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Black carbon emission and transport mechanisms to the free troposphere at the La Paz/El Alto (Bolivia) metropolitan area based on the Day of Census (2012)

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ABSTRACT

Urban development, growing industrialization, and increasing demand for mobility have led to elevated levels of air pollution in many large cities in Latin America, where air quality standards and WHO guidelines are frequently exceeded. The conurbation of the metropolitan area of La Paz/El Alto is one of the fastest growing urban settlements in South America with the particularity of being located in a very complex terrain at a high altitude. As many large cities or metropolitan areas, the metropolitan area of La Paz/El Alto and the Altiplano region are facing air quality deterioration. Long-term measurement data of the equivalent black carbon (eBC) mass concentrations and particle number size distributions (PNSD) from the Global Atmosphere Watch Observatory Chacaltaya (CHC; 5240 m a.s.l., above sea level) indicated a systematic transport of particle matter from the metropolitan area of La Paz/El Alto to this high altitude station and subsequently to the lower free troposphere. To better understand the sources and the transport mechanisms, we conducted eBC and PNSDs measurements during an intensive campaign at two locations in the urban area of La Paz/El Alto from September to November 2012. While the airport of El Alto site (4040 m a.s.l.) can be seen as representative of the urban and Altiplano background, the road site located in Central La Paz (3590 m a.s.l.) is representative for heavy traffic-dominated conditions. Peaks of eBC mass concentrations up to 5 $\mu g\, m^{-3}$ were observed at the El Alto background site in the early morning and evening, while minimum values were detected in the early afternoon, mainly due to thermal convection and change of the planetary boundary layer height. The traffic-related eBC mass concentrations at the road site reached maximum values of 10–20 $\mu g\, m^{-3}$. A complete traffic ban on the specific Bolivian Day of Census (November 21, 2012) led to a decrease of eBC below 1 $\mu g\, m^{-3}$ at the road site for the entire day. Compared to the day before and after, particle number concentrations decreased by a factor between 5 and 25 over the particle size range from 10 to 800 nm, while the submicrometer particle mass concentration dropped by approximately 80%. These results indicate that traffic is the dominating source of BC and particulate air pollution in the metropolitan area of La Paz/El Alto. In general, the diurnal cycle of eBC mass concentration at the Chacaltaya observatory is anti-correlated to the observations at the El Alto background site. This pattern indicates that the traffic-related particulate matter, including BC, is transported to higher altitudes with the developing of the boundary layer during daytime. The metropolitan area of La Paz/El Alto seems to be a significant source for BC of the regional lower free troposphere. From there, BC can be transported over long distances and exert impact on climate and composition of remote southern hemisphere.

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1. Introduction

Partic late black carbon (BC) plays an important role in air q ality and in the radiative balance of the Earth (Bond et al., 2013). Besides the harmf lness of BC particles as carriers of toxic trace compo nds s ch as metals and polycyclic aromatic hydrocarbons, partic late BC is the strongest anthropogenic absorber of solar light in the atmosphere. However, the q antification of climate forcing d e to atmospheric BC as a light-absorbing compo nd reveals to be still limited (IPCC; https://ar5-syr.ipcc.ch/). Uncertainties in emission inventories imply that predicting particle mass concentrations of elemental carbon (or BC) as well as its temporal and spatial resol tion remain a major problem. F rthermore, an improved knowledge of BC emitted and/or transported into the free troposphere might be of importance d e to its significantly long residence time there. This co ld therefore also affect regions located far away thro gh long-range transport. In addition to emission fl xes, q antifying radiative forcing from BC also req ires knowledge of its vertical distrib tion.

