A study of the combined impact of boundary layer height and near-surface meteorology to the CO diurnal cycle at a low mountaintop site using simultaneous lidar and in-situ observations

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Abstract

Evaluations of air pollutants and trace gas measurements over mountaintop sites and their application in inverse transport models to estimate regional scale fluxes are oftentimes challenging due to the influences associated with atmospheric transport at both local and regional scales. The objective of this study is to investigate the diurnal cycle pattern of CO mixing ratio over a low mountaintop influenced by: (1) two different convective boundary layer (CBL) regimes (shallow and deep) and associated growth rates over the mountaintop, (2) the combined effect of a deep CBL with and without diurnal wind shift, and (3) slope flows and associated air mass transport. For this purpose, we used simultaneous measurements of lidar-derived CBL heights, standard meteorological variables, and CO_2 and CO mixing ratio from Pinnacles, a mountaintop monitoring site in the Appalachian Mountains. We used both water vapor and CO_2 mixing ratio as tracers for upslope flow air masses. We used case studies to focus on two different scenarios of daytime CO mixing ratio variability: (1) a gradual increase in the morning with a maximum in the afternoon, and (2) a gradual decrease in the morning with a minimum in the late afternoon. The second scenario is similar to the CO variability observed atop tall towers in flat terrain.

Using the lidar-derived CBL height evolution and in situ CO, CO_2 and meteorological measurements over the mountaintop, we found that the upslope flow air masses arriving at the mountaintop in the morning affect the CO mixing ratio variability during the remaining part of the diurnal cycle. These findings help introduce a conceptual framework that can explain and differentiate the opposite patterns (i.e. daytime increase versus daytime decrease) in the CO diurnal cycles over a mountaintop site affected by upslope flows and provide new roadmaps for

monitoring and assimilating trace gas mixing ratios into applications requiring regionally-representative measurements.

1. Introduction

Trace gas measurements at mountaintop locations are valuable as they help determine background mixing ratios in the free atmosphere (FA) which are important for studies of long-range impacts of upwind source regions. However, greenhouse gases (GHG) such as carbon dioxide (CO_2) and trace gases such as carbon monoxide (CO) and O_3 are affected by site-specific meteorological conditions in mountainous terrain (e.g., Schmitt and Volz-Thomas, 1997; Lee et al., 2015; Sullivan et al., 2017), synoptic scale transport, e.g., via frontal passages (e.g., Pillai et al., 2011), and thermally driven recirculation pattern in the mountain-valley atmosphere (e.g., De Wekker et al., 2009; Sullivan et al., 2016). Additionally, air pollutants in mountainous areas include harmful airborne substances that threaten human health, harm vegetation, animals or structures, or affect visibility (Whiteman, 2000). However, our knowledge of the effect of complex terrain on air pollution in mountainous areas remains limited due to sparse observations (Lee, 2015) and to difficulties with numerical simulations in these areas (e.g., Desai et al., 2010; Steyn et al., 2012; Lin et al., 2016).

In mountainous regions, terrain-induced atmospheric processes can influence the diurnal cycle of trace gas mixing ratios. For example, flows along the valley and slopes are generated due to horizontal temperature gradients arising from heating and cooling of valley atmospheres and the atmosphere adjacent to sloping terrain. These flows are directed upvalley and upslope during daytime and downvalley and downslope at night (e.g., Whiteman, 2000). The mountaintop measurements of CO, CO_2, O_3, water vapor, aerosols, and other tracers are influenced by these flows, i.e. upslope flows bring air from the adjacent lowland boundary layer up to the summits (e.g., Fischer et al., 2004). Several investigators (e.g., Keeling et al., 1976; De Wekker et al., 2009) found that CO_2 mixing ratio time series exhibited a pronounced afternoon minimum in summer, which they partly attributed to the transport of CO_2 depleted air via upslope flows. Understanding these influences is important to better estimate the regional scale fluxes of CO_2 where CO is used to distinguish anthropogenic CO_2 from biogenic CO_2 (e.g., Andrews et al., 2014).

Previous studies focusing on CO and CO_2 mixing ratio variability over high-altitude sites, including Jungfraujoch (~ 3500 m mean sea level (MSL)) in the Swiss Alps (e.g., Dils et al., 2011), Nainital (~ 2000 m MSL) in the central Himalayas (e.g., Sarangi et al., 2014) and Mauna Loa (3397 m MSL) in Hawaii (e.g., Atlas and Ridley, 1996), illustrate that these sites mostly sample free atmospheric (FA) air except on days when the convective boundary layer (CBL) height is relatively large. The CO mixing ratio oftentimes reaches a maximum in the late afternoon hours (e.g., ~18:00 LST) due to the impact of upslope flows bringing polluted air from the adjacent valleys and plains (e.g., Dils et al., 2011). For low mountaintop sites like Ochsenkopf (1022 m MSL, situated in the Fichtelgebirge mountain range in Germany), the impact of upslope flow on the tracer mixing ratios is common throughout the year except in winter (Pillai et al., 2011). However, the role of CBL height variability over the mountaintop on CO mixing ratios on diurnal time scale has not been properly addressed using observational findings. Only recently have researchers emphasized a conceptual framework to illustrate CO diurnal cycle pattern over mountaintop sites (e.g., Bamberger et al., 2014, 2017; Lin et al., 2016) as was performed for CO_2 diurnal pattern over flat terrain (e.g., Pino et al., 2012; Haszpra et al., 2015).

Complex meteorology and lack of observations are important hurdles to study exchange processes in a mountain-valley atmosphere system. Empirical work illustrating the combined impacts of both meteorology and CBL height variability and relevant dynamics on the CO diurnal cycle is very limited. While several studies report CO variability on diurnal, synoptic and seasonal time scales, we are unaware of studies that demonstrate specifically the importance of continuously monitored mountaintop CBL heights on CO variability. Furthermore, the driving factors that yield contrasting patterns (i.e. daytime increase versus daytime decrease) in the diurnal cycles of trace gases, including CO, have so far not been explained. In this work, we emphasize a process-based framework by investigating CO mixing ratio measurements on a mountaintop monitoring site in the Blue Ridge Mountains in northwestern Virginia that we refer to as Pinnacles, (38.61 N, 78.35 W, 1017 m MSL). The objective of this study is to investigate diurnal CO patterns influenced by (1) daytime CBL height variability and growth rate, (2) the slope wind system in the mountain-valley atmosphere, and (3) prevailing synoptic settings including on site meteorological conditions, in particular, a horizontal wind shift. We use continuous high-resolution lidar measurements at Pinnacles to investigate the CBL height variability during four selected days. CO and CO_2 measurements and other meteorological measurements were collected from a 17 m walkup tower that was established at Pinnacles in May 2008.

2. Basic concept and hypothesis

Based on the previous studies on trace gas measurements over complex terrain, we consider CO mixing ratios to be a good proxy for boundary layer mixing processes. Figure 1 presents a conceptual framework for the general mechanisms governing the CO diurnal cycle on a tall tower located in flat terrain and on a low mountaintop site. During the morning transition period,

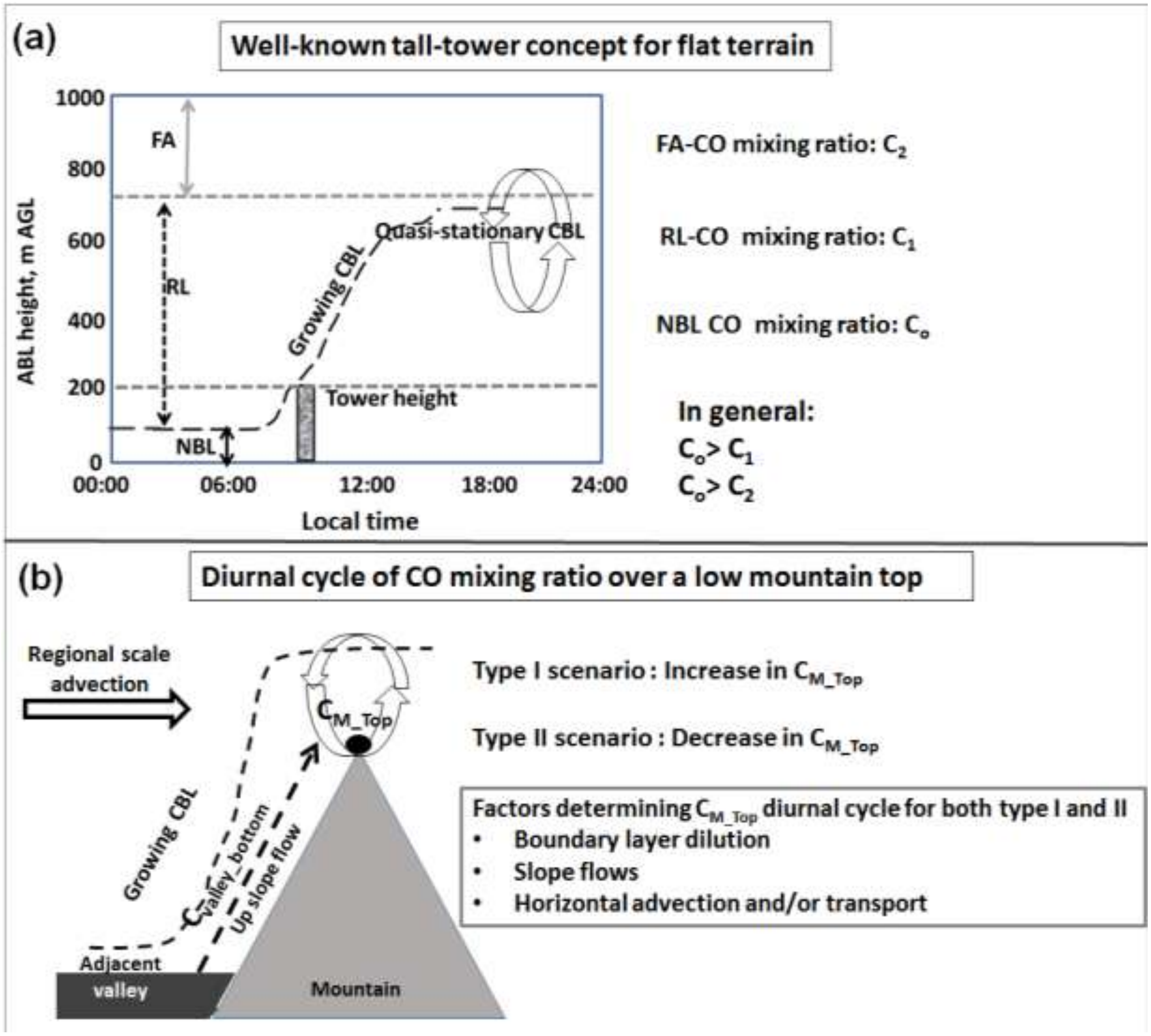

Fig. 1. *Schematics of the general mechanisms governing the diurnal cycle variability of CO mixing ratio on a tall tower in flat terrain (a) and on a low mountaintop site (b). NBL, RL, and FA denote the nocturnal boundary layer, residual layer, and free atmosphere, respectively. C0, C1, and C2 denote CO mixing ratios in the NBL, RL, and FA, respectively. In the top figure, horizontal dashed lines mark the levels of the tower top and of the quasi-stationary height of daytime well-mixed CBL and vertically-aligned arrows mark the NBL, RL and FA. The curved dashed line and thick circular arrows in both figures illustrates the growing CBL and entrainment mixing at the CBL top, respectively. CO mixing ratios at the valley and at the mountaintop site just before sunrise are referred to as* C_{valley_bottom} *and* C_{M_Top}*, respectively. The diurnal cycle of* C_{M_Top} *responds to the CBL dynamical processes, in particular, CBL height and air mass from adjacent valley transported via upslope flow. Type I and II scenarios refer to increase and decrease of* C_{M_Top}*, respectively due to the combined impact of boundary layer dilution, slope flows (dashed arrow aligned along the mountain slope) and regional scale advection (horizontally aligned thick arrow).*

polluted nocturnal boundary layer (NBL) air reaches the tower top, illustrating a morning peak in the CO mixing ratio variability. After the CBL begins growing, the CO mixing ratio at the tower top starts decreasing under the assumption that CO mixing ratio is higher in the NBL than in the residual layer (RL); CO continues to decrease due to the dilution effect until the late afternoon hours when the CBL attains a quasi-stationary state, yielding a daytime minimum mixing ratio until the evening transition period when the NBL starts developing.

