The impact of the afternoon planetary boundary-layer height on the diurnal cycle of CO and CO_2 mixing ratios at a low-altitude mountaintop

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Abstract: Mountaintop trace-gas mixing ratios are oftentimes assumed to represent free-atmospheric values, but are affected by valley planetary boundary-layer (PBL) air at certain times. We hypothesize that the afternoon valley-PBL height relative to the ridgetop is important in the diurnal cycle of mountaintop trace-gas mixing ratios. To investigate this, we use, 1) four-years (1 January 2009 – 31 December 2012) of CO and CO_2 mixing-ratio measurements and supporting meteorological observations from Pinnacles (38.61 °N, 78.35 °W, 1017 m a.s.l.), which is a monitoring site in the Appalachian Mountains, 2) regional O_3 mixing-ratio measurements, and 3) PBL heights determined from a nearby sounding station. Results reveal that the amplitudes of the diurnal cycles of CO and CO_2 mixing ratios vary as a function of the daytime maximum valley-PBL height relative to the ridgetop. The mean diurnal cycle for the subset of days when the afternoon valley-PBL height is at least 400 m below the ridgetop shows

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a daytime CO mixing-ratio increase, implying the transport of PBL air from the valley to the mountaintop. During the daytime, on days when the PBL heights exceed the mountaintop, PBL dilution and entrainment cause CO mixing ratios to decrease. This decrease in CO mixing ratio, especially on days when PBL heights are at least 400 m above the ridgetop, suggests that measurements from these days can be used as with afternoon measurements from flat terrain in applications requiring regionally-representative measurements.

Keywords: Carbon dioxide; Carbon monoxide; Mountaintop monitoring; Planetary boundary-layer height

1 Introduction

Mixing processes within the planetary boundary layer (PBL) affect the exchange of heat, moisture, momentum, trace gases, and aerosols between the Earth's surface and adjacent free atmosphere (e.g. Stull 1988). The PBL height represents the height to which these turbulent mixing processes occur. Over flat terrain and assuming a higher trace-gas mixing ratios in the PBL than in the overlying free atmosphere, growth of the daytime PBL causes free atmospheric air to be entrained into the PBL, causing mixing ratios of passive trace gases to decrease (e.g. Pochanart et al. 2003, Elanksy et al. 2007, Popa et al. 2010, Pal 2014, Pal et al. 2015, Berhanu et al. 2016, Chandra et al. 2016, Sreenivas et al. 2016). For this reason, the PBL height is an essential parameter describing the vertical mixing of trace gases and pollutants in air quality dispersion studies (e.g. Dabberdt et al. 2004, Koffi et al. 2016).

Over mountaintops, the relationship between PBL height and the diurnal cycle of aerosols and trace gases is more complex because of local and mesoscale transport processes occurring in these areas (e.g. Rotach and Zardi, 2007, van der Molen and Dolman, 2007, De Wekker et al.

2009, Steyn et al. 2013, Pal et al. 2014, 2016). Thus, the diurnal cycle of trace-gas species, assuming that there are no local sources or sinks affecting the trace-gas mixing ratio, is governed by the trace-gas mixing ratio over the surrounding lower terrain via vertical and horizontal mixing. Consequently, the diurnal trace-gas cycle over mountaintops is much different than over flat terrain. In situations when the valley-PBL top remains below the mountaintop, there is oftentimes no clear diurnal trace-gas cycle. In these situations, mountaintop trace-gas mixing ratios are often assumed to be representative of free-atmospheric mixing ratios, as has been shown in trace gas and aerosol observations from tall mountaintops (e.g. Baltensperger et al. 1997, Lugauer et al. 1998).

In other situations, PBL air in adjacent valleys has a significant impact on the mountaintop trace-gas cycle. During the daytime, polluted PBL air from within the valley is transported to the mountaintop via growth of the valley PBL and thermally-driven upslope flows. Previous studies have found that these processes influence the diurnal cycle of carbon dioxide (CO_2) mixing-ratios observed at nearby mountaintops (e.g. Keeling et al. 1976, Thoning et al. 1989, De Wekker et al. 2009) and affect the presence of the daytime minimum CO_2 mixing-ratio (e.g. De Wekker et al. 2009; Pal et al., 2017). Other trace gas and aerosol species exhibit an increase in mixing-ratio at mountaintop sites due to the arrival of valley-PBL air at the mountaintop via growth of the valley PBL and thermally-driven upslope flows. The observed increase has been reported for many trace-gas species, including carbon monoxide (CO) (e.g. Weiss-Penzias et al. 1996, Forrer et al. 2000, Lin et al. 2011, MacDonald et al. 2011), ozone (O_3) (e.g. Sullivan et al. 2016), methane (e.g. Necki et al. 2003; Bamberger et al. 2017), gaseous mercury (e.g. Obrist et al. 2008), as well as aerosols (e.g. Baltensperger et al. 1997, Bukowiecki et al 2016). The amplitude and timing of this increase vary seasonally. The increase is typically largest during the summer when the valley PBL is deep and exceeds the mountaintop height, but may be non-existent during the winter when the valley PBL is very shallow and remains below the mountaintop. In the latter scenario, the mountaintop remains in the free atmosphere throughout the day (e.g. Baltensperger et al. 1997, Lugauer et al. 1998, Henne et al. 2008a, Henne et al. 2008b). Oftentimes, there is a corresponding night-time decrease in CO mixing ratio (e.g. Gao et al. 2005, Balzani Lööv et al. 2008, Henne et al. 2008b) and aerosols (e.g. Baltensperger et al. 1997, Bukowiecki et al 2016) because sinking motions transport free-atmospheric air to the mountaintop (e.g. Schmidt et al. 1996).

Identifying representative measurements is important for a number of applications including, e.g. atmospheric chemistry studies (e.g. Novelli et al. 1998), air quality studies (e.g. Dabbert et al. 2004), and carbon cycle studies (e.g. Andrews et al. 2014). One of the simplest filtering approaches is to remove measurements made during the daytime and only assimilate night-time measurements from mountaintops (e.g. those made between 0000 and 0400 local standard time [LST]) into these applications (e.g. Peters et al. 2010). The major assumption of this approach is that night-time measurements made at mountaintops are representative of the free atmosphere (e.g. Schmidt et al., 1996). In addition to filtering trace-gas measurements by time of day, statistical filtering techniques, e.g. removing outliers, using low-pass filters (e.g. Thoning et al. 1989), filtering measurements made when there are strong local vertical trace-gas gradients and excessive hourly variances present in the measurements (e.g. Brooks et al. 2012), have been developed to identify regionally-representative trace-gas measurements. Meteorological analyses have also been used to identify measurements affected by local sources, including performing trajectory analyses to identify source regions of elevated trace-gas mixing ratios (e.g. Forrer et al. 2000, Zellwegger et al. 2003), and distinguishing between upslope and downslope flows using in situ meteorological measurements (e.g. Henne et al. 2008a). However, to the best of our knowledge, no study has used knowledge of daytime PBL heights to identify regionally-representative trace-gas measurements from mountaintops.

Following the aforementioned studies, one may hypothesize that the diurnal trace-gas cycle at mountaintops depends on the maximum daytime PBL height in the adjacent low-lying terrain relative to the ridgetop height. This dependency can then be used in helping identify regionally-representative mountaintop trace-gas measurements. Recent studies have begun to address this hypothesis using mountaintop CO mixing ratio and accompanying in situ meteorological measurements. Lee et al. (2015) found that, for a mountaintop site in north-western Virginia, USA, referred to as the Pinnacles site, CO mixing ratios decreased during the daytime on clear fair weather days. Pollutants contained within the valley PBL arrived at the mountaintop in these cases, but PBL mixing and dilution effects produced a decrease in mountaintop CO mixing ratios.

In the present study, we follow up on these analyses by investigating how these mountaintop trace gas changes depend on the daytime maximum PBL height relative to the ridgetop height. We address this question for both CO and CO_2 mixing ratios and use four years of measurements accompanied by collocated meteorological measurements from the Pinnacles site and also meteorological measurements from surrounding locations. These measurements allow for a process-based study, rather than a climatological overview of the trace-gas measurements at the Pinnacles site that previous studies have provided (i.e. Lee et al. 2015). The Pinnacles site is an ideal location to investigate the influence of the PBL height relative to the ridgetop on the observed trace-gas cycle because the PBL height can either be well below or well above the ridgetop (e.g. Lee and De Wekker 2016). Furthermore, the CO_2 mixing-ratio measurements from the Pinnacles site are currently used to estimate regional- to continental-scale carbon fluxes in CarbonTracker, an inverse carbon transport model that assimilates observations from regionally-representative trace-gas monitoring sites located in flat terrain (e.g. Peters et al. 2007) and at mountaintops (e.g. Lin et al. 2017). Careful selection of trace-gas measurements and their degree of representativeness from sites such as Pinnacles is necessary to improve the surface fluxes calculated by these models.

