Carbon Dioxide in the Free Troposphere and Boundary Layer at the Mt. Bachelor Observatory

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ABSTRACT

We use data for 2012–2014 from the Mt. Bachelor Observatory (MBO) in central Oregon to understand variations in carbon dioxide (CO₂) in the free troposphere (FT) and boundary layer (BL). The goals of this analysis are to identify and examine CO₂ in FT and BL air, events due to wildfires, the role of transport patterns, and the variation of CO₂ seasonally. For all seasons, we found that FT air has higher average CO₂ mixing ratios compared to BL air. FT air was most often seen during the night and early morning at MBO (20-8 PST) while BL air was most often observed during the afternoon and evening (12-20 PST). Winter and spring showed the highest mixing ratios of CO₂ while summer and fall showed the lowest mixing ratios. The maximum diurnal change in CO₂ was found during spring and summer. HYSPLIT back-trajectories and a cluster analysis of those trajectories were initiated for spring months. Based on this analysis, the spring clusters with the highest ozone and lowest water vapor mixing ratios were associated with the highest mixing ratios of CO₂. Four case studies of CO₂ variations are presented: a long-range transport event observed at MBO and three wildfire events. In one large fire event, CO₂ showed a large enhancement and was well correlated with CO. In another fire event, CO₂ was observed to decrease, suggesting that depletion in BL air by surface uptake can counteract the enhancements from wildfire emissions.

Keywords: Carbon dioxide; Greenhouse gases; Mountain-top observatory; Biomass burning; Long-Range transport; Free troposphere; Boundary layer.

INTRODUCTION

Carbon dioxide (CO₂) is an important and long-lived greenhouse gas that has shown an appreciable increase in atmospheric concentration since pre-industrial times (from ~280 ppm in the 19th century to ~396 ppm in 2013) (WMO, 2014). Keeling et al. (1976) and Goldman (1974) demonstrated that CO₂ at Mauna Loa was increasing consistently every year in excess of 1 ppm year⁻¹ based on measurements taken between 1968 and 1972. According to Thoning et al. (1989), the rate increased after 1974 to 1.42 ppm year⁻¹ at Mauna Loa. In the fifth IPCC report, a global increase of 2.0 ± 0.1 ppm of CO₂ year⁻¹ between 2002 and 2011 was reported (IPCC, 2014). For the last decade (2003–2013), the WMO (2014) reported an increase of ~2.1 ppm of CO₂. Increasing atmospheric CO₂ concentrations in combination with the debate over carbon fluxes and atmospheric residence time of CO₂ suggests that detailed observations of CO₂ transport and vertical profiles must be made to better understand carbon cycling in the Earth system (Sonnemann and Grygalashvyly, 2013; Friend et al., 2014).

Emissions of CO₂ can come from either natural sources (e.g., carbon cycling through the atmosphere, wildfires, ocean, soil,) or anthropogenic sources (e.g., combustion of fossil fuels, cement production). The primary sources and sinks of CO₂ are near the surface of the Earth (Machida et al., 2002; Li et al., 2014). Near the surface, photosynthesis can draw down atmospheric CO₂ or combustion of fossil fuels can cause an increase in concentration. Because CO₂ has a sufficiently long atmospheric lifetime (not readily removed) and is produced and removed near the surface, it can be used as a tracer of long-range pollution transport (Sidorov et al., 2002). Measurements of CO₂ in the free troposphere are important in understanding the carbon cycle and provide insight into vertical distribution (Tans et al., 1990; Wang et al., 2007; Gurk et al., 2008; Font et al., 2010). This type of data can be used for inverse modelling of CO₂ sources and sinks along with model validation.

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Numerous types of sites have been used to measure atmospheric CO₂, such as: surface observatories (Idso et al., 2001; Newman et al., 2008; Ramonet et al., 2010; Rice and Boström, 2011; Pérez et al., 2012), balloon soundings (Bischof et al., 1980; Li et al., 2014), aircraft measurements (Bischof et al., 1980; Lloyd et al., 2002; Machida et al., 2002; Sidorov et al., 2002; Gurk et al., 2008; Shashkov et al., 2011; Sun and De Wekker, 2011; Sweeney et al., 2015), tall towers (Bakwin et al., 1995; Haszpra et al., 2005; Haszpra et al., 2012), and mountain-top observatories (Goldman, 1974; Thoning et al., 1989; Sturm et al., 2005; De Wekker et al., 2009; Ramonet et al., 2010; Brooks et al., 2012). Even though there are numerous methodologies for the measurement of CO₂ and data on atmospheric CO₂ concentrations in conditions other than in a well-mixed planetary boundary layer (Haszpra et al., 2012), because FT/BL exchange varies by season and by day, long-term, high-altitude, observations of CO₂ are important in understanding the atmospheric CO₂ cycle (Gurk et al., 2008; Font et al., 2010; Haszpra et al., 2012). Here, we present mountain-top observations of CO₂ from the Mt. Bachelor Observatory (MBO) in central Oregon, U.S.A, from 2012 through 2014.