Similar to the CO diurnal cycle on a tall tower, mountaintop measurements are also affected by the CBL dilution effect via boundary layer growth and by horizontal advection. Additionally, vertical transport by upslope flow affects mountaintop trace gas measurements in mountainous regions and causes a daytime peak in the CO mixing ratio which is similar to the arrival of NBL air reaching the tall tower top during the morning transition. During nighttime, the top of a tall tower usually remains either in the RL or in the NBL depending on the NBL height. In contrast, mountaintops generally sample either FA or RL air depending on the daytime CBL height variability. This is because of the subsiding motions generated by downslope flows at the mountaintop that transport FA air to mountaintop level (e.g., Pillai et al., 2011). Therefore, a traditional NBL does not develop over a mountaintop and instead nighttime mountaintop measurements are considered representative of FA or RL measurements (Whiteman, 2000).

Nevertheless, we hypothesize that the tall tower concept can be applied to explain the CO mixing ratio variability over a mountaintop site under certain conditions that require knowledge of the CBL height diurnal cycle at the mountaintop location. Additionally, for flat terrain, Pino et al. (2012) outlined the importance of considering near-surface CO_2 mixing ratios in the early morning to interpret the observed CO_2 variability during the afternoon over flat terrain. Similarly, the CO variability during the morning transition period at low mountaintops also depends on the nighttime CO mixing ratios at the site before the arrival of adjacent valley air. In this context, low mountaintop sites refer to the ridges that are located around 500-1000 m above adjacent valleys or plains and include, e.g., Ochsenkopf (1022 m MSL, a monitoring station in the Fichtelgebirge Mountains of northern Bavaria in Germany) (e.g., Thompson et al., 2009), Hornisgrinde (1161 m MSL) in the Black Forest of Germany (Vögtlin et al., 1996), and Pinnacles in the Appalachian Mountains of the eastern US (e.g., Lee et al., 2012), the site we focus on in the current study.

Figure 1 illustrates that during the morning transition period, the valley air with C_{valley_bottom} reaches the mountaintop and mixes with the air with C_{M_Top}. In general, C_{M_Top} measurements in the morning before upslope flow arrives at the site help identify NBL-CO mixing ratio and determine which layer (RL or FA) of the atmosphere is being sampled. It is therefore considered a quantifiable tracer of the atmospheric dynamics occurring in the mountain-valley atmosphere. We consider two types of diurnal scenarios affected by mountaintop meteorological conditions and CBL regime: (1) daytime increase in C_{M_Top} (type I scenario resembling NBL air reaching tall tower top in the morning), and (2) a decrease in C_{M_Top} (type II scenario resembling CBL dilution effect in flat terrain). Additionally, we also hypothesize that, C_{M_Top} during type I and II scenarios is influenced by the combined effect of (1) local meteorological conditions, (2) arrival of different air masses at the mountaintop via either upslope flow or horizontal transport, and finally (3) CBL height and growth rate. In this paper, we use some case studies to illustrate the processes playing a dominant role in governing the CO diurnal cycle for both type I and II scenarios.

3. Experimental site, instruments and data sets

The data sets were collected on a 17 m walkup tower located at Pinnacles, a forested mountaintop site in the Shenandoah National Park (SNP) of the Blue Ridge Mountains of Virginia. The research station at Pinnacles was established in May 2008 along a ridgeline at an elevation of 1017 m (38.61°N, 78.35°W) in the north-central section of SNP. Further details on the infrastructure of the Pinnacles station, geography, and climatology of the region are reported in Lee et al. (2012, 2015).

The tower is outfitted with a suite of instruments, including meteorological sensors and micrometeorological instruments, a Thermo Electron 48C Trace Level CO Analyzer for measuring CO mixing ratios at three levels (5, 10, 17 m above ground level (AGL)), and a Li-COR 7000 closed path gas analyzer for CO_2 mixing ratios at these same three levels (e.g., Lee et al., 2012; Andrews et al., 2014). The meteorological sensors include a Campbell Scientific 3D Sonic anemometer (CSAT3) combined with LI-COR 7500 open-path gas analyzer for CO_2, latent, and sensible heat fluxes, Hukseflux four-component net-radiation sensor for incoming and outgoing short- and long wave radiation, MetOne 034B cup and vane anemometer for horizontal wind speed and direction, Vaisala HMP45 probe for humidity and temperature, a Vaisala CS105 for pressure, and a TR-525I tipping bucket rain gauge. For each collected variable, a set of quality assurance and quality control procedures was implemented. More detailed information about the trace gas and meteorological data sets, as well as the quality control algorithms implemented, can be found in Lee (2015).

When CBL height measurements over mountaintop sites are concerned, previous studies mainly used maximum CBL height derived from nearby rawinsonde profiles (Lee and De Wekker, 2016), from numerical model simulations (e.g., Pillai et al., 2011), from lidar measurements in an adjacent valley (e.g., Gallagher et al. 2012), or from combined lidar and radar observations from adjacent plains (e.g., Sullivan et al., 2016). However, the potential of continuous monitoring of CBL height using ground-based profilers (e.g., lidar, radar, sodar, wind profiler) over mountaintop sites for elucidating the CO diurnal cycle characteristics has not been addressed. At Pinnacles, a Leosphere ALS-300 eye-safe aerosol lidar was occasionally deployed at the site for monitoring CBL height over the region. The lidar system installed at the site operates at a wavelength of 355 nm (UV range) and provides profiles of relative particle backscatter at temporal and vertical resolutions of 1 minute and 15m, respectively. During post-processing, profiles of range-squared corrected backscatter signal intensities were used to estimate CBL heights by applying the Haar wavelet algorithm (Pal et al., 2014, 2015).

Using aerosols as tracers for CBL mixing processes, the Haar wavelet algorithm has been used for nearly two decades to estimate CBL height from aerosol lidar observations (e.g., Cohn and Angevine, 2000; Pal et al., 2009, 2015). Based on a sensitivity test that is typically done for Haar wavelet method, we used a dilation of 150 m for the analysis; the time resolution between two profiles is 1 minute, and the range resolution in the backscatter data is 15 m. The dilation value depends on several factors: (1) temporal and spatial resolution of the lidar signal profiles, (2) signal to noise ratio; (3) atmospheric conditions revealing particle backscatter strengths, and (4) limit of wavelet covariance transform integration. We tested various dilations (a in the wavelet transformation equation, see e.g Cohn and Angevine, 2000; Pal et al., 2010) and found 150 m to be appropriate where multiple peaks in the wavelet coefficients were absent yielding the most appropriate location of maximum gradient in altitude, i.e. top of the CBL. For further discussion on the wavelet application for determining CBL heights, readers are referred to Davis et al. (2000) and Pal et al. (2010).

In this study, we use lidar measurements collected on selected clear sky days in 2009 to investigate the impact of CBL height on the CO mixing ratio variability on a diurnal time scale. Full overlap of the transceiver of the lidar system is attained at a height of ~ 200 m AGL, and thus estimates of CBL height below this height cannot be made with the lidar system (e.g., Behrendt et al., 2005; Pal, 2014).

4. Meteorological conditions

An overview of the near-surface meteorological conditions is presented in Table 1, which reports the daily maximum, minimum temperature, diurnal temperature range, clearness index based on the incoming solar radiation (Whiteman et al., 1999), regimes of diurnal wind shift, and times of sunrise and crossover of sensible heat fluxes (SHF) (i.e., the time when sensible heat flux changes sign). A clearness index of more than 0.6 was observed at the site on all the days confirming the absence of significant cloud cover during the daytime (Table 1).

For obtaining a general overview on the prevailing synoptic settings for those case studies, we used 3-hourly surface reanalysis charts produced by NOAA-HPC. Prevailing synoptic conditions on all four selected days of interest were characterized by near-surface anti-cyclonic flow in the region around Pinnacles (Fig. 2). In particular, on 21 May and 21 October 2009, there was an anti-cyclone located over the Mid-Atlantic; on 5 and 14 September 2009, the anti-cyclone was positioned over the upper Midwest.

Unfortunately, there were no rawinsonde observations from the adjacent Page Valley on any of the four case study days reported here. Lee and De Wekker (2016) used nearby rawinsonde profiles to estimate maximum CBL heights in the Page Valley. Nevertheless, using only daytime maximum CBL heights, one cannot infer boundary layer transport and mixing processes of trace gases at a mountaintop site in detail. For instance, to understand the impact of CBL regimes on the CO mixing ratio during the entire diurnal cycle, it is important to have information on CBL growth rate, CBL height variability including entrainment processes, and upslope flows. Thus, a complete picture of daytime evolution of CBL heights over mountaintop, obtained in this study using continuous lidar measurements, is a pre-requisite to address our research goals.