2 Site Description and Datasets

2.1 Site Description

The Pinnacles site (38.61 °N, 78.35 °W, 1017 m above sea level (a.s.l.)) is a mountaintop site with a 17-m tower from which meteorological and trace-gas measurements have been made since 2008. The site is located in the Virginia Blue Ridge Mountains, which are along the eastern flank of the Appalachians in the eastern USA. The mountain ridge on which the Pinnacles site is located ranges in height from 1000 to 1200 m a.s.l. and is about 800 m above the surrounding valley and plain. The Page Valley, part of the larger Shenandoah Valley, is located west of the Pinnacles site; the Virginia Piedmont is located east of the Pinnacles site. The area immediately surrounding the Pinnacles site is a mixed deciduous forest with a mean canopy height of about 14 m, while the adjacent lowlands are comprised of mixed deciduous forests and cropland. Further details about the site and surrounding region are found in, e.g. Lee et al. (2012) and Lee et al. (2014).

2.2 CO Mixing-Ratio Measurements

CO and CO_2 mixing-ratio measurements at the Pinnacles site began in late August 2008 at 5, 10, and 17 m a.g.l. (above ground level) through a collaboration with the NOAA Earth System Research Laboratory. The measurement system and in situ calibrations have already been described by Lee et al. (2015), and a detailed description of the measurement uncertainties is discussed in Andrews et al. (2014). In the present study, we used 30-min means of the CO and CO_2 mixing-ratio data collected 17 m a.g.l. during the site's first four full years of operation, i.e. 1 January 2009 through 31 December 2012. Much of our focus is on CO mixing ratio rather than CO_2 mixing ratio because, during the growing season, CO_2 mixing ratio is affected both by PBL-dilution and entrainment as well as photosynthetic uptake occurring on site and along upwind forested mountain slopes (e.g. Sun et al. 2007), which complicate the interpretation of the diurnal cycle. Because CO mixing ratio is unaffected by local uptake, it is a more suitable candidate than CO_2 mixing ratio for investigating PBL mixing and transport processes over mountainous terrain.

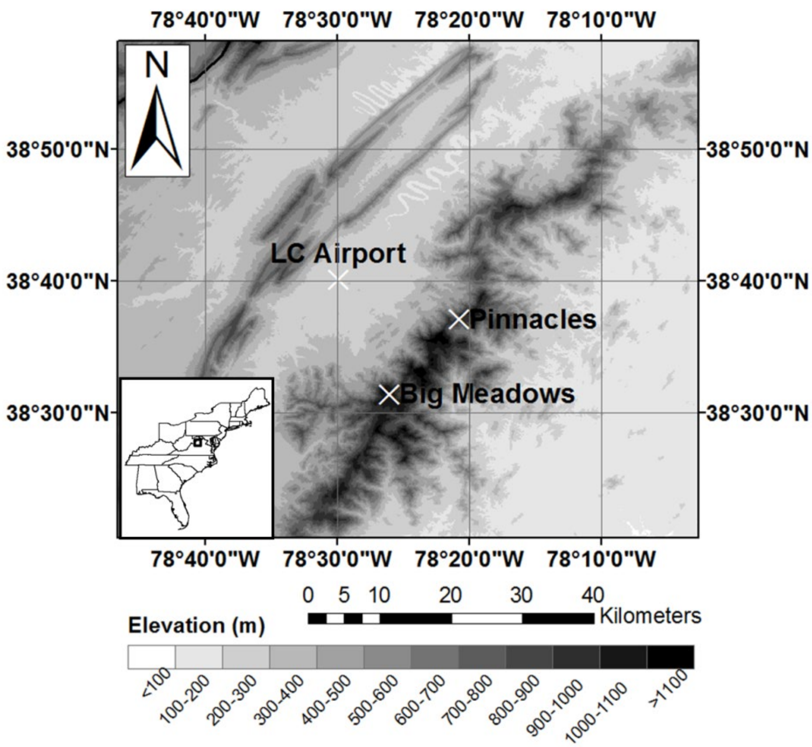

Fig 1 Topographic map indicating the location of the Pinnacles site relative to the Big Meadows site and the Luray Caverns (LC) airport (white X's). Shading shows elevation a.s.l. The inset map at the bottom left indicates the study location, denoted by a black box, in the eastern USA.

2.3 Supplemental Measurements

To help interpret the diurnal CO and CO_2 mixing-ratio cycle, we used supplemental meteorological and trace-gas measurements. Meteorological measurements at the Pinnacles site began in July 2008 and include temperature, humidity, wind speed and direction, rainfall, pressure, incoming and outgoing shortwave and longwave radiative fluxes, and fluxes of sensible heat, latent heat, and CO_2 mixing ratio. In addition to measurements from the Pinnacles site, we used meteorological and trace-gas measurements from nearby monitoring sites. Mountaintop O_3 mixing-ratio measurements were obtained from the Big Meadows site (38.52 °N, 78.44 °W, 1079 m a.s.l.), located on the same ridgeline 14 km south of the Pinnacles site, and from the Page

Valley (Fig. 1) at the Luray Caverns airport (38.66 °N, 78.50 °W, 275 m a.s.l.), located 13 km west of the Pinnacles site. At both the Big Meadows site and the Luray Caverns airport, O_3 mixing ratios were measured 10 m a.g.l. using a Thermo Environmental Instruments Model 49i UV photometric O_3 analyzer that has a 1-ppb precision, a 20-s response time, and span drift of <1%. The data record at the Big Meadows site for the period of interest was mostly complete, although there existed a data gap between late February and April 2010. At the Luray Caverns airport, hourly O_3 mixing ratios were sampled from 1 April through 31 October annually.

3 Methods

3.1 Determining PBL Heights near the Mountaintop

Reliable PBL height estimates over the Page Valley, which is most often upwind of the Pinnacles site based on previous studies of the site's climatology (e.g. Lee 2015; Lee et al. 2015), are required to investigate the role of the valley PBL on the trace-gas cycle at the Pinnacles site. In the Page Valley, there exists no PBL height observations for the entire period of interest. One approach is to assume that PBL heights obtained from a nearby sounding station, where twice-daily rawinsonde observations are made, are representative of the region (e.g. Hondula et al. 2013). However, the spatial variability in PBL heights needs to be carefully assessed when using this approach. Lee and De Wekker (2016) found that mean afternoon PBL heights over the Page Valley are 200-400 m larger than the PBL heights estimated using observations from the nearest sounding station, located at Dulles airport (38.98 °N, 77.49 °W, 87 m a.s.l.) 90 km north-east of the Page Valley. Greater PBL heights over the Page Valley than near Dulles airport arise due to higher terrain and drier conditions in the Page Valley. Accounting for these PBL height differences is necessary to obtain the most reliable PBL height estimates for the Page Valley. Thus, to estimate PBL heights over the Page Valley, we used 0000 UTC (UTC = LST + 5)

Dulles airport rawinsonde observations and followed the approach developed by Lee and De Wekker (2016) to remove the early-evening near-surface stable layer oftentimes present in the sounding. We then calculated the bulk Richardson (R_b) number and determined the afternoon PBL height at Dulles airport as the first height where R_b exceeded a critical threshold, R_c, which we set to 0.25 (Vogelezang and Holtslag, 1996). The approach has been found to yield PBL heights that agree well with afternoon PBL heights obtained from reanalysis products and aircraft observations (i.e. Lee and De Wekker 2016) and has recently been used to develop a climatology of afternoon PBL heights over the contiguous USA (Lee and Pal 2017).

To determine PBL heights over the Page Valley site from the afternoon Dulles Airport PBL height, following Lee and De Wekker (2016), we computed the difference in the daily 2100 UTC PBL height between the grid box in the North American Regional Reanalysis (Mesinger et al. 2006) containing the Page Valley and the grid box containing Dulles Airport for the period 2009-2012. Based on the analyses presented in Lee and De Wekker (2016), we determined a seasonal correction factor that represents the mean difference in PBL height as a function of season (Table 1) and applied this correction to the afternoon PBL heights estimated from the 0000 UTC rawinsonde at Dulles Airport.

3.2 Interpreting Mountaintop Trace-gas Measurements

To help interpret the mountaintop trace-gas diurnal cycles, we subtracted the daily mean from each day before averaging the values together to generate composites. Removing the daily means allows for a better investigation of the dominant physical processes affecting the daily trace-gas cycle on diurnal time scales and removes the major influence of processes affecting trace-gas mixing ratios at longer time scales. For CO_2 mixing ratio, these processes include the seasonal cycle in vegetative photosynthetic uptake and respiration (e.g. Lee et al. 2012), whereas the seasonality of hydroxyl radicals and anthropogenic emissions affects the seasonal cycle in CO mixing ratio (e.g. Thompson et al. 1992; Novelli et al. 1998).

Once we removed the daily means and calculated the standard errors (*SE*), we investigated the role of the PBL height on the diurnal CO_2 and CO mixing ratio cycle for all days, regardless of the presence or absence of a wind-direction shift. Distinguishing between days with wind-direction shifts and days without wind-direction shifts is important because of the role that wind-direction shifts have on the observed trace-gas cycle at the site (Lee et al. 2015). The wind climatology from the site shows a backing from the north-west in the early morning to the south-west during the daytime. This wind-direction shift occurs on a regional scale and is not a result of local, thermally-driven flows. The wind-direction shift has been found to correlate with trace-gas cycle (in particular an increase in CO mixing ratio which makes it difficult to isolate the role of PBL height on the diurnal CO and CO_2 mixing ratio cycle. Thus, following Lee et al. (2015), we also identified days without a wind-direction shift and that also had clear skies, using a clearness index (e.g. Whiteman et al. 1999), and compared these days to the set of days that included cloudy days and days with wind-direction shifts.