Our study examines the FT/BL mixing ratios, sources and sinks of CO₂, and seasonal variations. Our purpose is to answer the following four scientific questions:

1. How does the short-term CO₂ record seen at MBO compare with other mountaintop sites?
2. How does CO₂ vary in FT/BL air and how does this vary seasonally?
3. How does CO₂ vary with transport patterns? Is there a transport pattern that shows enhanced/depleted CO₂ mixing ratios?
4. How do fire emissions contribute to enhanced CO₂ mixing ratios? Why do some fires plumes show no CO₂ enhancement?

**METHODS**

**Measurements Conducted at MBO**

The Mt. Bachelor Observatory (43.979°N, 121.687°W, 2763 m above sea level (asl)) is located in central Oregon, U.S.A, with measurements being taken in the summit lift building of the Mt. Bachelor Ski Resort. A suite of measurements (including carbon monoxide (CO), ozone (O₃), aerosol scattering, and more) have been made continuously at the summit site since 2004. Other measurements (including NOₓ, NOy, and PAN) are taken during specific seasons or intensive campaigns. Continuous CO₂ observations began in 2012. Past studies using MBO observations have focused on long-range transport of Asian pollution (Jaffe et al., 2005; Weiss-Penzias et al., 2006; Weiss-Penzias et al., 2007; Fischer et al., 2009), mercury (Swartendruber et al., 2006), O₃ (Ambrose et al., 2011), and CO (Gratz et al., 2015). In all of these studies, the FT/BL exchange was considered, especially in the studies performed at MBO by Reidmiller et al. (2010) and Weiss-Penzias et al. (2006). The location of the observatory makes it ideal for the measurement of clean air masses and trans-Pacific transport with little local anthropogenic influences upwind (Weiss-Penzias et al., 2006; Ambrose et al., 2011; Gratz et al., 2015). The prevailing Pacific High Pressure system and predominately westerly winds provide frequent opportunities to sample long-range transport of pollutants during spring (Stohl et al., 2002; Jaffe et al., 2003). Summer allows for measurements of more local, continental/marine transport, which includes biomass burning influences, especially during upslope airflow (Weiss-Penzias et al., 2007; Wigder et al., 2013; Baylon et al., 2015). All measurement times presented herein are in local standard time. The local time at MBO is Pacific Standard Time (UTC-8h for PST). For this analysis, we use ppmv = μmol/mol by volume and ppbv = nmol/mol by volume as abbreviations for dry-air mole fraction.

We focus on measurements made at MBO between 2012 and 2014. During this period, CO₂ and CO measurements were made using a Picarro G2302 Cavity Ring-Down Spectrometer. Calibrations were performed every 8 hours using three different NOAA calibration gas standards, which are referenced to the World Meteorological Organization’s (WMO) mole fraction calibration scale (Gratz et al., 2015). Additionally, O₃ measurements were made by dual UV instruments, a Dasibi 1008 RS and an Ecotech Serinus 15 (Weiss-Penzias et al., 2006; Ambrose et al., 2011; Gratz et al., 2015). Weekly 1-hour automated zeros were performed with an ozone scrubber cartridge, while manual calibrations were performed at 6-month intervals using a Washington State Department of Ecology transfer standard (Serial Number #6452), which was calibrated to the EPA Region 9 Standard Reference Photometer (Gratz et al., 2015). The total uncertainty for O₃ is ± 2% (Ambrose et al., 2011) with a method detection limit (MDL) of 1.57 ppbv.

Aerosol scattering was measured by a TSI Model #3563 Integrating Nephelometer. Observations from this instrument are described in Fischer et al. (2011) and Gratz et al. (2015).