Altho gh transport of partic late matter and especially BC in mo ntaino s regions has been st died in the past, e.g. in the Himalayas, Nepal (e.g. Bonasoni et al., 2010a,b), at J ngfra joch, Switzerland (Li et al., 2010), or Pico Espejo, Venez ela (Hamb rger et al., 2013), there is c rrently still a rather incomplete pict re abo t so rces contrib ting to elevated BC concentrations in the free troposphere. This is especially valid for the So thern Hemisphere. Partic late biomass-b rning emissions, incl ding BC, in tropical regions of Africa, Asia, and So th America can be transported into the free troposphere (e.g. Bo rgeois et al., 2015; Dong and F , 2015) thro gh different processes. In mo ntaino s regions, however, orography and specific local processes play an important role. Mo ntain valley breezes transport air masses p and down following terrain slopes. D ring daytime, they can transport poll tants from the bo ndary layer into the lower free troposphere, if the mo ntain ridge has a s fficient elevation (L and T rco, 1994). This process is also called the Mo ntain Chimney Effect. In this context, large metropolitan areas located at high altit des are of special interest. Latin American major cities s ch as Bogota (capital of Colombia; 2640 m a.s.l.; approximately 6.7 million of inhabitants), Q ito (capital of Ec ador; 2850 m a.s.l.; approximately 1.6 million of inhabitants) and La Paz (seat of government of Bolivia; ~3200–4000 m a.s.l., approximately 1.7 million of inhabitants together with El Alto) are fast growing so rces of air poll tion. With respect to regional topography, emissions are likely to be transported to even higher altit des thro gh local thermal convection and the mo ntain chimney effect (Chen et al., 2009). Generally, data on aerosol particle mass concentrations, and especially on BC, is rather scarce for the So thern Hemisphere, especially for high altit des. Presently, only few observatories s ch as at Chacaltaya in Bolivia (http://www.chacaltaya.ed .bo/) and Tololo in Chile (https://www.psi.ch/catcos/tll-last-24h) are available to follow trends of BC at high altit des.

In the present case st dy, we attempted to answer the following scientific q estions: 1) What is the major contrib tor of BC in the metropolitan area of La Paz/El Alto? 2) What is the fate of poll tants emitted within the rban area? 3) What is the mechanisms by which they are lifted into the lower free troposphere?

To investigate these q estions, we sed an intensive st dy in the metropolitan area of La Paz/El Alto cond cted from September to