Because the uncertainties in monthly PBL height estimates in this region can be as large as 400 m (Lee and De Wekker 2016), we classified days with PBL heights below the ridgetop when the PBL height was at least 400 m below the maximum height of the mountain ridge (1200 m), and we classified days with PBL heights above the ridgetop when the PBL height was at least 400 m above the ridgetop height. Thus, days with PBL heights <800 m a.s.l. and >1600 m a.s.l. were classified as below the ridgetop and above the ridgetop, respectively. Altering these threshold values by ±200 m did not significantly affect the mean diurnal CO or CO_2 mixing-ratio cycles on these subsets of days.

To understand the role of valley-PBL air on the diurnal CO and CO_2 mixing-ratio cycles, we used mountaintop measurements of specific humidity (*q*) and mountaintop and valley measurements of O_3 mixing ratio. We used O_3 mixing ratio and specific humidity measurements since they can be used as tracers of PBL air (e.g. Weiss-Penzais et al. 2006) and because CO and CO_2 mixing-ratio measurements were unavailable from the valley. We computed differences in O_3 mixing ratio between the mountaintop and valley to discern valley-PBL influences on the mountaintop measurements. Large O_3 mixing-ratio differences (e.g. >20 ppb) imply less influence of valley-PBL air on the mountaintop measurements; small O_3 mixing-ratio differences (e.g. ≈ zero) suggest that valley-PBL air reaches the mountaintop and affects the mountaintop trace-gas measurements.

4 Results

4.1 Seasonal PBL Height Cycle

During the four-year period of interest, PBL heights in the 0000 UTC Dulles airport sounding range from <500 m a.s.l. to >2500 m a.s.l. (Fig. 2a). PBL heights range from 500 to 2000 m a.s.l. in the winter, with mean values around 1000 m a.s.l. PBL heights are largest in the spring and summer, when maximum values are around 2300 m a.s.l. The seasonal cycle in PBL heights closely follows the seasonal cycle of sensible heat flux and has been investigated in previous work (Lee and De Wekker, 2016). Afternoon (1200-1600 LST) sensible heat flux computed at the Pinnacles site is typically 50 W m^{-2} in the winter when PBL heights are smallest, but is largest in the late spring and early summer when mean afternoon sensible heat flux is typically around 200 W m^{-2} (Fig. 2b). In the discussion that follows, we consider situations in which the

PBL heights are well below or well above the ridge height, i.e. <800 m a.s.l. and >1600 m a.s.l., respectively. Over the total 4-year period, these situations occurred 24% and 32% of the time, respectively, for all days (i.e. regardless of if the day was cloudy or if there was a wind-direction shift present).

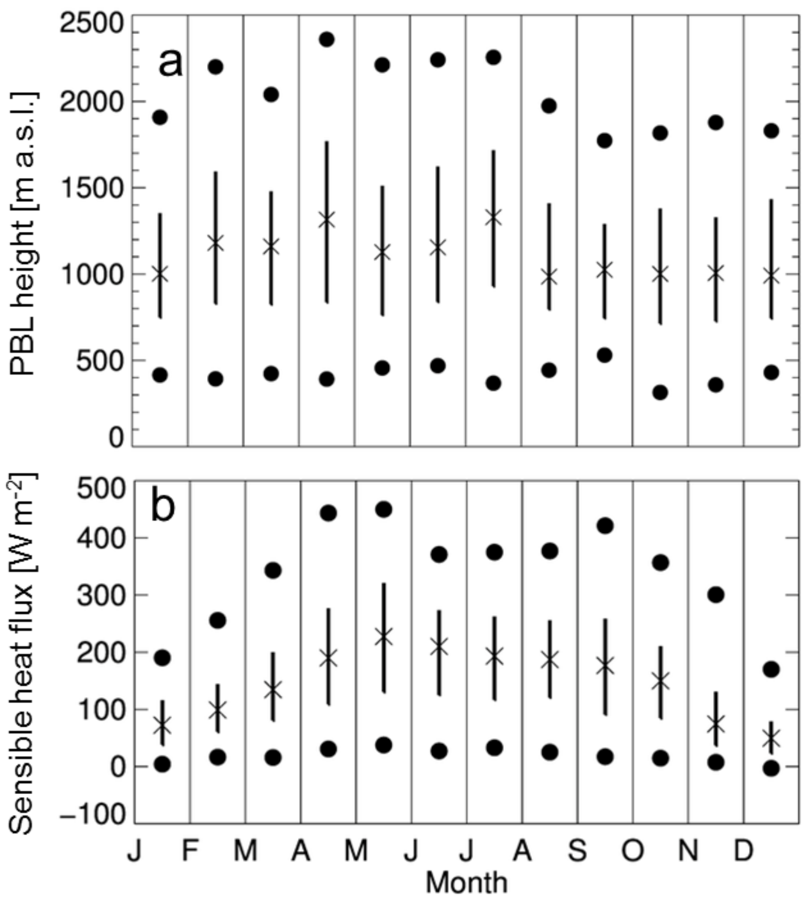

Fig 2 PBL height percentiles, computed over the period 1 January 2009 – 31 December 2012, as a function of time of year after removing the near-surface stable layer from the 0000 UTC Dulles airport sounding following Lee and De Wekker (2016) (a). Panel (b) shows afternoon (1200-1600 LST) the sensible heat flux from the Pinnacles site. X's indicate medians; black bars extend out to the 25th and 75th percentiles. Dots indicate 5th and 95th percentiles. The sensible heat flux is the mean over eight 30-min averages between 1200 and 1600 LST, whereby the first average is from 1200-1230 LST and the final 30-min average is from 1530-1600 LST.

4.2 Overview of CO and CO_2 Mixing-Ratio Measurements

The mean seasonal and diurnal cycles of CO mixing ratio at the Pinnacles site have been described in previous work (Lee et al. 2015), and characteristics of the mean seasonal and diurnal CO_2 mixing-ratio cycle have been described by Lee et al. (2012) and Lee (2015). Briefly, CO mixing ratios are typically highest in March and lowest in October (not shown) which is consistent with findings from other mid-latitude continental monitoring sites (e.g. Popa et al. 2010, Cristofanelli et al. 2013). The mean diurnal CO mixing-ratio cycle at the Pinnacles site is characterized by a daytime CO mixing-ratio increase, which is a common feature of other mountaintop monitoring sites at which valley-PBL air affects mountaintop trace-gas mixing-ratios (e.g. Atlas and Ridley, 1996, MacDonald et al. 2011). The CO mixing-ratio increase occurs in all seasons and has the smallest amplitude in the summer (4.0 ppb) and largest amplitude in the winter (7.1 ppb) (Lee et al. 2015), which is inconsistent with the diurnal CO mixing-ratio cycle at mountaintops taller than Pinnacles (e.g. Forrer et al. 2000, Henne et al. 2008b, Ou-Yang et al. 2014). At mountaintops taller than Pinnacles, deeper PBL heights during the summer than during the winter allow for valley-PBL air to be transported to the mountaintop, causing the largest CO mixing-ratio increases during the summer. Additionally, previous work at the Pinnacles site has found large day-to-day CO mixing-ratio variability which arises due to synoptic scale transport (Lee et al. 2012) and mesoscale circulations (Lee et al. 2015).

In contrast to CO mixing ratio, previous studies on CO_2 mixing ratio at the Pinnacles site have shown that seasonal changes are strongly correlated with seasonal changes in uptake and respiration (Lee et al. 2012). Consistent with other continental locations (e.g. Greco and Baldocchi 1996; Schmidt et al. 2014; Berhanu et al. 2016; Chandra et al. 2016; Sreenivas et al. 2016), mean CO_2 mixing ratios are typically highest in winter and lowest in the summer. On diurnal time scales, there is a daytime decrease caused by local to regional photosynthetic uptake occurring during the growing season. There is also large day-to-day variability in CO_2 mixing ratios due to mesoscale to synoptic scale transport processes that result in hourly CO_2 mixing-ratio changes sometimes exceeding 20 ppm (Lee et al. 2012) which is in agreement with findings reported at other forested mountaintop monitoring sites (e.g. Pillai et al. 2011; Brooks et al. 2012).

4.3 Effect of PBL Height on the Diurnal CO and CO_2 Mixing-Ratio Cycle

4.3.1 CO Mixing-Ratio Diurnal Cycle

We found significant differences in the mean diurnal CO mixing-ratio cycle that depend on, 1) whether the PBL is below the ridgetop or the PBL is above the ridgetop, and 2) whether or not the day is a fair weather day with constant wind directions (Fig. 3). The same diurnal trends are found when computing the medians; in the present paper, we discuss the diurnal trends in the means for consistency with previous work at the site (e.g. Lee et al. 2012, Lee et al. 2015). When all days are considered (i.e. independent of the presence of fair weather conditions or presence of a wind-direction shift at the site), there is a daytime increase in the mean diurnal CO mixing-ratio cycle on days when the PBL height is below 800 m a.s.l. On these days, CO mixing ratios increase from a minimum around 0700 LST to a maximum at 1900 LST (Fig. 3a). In contrast, daytime CO mixing ratios show a small decrease when the PBL height is above 1600 m a.s.l., but both cases show nearly constant CO mixing ratios after 1900 LST that suggest that the mountaintop is sampling air from the residual layer or the free atmosphere.