Temperature and relative humidity (RH) measurements were made by a Campbell Scientific HMP45C probe, which was sheltered from icing. Water vapor mixing ratios (g kg⁻¹) were calculated using the equations by Bolton (1980). Pressure data was measured using a Vaisala PTB101B Pressure Transmitter. The estimated accuracy of the temperature, RH, and pressure measurements are: ± 0.4°C, ± 3% RH, and ± 0.5 mbar, respectively (Ambrose et al., 2011).

**HYSPLIT Back-Trajectories and Cluster Analysis**

Five-day air mass back-trajectories were computed every hour for 2012–2014 using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model Version 4 (Draxler and Hess, 1998). For this time period, we used the Global Data Assimilation System (GDAS) 1° × 1°
gridded meteorological data from the National Oceanographic and Atmospheric Administration’s Air Resources Laboratory (NOAA-ARL). Within GDAS, the grid box containing MBO is located at approximately 1300 m asl. Therefore, we initiated back-trajectories at 1500 m above ground level (agl) to represent the approximate altitude at MBO (2.8 km asl) (Ambrose et al., 2011).

With the trajectories from 2012 through 2014, we used a HYSPLIT Cluster Analysis to determine the predominant FT meteorological patterns observed at MBO and their relationship to average mixing ratios of CO₂, water vapor, O₃, and pressure. The cluster analysis was accomplished by using trajectories starting every hour between 20 and 4 PST (nighttime) and only using every fourth endpoint within each trajectory to decrease computing time. Hourly observation of CO₂, water vapor, O₃, and pressure from MBO were then compared with the clusters identified by the analysis.

An important caveat to the 3-D HYSPLIT back-trajectories should be noted. According to Font et al. (2010) and Stohl et al. (2004), back-trajectories can suffer from artificial mixing (due to improper meteorological inputs) and, after 4–5 days back, the structure of a coherent plume can be lost. Without the simultaneous analysis of trace gases, back-trajectories by themselves cannot accurately describe FT/BL mixing.

**Boundary Layer vs. Free Troposphere Water Vapor Criterion**

For the purposes of this analysis, we assumed a water vapor criterion to distinguish between FT and BL air based on work by Ambrose et al. (2011) who compared nearby sounding data to MBO water vapor distributions. The FT/BL water vapor criterion established by Ambrose et al. (2011) for each season is: DJF = 3.28 g kg⁻¹, MAM = 3.28 g kg⁻¹, JJA = 5.40 g kg⁻¹, and SON = 4.12 g kg⁻¹. Above this water vapor criterion, an air mass sampled at the MBO summit is considered to be BL-influenced, while below this criterion, an air mass is considered to be FT-influenced. For our analysis, we have interpolated between the seasonal values given above into a monthly criterion and used this to distinguish between FT and BL air (Table S1).

**Statistical Methods**

We used a one-way ANOVA and a multiple comparison analysis to determine the significance of each cluster identified by the HYSPLIT cluster analysis. All clusters were determined to be significantly different (p-value ≤ 0.05) using the one-way ANOVA. However, not all clusters have significantly different tracer mixing ratios (i.e., CO₂, water vapor, O₃, and pressure). A more detailed discussion of these results can be found in the Cluster Analysis section.

**RESULTS AND DISCUSSION**

**3-Year Overall Analysis**

Fig. 1 shows the average monthly CO₂ mixing ratios at MBO. The average monthly CO₂ mixing ratios at MBO are separated between BL (blue circles) and FT (red squares) values based on the water vapor criterion presented previously. As observed by others before, minimum CO₂ mixing ratios for both BL and FT averages occur each year during either summer or fall when there is the most drawdown of CO₂ by vegetation near the surface, while maximum CO₂ mixing ratios occur during early spring due to a buildup of CO₂ (via respiration, fuel burning, etc.) (Keeling et al., 1976; Thoning et al., 1989; Tans et al., 1990; Lloyd et al., 2002; Gurk et al., 2008; Ramonet et al., 2010; Shashkov et al., 2011; Brooks et al., 2012; Haszpra et al., 2012). For 2013 and 2014, the peak-to-peak amplitude of the CO₂ seasonal cycle (highest monthly mean – lowest monthly mean) at MBO is 8.07 and 8.45 ppmv, respectively.

