2$ and $CH_4$ observations from SCI, VIC, and LJO. Overall, Figure S4 shows that a large fraction of measurements from all three sites have hourly standard deviations <0.3 ppm $CO_2$ and <3 ppm $CH_4$. During 2015, 70%, 42%, and 30% of the data had a 1 hour S.D. <0.3 ppm $CO_2$, 67%, 57%, and 42% of the data had a 1 hour S.D <3 ppb $CH_4$, and 60%, 35%, and 29% of the data met both criteria for the SCI, VIC, and LJO sites, respectively. Because a significant fraction of the data from each site is within these limits ($\sim$30% or more), we applied them to all three sites. This means our $CH_4$ filter limit was reduced from 5 ppb to 3 ppb $CH_4$ (which is more reasonable considering the average analytical uncertainty in the $CH_4$ observations was only $\sim$1 ppb at LJO during 2015, see Table 6 in the revised manuscript). For SCI, all other original filter criteria were retained (one hour S.D. of 0.3 ppm $CO_2$, hour-to-hour stability cutoff of 0.25 ppm $CO_2$ based on Thoning et al., 1989, and 6 hours of persistent "background" conditions). Overall, we found that the LJO and VIC were most sensitive to filter criteria 2 and 3 (the hour-to-hour stability and number of consecutive hours with stable conditions). We performed tests varying the hour-to-hour stability between 0.25 and 0.5 ppm $CO_2$ and the number of consecutive hours from 3 to 6 hours and analyzed the results. For LJO, the original filter criteria did not produce large gaps (i.e., >1 month). Furthermore, increasing the allowable hour-to-hour stability or decreasing the number of consecutive hours sometimes resulted in a few anomalously high CO2 and/or CH4 observations being included in the result, which was unfavorable (and likely due to a persistent polluted air mass passing over the site rather than clean background air). For these reasons, we decided to keep the same filter criteria for both LJO and SCI. For VIC, we noticed that applying the same filtering criteria as SCI and LJO produced large gaps in the selected background observations, sometimes over an entire season in summer months, which would make the background estimate highly uncertain. In order to reduce gaps in the VIC background observations to <=1 month, we used the following criteria: 1) hour-to-hour stability equal to 0.5 ppm CO2 and 2) number of consecutive hours with stable conditions equal to four hours. With these changes, there are no longer significant gaps in the CO2 or CH4 records used to generate the smooth curve fits. Overall, we believe the final results from our revised background analysis are very reasonable for the intended purposes. Furthermore, the agreement between the background estimates from the marine and continental sites –which all exhibited very different variability in CO2 and CH4 mole fractions – serves as a metric of success in our approach.

Summary of MS changes for this comment:

P. 15 (Section 4.1, line 17-28): “LJO and SCI “Marine” Background and VIC “Continental” Background Estimates: The LJO, SCI, and VIC air observations were filtered according to statistical criteria based on the variability in the hourly average data (see Supplementary materials). As shown in Figure 3, the CO2 and CH4 observations from SCI exhibit much less variability compared to VIC and LJO. Figure S4 shows histograms of the hourly standard deviations for the SCI, VIC, and LJO observations. As discussed earlier, the variability in the LJO record is more like an urban/suburban site than a background site. This is primarily due to along-shore transport from the north and the proximity to other local sources (including a large landfill immediately to the



east). After applying the selection criteria respective to each site, the CCGCRV curve fitting software was used to estimate a "smooth curve" fit to the selected observations (Thoning et al., 1989; http://www.esrl.noaa.gov/gmd/ccgg/mbl/crvfit/crvfit.html). The curve-fitting parameters are described further in the Supplementary materials. The full time series, selected data and "smooth curve" results are shown in Figure 3 and the final smooth curve results for each site are shown in Figure 4 (panels a-b). We discuss the uncertainty in the smooth curve estimates in Section 6.2 (see also, Figure S10).”

Supplementary materials (Section 3, P. 4-5): Added details described above regarding the filtering criteria for each site. Also, added Figure S4 showing histograms of the 1 hour S.D. for the CO2 and CH4 observations from SCI, LJO and VIC.

We also removed the following sentences as the gaps at VIC are no longer relevant to the discussion in this paper:

Abstract: “We also show that continental sites may not be relevant for selecting background observations during summer months due to the prevalence of onshore flow, which could transport CO2 and CH4 from the LA Basin to relatively remote sites.”