Notable differences are present when we selected fair weather days with constant wind directions (Fig. 3b), i.e. days on which we expect there to be the largest sensitivity in trace-gas variability to differences in PBL height. Whereas the amplitude of the CO mixing-ratio increase on days when the PBL height is below the ridgetop is comparable between all days and fair weather days with constant wind directions (9.5 ppb vs 9.0 ppb), CO mixing ratios on fair weather days with PBL heights below the ridgetop height decrease following a 1300 LST maximum. Additionally, on days with PBL heights above the ridgetop height, the mean decrease (6.2 ppb) is larger on fair weather days with constant wind directions (c.f. Fig. 3b) than the mean decrease for all days (c.f. Fig. 3a). On these days with a large afternoon decrease in CO mixing ratios, PBL dilution and entrainment cleaner free atmospheric air is likely to be the dominant driver of the diurnal CO mixing-ratio cycle, as shown in recent case studies from the site (Pal et al. 2017). Also, we note that the diurnal changes on these sets of days, including the short-lived peak around 1300 LST on days with a shallow PBL, are much larger than the standard errors.

4.3.2 CO_2 Mixing-Ratio Diurnal Cycle

In the case of CO_2 mixing ratios, there is a decrease during the daytime both on days when the PBL height is below the ridgetop and on days when the PBL height is above the ridgetop, regardless of whether or not fair weather days are considered (Fig. 3c; Fig. 3d). Maximum CO_2 mixing ratios are observed between 0200 LST and 0600 LST, whereas the minimum in CO_2 mixing ratios occurs around 1600 LST. When the PBL is below the ridgetop, the amplitude of the diurnal CO_2 mixing-ratio cycle is 2.5 ppm when all those days are considered, but is 4.8 ppm on fair weather days with constant wind directions. Uncertainties are small on both subsets of days compared with the amplitude of the changes in the mean cycles; standard errors are <0.6 ppm for both subsets of days. In addition, both subsets of days with PBL heights below the ridgetop have a short-lived CO_2 mixing-ratio increase around noon. However, there is no such increase when the PBL exceeds the ridgetop. When all days with PBL heights exceeding the ridgetop are considered, the amplitude of the mean diurnal cycle is 4.6 ppm, but is 6.1 ppm on fair weather days with constant wind directions. We attribute the larger amplitude of the mean diurnal CO_2 mixing-ratio cycle on fair weather days to a combination of mixing within the daytime PBL and also to greater uptake occurring both at the site and along upwind forested mountain slopes, which has been found to explain daytime CO_2 mixing-ratio decreases at other mountaintop sites (e.g. Sun et al. 2007). Night-time CO_2 mixing ratios are characterized by an increase that occurs independently of the daytime maximum PBL height relative to the ridgetop and can be attributed to, e.g. on-site respiration in the growing season.

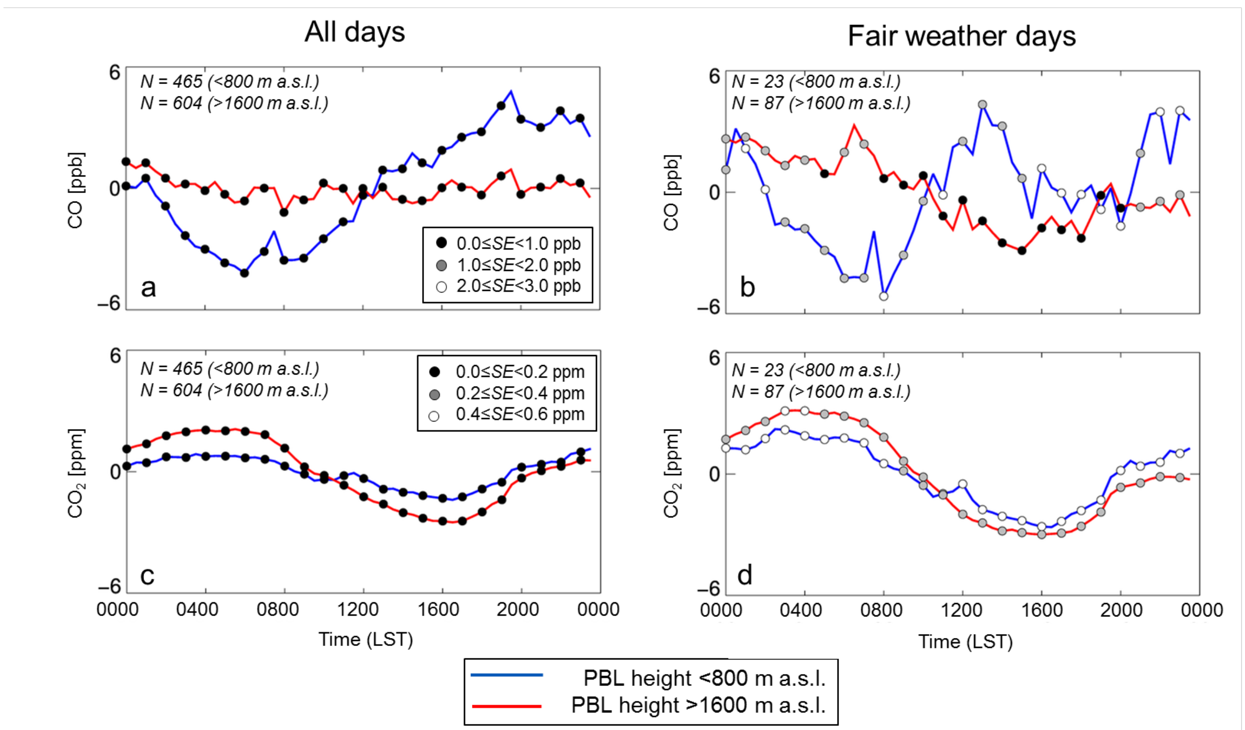

Fig 3 Mean diurnal cycle in CO mixing ratio, measured 17 m a.g.l., for PBL heights <800 m (blue line) and for PBL heights >1600 m (red line) for all days over the period 1 January 2009 – 31 December 2012 (a) and for the subset of fair weather days with constant wind directions (b). Same for panels (c) and (d) but for CO_2 mixing ratio measured 17 m a.g.l. at the Pinnacles site. The number of cases of PBL height <800 m a.s.l. and PBL height >1600 m a.s.l., *N*, is noted in each panel. The circles represent the standard error in the measurements, and the legend for each species is shown on panels (a) and (c). For brevity, the standard error is shown every 60 min rather than every 30 min.

4.3.3 Seasonal Differences between CO and CO_2 Mixing-Ratio Diurnal Cycles

Because the seasonal cycle of CO_2 mixing ratios is strongly affected by photosynthetic uptake and respiration during the growing season, we differentiated between the mean diurnal cycles in the two contrasting seasons (summer and winter) for the subset of days with PBL heights below the ridgetop and for the subset of days with PBL heights above the ridgetop. We found that the amplitude of the diurnal CO_2 mixing-ratio cycle is largest on fair weather days with PBL heights exceeding the ridgetop height during the summer (Fig. 4), whereas diurnal CO_2 mixing-ratio changes are smallest on days with deep PBL heights during the winter (Fig. 5). Most notable, however, is a daytime CO_2 mixing-ratio increase during the winter when the PBL remains below the ridgetop that begins around 1100 LST and leads to maximum CO_2 mixing ratios around 1800 LST (Fig. 5c). A CO_2 mixing-ratio increase is also observed in summer (Fig. 4) but is much less pronounced and shorter-lived than in winter. Regardless of whether the PBL is below the ridgetop or is above the ridgetop, CO and CO_2 mixing ratios closely follow the same cycle during the winter which indicates that, when CO_2 uptake is absent, CO and CO_2 mixing ratios behave as similar tracers of atmospheric dynamics at the site. The similar behaviour of the diurnal CO and CO_2 mixing-ratio cycles during the winter, particularly the daytime CO and CO_2 mixing-ratio increase on days with PBL heights below the mountaintop suggests that they are mainly influenced by polluted air arriving at the mountaintop during the daytime from the adjacent valleys. We hypothesize that its origin can be traced to the upwind adjacent valley; we investigate this hypothesis in more detail in the next section.