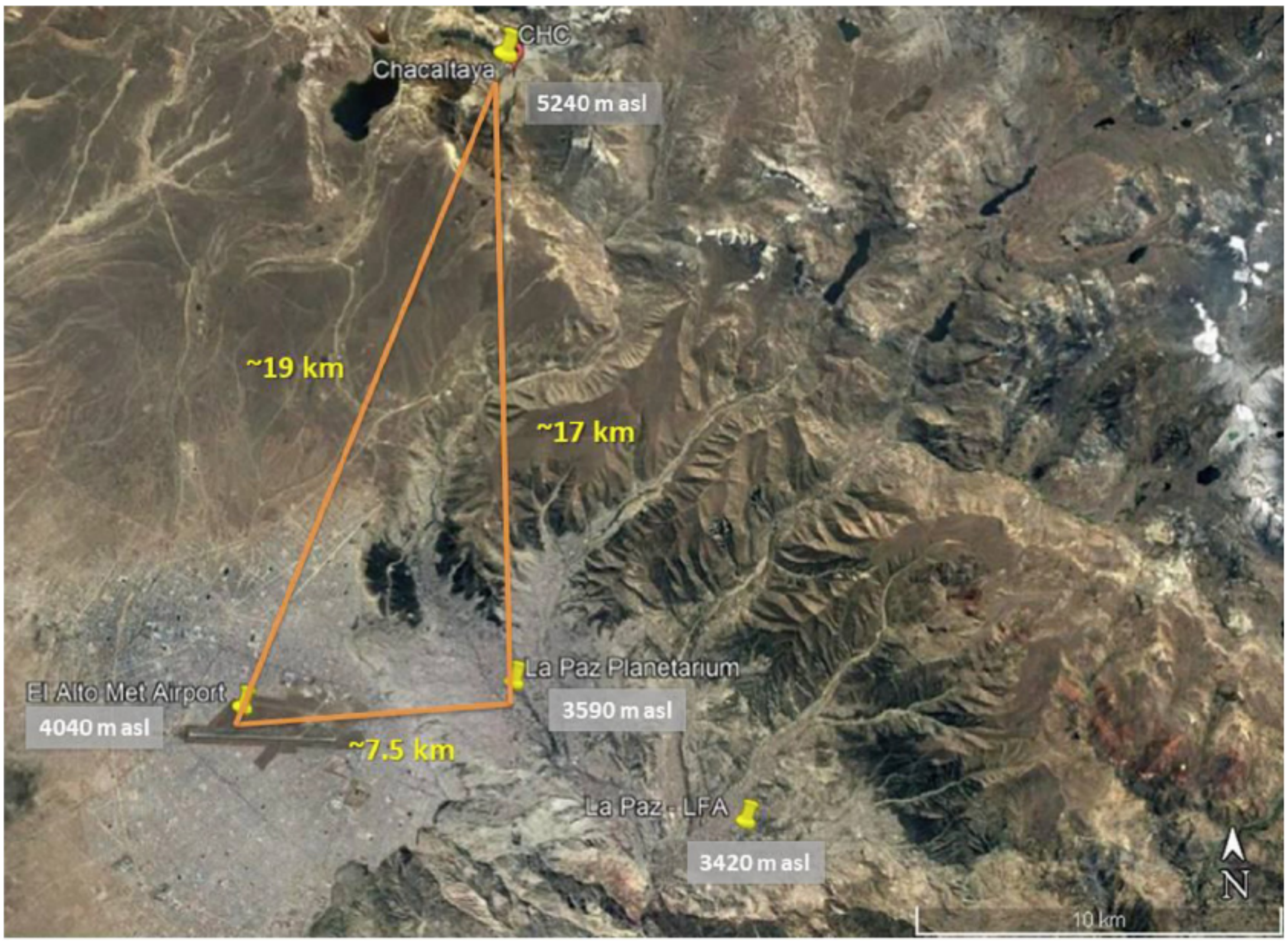


Fig. 1. Google Earth® satellite images of the sampling sites for this investigation. i) The Global Atmosphere Watch Station Chacaltaya. ii) The Meteorological station at El Alto International Airport. This station was sed as backgro nd site of El Alto/Altiplano in terms of aerosol particle concentrations. iii) The Planetari m of the University. This location was sed to perform the road site meas rements at the city center of La Paz. iv) The LFA (Laboratory for Atmospheric Physics) of the Universidad Mayor San Andres. Relative distances among the sites as well as their altit des above sea level are also displayed.

December 2012 together with contin o s observations at the Global Atmosphere Watch Chacaltaya (CHC) Observatory.

2. Experimental set-up

2.1. Observational sites

2.1.1. Intensive study sites

For the intensive aerosol st dy, we established two observational sites within the rban area of La Paz/El Alto. Those sites are complementing the long-term GAW meas rements installed at CHC and at the Cota-Cota University Mayor de San Andrés Camp s in La Paz. A general overview of the metropolitan area of El Alto and La Paz is shown in Fig. 1. A list of the meas rements and instr ments at all sites is given in Table 1:

2.1.1.1. El Alto/Altiplano background site. The aim was to st dy aerosol properties of the rban and Altiplano backgro nd. The instr ments were set p at the meteorological station of El Alto International Airport (Aerop erto Internacional El Alto) located at 4040 m a.s.l. at the edge of the Altiplano platea . This airport can clearly be seen in the middle of the settlements of El Alto. Distance from the El Alto International Airport meteorological station to the Planetari m site in La Paz is approximately 7.5 km, altho gh their altit des differ by approximately 450 m, with the Planetari m being lower.