Table 1*: A summary of the near-surface meteorological conditions on the four case study days. CI: Clearness index, T_{max}: Daily maximum temperature, T_{min}: Daily minimum temperature, DTR: Diurnal temperature range calculated by subtracting T_{min} from T_{max}, SHF: Sensible heat flux*

Date in 2009	**Diurnal temperature parameters (˚C)**			**CI**	**Wind direction or observed wind shift**	**Local standard time**	
	T_{max}	**T_{min}**	**DTR**			**Sunrise**	**SHF crossover**
14 Sept	20.66	13.53	7.13	0.77	Westerly (no wind shift) with decreasing wind speed	06:55	07:30
21 May	20.34	13.28	7.06	0.85	Wind shift from NW to SE	06:05	06:25
5 Sept	21.14	16.23	4.91	0.62	Wind shift from NNW to SE	06:50	07:55
21 Oct	18.02	14.21	3.79	0.75	Wind shift from NW to SE	07:30	08:15

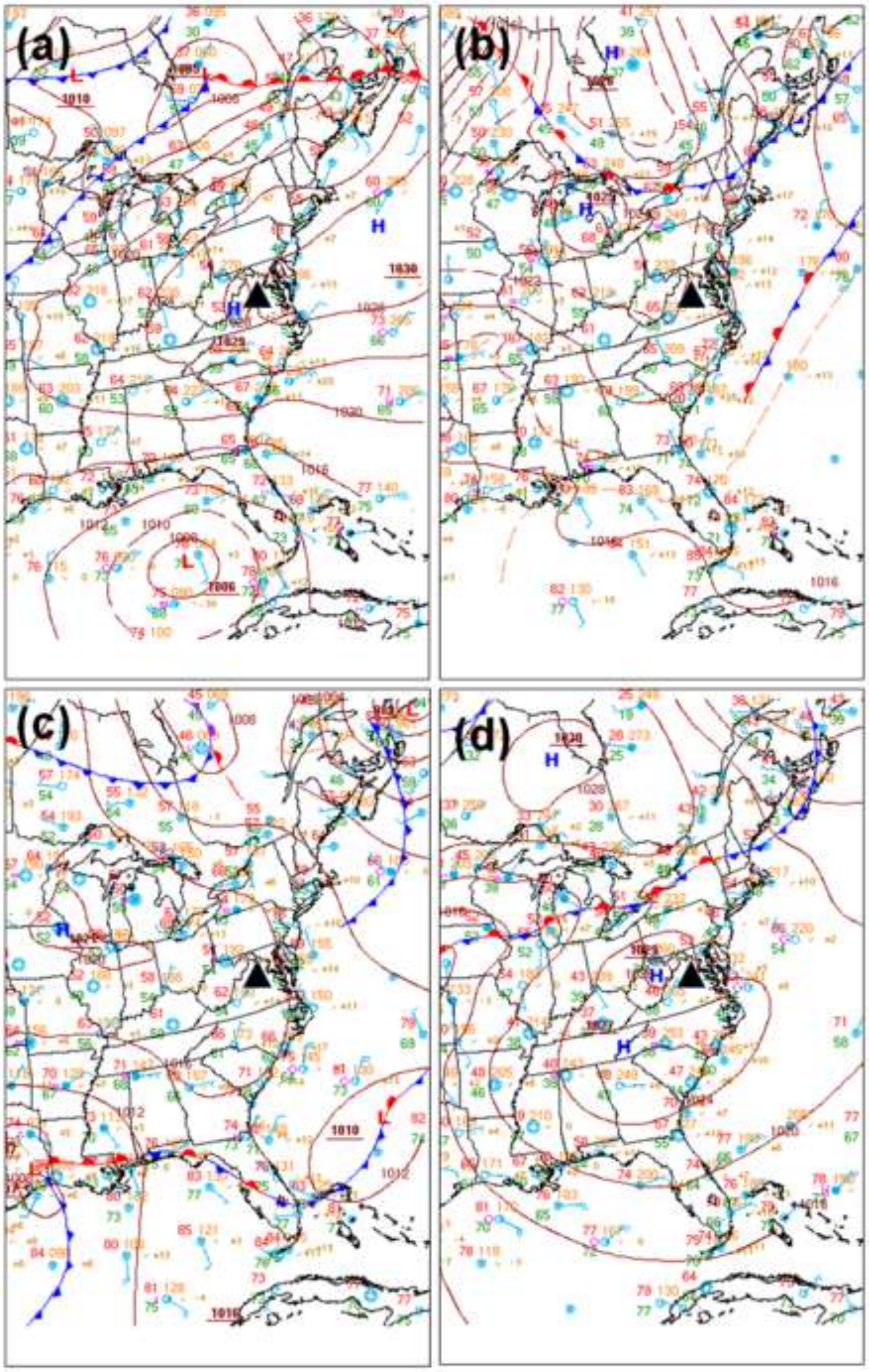

Fig. 2. *Surface synoptic charts at 12:00 UTC (07:00 LST) on 21 May 2009 (a), 5 September 2009 (b), 14 September 2009 (c), and 21 October 2009 illustrating fair weather high-pressure, anticyclonic synoptic settings on all four days. The location of Pinnacles is denoted by black triangle. Figures courtesy of <hpc.ncep.noaa.gov>.*

5. Results and discussion

5.1 Case I: Impacts primarily related to boundary layer dilution (14 Sept 2009)

Case I on 14 September 2009 is characterized by clear-sky anticyclonic conditions with weak to moderate westerly winds (Fig. 3). In particular, wind speed observed at 17 m AGL at Pinnacles was rather constant around 1.2 ms^{-1} until 16:00 LST (LST=UTC-5:00); afterwards the wind weakened and remained around 0.5 ms^{-1} while there was a slight backing from northwesterly to southeasterly. Near-surface meteorological measurements reveal that the morning and evening crossover of sensible heat fluxes took place at 07:45 and 17:00 LST, respectively, while sunrise and sunset on this day were around 07:00 and 18:30 LST, respectively. The diurnal temperature range was 9 ˚C while daytime maximum temperature was 22.5 ˚C.

The time-height cross-section of the lidar measured range-square corrected signals over Pinnacles on this day exhibits a clear-sky CBL regime over the site (Fig. 3). The CBL heights derived using Haar wavelet method on the lidar-derived aerosol backscatter profiles are overlaid (black solid line). Lidar measurements display a “textbook-style” CBL development over the site with a maximum quasi-stationary CBL height about 1250 m AGL. We have also compared the lidar-based CBL height estimates with the CBL height measured at the nearest rawinsonde site (Dulles airport, IAD); relevant results and discussion can be found in Appendix A.

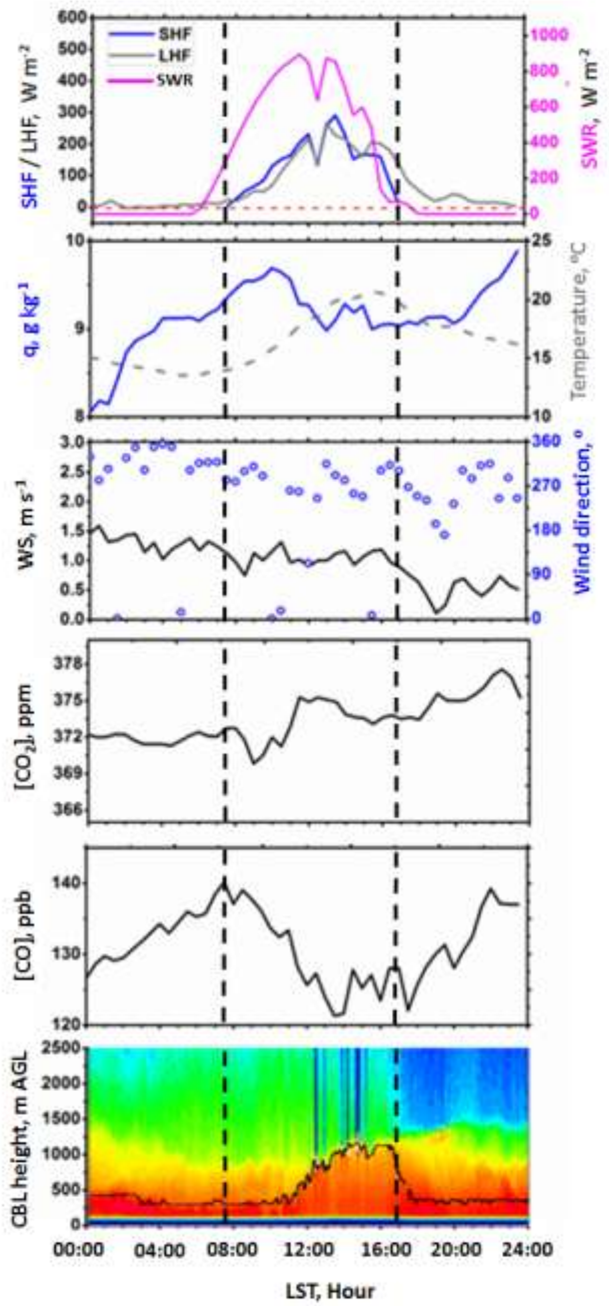

Fig. 3. *Diurnal cycles of CO_2, CO, water vapor mixing ratio (q), relative humidity at 17 m AGL on the tower, heat fluxes and incoming solar radiation, and horizontal wind speed and direction along with the lidar-measured CBL height at Pinnacles on 14 September 2009. The CBL on this day reaches a maximum quasi-stationary height of about 1250 m AGL. In the lidar-backscatter image, cold to warm color denotes lower to higher backscatter intensity. Vertically aligned dotted lines mark the morning and evening transition period determined using the heat flux crossover times.*

We were not able to monitor CBL height <200 m at the site during the measurement period due to incomplete overlap as mentioned before. It can be seen that after 11:00 LST, the CBL height grew at a rate of about 240 m hr^{-1}. Between the morning transition period and the early afternoon hours, the CO mixing ratio of 140 ppb at 07:45 LST decreased by 15 ppb to a quasi-stationary mixing ratio value of 125 ppb between 13:00 and 16:00 LST; this decrease is larger than the total uncertainty (i.e., < 6 ppb [Andrews et al., 2014]) of the CO measurements. This decrease of more than 10 % in CO mixing ratio is consistent with the boundary layer dilution effect. This type of CO diurnal cycle corresponds to the type II scenario (Fig. 1), which is very similar to the observed CO variability on tall tower tops in flat terrain (e.g., Popa et al., 2010). Additionally, measurements of both clearness index and sensible heat flux at the site on this day confirm the presence of a convectively driven boundary layer regime.

After 13:00 LST when the CBL top reached its daytime maximum, the CO mixing ratio remained constant around 125 ppb. The CO diurnal cycle at other mountaintop locations often evinces a continuous increase in CO mixing ratios with a daytime maximum due to upslope flows advecting polluted low elevation air from adjacent valleys (e.g., Gao et al, 2005; Henne et al., 2008; Ou-Yang et al., 2014). For the observations presented here, the initial pre-sunrise CO mixing ratio in the atmosphere above the mountaintop is high (~ 140 ppb), and the CO mixing ratio does not increase further after the air mass from the adjacent valley reaches the mountaintop around 09:00 LST. This fact is also evident from the CBL height development, water vapor mixing ratio (q), and CO_2 variability. In contrast, a decrease in the CO mixing ratios was observed from the morning transition period until the early afternoon, which suggests that due to the prevailing deep CBL over the site, the boundary layer dilution effect outweighs the effect due to upslope flows.

It should be noted that a steady rise in CO in the very early morning (i.e. between 00:00 and 06:00 LST) might correspond to morning local vehicular traffic or campfires near the mountaintop site. One potential source for local vehicular traffic Skyline Drive, a scenic tourist road in the Shenandoah National Park that runs southwest-northeast about 100 m southeast of Pinnacles. However, any vehicular emissions from this road would be advected away from the site because of the northwesterly winds observed between 0000 and 0600 LST on this day.