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*Fig. 1. MBO Average Monthly CO₂* Average monthly CO₂ mixing ratios at Mt. Bachelor Observatory distinguished between Boundary Layer (BL) and Free Troposphere (FT) by the water vapor criterion for 2012–2014. Monthly BL values are shown by blue circles while FT values are shown by red squares.
In 2012, we see lower mixing ratios of CO\(_2\) in the BL compared with FT during the summer. However, in 2013 we see similar summer BL and FT mixing ratios, and in 2014 we see higher mixing ratios in the summer BL compared with the FT. To explain this, we look at the average O\(_3\), CO, and aerosol scattering concentrations in the BL versus FT for each month between 2012 and 2014 (see Fig. S1). In Fig. S1, summer 2012 data shows a higher average CO mixing ratios in the FT compared to the BL. In the summer of 2014, however, both CO and aerosol scattering are higher on average in the BL versus in the FT. This suggests a significant fire influence in 2014 which affected the average CO\(_2\) mixing ratio in the 2014 summer months. We can also compare these results with Fig. 5 in Sweeney et al. (2015). Within this figure, Sweeney et al. (2015) shows annual climatological CO\(_2\) vertical profiles from 16 sites in the NOAA/Earth System Research Laboratory (ESRL) Global Greenhouse Gas Reference Network Aircraft Program. We can compare specifically with the Trinidad Head (THD) site, which is nearest to MBO. When looking at the deviation of CO\(_2\) from the deseasonalized trend at Mauna Loa Observatory (MLO), we see that MBO correlates well with west coast sites like THD (average difference in monthly BL vs. FT CO\(_2\) is \(\pm\) 0.5% for all months). A correlation between MBO and west coast sites like THD suggest the BL seasonal cycle is less pronounced at MBO compared with sites further inland due to marine influences.

Annual average CO\(_2\) mixing ratios at MBO are increasing by 1.48 ppmv per year based on our short record. Fig. 2 compares the average monthly CO\(_2\) mixing ratios at MBO with two other mountain sites: MLO in Hawaii, U.S.A. (19.54°N, 155.58°W, 3397 m asl) and The High Altitude Station at Jungfraujoch (JFJ) in Switzerland (46.548°N, 7.984°E, 3450 m asl). MLO is operated by NOAA’s ESRL: Global Monitoring Division (GMD) (Tans and Keeling, 2015). The High Altitude Station at JFJ is operated by the International Foundation High Altitude Research Stations: Jungfraujoch and Gornergrat (HFSJG) (Leuenberger, 2015). Fig. 2 shows that the summer minimum of CO\(_2\) is shifted earlier at MBO and JFJ compared with MLO. Sweeney et al. (2015) discusses a significant temporal lag at MLO relative to BL observations in North America. This offset highlights an earlier summer CO\(_2\) minimum for high latitude sites in North America compared with MLO. Based on our data in Fig. 2, both sites, MBO and JFJ, show an earlier summer CO\(_2\) minimum compared with MLO. Overall, both MLO and JFJ show a statistically significant correlation (p-value \(\leq\) 0.05) with MBO CO\(_2\) mixing ratios.

**Average Diurnal Variations of CO\(_2\) at MBO**

Fig. 3 shows the average diurnal CO\(_2\) and water vapor mixing ratios and number of hours of FT and BL air for each season at MBO between 2012 and 2014. From Fig. 3, we can discern that average CO\(_2\) mixing ratios peak at night and into morning hours (20-8 PST), while minimum CO\(_2\) mixing ratios occur in mid- to late evening (12-20 PST). MBO shows this consistent diurnal pattern independent of season, unlike JFJ where the diurnal pattern shifts with the seasons (Sturm et al., 2013). A more consistent diurnal pattern at MBO suggests that MBO receives more marine-influence, background air than JFJ. The peak in CO\(_2\) usually coincides with low water vapor mixing ratios and, therefore, (based on our water vapor criterion) more hours in the FT. This indicates a higher mixing ratio of CO\(_2\) in the FT, consistent with Font et al. (2010), Gurk et al. (2008), and Haszpra et al. (2012). Highest FT CO\(_2\) mixing ratios occur during winter and spring. This is consistent with a buildup of CO\(_2\) in the FT during spring because of less draw down near the surface in winter and spring (Gurk et al., 2008; Haszpra et al., 2012). Lowest FT CO\(_2\) mixing ratios occur during summer.
Fig. 3. Average Diurnal CO₂ and Water Vapor Mixing Ratios at MBO for All Seasons in 2012–2014

Graphs are distinguished by season: (a) Winter (DJF), (b) Spring (MAM), (c) Summer (JJA), and (d) Fall (SON). Data in each graph are hourly averages over 2012–2014 at MBO. Average hourly CO₂ mixing ratios are shown by blue circles and water vapor mixing ratios are shown by green triangles. Number of hours in the FT or BL for each season is shown by bars in transparent purple and solid red, respectively. Each bar represents the sum of the number of hours in either the FT or BL for each overall seasonal hour at MBO. Average nighttime hours during each season are shaded grey.