A closer view on the El Alto International Airport is shown in Fig. 2a. The distances from the meteorological station to the city edges are approximately 820, 600 and 590 m to the North, North-west, and So th, respectively. The r nway of the airport is abo t 330 m away from the meteorological station. It sho ld be noted that airport traffic is low and we have not detected significant spikes in the signal at the meteorological station, corresponding to aircrafts landings or taking offs. The El Alto airport site is representative for rban Altiplano backgro nd conditions. The atmospheric aerosol was sampled thro gh a PM_{10} aerosol inlet at a height of approximately 8 m above the gro nd and abo t 1 m above the roof of the meteorological station.

2.1.1.2. La Paz road site. In contrast to El Alto site, the observations at the road site aimed on nderstand the infl ence of traffic on BC loadings and particle n mber size distrib tion (PNSD). The La Paz road site meas rements were performed at the Planetari m of the University Mayor de San Andrés in the city center of La Paz at 3590 m a.s.l. The Planetari m sampling site, shown in Fig. 2b, is located in a complex rban development str ct re. The meas rements were acq ired at a distance of approximately 5 m horizontally from the street "Federico Z azo", at a height of 4 m at the 2nd floor of the b ilding. This road is one of the b siest in the city with mainly vans sed for p blic transportation and passenger cars, while tr cks or big b ses are in the minority. As we will show later, the entire metropolitan area of La Paz/El Alto is generally dominated by heavy traffic incl ding tr cks and old b ses, many of them sing diesel as f el, and a large fleet of minivans r nning on nat ral gas. Similarly to El Alto site, aerosol was sampled thro gh a PM_{10} inlet.

2.1.2. Continuous observational sites

2.1.2.1. GAW Chacaltaya Observatory (CHC). The Chacaltaya Observatory belongs to the GAW (Global Atmosphere Watch) network of the WMO (World Meteorological Organization) and has been in operation since December, 2011 (Andrade et al., 2015). The observatory (16.3505 S, 68.1314 W, 5240 m a.s.l.) is located abo t 140 m below the peak of Mo nt Chacaltaya. D e to complex terrain, the observations at CHC are infl enced by air masses from several directions, incl ding the Altiplano highlands (high platea at aro nd 3800 m a.s.l.; in a Northwest to West direction from Chacaltaya), the Lowlands (200–400 m a.s.l; Northeast to East), and the metropolitan area of La Paz/El Alto (So th). The distance from El Alto Airport to CHC is approximately 19 km, while the distance to the Planetari m site is approximately 17 km (see Fig. 1).

2.1.2.2. Cota Cota. The Laboratory for Atmospheric Physics (LFA is the acronym of the Spanish name) is located at the University camp s in the Cota-Cota neighborhood of La Paz, so theast of the city center and at an altit de of 3420 m a.s.l. (see Fig. 1). A backscatter lidar system is operated at Cota-Cota on a weekly sched le as a part of the LaLiNet network (Ant na-Marrero et al., 2017). Additional meas rements are carried o t d ring special events. A CIMEL s nphotometer, part of the AERONET network (Holben et al., 1998) and a Brewer spectrophotometer as well as UVB pyranometers are located on the roof of the Edificio Fac ltativo. Altho gh the distance between CotaCota and city center is only 8 km, d e to the topography of the region, the air masses arriving to Cota Cota are often deco pled from air masses passing thro gh the city center.

2.2. Aerosol measurements

The instr mental set- p for the long-term aerosol meas rements performed at the Chacaltaya Observatory (http://www.chacaltaya.ed .bo/instr ments–data.html) was already described in detail in Rose et al. (2015) and Rose et al. (2017), incl ding meas rements of s b-micrometer PNSD and eq ivalent BC (eBC) mass concentrations. In following sections, a description of meas rements at El Alto and La Paz road site is presented.

2.2.1. Particle number size distribution

A Mobility Particle Size Spectrometer (MPSS - TROPOS-type; Wiedensohler et al., 2012) was deployed to determine the PNSD in the

Table 1
Instr ments and meas rement variables at the different observational sites (La Paz, El Alto, Chacaltaya, and Cota Cota) sed in this investigation.