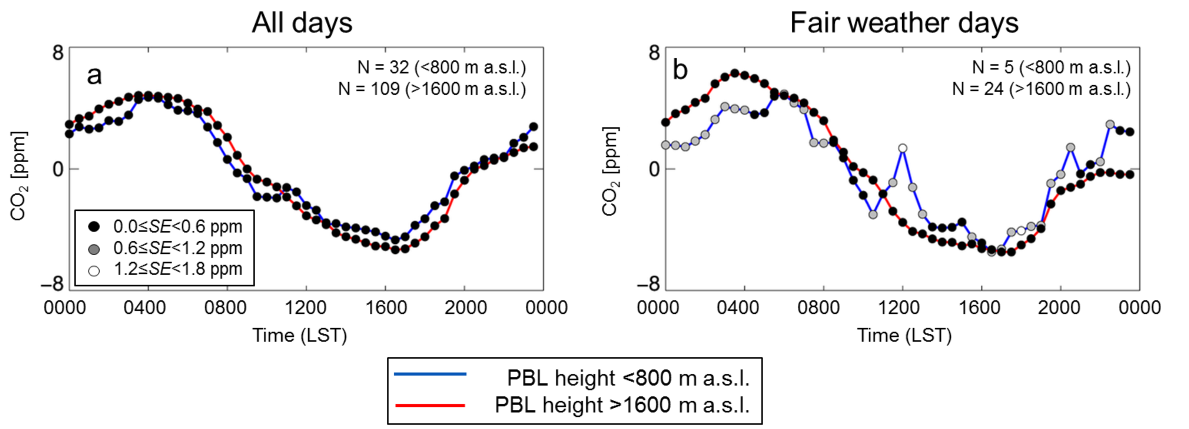

Fig 4 Diurnal CO_2 mixing-ratio cycle for all days (a) and for the subset of fair weather days with constant winds (b) for the summer (1 June – 31 August) months. The circles represent the standard error in the measurements.

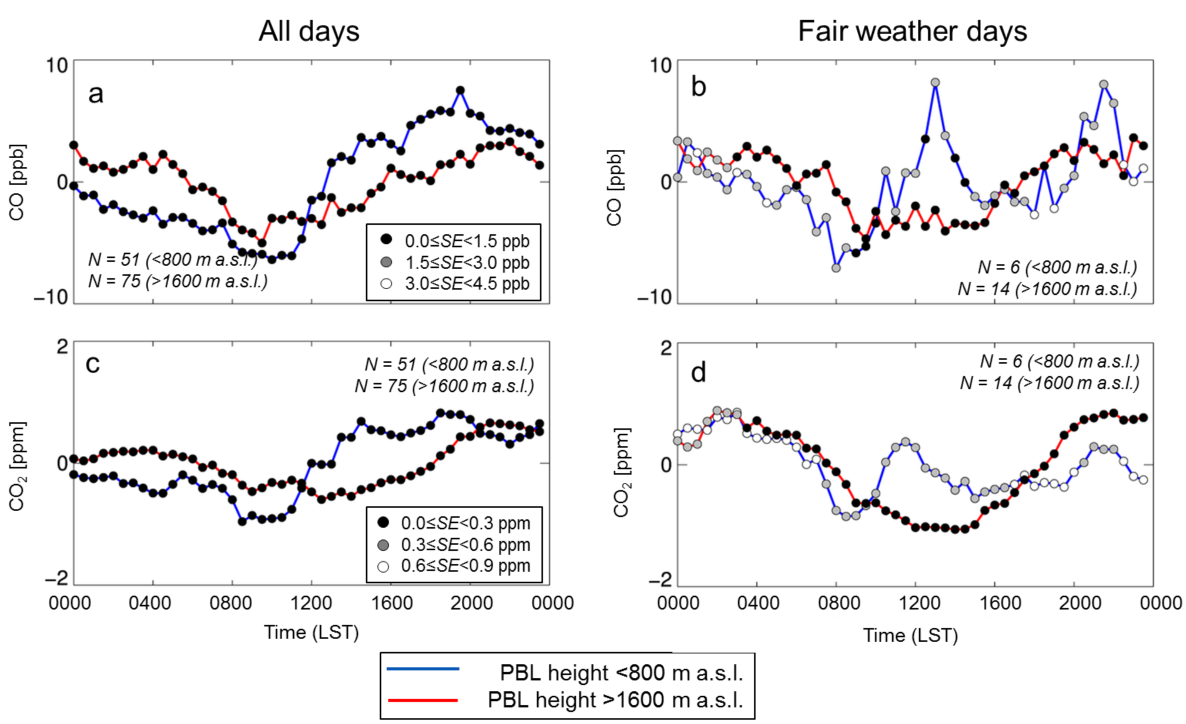

Fig 5 Same as Fig. 3 but only for days during the winter months (1 December – 28 February).

4.4 Indicators of Valley-PBL Air Impacting the Mountaintop Measurements

In the previous section, we discussed the diurnal CO and CO_2 mixing-ratio cycles as a function of PBL height relative to the mountaintop height. These diurnal CO mixing-ratio changes closely follow changes in specific humidity (q) on the subset of fair weather days with constant wind directions for both the subsets of days with PBL heights below the ridgetop and for the subset of days with PBL heights above the ridgetop (Fig. 6b). On days with the PBL height below the ridgetop, the simultaneous CO mixing ratio and specific humidity increases indicate that these days are characterized by vertical transport and mixing of valley-PBL air to the mountaintop (e.g. Weiss-Penzias et al. 2006). Previous studies (i.e. Lee and De Wekker 2016) from the site have found, through the combined use of observations and numerical simulations, that these cases are characterized by a daytime PBL that parallels the underlying terrain. Shallow daytime PBLs that closely parallel the underlying terrain have also been reported in studies involving other mountaintops (e.g. De Wekker 2002; De Wekker and Kossman 2015). The transport of valley-PBL air to the mountaintop within this shallow terrain-following daytime PBL results in a short-lived increase in CO_2 mixing ratio that corresponds with the peak in specific humidity and has been attributed in previous studies at the site to upslope flows (Pal et al. 2017). In contrast, the decrease in passive tracers like specific humidity that accompanies the decrease in CO mixing ratio on days with the PBL height above the ridgetop, as well as the absence of a noontime increase in CO_2 mixing ratio, implies that PBL dilution and entrainment overwhelm the transport of polluted valley-PBL air to the mountaintop via convective mixing and upslope flows.

The relationships between CO mixing ratio and specific humidity, as well as CO_2 mixing ratio and specific humidity, as a function of PBL height relative to the ridgetop are less clear when all days in the period of record are considered (Fig. 6a). When the PBL height is below the ridgetop, both CO mixing ratios and specific humidity increase beginning around 0700 LST, whereas CO_2 mixing ratios decreases (c.f. Fig. 3c). However, specific humidity remains somewhat constant between 1200 LST and 1900 LST, but during this time CO mixing ratios kept increasing and CO_2 mixing ratios decrease (c.f. Fig. 3a, 3c). On fair weather days with constant wind directions and PBL tops below the ridgetop, CO mixing ratios and specific humidity increase after the onset of stable boundary-layer development around sunset to a secondary maximum around 2300 LST (c.f. Fig. 3b, Fig. 6b). In the case of CO_2 mixing ratio, respiration also contributes to the nocturnal CO_2 mixing-ratio increase.

When days with PBL heights above the ridgetop height are considered irrespective of wind-direction shift or the day's clearness index, CO mixing ratio and specific humidity decrease throughout the entire night. However, the amplitude of the CO mixing ratio decrease on the subset of fair weather days with constant wind directions is about 4 ppb larger than the mean CO mixing ratio cycle of all days with PBL heights exceeding the ridgetop height. One possible reason for this larger CO mixing ratio decrease is more pronounced nocturnal downslope flows under fair weather conditions (e.g. Zardi and Whiteman, 2013) which result in a transport of clean free atmospheric air to the mountaintop (e.g. Schmidt et al. 1996).

O_3 mixing ratios at a nearby mountaintop (at the Big Meadows site, located about 14 km south of the Pinnacles site but at a similar elevation; see Section 2.3) and a valley site also show significant differences in their diurnal cycles that depend on 1) whether or not the day is a fair weather day, and 2) PBL height (Fig. 6c, 6d, 6e, 6f). At the mountaintop, the amplitude in the diurnal O_3 mixing-ratio cycle is larger on fair weather days with PBL tops exceeding the ridgetop height (Fig. 6c, 6d). In contrast, the amplitude of the diurnal O_3 mixing-ratio cycle at the valley site is largest on fair weather days with PBL tops below the ridgetop (Fig. 6f) due to an increase in pollutant mixing ratios within a shallow PBL that favors O_3 production. Also note that the amplitude of the diurnal O_3 mixing-ratio cycle in the valley is much larger than at the mountaintop (cf. Fig. 6e, 6f and Fig. 6c, 6d).