During summer and fall with lofted air that has been near the surface recently where CO₂ is being removed. Winter and fall show a much smaller diurnal variation in CO₂ (ΔCO₂ are 0.40 ± 0.10 and 1.26 ± 0.22 ppmv, respectively) and water vapor due to reduced uptake in the BL and greater atmospheric mixing. Spring and summer show the largest diurnal variations (ΔCO₂ are 3.23 ± 0.29 and 2.56 ± 0.26 ppmv, respectively) due to uptake and respiration by vegetation. Over the whole year, minimum CO₂ mixing ratios usually coincide with high water vapor mixing ratios and, therefore, more hours in the BL. These time periods usually include daytime upslope flow to the summit from the more moist BL air. CO₂ mixing ratios are lower in the BL due to vegetation uptake near the surface with the lowest mixing ratios during summer (which is when vegetation has its maximum uptake of CO₂). Note that these seasonal averages smooth out any pollution source observed at MBO affecting either FT or BL air. Case studies will be provided for specific pollution/transport events observed at MBO and their corresponding CO₂ response.

Cluster Analysis of Back-Trajectories Originating at Mt. Bachelor

Fig. 4 shows clusters for back-trajectories in April and May (AprMay) from 2012 through 2014. We focus on spring clusters because each cluster was found to be unique and statistically relevant, whereas, clusters in other seasons were either not found to be statistically relevant or did not
provide new conclusions. AprMay contained 1,647 back-trajectories (with none excluded) from the cluster analysis. Only trajectories between 20 and 4 PST (nighttime) were used for this analysis. Since FT/BL exchange is difficult to characterize in back-trajectories, we only used nighttime trajectories to better understand FT patterns (downslope flow and FT conditions dominate nighttime data). All clusters were determined to be significantly different (p-value \( \leq 0.05 \)) using a one-way ANOVA.

For AprMay, the clusters are ordered from highest average CO2 (cluster 1) to lowest (cluster 5). Figs. S2 and S3 also show height and average trajectory maps for each cluster, respectively. By choosing April and May for these clustered trajectories, we increased the likelihood of influence by mid-latitude cyclones and the Pacific High Pressure system that circulates air off the Pacific coast (Stohl et al., 2002; Liang et al., 2004; Zhang et al., 2008). Cluster 1 shows relatively high CO2, O3, and pressure and low average water vapor. This cluster includes a smaller number of individual trajectories, but does reflect an important pattern for CO2. This pattern includes events with long-range transport of anthropogenic pollution due to the high average CO2 and O3 mixing ratios indicating anthropogenic pollution and low water vapor indicating FT transport. Cluster 1 is likely associated with subsidence in the Pacific High Pressure system. High O3 and low water vapor mixing ratios also suggest mixing with upper tropospheric/lower stratospheric (UT/LS) air. In Cluster 1, water vapor and O3 were determined to be significantly different from all other clusters based on the multiple comparisons test (p \( \leq 0.05 \)). In contrast, Cluster 5 shows an average air mass with low CO2 and O3 mixing ratios along with high water vapor. This would suggest that the average trajectory in this cluster was associated with BL transport that removed CO2. This assumption is consistent with the height and trajectory figures (BL, upslope flow near MBO). For AprMay, CO2 was determined to be significantly different from all other clusters. Cluster 3 is similar to cluster 5 except with higher CO2 mixing ratios. This suggests that cluster 3 experienced less CO2 uptake, which is consistent with this trajectory being mostly marine-influenced. Clusters 2 and 4 are similar; however, higher CO2 mixing ratios in cluster 2 could be caused by more FT influence. Overall, for higher CO2 mixing ratios, we tend to see higher O3 and lower water vapor mixing ratios indicating anthropogenic emissions and long-range FT transport.