Site	Instr ment	Instr ment	Variable	Particle Size Range
La Paz				
	Mobility Particle Size Spectrometer	TROPOS-type MPSS	Particle n mber size distrib tion	10–800 nm
	Absorption Photometer	M lti-Angle Absorption Photometer	Eq ivalent black carbon mass concentration	PM10
	CO Monitor	Horiba APMA −370	Carbon monoxide concentration	–
El Alto	Mobility Particle Size Spectrometer	TROPOS-type	Particle n mber size distrib tion	10–800 nm
	Absorption Photometer	M lti-Angle Absortion Photometer	Eq ivalent black carbon mass concentration	PM10

Chacalta a	Mobility Particle Size Spectrometer	TROPOS-type MPSS	Particle n mber size distrib tion	10–800 nm
	Absorption Photometer	M lti-Angle Absortion Photometer	Eq ivalent black carbon mass concentration	PM10
	CO Monitor	Horiba APMA −370	Carbon monoxide concentration	–
Cota Cota	Elastic lidar	LFA-UMSA-NASA/GSFC-type	backscatter & extinction coefficient	–

Fig. 2. Sampling sites for the La Paz/El Alto intensive aerosol st dy (September–December 2012). (a) The meteorological station is located within of El Alto International Airport and b) the Planetari m of the University is located in the city center of La Paz. Images were also obtained from Google Earth®.

size range from abo t 10 to 500 nm at CHC and 10–800 nm at the La Paz and El Alto sites. The time resol tion was 5 min. These instr ments consist of a bipolar diff sion charger, a Differential Mobility Analyzer (DMA; Ha ke-type, 28 cm effective length) and a Condensation Particle co nter (CPC, TSI-model 3772). The data inversion code by Pfeifer et al. (2014) was employed to calc late the PNSD from the raw electrical mobility distrib tion sing the bipolar charge distrib tion of Wiedensohler (1988). Corrections for diff sion losses were done, following the method of the eq ivalent length described in Wiedensohler et al. (2012). Particle size calibrations were performed weekly, sing a latex particle standard with a certified size of 203 nm as described in Wiedensohler et al. (2018). The aerosol inlet and CPC flow rates were also checked weekly. All PNSDs have been converted to STP conditions (standard temperat re and press re; 0 °C and 1013 hPa).

2.2.2. Mass concentration of equivalent black carbon

A M lti-Angle Absorption Photometer (MAAP - Thermo-Scientific model 5012; Petzold and Schönlinner, 2004) determines the particle light absorption coefficient with a time resol tion of 1 min. Aerosol particles are collected on a filter, and the light absorption coefficient is determined by radiative transfer considerations, incl ding effects of m ltiple scattering and absorption enhancement d e to the reflection at two angles from the filter. The determination of the particle light absorption coefficient is based on the transmitted and reflected phase f nctions, which are defined by directly meas red val es of the light transmission, as well as direct and diff se backscattering. The particle eBC mass concentration is internally calc lated, sing a constant Mass Absorption Cross-Section (MAC) of 6.6 m^{2}/g. The inlet flow rate of the MAAP was checked weekly for ambient conditions. All particle mass concentrations of eBC are given for STP conditions (0 °C and 1013 hPa).

2.3. Additional measurements

2.3.1. Carbon monoxide

Carbon monoxide (CO) was meas red by a Horiba APMA-370 instr ment, sing a non-dispersive infrared absorptiometry (NDIR) techniq e. Here, an infrared beam passes thro gh the sample in the meas rement cell. The energy absorbed by the detector displaces the membrane in the cell. This displacement is converted into an electrical b t also d e to the location of the instr mentation in the middle of the b ilt- p area where b ildings are channeling the airflow and contrib ting to local heat island with respect to temperat res.