In general, *q* showed similar variability as the CO mixing ratios, with an increase/decrease in water vapor accompanied by an increase/decrease in CO levels. In particular, the decrease in CO is coincident with the simultaneous decrease in water vapor mixing ratio at the site. Water vapor is also conserved on time scales of CBL mixing, so we examine this tracer along with CO and perform regression analysis between these two parameters. The correlation coefficient (*r*) between the time series of CO and *q* for the period between sunrise and sunset was 0.59. Ou-Yang et al. (2014) found similar variability in the seasonal mean diurnal cycles of *q* and CO for a high-mountain background station in East Asia, and Weiss-Penzais et al. (2006) also found this for Mt. Batchelor Observatory. However, they did not perform any correlation analyses; thus it was not possible to objectively compare their findings with the results presented here. We note that a daytime peak in CO_2 is due to the absence of or only weak CO_2 uptake via photosynthesis during the fall so that the air mass arriving at the site from the adjacent valley due to upslope flows is not CO_2 depleted. This is unlike cases in summer months as discussed, for example, in De Wekker et al. (2009) where a decrease is observed in CO_2 at a mountaintop site in the Colorado Rockies due to photosynthetic CO_2 uptake.

5.2 Case II: Impacts corresponding to slope flows (21 May 2009)

The lidar observations during case II on 21 May 2009 indicate the evolution of a shallow CBL over the site with a maximum CBL height of 550 m AGL around 12:00 LST remaining quasi-stationary for more than 4 hours until 16:30 LST (Fig. 4). The morning CBL growth rate (90 m hr^{-1}) was slower than for case I (240 m hr^{-1}). The CBL height at IAD using the 19:00 LST sounding on 21 May was 1306 m MSL, using the approach in Lee and De Wekker (2016); see Appendix A for further details.

Starting at 06:30 LST in the morning, both CO mixing ratios and q exhibit an increasing trend until 12:00 LST when the CBL reached its daytime maximum value. This increasing trend illustrates the impact of upslope flow on the CO mixing ratios. The correlation between CO and q was higher (r = 0.75) than for case I. The CO mixing ratio increased from an initial value of 116 ppb to 155 ppb at 13:00 LST. This large increase in CO mixing ratio may be attributed to transport from local upwind source regions and corresponds to type I scenario (Fig. 1). Also, in contrast to case I, the CO_2 diurnal cycle for this case evinces noticeable impact of upslope flow and associated photosynthetic uptake on the diurnal variability with a more prominent decrease in daytime CO_2 mixing ratios as discussed in previous studies for situations in the growing season (e.g., De Wekker et al., 2009; Lin et al., 2016). Additionally, to help determine local sources of CO, we have also investigated the possible local influences from a nearby road (Skyline drive) on the CO mixing ratio at Pinnacles (see Appendix B for further discussion).

The increase indicates that CO mixing ratios in the valley air mass reaching the mountaintop via vertical transport and mixing were higher than at the mountaintop, so boundary layer dilution did not have a significant impact on the mountaintop trace gas mixing ratios until 13:00 LST. Thus,

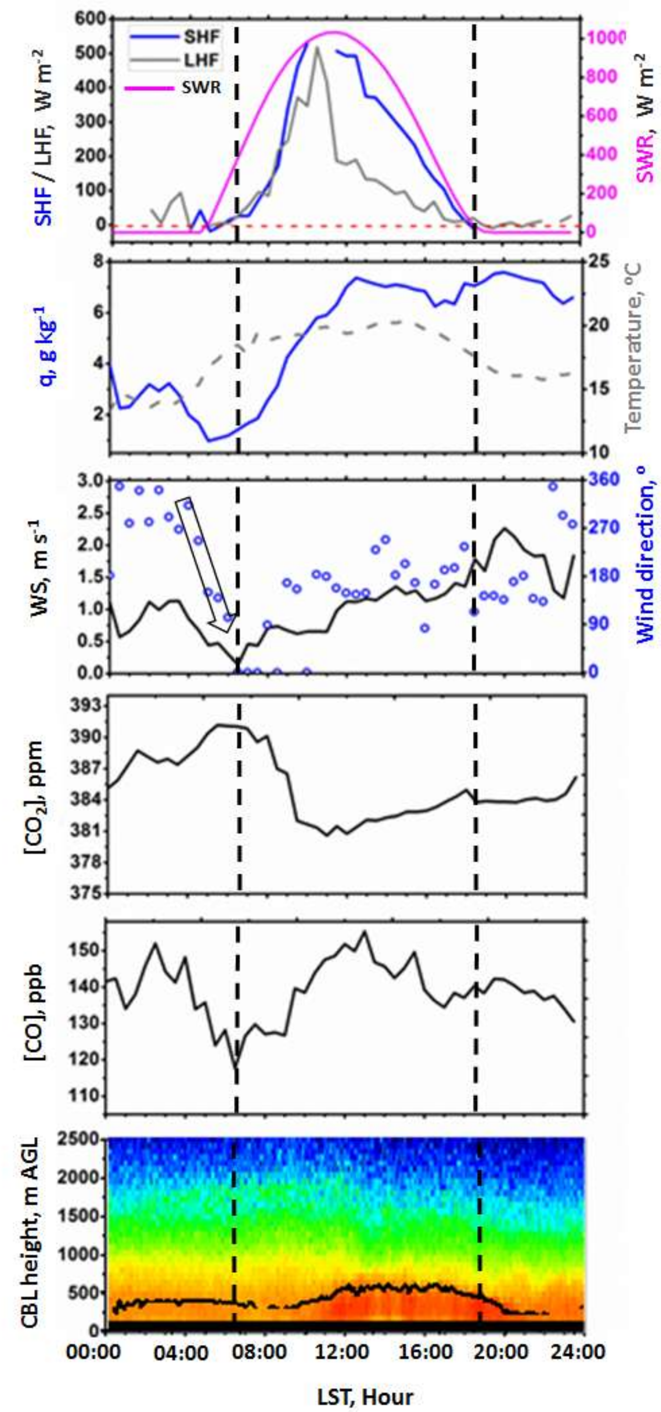

Fig. 4. *Same as Fig. 3 but for measurements on 21 May 2009 illustrating CO variability in the presence of a shallow CBL (~ 550 m AGL).Horizontal wind shift is marked by the black arrow in the third panel.*

we infer that the mountaintop measurements are mainly influenced by valley air during a time period until 12:00 LST when continuous development of the CBL height over the mountaintop was observed based on the lidar measurements. In a very recent study, using the measurements from concurrent DISCOVER-AQ (Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality) and FRAPPE (Front Range Air Pollution and Photochemistry Experiment) campaigns in northern Colorado, Sullivan et al. (2016) also illustrated similar impacts of thermally driven flow throughout the day. Their study, which mainly reported on O_3 concentrations, highlighted the role of slope winds on bringing pollutants from the Colorado Plains toward the foothills of the Rocky Mountains.

In the afternoon hours between 13:00 and 17:00 when the CBL height remained quasi-stationary around its daytime maximum value, both CO and q mixing ratios decreased. In particular, the CO mixing ratio decreased by around 20 ppb due to the dilution effect. Thus, on a day with a relatively shallow CBL over the mountaintop, the CO mixing ratio is affected by upslope flows during the growing CBL regime and by the dilution effect when CBL reaches its daytime maximum until the late afternoon. However, in the deep CBL scenario (i.e. case I), the CO at the mountaintop was influenced mainly by the CBL dilution effect.

The CO diurnal cycle feature during the morning transition period observed for case II is similar to the CO measurements at the tops of tall towers in flat terrain: vertical transport and mixing of polluted NBL air to the tower top increases the CO mixing ratio until the time when the CBL height reaches the tower height during the late morning or early afternoon hours (e.g., Yi et al., 2000; Pal et al., 2015; Pal and Haeffelin, 2016). However, for tall tower measurements in flat terrain, the tracer mixing ratios remain in their equilibrium level during the quasi-stationary CBL regime whereas for the mountaintop site the CO mixing ratios continue decreasing due to CBL dilution until 17:00 LST.

The CO diurnal cycle feature for Case II is unlike the diurnal cycle reported by, e.g., Gao et al. (2005) at Mount Tai in China where they attributed the elevated afternoon mixing ratios of CO to the transport of boundary layer pollution to the summit of the mountain due to daytime upslope flows and the growth of CBL. In that case, the dilution effect was not able to overcome the increase in CO due to upslope flows. Nevertheless, Gao et al. (2005) did not investigate the mountaintop CBL evolution as we have presented here using continuous lidar measurements.

Additionally, it should be noted that the CO mixing ratio between 01:00 and 04:00 LST appears to be as large as during the daytime upslope regime on this day, which suggests that during a time period without upslope flows, near peak CO is sampled which most likely can be attributed to the RL CO mixing ratio at the site. Then, between 03:00 and 06:00 LST, i.e. near sunrise but before upslope flow can properly occur, CO begins to decrease. This decrease occurs simultaneously with a wind shift from northwesterly to southeasterly illustrating the impact of local-scale transport processes on the CO mixing ratio at the monitoring site. This suggests air masses being transported downslope by the cold drainage flow at night affecting the CO mixing ratio at the site in the early morning. Water vapor mixing ratio also decreases by 2 g kg^{-1} during the same period (i.e. between 03:00 and 06:00 LST).

5.3 Case IIIa: Impacts corresponding to horizontal transport (5 September 2009)

Very different meteorological conditions and trace gas variability were observed during case IIIa on 5 September 2009 than during the previous two cases. During this case, a clearly visible daytime horizontal wind shift from northwesterly to southeasterly occurs at the site (Table 1 and

Fig. 5). Using 4-years long measurements, recently, Lee et al. (2015) concluded that the horizontal transport of CO outweighs the dilution effect resulting in a daytime increase in the CO mixing ratio due to wind shift. In the present context, CO variability during case IIIa at Pinnacles (i.e. C_{M_Top} mentioned in Fig. 1) corresponds to type I scenario (section 2) where a clearly visible increase in CO mixing ratio is revealed starting around 12:00 LST. The temporal variability of CBL height over the site and its influence on the CO mixing ratios were not investigated in Lee et al. (2015). In addition, Pal et al. (2014) found for a valley location that regular wind shifts due to thermally driven valley flows affect the variability of ultrafine aerosol particles where advection outweighs the contribution of CBL mixing. These two recent studies motivated us to further investigate the impact of wind shifts on the CO mixing ratio on diurnal time scales using concurrent lidar and meteorological measurements at Pinnacles. Consequently, we selected two cases with well-defined diurnal wind shift.

Lidar measurements were not available during case IIIa for the period between midnight and noon. However, CBL height measurements during the afternoon reveal the development of a deep CBL over the site. The CBL height shows a daytime maximum of 1500 m AGL around 15:00 LST when low level clouds appeared at the site. At this time, the horizontal wind started backing from northwest to southeast. Very low wind speeds (~ 0.5 ms^{-1}) were observed during the first half of the day. After 16:00 LST, the wind speed increased from 0.5 to 1.5 ms^{-1} and remained southeasterly until midnight.