**Case Study: Asian Long-Range Transport Event at MBO – 4/19/2014**

Typically during spring, trans-Pacific transport of pollutants to the western U.S. is at its maximum, which brings high concentrations of CO2 from emission sources in Asia (Jaffe et al., 1999; Stohl et al., 2002; Liang et al., 2004; Jaffe et al., 2005; Zhang et al., 2008; Fischer et al., 2009; Lin et al., 2012; Gratz et al., 2015). It is interesting to note that in the AprMay case, cluster 1 includes a case of FT Asian long-range transport with subsidence of the air mass to MBO. Fig. 5 shows a typical Asian Long-Range Transport (ALRT) event seen at MBO on April 19, 2014. During this event, a significant increase in CO2 (approximately 10 ppmv in 5 hours) is accompanied by an increase in CO, aerosol scattering and O3 along with a decrease in water vapor. With a CO enhancement of approximately 90 ppbv, this gives a with fossil fuel emissions (Suntharalingam et al., 2004). Back-trajectories and data are given in Fig. S4 and Table S2, respectively. Fig. S4 indicates low elevation transport over Asia for several days then lofting of the air mass into the FT for transport to MBO. This is consistent with the
Fig. 5. Case Study: Asian Long-Range Transport at MBO – 4/19/2014 A specific case of Asian Long-Range Transport (ALRT) at MBO is shown. All values are hourly averages. CO₂ is shown in blue, CO in red, O₃ in yellow, aerosol scattering in black, and water vapor in green. The same style is used for all other case study figures unless otherwise specified.

Case Study: Wildfire with CO₂ Enhancement in the BL – 8/28/2014

Fig. 6 shows a wildfire event observed at MBO on August 28, 2014. (No ozone data were available for this event.) Very high mixing ratios of CO₂, CO, aerosol scattering, and water vapor are observed at MBO during this fire event. The CO₂ enhancement during this fire event was approximately 40 ppmv, while the aerosol scattering and CO enhancement were approximately 3500 Mm⁻¹ and 4500 ppbv, respectively. This gives a CO₂/CO enhancement ratio of 8.9. Wildfires have average CO₂/CO enhancement ratios of approximately 5–20 for all fires, or approximately 12 for temperate forest fires (Akagi et al., 2011). Thus, our enhancement ratio of 8.9 is similar to the ratio for temperate fires. The high water vapor mixing ratio suggests BL transport, which is consistent with the back-trajectories. Aqua MODIS imaging confirm a fire in southwest Oregon associated with a very large plume (Figs. S5 and S6, MODIS fire detection and imagery, respectively). All back-trajectories also encounter this plume (Fig. S7). In this case, the wildfire plume was very concentrated, and the CO₂ enhancement was sufficiently large to be seen above any variations due to FT/BL exchange.

Case Study: Wildfire/Pollution Event without a CO₂ Enhancement in the BL – 5/9/2013

Fig. 7 shows an example of a wildfire/pollution case observed on May 9, 2013. In this pollution event, CO₂ and O₃ decrease while CO and water vapor increase. Aerosol scattering is also correlated with CO and anti-correlated with CO₂ during this event. Back-trajectories for this event reveal a path extending back through eastern Oregon, Idaho, and into Montana where the air mass could have encountered a few small fires or local pollution (Back-trajectories and MODIS fire detection are shown in Figs. S8 and S9, respectively). These trajectories also passed over a very large forested area. This would suggest a loss of CO₂ and O₃ combined with a local pollution source. This type of event shows that not all fire/pollution events will correspond to an increase in CO₂ if the enhancement is modest compared to the FT/BL variations.