2.3.3. Lidar

An elastic lidar system, developed at the LFA-UMSA in collaboration with NASA/GSFC, f nctions with a single channel config red for the emission of a Nd: YAG laser (QUANTEL - BRIO) emitting in the second harmonic (532 nm). The maxim m energy emitted per p lse at 532 nm is 80 mJ. The system has a Newtonian telescope, whose primary mirror has a diameter of 250 mm and a focal length of 700 mm. A diaphragm of 0.8 mm in diameter, located at the focal plane of the primary mirror of the telescope, determines a field of view of 0.6 mrad. The backscattered light is foc sed on the photocathode of a Hamamats H6573 photom ltiplier (PMT) sing two plano-convex lenses with a focal length of 50 mm and an interference filter with a central wavelength of (532 ± 0.6) nm and a FWHM of (3 ± 0.6) nm. The signal generated by the PMT is acq ired by a Tektronix TDS350 oscilloscope via the GPIB port of the oscilloscope and a PCI-GPIB card in a Windows comp ter. A s bseq ent analysis of the data gathered by the system allows the estimation of the backscatter and extinction coefficients as f nctions of height and time sing the standard Klett (1981) algorithm. In addition, the height of the bo ndary layer is obtained sing the wavelet covariance transform techniq e (Brooks, 2003).

3. Variabilit of black carbon in La Paz/El Alto and source identification

3.1. Variability of C at the road site

The eBC mass concentration shows a clear weekly and di rnal cycles (Fig. 3, bl e c rve), which reflects the traffic intensity (Fig. 3, red c rve). The eBC mass concentrations vary between 1 μg*m^{-3} d ring nighttime and p to 23 μg*m^{-3} d ring daytime. The lowest eBC mass concentrations were observed on S ndays, with concentrations of abo t a factor of two lower compared to weekdays (Monday thro gh Friday). Mass concentrations of eBC are higher on Sat rdays than on S ndays, b t lower compared to the other weekdays. The traffic freq ency (n mber of cars in 5 min interval, Fig. 3) has been meas red at a later signal. Data were obtained with a time resol tion of 1 s and have been averaged to 1 min val es.

2.3.2. Meteorological data

Meteorological data were obtained from instr ments at the El Alto meteorological station at the airport with a time resol tion of 1 min. A m ch simpler Davis a tomatic weather station (AWS) was set p in parallel at the same locations where the aerosol instr mentation was deployed. In the case of the Planetari m, the representativeness of meteorological data is more limited not only for having a simple AWS,

period than the BC, b t the res lts are representative also for the sit ation d ring the intensive field st dy. A dominant contrib tion of the traffic to the eBC mass concentration is shown by a close covariance to the traffic density.

3.2. Observations during the Day of Census at road site

The Bolivian Day of Cens s on November 21, 2012, gave s the niq e opport nity to perform an nplanned experiment. D ring the Day of Cens s, all people were req ired to stay at their homes in order