The observed wind shift at the site around 12:00 LST (northwesterly to southeasterly) is most likely not suggestive of slope flows on this day at the site. For instance, the occurrence of the low-level clouds influenced both the sensible and latent heat fluxes as well as the near-surface temperature measurements. In particular, the diurnal cycle of sensible heat flux was disrupted on

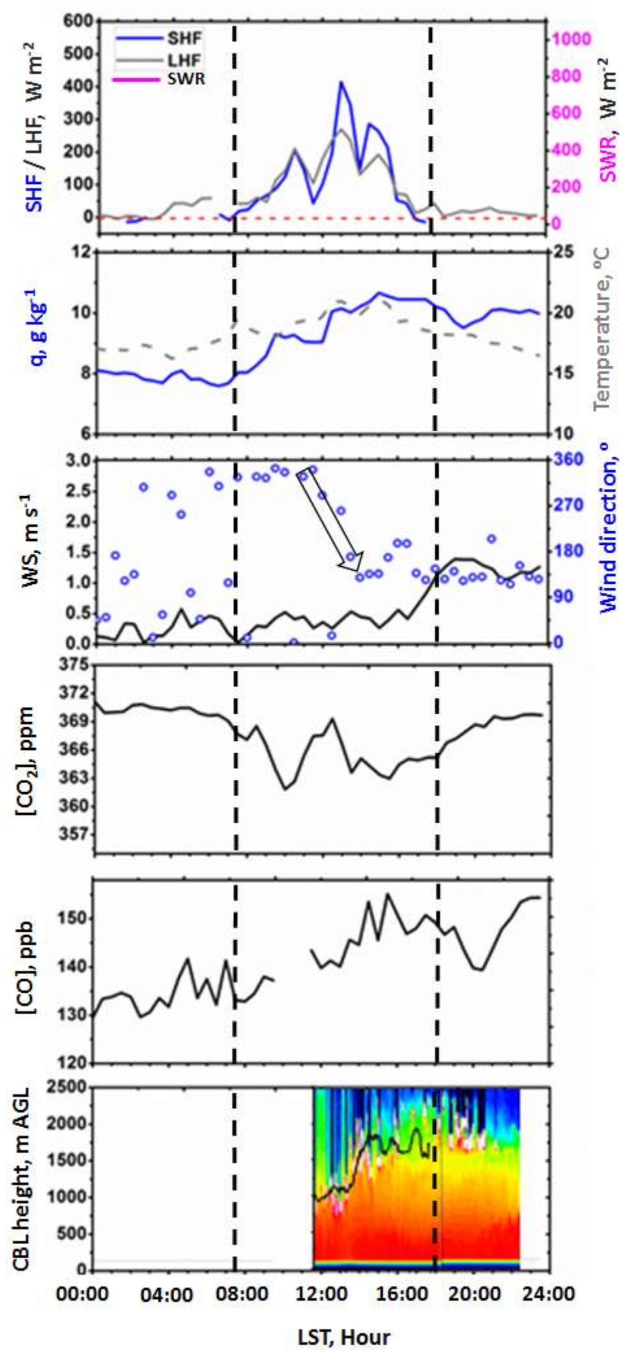

Fig. 5. *Same as Fig. 3 but for measurements on 5 September 2009 for case IIIa revealing the influence of daytime horizontal wind shift from (northwesterly to southeasterly) on the CO variability. The development of a deep CBL (1500 m AGL) on this day over the site is also visible. Horizontal wind shift is marked by the black arrow in the third panel.*

this day, contrary to the two previous cases. The daytime maximum and nighttime minimum temperatures were 21 ˚C and 16 ˚C, respectively, and showed no prominent diurnal cycle that had been observed in the other cases. Additionally, synoptic surface analyses also indicated similar wind shift at other sites over the adjacent plains (not shown).

During case IIIa, the CO mixing ratio increased by 10 ppb between 08:00 and 11:00 LST whereas during the afternoon between 12:00 and 15:00 LST, a relatively larger increase (15 ppb) in CO was observed, and CO mixing ratios peaked at 150 ppb. The q variability was similar to the CO variability with a maximum q of 11 g kg^{-1} at 16:00 LST, remaining high until midnight. The correlation between CO and q variability was higher during this case study than during the two other cases, with r of 0.82.

This case appears to completely conflict the mechanism described in Case I that also had a deep CBL over the site. Specifically, we did not observe dominant signatures of boundary layer dilution effect on CO diurnal cycle exhibiting daytime decrease during case IIIa. We investigated the role of the shift in the horizontal wind (northwesterly to southeasterly) to the increase in CO mixing ratio starting at 10:00 LST. To this end, we performed a trajectory analysis of case IIIa using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Hess, 2004), which we initialized using 12 km wind fields from the North American Model (NAM) as displayed in Fig. 6. We ran HYSPLIT backward 72 hr using a starting height of 100 m AGL following previous studies in the region (i.e., Lee et al. 2012; Lee et al. 2015). We performed two runs: one for the morning when northwesterly winds were observed at Pinnacles, and another for the afternoon when southeasterly flows were present. Both runs yield the differences in wind direction early on in the backward trajectory analysis and the trajectory goes over a very different area. However, both runs suggest the Northeast is a source region here.

Similar findings on the impact of horizontal transport on CO measurements at Pinnacles were previously reported by Lee et al. (2012). These results suggest that the CO and *q* variability were mainly governed by the transport of a different air mass associated with the horizontal wind shift. In particular, along with the primary maximum in the CO mixing ratio in the late afternoon (~ 150 ppb around 15:00 LST), several secondary peaks were also present. Therefore, it is likely that the boundary layer dilution effect during the late afternoon did not have a clear impact on the trace gas variability at the site for case IIIa as was evident for case I, although in both cases a deep boundary layer (1200 m AGL) prevailed.

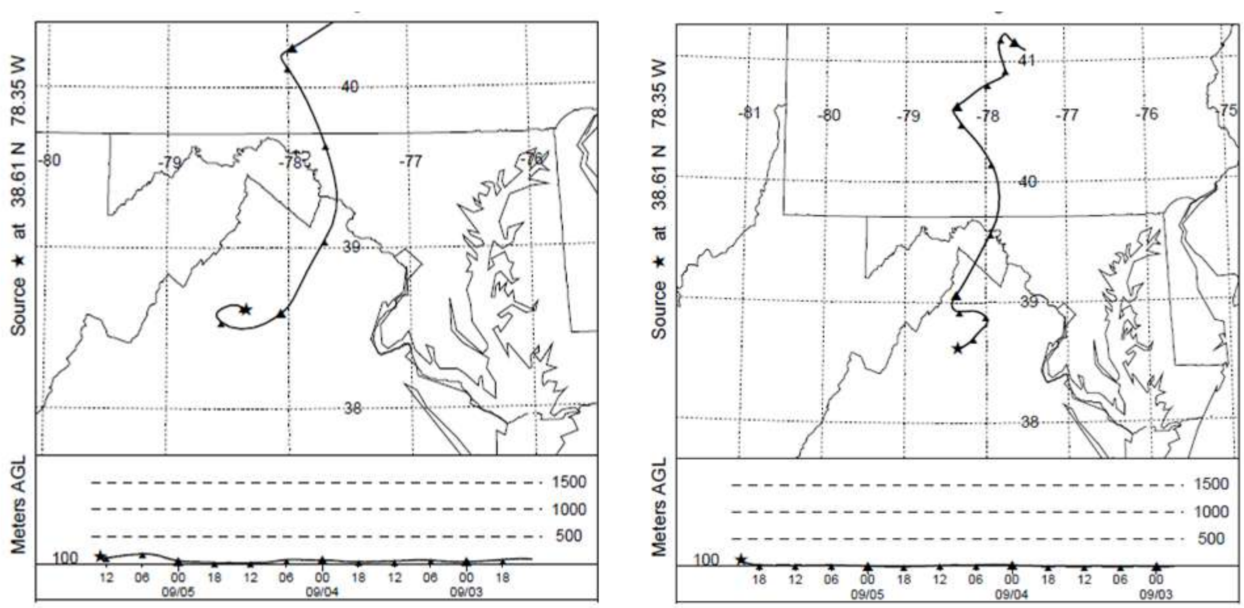

Fig. 6. *72 Hour backward trajectory based on NOAA HYSPLIT model using NAM (12 km horizontal resolution) meteorological data, initialized 100 m AGL for 13:00 UTC (08:00 LST, 5 Sep 2009), (left) and 21:00 UTC (16:00 LST), (right). Model vertical velocity was used for vertical motion calculations for both scenarios. Height of trajectory AGL is shown in the bottom portion of the figure. Source of the images http://ready.arl.noaa.gov/HYSPLIT.php.*

5.4 Case IIIb: Impacts corresponding to horizontal transport (21 October 2009)

To further illustrate the role of horizontal wind shift on CO mixing ratios, we considered another case (i.e., case IIIb, 21 October 2009). During case IIIb, a similar wind direction shift was observed at the site but occurred during the morning transition period around 10:00 LST (Fig. 7). Case IIIb was characterized by cloud free conditions with a clear diurnal cycle in the incoming solar radiation, sensible heat flux, and other meteorological variables at the site (Table 1). However, the CBL was shallower than in previous case (case IIIa) with a daytime maximum CBL height of ~ 500 m AGL.

The prevailing northwesterly wind started backing at 10:00 LST and became southeasterly at around 12:00 LST. Between 09:00 and 17:00 LST, CO mixing ratios steadily increased from an average value of around 90 ppb to a maximum value of around 120 ppb; thus corresponds to type I scenario (Fig. 1). The increase in CO mixing ratio of more than 30 ppb is larger than the total uncertainty (i.e., < 6 ppb) of the instrument. The water vapor mixing ratio increased in a very similar way as CO from its early morning value of 2.5 g kg^{-1} to a quasi-steady afternoon value of 5.5 g kg^{-1}. A correlation coefficient between CO and q of 0.91 confirms their similar (or almost identical) temporal variability between sunrise and sunset on this day. After 17:00 LST when the horizontal wind became westerly, both CO and water vapor mixing ratios started to decrease due to downslope flows transporting cleaner FA air masses to the site.