Case Study: Wildfire with CO₂ Enhancement in the FT – 8/31/2012

Fig. 8 shows a FT wildfire event observed at MBO on August 31, 2012, that had an appreciable increase in CO₂. During this fire event, water vapor decreases (showing a descent from the FT to the MBO summit), while CO₂, CO, O₃, and aerosol scattering increase simultaneously. CO is also significantly enhanced compared to the typical FT values for summer (average background CO is approximately 100 ppbv at MBO). Back-trajectories confirm a synoptic influence and subsiding FT air that has passed over a fire located in southwest Oregon (Fig. S10). Aqua MODIS imaging also confirm the fire plume and event in southwest Oregon (Fig. S11). Considering that the normal response of FT subsidence at the MBO summit is an increase in CO₂, how can we distinguish between an enhancement of CO₂ due to the fire event and a normal increase in CO₂ mixing ratios when there is an exchange of BL to FT air? We calculated the median FT enhancement (relative to the BL) in CO₂ for all August data to be 1.49 ± 0.59 ppmv. For this particular fire event, the total enhancement of CO₂ was 6.26 ± 1.55 ppmv. This indicates that approximately 4.77 ppmv decrease in water vapor seen at MBO (< 1.5 g kg⁻¹) during the event. All components for the April 19, 2014 event are indicative of ALRT.
Fig. 6. Case Study: Wildfire with CO2 Enhancement in the BL – 8/28/2014 A specific case of enhanced CO2 in the BL associated with transport of a biomass burning plume to MBO is shown. All values are hourly averages. O3 data were not available during this event.

Fig. 7. Case Study: Wildfire/Pollution Event without a CO2 Enhancement in the BL – 5/9/2013 A specific case of polluted air transported to MBO shows a decrease of CO2 inside the plume. All values are 5-minute averages.
of CO2 was most likely enhanced due to the fire plume. We can also estimate the CO2 enhancement due to fires by using the previously mentioned enhancement ratio. For a CO2/CO enhancement ratio of 12 (typical temperate forest values given by Akagi et al. (2011)) and a CO enhancement of 250 ppbv, we estimate a wildfire enhancement of CO2 of 3 ppmv, which is similar to our calculated value.

CONCLUSIONS

Using data from MBO between 2012 and 2014, we analyzed variations in CO2 from both the FT and BL. Our main conclusions are:

1. At MBO, CO2 mixing ratios are increasing by 1.48 ppmv of CO2 year⁻¹ with an average annual peak-to-peak amplitude based on monthly means of 8.26 ppmv.
2. The seasonal cycle at MBO shows a similar pattern compared with other mountain-top observatories (Mauna Loa Observatory (MLO) and Jungfraujoch (JFJ)). However, the data from MBO and JFJ are more similar in that both show an earlier summer CO2 minimum compared with MLO (Sweeney et al., 2015).
3. The diurnal pattern of FT/BL air at MBO shows that, on average, FT air has a higher mixing ratio of CO2 than BL air. In all seasons, FT air was most often seen at night and during the early morning at MBO (20-8 PST), while BL air was most often observed during the afternoon and evening (12-20 PST). Winter shows the least diurnal amplitude due to minimal CO2 uptake in the BL, while spring and summer show the largest diurnal amplitude due to greater BL uptake. Winter and spring show the highest mixing ratios of CO2, while summer and fall show the lowest mixing ratios of CO2.
4. Based on the HYSPLIT cluster analysis of nighttime spring trajectories, we determined that for high CO2 mixing ratios, we tend to observe higher O3 and lower water vapor mixing ratios indicative of long-range, FT transport. Conversely, for low CO2 mixing ratios, we tend to observe lower O3 and higher water vapor mixing ratios with higher pressure. Low CO2 mixing ratios for these events suggest BL transport and uptake of CO2.
5. Three wildfire cases were observed with and without an enhancement in CO2. The event without CO2 enhancement suggests that not all wildfire/pollution events will correspond to an increase in CO2 if the enhancement is modest compared to the FT/BL variations. Additionally, the estimated CO2 enhancements due to wildfire emissions are consistent with known CO2/CO enhancement ratios (Suntharalingam et al., 2004; Akagi et al., 2011).
6. One case study showed a specific example of enhanced CO2 associated with Asian long-range transport (ALRT). This event was observed in the cluster with higher O3 and lower water vapor mixing ratios, corresponding to high CO2 mixing ratios. The CO2/CO enhancement ratio for this event is consistent with fossil fuel emissions (Suntharalingam et al., 2004) and back-trajectories provide
corroboration, indicating low elevation transport over Asia before FT transport to MBO.

While this work provides information on FT/BL mixing ratios of CO₂, continued long-term observations at sites like MBO will allow us to determine sources and sinks of CO₂ through the acquisition of transport and vertical profile data for a better understanding of the carbon cycle. Future research at MBO, and sites like it, to address sources and sinks of carbon cycling should include: C-isotope measurements to identify sources, better understanding of surface exchange, and chemical tracer analysis of wildfire events.

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SUPPLEMENTARY MATERIALS

 Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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