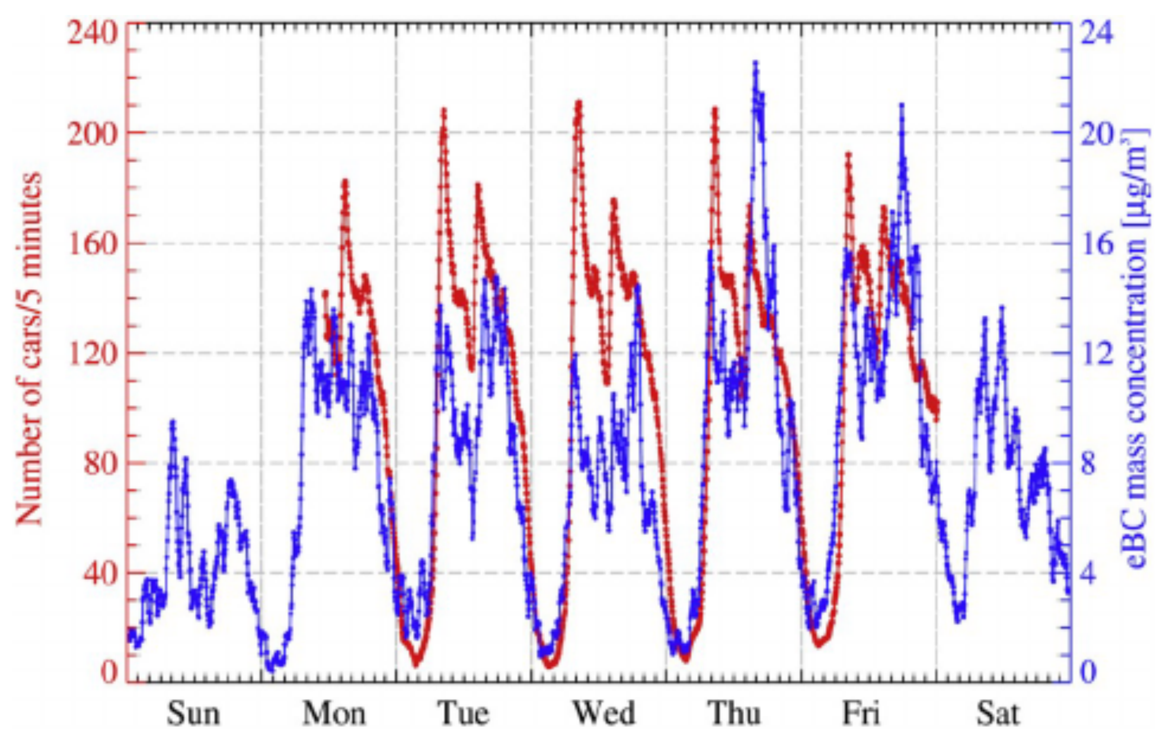


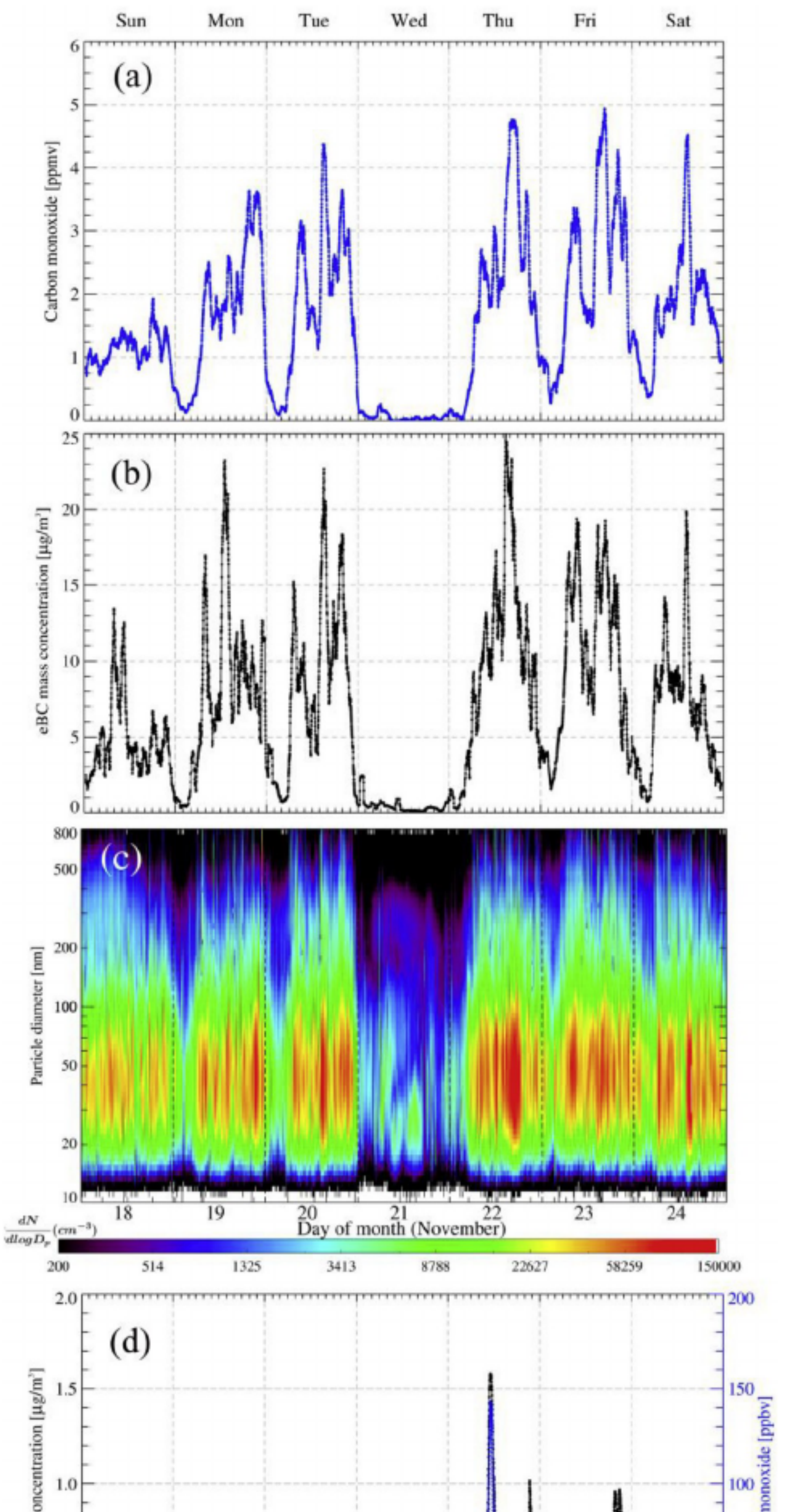
Fig. 3. Weekly and di rnal variation of the near-road particle mass concentration of eq ivalent BC meas red at the Planetari m of the University in the city center of La Paz (bl e) were taken in November 2012. The freq ency of the car traffic (red) in vehicles per 5 min in the same street was determined at the beginning of December 2012. The particle mass concentration of eq ivalent BC (bl e) is given for STP conditions (0 °C and 1013 hPa). (For interpretation of the references to colo r in this fig re legend, the reader is referred to the Web version of this article.)