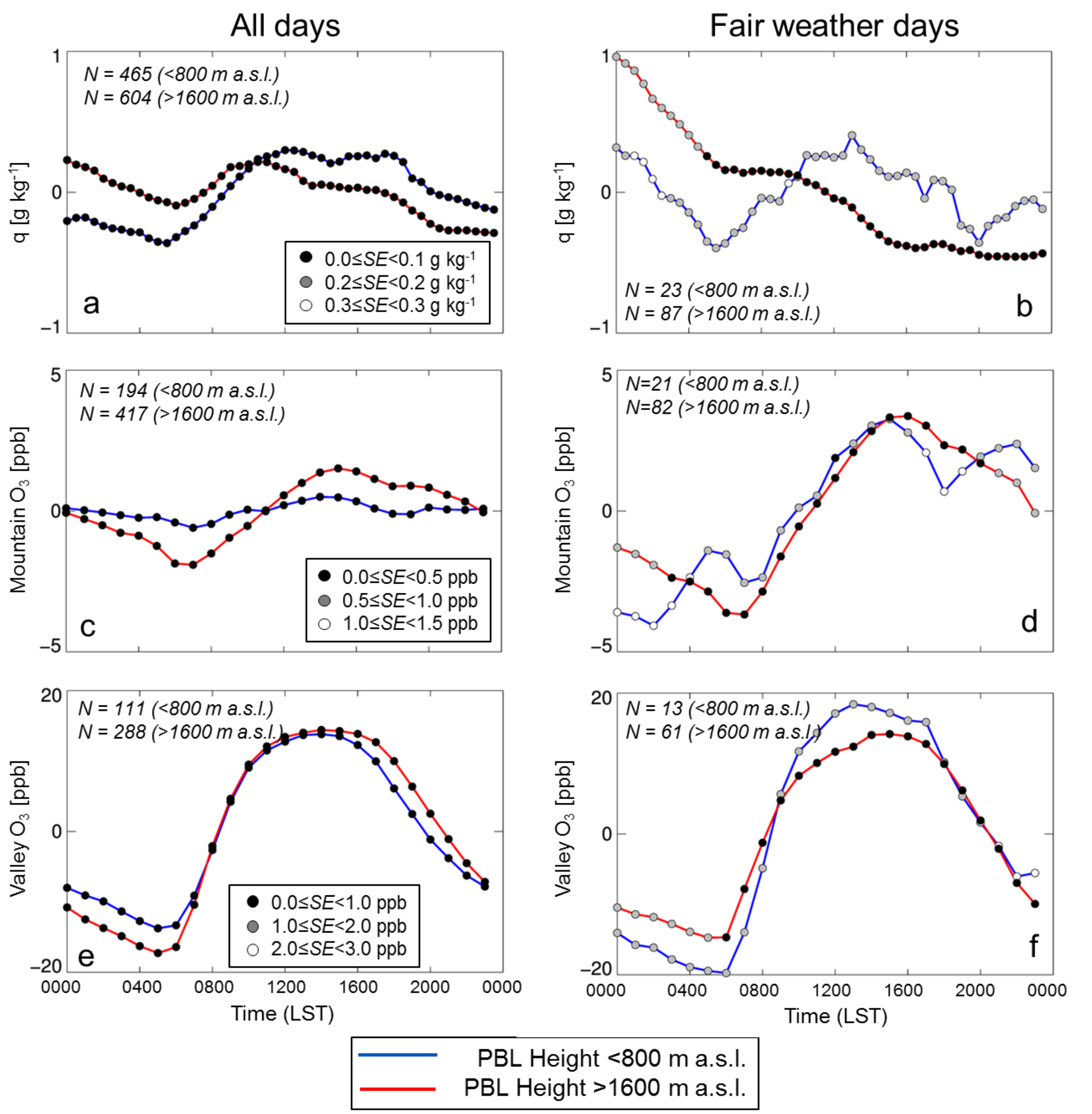

Fig 6 Mean diurnal cycle in specific humidity, measured 17 m a.g.l., for PBL heights <800 m (blue line) and for PBL heights >1600 m (red line) for all days (a) and for the subset of fair weather days with constant wind directions (b) independent of season for 1 Jan 2009 – 31 Dec 2012. Panels (c) and (d) show O_3 mixing ratio at the mountaintop

(the Big Meadows site), and panels (e) and (f) show O_3 mixing ratio at the valley site (Luray). The number of cases of PBL height <800 m a.s.l. and PBL height >1600 m a.s.l., *N*, is noted in each panel. The circles represent the standard error in the measurements and are shown in the bottom right of panels (a), (c), and (e) for specific humidity, mountaintop O_3 mixing ratios, and valley O_3 mixing ratios, respectively. Note that the daily means are removed.

The role of valley-PBL air on the mountaintop trace-gas mixing ratios is further investigated by computing the difference in O_3 mixing ratios between the mountaintop and valley. O_3 mixing ratios are 20-30 ppb greater at the mountaintop than in the valley during the night-time (Fig. 7) which has previously been attributed to deposition (e.g. Reitebuch et al. 2000, Mayer et al. 2008) and to enhanced O_3 depletion by nitric oxide in valleys (e.g. Broder and Gygax, 1985, Wunderli and Gehrig, 1990, Vögtlin et al. 1996). Additionally, previous studies have shown that the greater nocturnal O_3 mixing ratios at mountaintops occur because the mountaintops are exposed to O_3-rich free atmospheric air via downslope flows (e.g. Zaveri et al. 1995) and elevated O_3 layers which oftentimes form over mountainous terrain (e.g. Neu et al. 1994, McKendry and Lundgren 2000). O_3 mixing-ratio differences between the mountaintop and valley become smaller beginning around sunrise and are smallest from about 1000-1700 LST (typically <2 ppb). The small differences are attributed to the mixing of transported valley-PBL air with the air mass at the mountaintop, as reported in previous studies for other mountaintop sites, e.g. Hohenpeissenberg (998 m a.s.l.) (Mayer et al. 2008). We note that these transport processes occur independently of PBL height relative to the mountaintop and independently of the presence of fair weather conditions at the site (Fig. 7b). This finding most likely indicates that valley-PBL air arrives at the mountaintop regardless of the PBL height relative to the mountaintop, and that the mountaintop and valley measure similar trace-gas mixing ratios during the daytime.

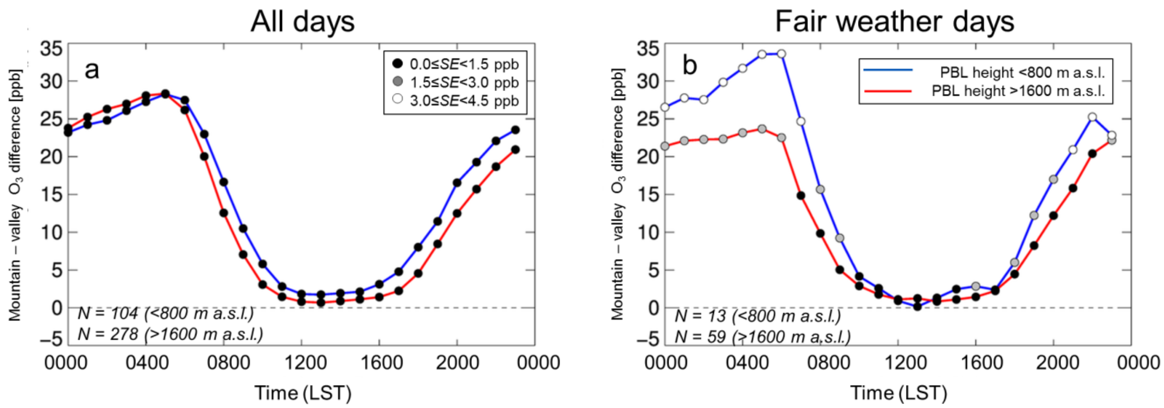

Fig 7 Diurnal cycle in O_3 mixing-ratio difference between the mountaintop and valley for days with PBL heights <800 m (blue line) and for PBL heights >1600 m (red line) for all days (a) and for the subset of fair weather days with constant wind directions (b). The circles represent the standard error in the measurements.

4.5 Effect of PBL Height on Diurnal Contrasts in CO and CO_2 Mixing Ratios

To quantitatively investigate the impacts of PBL dilution and entrainment on the observed diurnal CO and CO_2 mixing ratios, we could determine the relationship between daily CO and CO_2 mixing-ratio amplitude and afternoon PBL height. However, the amplitudes represent the absolute change in CO and CO_2 mixing ratio occurring over the entire diurnal cycle and also include night-time processes, e.g. nocturnal sinking motions that transport free-atmospheric air to mountaintops (e.g. Schmidt et al. 1996). These processes can affect the trace-gas cycle independently of the maximum daytime PBL height. In addition, nocturnal respiration occurring at local to regional scale can impact the CO_2 mixing-ratio amplitude independently of PBL height. Therefore, to isolate the impact of processes occurring in the daytime PBL on the diurnal mountaintop CO and CO_2 mixing-ratio cycle, we computed the difference between mean afternoon (1200-1600 LST) and mean morning (0400-0800 LST) mixing-ratios rather than the daily amplitudes. There is an inverse relationship between this CO mixing-ratio difference and PBL height when all days are considered (r = -0.86, p < 0.01) and only when the PBL height exceeds 2000 m a.s.l., CO mixing ratios are typically lower in the afternoon than during the morning (Fig. 8a). On the subset of fair weather days with constant wind directions, there also exists an inverse relationship between PBL height and the daytime CO mixing-ratio difference (r = -0.67, p = 0.02) (Fig. 8b). Mean CO mixing ratios are about 4 ppb larger during the afternoon than during the morning on days when the PBL height is below the ridgetop because of the upward transport and mixing of pollutants. When the PBL height exceeds the ridgetop, afternoon CO mixing ratios are about 5 ppb lower than morning CO mixing ratios because pollutants are mixed over a volume of air that is larger than on days with a shallow PBL, thereby resulting in a decrease in trace-gas mixing ratios. This decrease is similar to what occurs over flat terrain (e.g. Pochanart et al. 2003, Popa et al. 2010, Pal 2014, Berhanu et al. 2016, Chandra et al. 2016, Sreenivas et al. 2016), and its implications are revisited in Section 5.