One general conclusion from the above results is that, due to a shift in the wind direction (from northwesterly to southeasterly), horizontal advection of a different air mass increases the CO mixing ratio at the site. However, increases in CO mixing ratios in both cases appear to be similar but not identical. In particular, (1) two different CO increases were observed: 20 ppb and

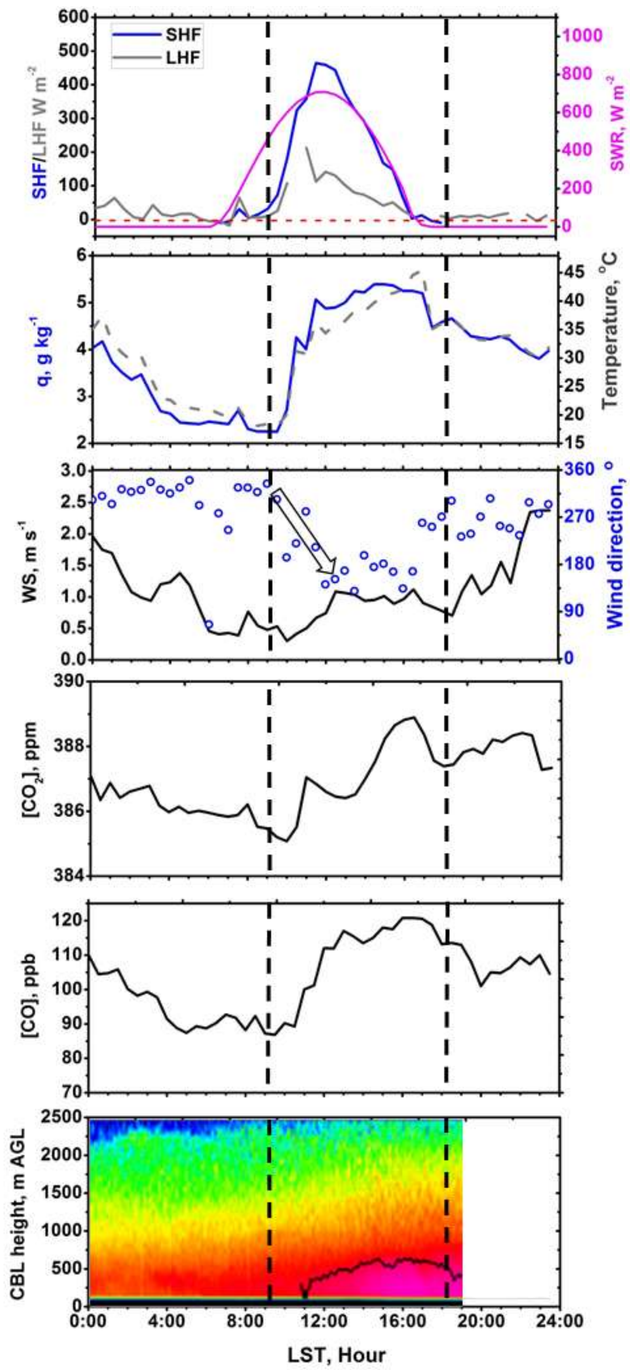

Fig. 7*: Same as Fig. 3 but for measurements on 21 October 2009 (case IIIb) illustrating the impacts of both wind directions shift during the morning transition period and a shallow CBL (600 m AGL) over the site during the afternoon hours. The initial CO mixing ratio was very low (90 ppb). Horizontal wind shift is marked by the black arrow on the third panel.*

35 ppb for case IIIa and case IIIb, respectively; (2) the initial CO mixing ratios (i.e. CO mixing ratio in the NBL at the site) for case IIIa and case IIIb were 130 and 85 ppb, respectively, so more polluted air masses were present during case IIIa than during case IIIb, and (3) lidar measurements confirmed a higher daytime maximum CBL height during case IIIa (1500 m AGL) compared to case IIIb (500 m AGL). Although for both cases the CO mixing ratio variability was substantially influenced by the air mass transported to the site, it appears that the boundary layer dilution effect had more impact on CO mixing ratio during case IIIa than during case IIIb. Thus, a larger increase and more accumulation in CO (35 ppb) were observed for case IIIb than for case IIIa. These results clearly underscore the importance of continuous monitoring of CBL height variability at a mountaintop site like Pinnacles.

Additionally, we have performed HYSPLIT analyses for case IIIb (21 Oct 2009) which showed clear evidence that different air mass source regions influenced the site during the daytime. 72 hour backward trajectories initialized at 0800 LST show descending trajectories that originated over the Midwest. Backward trajectories initialized at 1600 LST had shorter flow paths and had more contact with surface emissions over central Virginia, thereby helping to explain the marked increase in CO mixing ratios observed at the site during the afternoon.

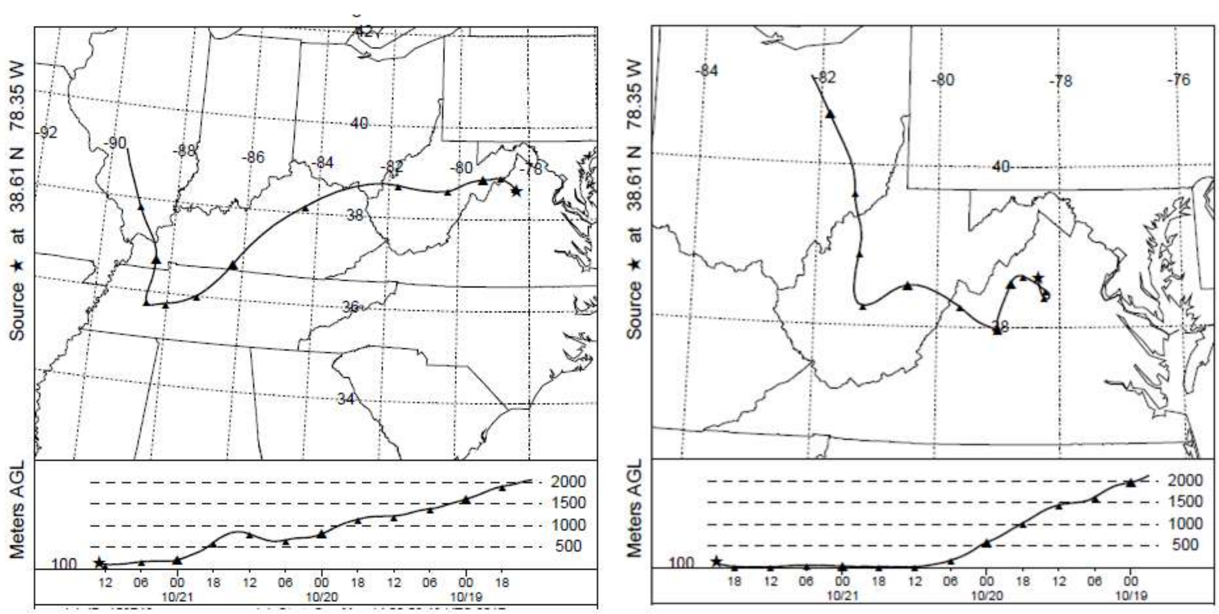

Fig. 8. Same as Fig. 6 but for 72 Hour backward trajectory, initialized at 100 m AGL for 13:00 UTC (08:00 LST, 21 Oct 2009), (left) and 21:00 UTC (16:00 LST), (right). Source of the images http://ready.arl.noaa.gov/HYSPLIT.php.

6. Generalization of the case studies

Using lidar-derived CBL height variability over a mountaintop site, we demonstrated for the first time the relation between CBL height and CO mixing ratio for a typical well-characterized situation at a low mountaintop site (Pinnacles). This investigation helped us provide detailed information on diurnal cycles of CO mixing ratios, in particular, contrasting CO diurnal cycles: daytime decrease (case I with daytime maximum CBL height of around 1200 m AGL) versus daytime increase (case II with daytime maximum CBL height of around 500 m AGL). Additionally, two cases (cases IIIa and IIIb) with diurnal wind shift illustrate the role of transport of a different air mass to the site on the elevated afternoon levels of CO and water vapor mixing ratios as was reported by Lee et al. (2015) although their work did not provide detailed information on the CBL height evolution at the site.

In recent studies, researchers have started examining the implications of using nocturnal versus daytime mountaintop measurements of GHGs and trace gases within model simulations (e.g. Lin et al., 2016). Additionally, very recently, Bamberger et al. (2017) investigated the application of mountaintop measurements to find regional representativeness GHG mixing ratios. Our findings further illustrate CO mixing processes in complex terrain, in particular over a site significantly perturbed via local scale flows. Two key aspects of the results presented in Section 5 are generalized here by evaluating four-year (2009-2012) long measurements of CO and meteorological conditions at Pinnacles: (1) correlation between daytime CO and water vapor mixing ratio evolution, and (2) general pattern of diurnal contrasts in CO mixing ratios.

6.1 Correlation between daytime CO and water vapor mixing ratio evolution

A linear regression analysis was carried out between CO and water vapor mixing ratio variability from sunrise to sunset on each day of the four-year period that we performed for the case studies presented in Section 5. Frequency distributions of the correlation coefficients (r) for different years are shown in Fig. 9. As discussed in Section 5, positive (negative) correlation coefficient implies that both CO and q vary similarly (differently). Numbers of cases vary from one year to the other; however, at least 70 % of the days in a year are covered (except in 2010 where number of days is 205).

Nevertheless, it can be concluded that 70 % (30 %) of the times in a year, CO and q shows a positive (negative) correlation coefficient illustrating the fact that like q, CO could be considered

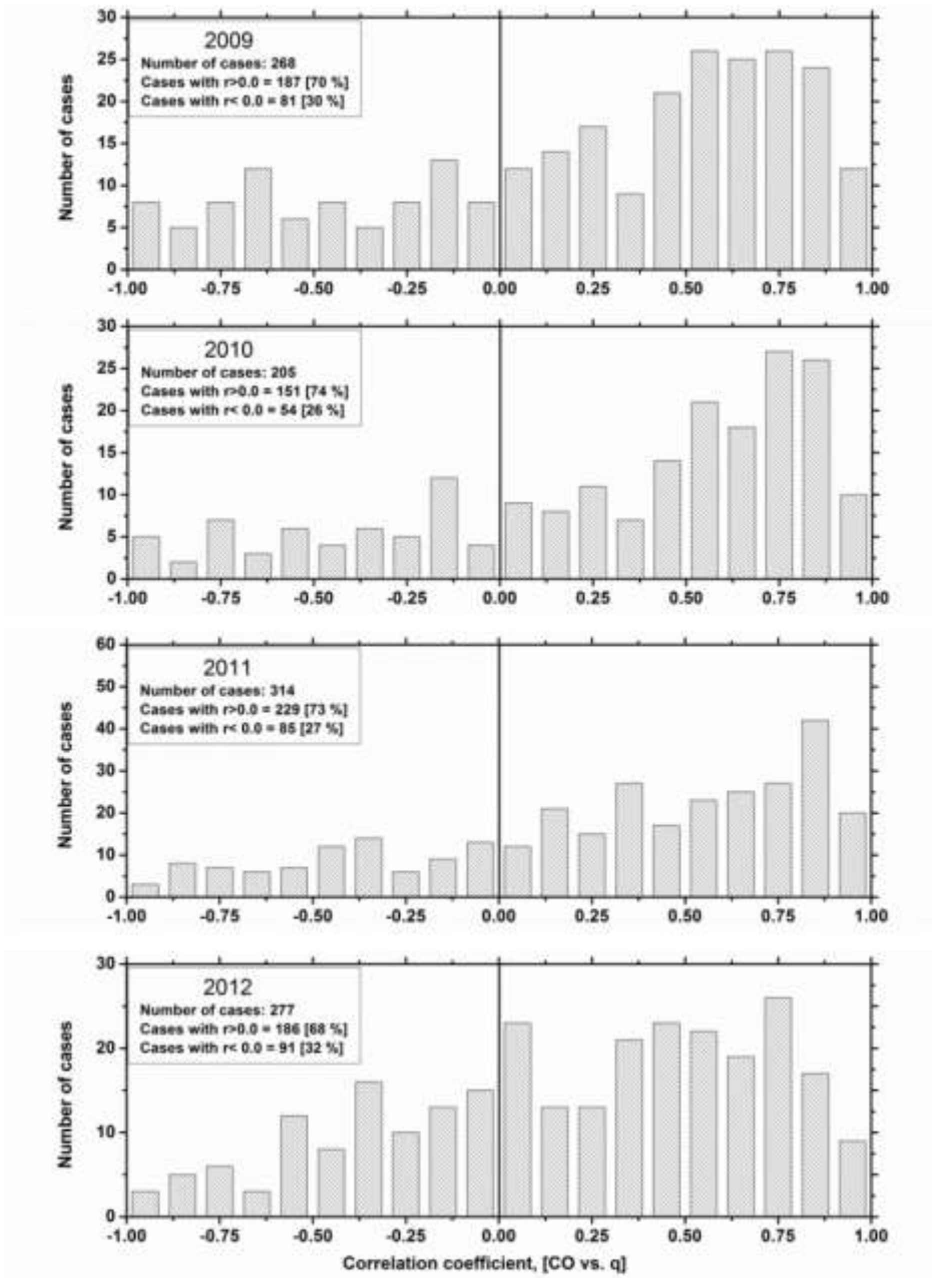

Fig. 9. *Distribution of r based on regression analyses between daily time series of CO and q between morning transition period to late afternoon on different days between 2009 and 2012. Number of cases in different years, two different r distributions with number of days and percentages with respect to the total number of days when observations were available are reported in each panel. Vertically-aligned solid grey line marks r = 0 showing no correlation between CO and q.*

a good tracer for studying boundary layer mixing processes including the impact of upslope flows in the mountainous regions. For instance, in 2009, positive (negative) r was found on 187 (81) days among 268 days. In section 5, it was found that available lidar-derived CBL height variability helped understanding the boundary layer regimes at the site for those cases. However, we do not have continuous lidar measurements for the four-year period (2009-2012). In future studies, we will therefore use model simulations of CBL height diurnal cycles and available meteorological measurements to illustrate possible mechanisms governing the nature of correlation coefficients on different days and seasons at the site.