P. 18, Section 4.3: “For VIC, there is virtually no CO2 or CH4 data meeting the selection criteria during the summer and early fall months.”

Section 4.3:

Author Response: We used the SCI background estimate to calculate the CO2 and CH4 enhancements because this turns out to be the site that samples marine background air most frequently near LA, and additionally, the results from SCI look plausible compared to other marine background estimates. While this may seem somewhat obvious after reading the manuscript, the analysis we conducted really served to explore whether SCI is a reasonable marine background site, which had not been demonstrated previously in the literature. In our analysis, we demonstrate that SCI is a good background site by analyzing results from SCI in comparison to the LJO and Pacific

MBL background curves, as well as two other potential continental background sites. Historically, LJO has been used as a background site for other gases; however, the continuous observations show LJO is frequently impacted by local sources of $CO_2$ and $CH_4$ (see Figure 2 in the manuscript). Applying our filtering criteria to both SCI and LJO offered a great test case for our methodology. A metric of success exhibited by our results is that we have achieved a reasonable level of convergence between all the background estimates (e.g., marine sites: LJO vs SCI and continental sites: MWO vs VIC), and overall the differences between the background estimates are now relatively small (see Figure 4 in the manuscript). To further address this comment, we changed the text on P. 19 (lines 10-13) in the manuscript, as follows: "SCI is the most representative of local marine background conditions for both $CO_2$ and $CH_4$ throughout the year. The LJO background curve also helps confirm that the background estimate from SCI is reasonable. Therefore, we use SCI as the background reference site to calculate $CO_2$ and $CH_4$ enhancements for the LA surface sites (see Section 5)."

Section 6.1.6:

Author Response (Comment 1): We removed the redundant text in the second paragraph.

Author Response (Comment 2): This comment refers to the fact that standard tanks that are measured during "pre-deployment" and "post-deployment" field checks. This is determined independently at the NOAA/ESRL laboratories, and these results do not indicate significant drift (see, e.g., Andrews et al., 2014). For clarification, we changed the text (now on P. 27, lines 22-24) as follows: "Andrews et al. (2014) report a mean difference between pre- and post-deployment tank calibrations of $CO_2$ and $CH_4$ for tanks prepared by the NOAA/ESRL laboratories."

Tables 5 and 6

Author Response: We assume the reviewer was referring to moving Tables 6 and 7 to the Supplement (the statistics for epsilon, or the slope estimates from individual



analyzers) since Tables 5 and 6 show very different results from one another. We moved Tables 6 and 7 to the Supplement (now Tables S2 and S3). As noted, these tables complement Figures S4 and S5.

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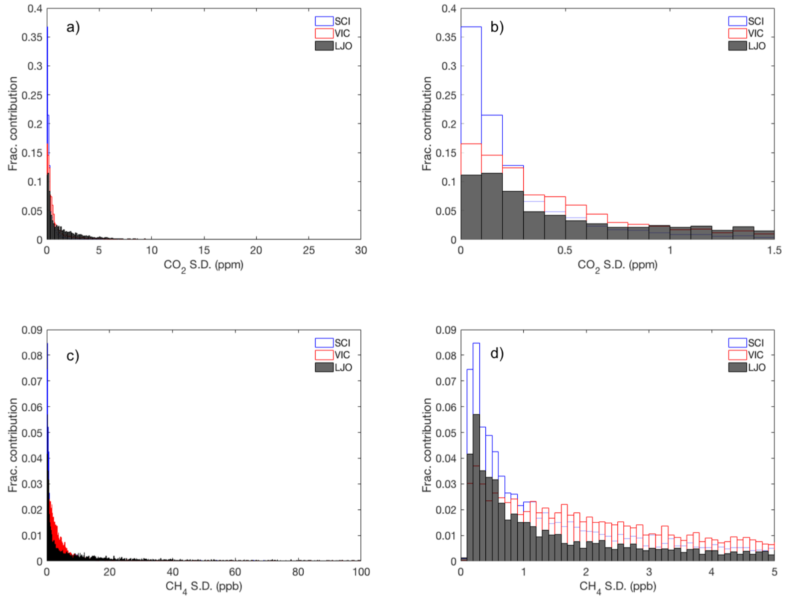


**Fig. 1.** Fig S4: Histograms of the S.D. of hourly CO2 (panels a and b) and CH4 (panels c and d) observations from SCI (blue), VIC (red), and LJO (grey). Left panels show all data (right panels, zoomed).