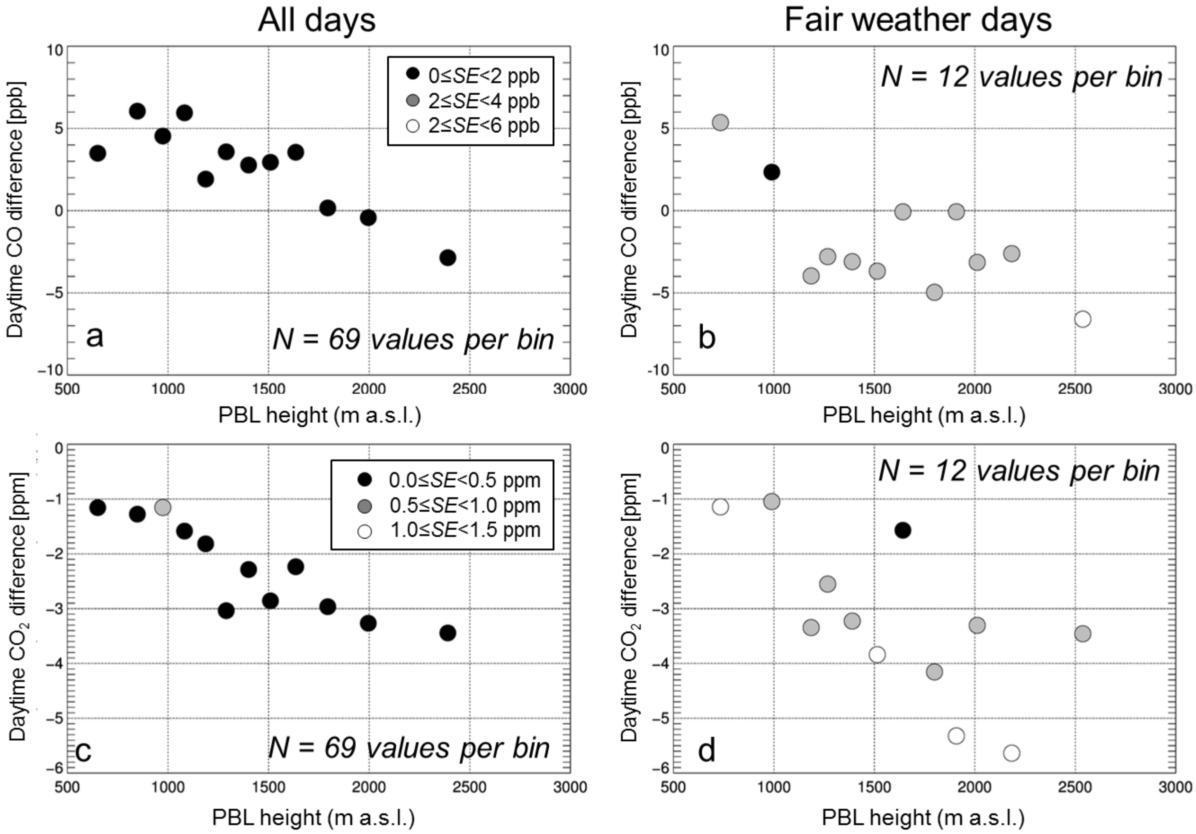

Fig 8 Mean difference between mean afternoon (1200-1600 LST) and mean morning (0400-0800 LST) CO mixing ratios as a function of PBL height for 1 January 2009 – 31 December 2012 for all days (a) and for fair weather days with constant wind directions (b). Same for panels (c) and (d) but for CO_2 mixing ratio. Data from all days represent 12 bins with 69 values per bin; data from fair weather days represent 12 bins with 11 values per bin.

There is also an inverse relationship between the PBL height in the difference between mean afternoon and mean morning CO_2 mixing ratios (r = -0.89, p < 0.01) when either all days are considered (Fig. 8c) or just the subset of fair weather days (r = -0.67, p = 0.02) (Fig. 8d), with a larger decrease in daytime CO_2 mixing ratio on days with deeper PBLs. The differences between the morning and afternoon are larger on the subset of fair weather days most likely due to larger on-site CO_2 fluxes along with deep PBL mixing occurring on days with stronger insolation (not shown).

Both when all days or only fair weather days with constant wind directions are considered, CO mixing ratios are lower in the afternoon than in the morning on days when the PBL height greatly exceeds the ridgetop height, i.e. is about 1 km above the ridgetop or at least 2000 m a.s.l. (Fig. 9a). The mean diurnal CO mixing-ratio cycle in both of these scenarios is characterized by a CO mixing-ratio maximum around 0730 LST, whereas the minimum CO mixing ratios occur around 1500 LST in both mean diurnal cycles (Fig. 9a). The decrease in the diurnal CO and CO_2 mixing-ratio cycles (Fig. 9b) both on all days and on the subset of fair weather days suggests the influences of PBL dilution and entrainment.

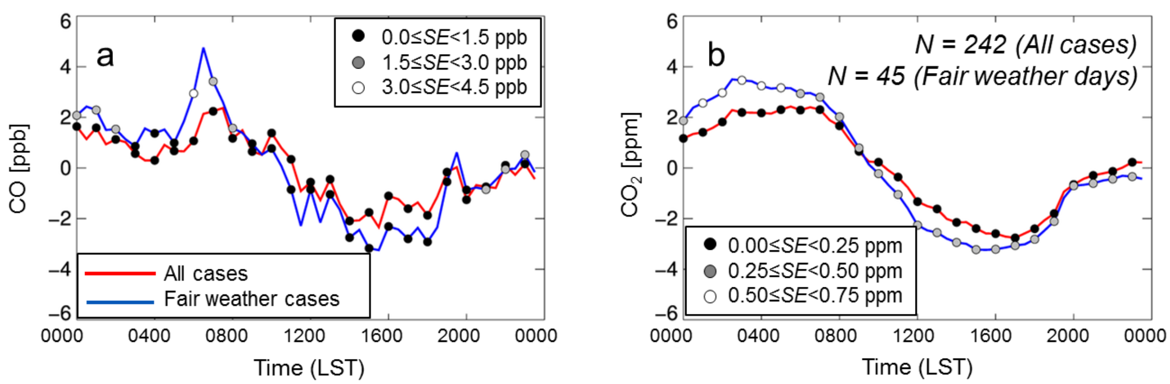

Fig 9 Diurnal CO (a) and CO_2 (b) mixing-ratio cycle on all days over the period 1 January 2009 – 31 December 2012 when PBL heights >2000 m a.s.l. (red line, N=242) and for the subset of fair weather days with PBL heights >2000 m a.s.l. and constant wind directions (blue line, N=45). The circles represent the standard error in the measurements. For readability, the standard error is shown every 60 min rather than every 30 min.

5 A Conceptual Framework Highlighting the Key Findings

We summarize our findings using a conceptual framework shown in Fig. 10 to illustrate the dominant physical processes affecting the diurnal cycle of trace gases, specifically CO mixing ratio, at mountaintops as a function of afternoon valley-PBL top relative to ridgetop height. In the conceptual diagram, we assume that the valley is the sole source of pollutants. We also assume that there are no chemical reactions, including photosynthetic uptake of CO_2 mixing ratio during summer, that either add or remove the trace gas from the atmosphere, and we neglect surface deposition. Therefore, the conceptual diagram that we present closely matches the diurnal CO mixing-ratio cycles shown in Figs. 3 and 9.

On days when the valley-PBL top remains below the ridgetop (Fig. 10a), pollutant transport from the valley to the mountaintop occurs via upslope flows and PBL mixing within a daytime PBL. The result is that pollutants are confined within this shallow PBL that parallels the underlying terrain throughout the day, as shown by the PBL tops during the mid-morning and mid-afternoon in Fig. 10a which correspond with times *t1* and *t2*, respectively. Between time *t1* and *t2*, pollutants are transported to the mountaintop which causes their mixing ratios at the mountaintop to increase (Fig. 10b). After time *t2*, local mixing occurring with the PBL at the ridgetop causes the pollutant mixing-ratios to decrease. The daytime increase occurs between times *t1* and *t2* is contrary to many previous studies that have reported little to no change in daytime trace-gas mixing ratios when the valley PBL remains below the ridgetop height (e.g. Forrer et al. 2000, Obrist et al. 2008, MacDonald et al. 2011).

A key difference between these previous findings from other mountaintops and our findings is that the previous studies were conducted using measurements from mountaintops with much greater topographic relief than the Pinnacles site, i.e. those that are typically at least 2-3 km in elevation and at least 1-2 km above the surrounding valley or plain (e.g. Keeling et al. 1976, Forrer et al. 2000, De Wekker et al. 2009, McClure et al. 2016, Zhu et al. 2016). Mountaintops with these topographic characteristics remain in the free atmosphere much of the time and are much more isolated from the effects of valley-PBL air because the maximum height of the valley PBL is at least several hundred metres below the ridgetop height. The Pinnacles site is affected by valley-PBL air much more frequently than taller mountaintops as the PBL height is at least 500 m over the ridgetop on about one-third of all days. Because of the daytime trace-gas increase that we observe at the Pinnacles site on days with PBL heights below the ridgetop, the daytime trace-gas measurements from the Pinnacles site, as well as other mountaintops with similar elevation above the surrounding valley and where the daytime maximum PBL height does not exceed the ridges, cannot be considered representative of free atmospheric values, but rather are representative of the local valley PBL. Therefore, these measurements should not be assimilated into e.g. inverse carbon transport models or air chemistry models that cannot resolve local to mesoscale processes.