6.2. General pattern of diurnal contrasts in CO mixing ratios

In this study as well as in a number of past studies, it was found that due to upslope flow contribution, CO mixing ratio at the mountaintop sites increases after morning transition and yields a daytime maximum peak (case II). However, within the case studies presented here, we demonstrated that for some situations the boundary layer dilution effect outweighs the upslope flow contribution in governing CO diurnal cycle and yields a daytime minimum (case I). Thus, using the four-year long measurements at Pinnacles we demonstrate how frequent the two different types of CO diurnal cycles (i.e. type I and type II scenarios in Fig. 1) occur at the site using daytime versus nighttime CO differences on different days. We believe these results would provide important information on the interplay between the nocturnal CO mixing ratios at the mountaintop versus the upslope flow contribution and boundary layer dilution.

First of all, daily mean nocturnal (daytime) CO mixing ratio is determined by averaging CO variability observed between 00:00 and 04:00 LST (12:00 and 16:00 LST). We refer to the difference between nighttime and daytime CO as the “CO contrast” on diurnal time scale. The daily CO contrast is obtained by subtracting the daytime mean from nighttime mean CO mixing ratio. As explained in section 5, a positive CO contrast implies a decrease in CO mixing ratios during the day, most likely explaining the impact of boundary layer dilution while a negative CO contrast implies an increase in CO mixing ratios during the day, most likely explaining the impact of upslope flows bringing more polluted adjacent valley air mass or via transport of a different air mass to the site.

Results obtained for the CO contrasts on different days between 2009 and 2012 are summarized in Fig. 10. For instance, in 2009, the number of days or cases showing a daytime increase (156 days among 322) is very similar to the number of cases showing a daytime decrease (166 days among 322) at the site illustrating comparable situations for both the impacts of upslope flows or transport processes and boundary layer dilution effect. It can also be seen that in other years these contributions remain comparable (i.e. ~ 50 %) suggesting the importance of continuously monitoring both meteorological conditions and CBL heights over the low mountaintop sites like Pinnacles. These results will help demonstrate the implications of assimilating nighttime versus daytime measurements within numerical models for low mountaintops. In future studies, using long-term measurements of CO contrasts and model-simulations of CBL height and meteorological conditions, we will investigate in detail the diverse nature of the reported CO contrasts.

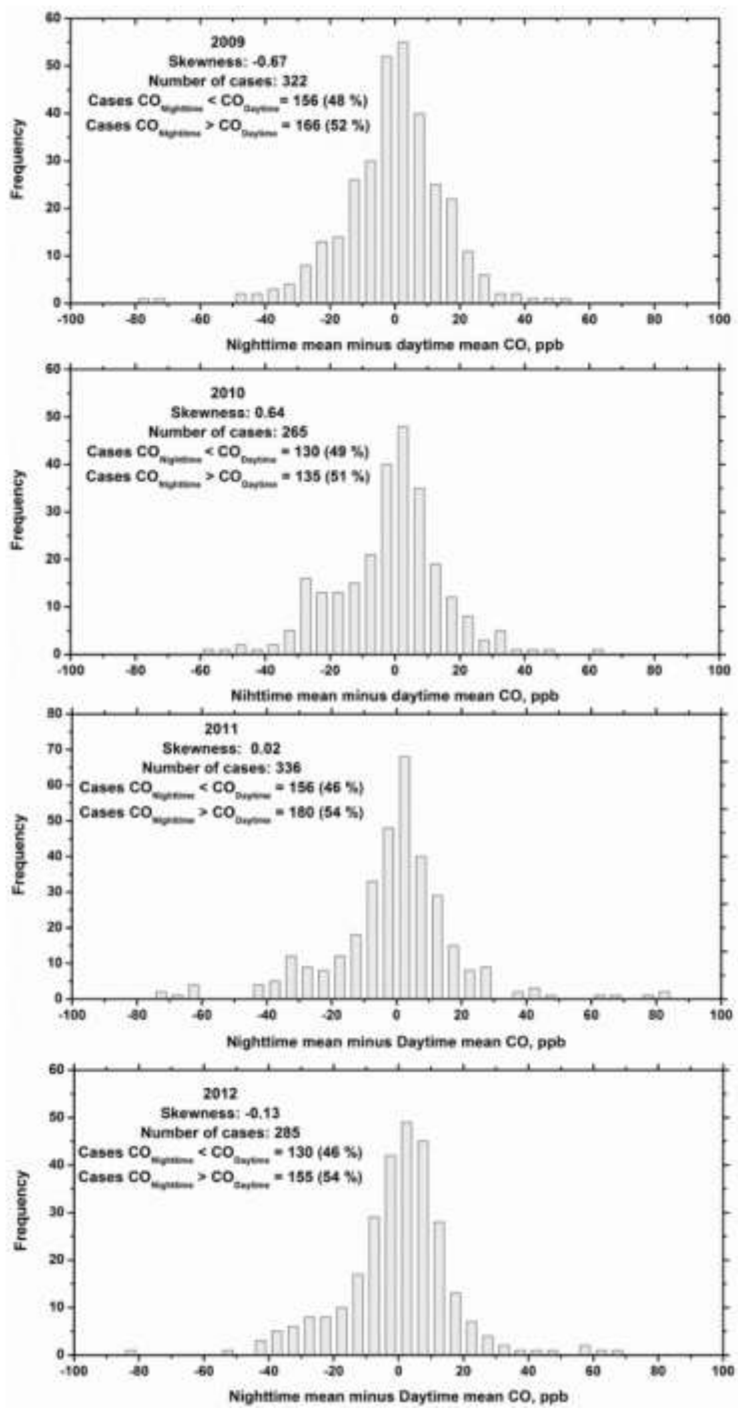

Fig. 10. *CO contrasts calculated by subtracting daytime mean CO mixing ratio from nighttime mean CO mixing ratio on different days for the period between 2009 and 2012. Numbers of cases in two different regimes of CO variability with their occurrences are also reported in each panel.*

7. Summary, conclusions and outlook

In the present study, we used selected case studies to investigate the impact of CBL dynamics on the diurnal variability of CO mixing ratio at a low mountaintop site. We hypothesized that CO diurnal cycle at the mountaintop site is affected by the combined impact of meteorological condition, slope flows, boundary layer depth and associated growth rate, and regional scale advection. We also considered two well-defined clearly two scenarios in the CO diurnal cycle: Type I scenario for increasing CO, and type II scenario for decreasing CO. Using three different cases, we find that the CO diurnal cycle during case I (decreasing CO), case II (increasing CO), and case III (increasing CO) is significantly affected by deep CBL mixing, upslope flow, and regional scale advection, respectively. A summary of the findings for the three cases is illustrated in Fig. 11 which clearly outlines the fact that one needs to untangle the influences of competing physical processes affecting mountaintop CO measurements to understand and simulate mountaintop tracer measurements. Investigating the three cases using the available observations facilitated a better understanding of the impacts of CBL dynamics on the CO diurnal cycle over the mountaintop site Pinnacles. In particular, we introduced a conceptual framework for the pollutant mixing processes in the mountain-valley atmosphere using the results based on case studies (Fig. 11).

For the first time, continuous and simultaneous lidar and CO measurements during the entire diurnal cycle were performed over a low mountaintop site. We found the following two main results: (1) for a case with initial CO mixing ratios of ~120 ppb in the morning and with a shallow afternoon CBL ~ 550 m AGL, a daytime increase in CO is observed, illustrating the

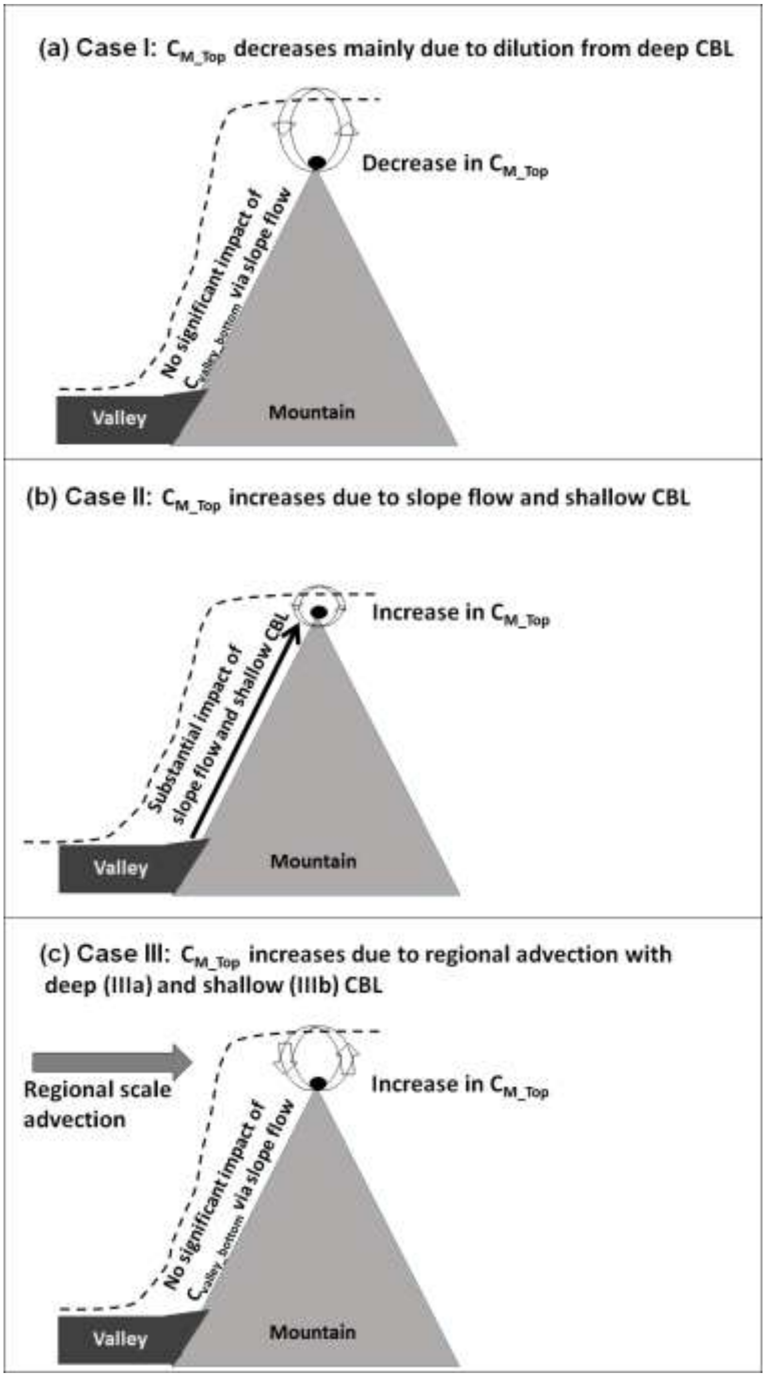

Fig. 11: *Summary of the findings for three cases presented in section 5. A decrease in CO mixing ratio (referred as* C_{M_Top} *in schematic) during case I occurs mainly due to deep CBL (a), an increase in CO during case II occurs due to slope flows marked with the black solid arrow (b), and an increase in CO during case IIIa and IIIb occur due to regional scale advection as marked by the horizontally aligned arrow (c). The curved dashed line and thick circular arrows in all panels illustrate the growing CBL and entrainment mixing at the CBL top, respectively.*