On days when valley-PBL heights exceed the ridgetop (i.e. >1600 m a.s.l.) (Fig. 10c), the PBL is initially parallel to the underlying terrain during the mid-morning, as shown by the PBL top at time *t1* in Figure 10c, like it is on days with PBL heights below the ridgetop. Pollutants are transported to the mountaintop during this time as evident by the short-lived maximum in CO mixing ratios. As the PBL grows deeper during the day and exceeds the ridgetop height, it does not parallel the underlying terrain, as shown by the PBL top at time *t2*. After the mid-morning maximum in pollutant mixing-ratios at time *t1*, we infer that pollutant transport via upslope flows becomes overwhelmed by PBL dilution and the entrainment of cleaner free atmospheric air on these days. Thus, mountaintop pollutant mixing ratios decrease between times *t1* and *t2* to an afternoon minimum on these days (Fig. 10d). This daytime trace-gas mixing ratio decrease is also contrary to findings from other mountaintops. The key difference between the Pinnacles site and other mountaintops is that other mountaintops where studies have been conducted are higher in elevation and extend higher above the surrounding valley/plain than the Pinnacles site (e.g. Forrer et al. 2000, Bukowiecki et al. 2016, McClure et al. 2016, Zhu et al. 2016). At mountaintops with these topographic characteristics, the valley PBL may reach the mountaintop during the daytime but the PBL is not deep enough above the ridgetop for mixing to dilute the pollutants and cause their mixing ratios to decrease.

We also note that the daytime pollutant mixing-ratio decrease at the Pinnacles site on days with PBL heights exceeding the ridgetop height is similar to the findings from tall towers in flat terrain (e.g. Schmidt et al. 2014, Pal et al. 2015, Berhanu et al. 2016). Our results on the deep PBL exceeding the ridgetop suggest that, although pollutants arrive at the mountaintop via upslope flows, the impact of these flows on the mountaintop measurements is overwhelmed by PBL dilution and entrainment of free atmospheric air. This same process occurs in flat terrain, where PBL dilution and entrainment cause a decrease in pollutant mixing ratios, and suggests that low-elevation mountaintops such as the Pinnacles site behave like tall towers. The same is also true for other mountaintops where the regional PBL exceeds the ridgetop height. Based on these findings, selecting days on which PBL heights over the adjacent valley or plains exceed the mountaintop height can be used as guidance for identifying trace-gas measurements representative of the regional PBL. Trace-gas measurements made during the afternoon on these days can then be used for assimilation into regional scale inverse carbon transport models and air chemistry studies.

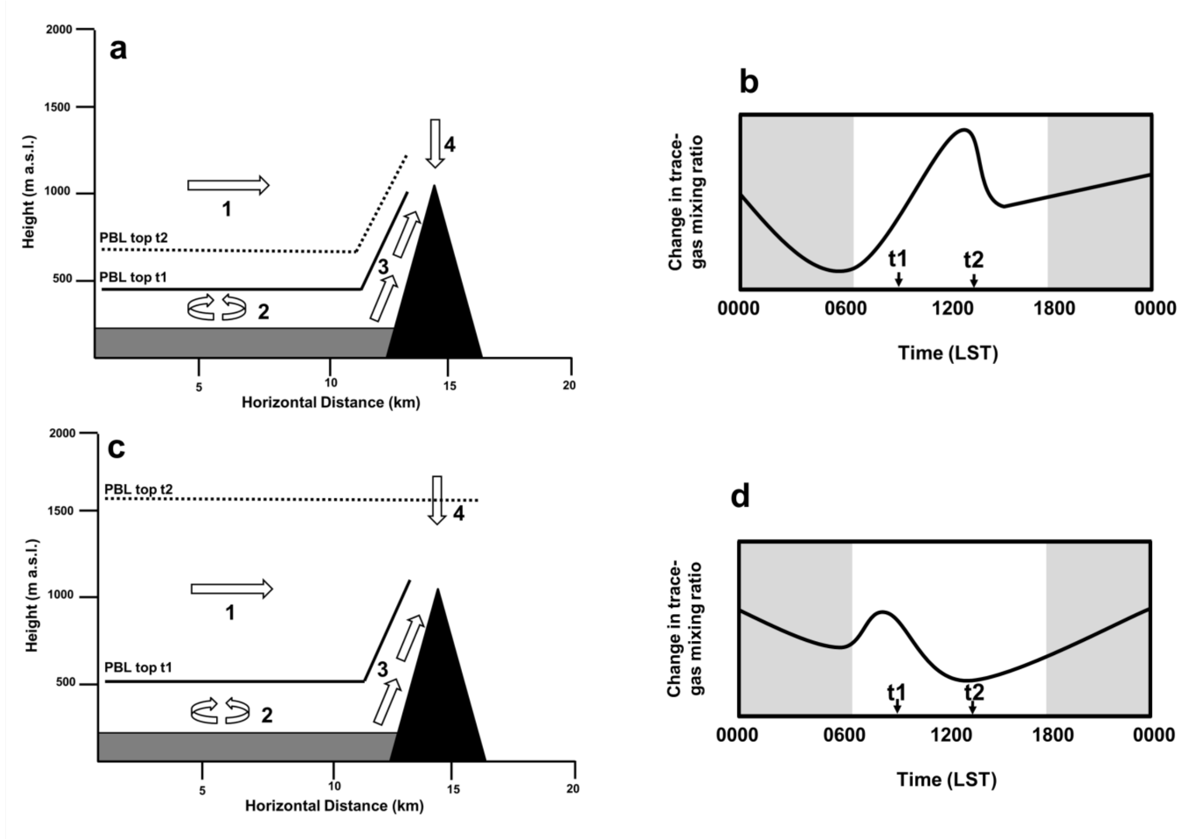

Fig 10 Conceptual diagram of dominant trace-gas transport mechanisms, assuming the valley (grey rectangle) is the sole source of pollutants, affecting the diurnal cycle of a passive trace gas as a function of PBL height relative to a 1000 m a.s.l. mountaintop (black triangle) on days when the height of the afternoon valley PBL remains below the mountaintop. The dominant transport mechanisms shown are synoptic-scale advection (1), convective mixing (2), upslope flows (3), and free atmosphere air entrainment (4) and are indicated with arrows. The PBL top at times *t1* and *t2* is shown by solid and dotted lines, respectively. These times are indicated on panel (b) which shows the near-surface diurnal trace-gas cycle starting with a set mixing ratio of trace gas and assuming no advection or sources. The shaded and non-shaded areas in this panel represent night-time and daytime, respectively. Same for panels (c) and (d) but for days when PBL height is much greater than the height of the mountaintop.

6 Summary and Conclusions

We presented the first study investigating the effect of the afternoon PBL height on the diurnal CO and CO_2 mixing-ratio cycle at a low mountaintop using measurements from a mountaintop trace-gas monitoring site (the Pinnacles site, in the Virginia Blue Ridge Mountains). We found that the diurnal cycle of CO mixing ratios is typically largest on days when the PBL height remained below the ridgetop (i.e., ≈1000 m a.s.l.) and is smallest on days when the PBL height exceeded the ridgetop by at least 400 m. On days when the valley-PBL height is below the ridgetop, there is a daytime CO mixing-ratio increase, as well as a short-lived increase in CO_2 mixing ratios during the winter, caused by the transport of polluted valley-PBL air to the mountaintop. On days when the valley-PBL height exceeds the ridgetop height, both CO and CO_2 mixing ratio decrease during the daytime due to dilution and entrainment that negate the influence of pollutant transport from the valley floor.

The results in this study provide additional insights into the use of trace-gas measurements from low-elevation mountaintops like the Pinnacles site in applications requiring regionally-representative values. The present study builds upon previous studies from the region (Lee et al. 2012, 2015, Pal et al. 2017) by helping to further understand the local scale to mesoscale meteorological processes affecting the trace-gas cycle at low mountaintops. The daytime CO mixing-ratio increase on days with PBL heights below the ridgetop, as well as the small differences in O_3 mixing ratio between the mountaintop and valley, suggest that the mountaintop is mostly influenced by valley-PBL air, and therefore the mountaintop trace-gas measurements are representative of the "local" valley atmosphere. Pollutants are also transported to the mountaintop during the daytime on days when the PBL exceeds the ridgetop height, but PBL dilution overwhelms the influence of upslope pollutant transport, causing CO and CO_2 mixing ratios to decrease. This behaviour in CO and CO_2 mixing ratios is also observed in measurements from tall towers (i.e. larger than a few hundred metres a.g.l., or more than about 10% of the daytime PBL depth) in flat terrain. The daytime decrease that we observed indicates that afternoon trace-gas measurements from low mountaintops made when PBL heights over the adjacent valley or plains exceed the ridgetop can be used in the same way that afternoon measurements from tall towers are used in applications requiring regionally-representative measurements.

7 Tables

Season	Correction (m)
Winter	+190
Spring	+210
Summer	+300
Fall	+250

Table 1 Seasonal correction factor applied to the Dulles Airport rawinsonde PBL height, based on findings from Lee and De Wekker (2016), to better approximate the daytime maxmimum PBL height over the Page Valley.

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