impact of upslope flow contribution (scenario I in schematic presented in Fig. 1). In another case, with initial CO of ~ 140 ppb and daytime CBL height of 1200 m AGL, the CBL dilution outweighs the upslope contribution, illustrating the impact of deep CBL mixing over the site (scenario II); (2) Comparison of two cases with and without horizontal wind shift, (case III and I, respectively), confirm the potentially dominant role of a wind shift and illustrates how elevated afternoon levels of CO and water vapor mixing ratios can be due to the transport of a different air mass to the site with no significant impact of the CBL dilution effect.

For typical meteorological conditions and CBL (e.g. case I with daytime maximum CBL height of 1250 m AGL), mountaintop CO measurements have characteristics of monitoring sites in flat terrain. On the other hand, for shallow CBL regime (case II with daytime maximum CBL height of 550 m AGL) over mountaintop, there are some similarities but also some differences with tall tower measurements. For instance, for tall tower measurements, CO mixing ratios remain in their equilibrium level during the quasi-stationary CBL regime in the early afternoon hours whereas for the mountaintop measurements the CO mixing ratios continue decreasing due to CBL dilution until very late in the day (17:00 LST in our case). This knowledge could be used in applications requiring regionally representative CO mixing ratio values.

Results presented in this work can help define fruitful criteria for emission regulations and create better quantitative information for the regulatory community. The wind shifts result in different upwind emission sources being sampled and can help estimate emissions and reduce flux estimate uncertainties over upwind areas.

This study suggests that the interpretation of observed CO diurnal cycles near the surface at mountaintop sites requires knowledge of the relationship between local CBL dynamics involving mountaintop and adjacent valleys and associated meteorological characteristics given the difficulty in resolving the terrain and flows in complex terrain. For instance, regression analysis between CO and *q* time series between sunrise and sunset showed positive *r* in all the cases. We carried out an investigation of the long-term data sets of both quantities and found that CO and *q* evinces a positive correlation coefficient on ~70 % of the days in any given year. Additionally, since the present study is based on four different cases with particular behavior in CO variability, one may wonder about the frequency of these two contrasting CO diurnal cycle features (daytime increase versus decrease in CO mixing ratios). Based on the investigation on the differences between the daily NBL CO and the daytime mean CO mixing ratios, we found that nearly 50 % of the days in any given year, mountaintop CO diurnal cycle exhibit a daytime increase and the rest of the days in a year exhibit a daytime decrease.

One of the limitations of the results presented here is that the aerosol lidar measurements at Pinnacles only account for daytime evolution of the CBL heights over the site as the full overlap of the lidar transceiver is attained at a height of 200 m. Thus, it was not possible to determine NBL height and consequently explore further the nighttime CO variability. Additionally, long-term continuous lidar measurements were not available at the site. Although this study is based on four selected cases illustrating concurrent observations of lidar-derived CBL heights, CO mixing ratio and meteorological measurements, it nonetheless underscores the important role of the impact of CBL height variability and slope winds on the CO mixing ratio at the mountaintop.

In future work, we will continue to broaden and generalize the results from the selected case studies by evaluating long-term measurements of CO available at the site in combination with estimates of nearby rawinsonde measurements of CBL heights. Such a study will be able to reveal the impact of regional scale CBL height relative to the mountaintop on CO variability.

Nevertheless, the present study provided detailed insights into the important factors and physical processes occurring in a mountain-valley atmosphere system. Such insights are helpful for addressing an important and compelling issue: can mountaintop measurements provide high quality data and spatial representativeness similar to a tall tower in a flat terrain? Within future studies, we will use numerical simulations (e.g., the Weather Research and Forecasting (WRF) model) to further examine the role of upslope flows on the mountaintop CO and CO_2 mixing ratios. Finally, while the present study has focused solely on the dynamical processes affecting the mountaintop CO mixing ratios, additional studies are needed to help quantify the potential role of atmospheric chemistry processes on the CO diurnal pattern at low mountaintops.

Acknowledgement

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Appendix A: CBL height derived using lidar at Pinnacles versus rawinsonde at IAD

There were no rawinsonde measurements from the adjacent Page Valley on any of the four case studies presented here. However, we took an advantage of the nearby rawinsonde measurements taken at 19:00 LST (00:00 UTC) at Dulles airport (IAD), located approximately 90 km northeast of Pinnacles near Washington, DC.

The CBL height at Dulles airport may be ill-defined around 19:00 LST, considering that NBL evolution has started around that time. Lee and De Wekker (2016) explained that near-surface stability is an important issue that needs to be considered in order to correctly estimate the afternoon CBL height using measurements at 19:00 LST. In their study, they hypothesized that the residual layer height observed at 19:00 LST is equivalent to the daytime maximum afternoon CBL height (Stull, 1988). Therefore, based on an objective method, they excluded the first few hundred meters of stable boundary layer measurements to derive the CBL height from the 19:00 LST rawinsonde measurements. We used their methodology to derive afternoon CBL height in this study. The CBL height based on IAD rawinsonde measurements can differ from the CBL height over Pinnacles because of the horizontal distance between the two sites (~ 100 km) and to the two different sampling times of these measurements. Lee and De Wekker (2016) showed typical differences of the CBL height between Dulles and the Page Valley of 200-400 m (higher over the Page Valley than at IAD).

For case I (14 Sep 2009) lidar measured daytime maximum CBL height was found to be ~ 1250 m AGL over Pinnacles (i.e. ~ 2250 m MSL), whereas CBL height from rawinsonde measurements at 19:00 LST, computed using the bulk Richardson number approach (Lee and De Wekker, 2016), was 1625 m MSL. For Case II (21 May 2009), the CBL height at IAD (1306 M MSL) was also lower than lidar-derived CBL height (~ 1600 m MSL) at Pinnacles. These differences in CBL height between the mountaintop and at IAD are consistent with findings by Lee and De Wekker (2016) who observed spatial heterogeneity in the CBL heights and discussed in detail the different factors responsible for these differences, including the distance between the two measurement sites and the effects of underlying land surface forcing.

Appendix B: Possible impact of local sources of CO at Pinnacles

One notable local source for CO measurements at Pinnacles is Skyline Drive, a scenic tourist road in the Shenandoah National Park that runs southwest-northeast about 100 m southeast of the monitoring site. As Skyline Drive is directly upwind of Pinnacles throughout much of the daytime on 21 May and 21 Oct, one may expect these local emissions to affect the mountaintop trace gas measurements. However, previous studies from the site have suggested that vehicular emissions from Skyline Drive are unlikely to have a significant effect on the mountaintop trace gas measurements from Pinnacles (i.e., Lee et al. 2012, 2015), as well as other nearby mountaintop monitoring sites, i.e. Big Meadows (e.g., Poulida et al., 1991; Cooper and Moody, 2000). For example, Lee et al. (2012) found that, despite weekends having 2-3 times the volume of traffic on weekdays, there were no statistically significant differences in trace gas mixing ratios by Skyline Drive. Additional analyses by Lee et al. (2015) confirmed this finding as well. They found that, even though vehicular emissions are typically higher during the summer and fall tourist seasons, CO increases occurred only several hours after the traffic maximum along Skyline Drive.

To investigate transport from more regional resources, e.g. upwind fires, we used Moderate Resolution Imaging Spectroradiometer (MODIS) (e.g. Justice et al. 2002) to determine the presence of fires in the region around Pinnacles on days when there is a marked CO increase (e.g., 21 May 2009 and 21 Oct 2009). Analyses of MODIS data for 21 May (Fig. A1a) and for 21 Oct (Fig. A1b) indicate the presence of fires upwind of Pinnacles that could have contributed to the daytime CO increase.

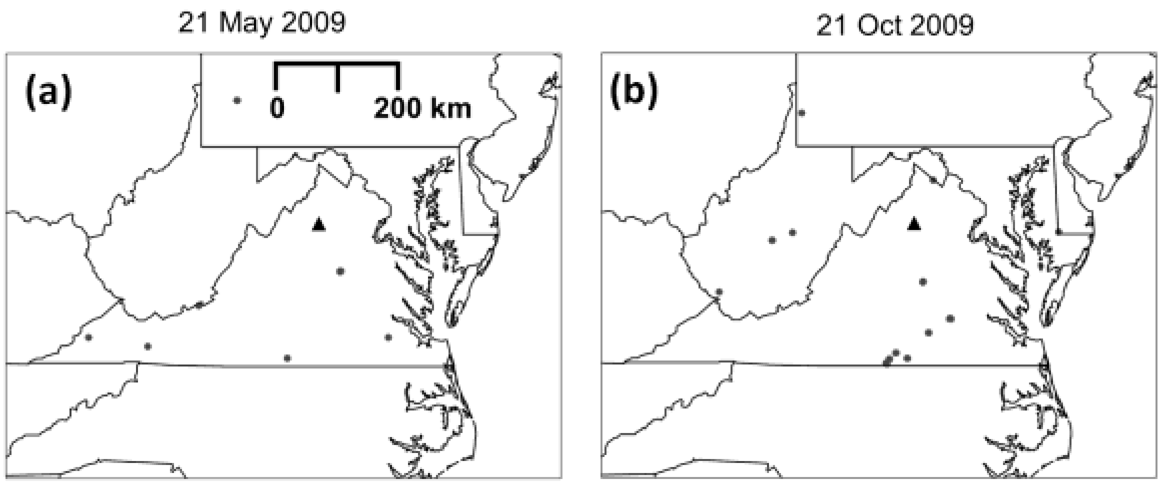

Fig A1: Locations of fires (grey dots) identified in MODIS relative to Pinnacles (black triangle) on 21 May 2009 (a) and 21 Oct 2009 (b).

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