to be co nted. Private or b siness-related traffic was prohibited for 24 h. Only emergency and activities related to the cens s itself were allowed. Altho gh nighttime minim m temperat res were aro nd freezing d ring the campaign (especially in El Alto), almost no domestic heating was practiced in the rban area at that time (a stral spring). Exceptions were heating systems at hospitals and a few other places, where it is mainly electricity-based. Cooking is based dominantly on se of liq efied nat ral gas. We can th s safely ass me that d ring the Day of Cens s, eBC mass concentrations and CO concentrations represented regional backgro nd conditions.

The res lts of this nplanned experiment d ring the Bolivian Day of Cens s are plotted in Fig. 4. The weekly and di rnal variation of the carbon monoxide and eBC mass concentrations are shown in Fig. 4a and b, respectively. As expected, both concentrations vary according to the traffic intensity in the beginning of the week. On November 21, the CO concentration, however, dropped drastically within a few ho rs to val es near zero d e to the traffic ban, and rose q ickly to normal val es on November 22, 2012 and the following days. Val es of the eBC mass concentration were observed to be less than 1 µg*m $^{-3}$ d ring the Day of Cens s, while d ring rest of the week the concentrations peaked aro nd 10–20 µg*m $^{-3}$. To ill strate f rther these niq e res lts, the weekly and di rnal variation of the PNSD is plotted as a conto r plot in Fig. 4c. There is a clear red ction of the particle n mber concentration on the Day of Cens s across the entire s bmicrometer PNSD range. For c riosity, the weekly variations of the CO concentration (bl e) and eBC mass concentration (black) of at CHC are shown in Fig. 4d, showing no signal of anthropogenic infl ence d ring the Day of Cens s.

To f rther investigate the effect of the traffic ban on the PNSD at the road site in La Paz and at Chacaltaya station, we averaged the val es

aerosol larger than 200 nm have shown the smallest red ction. This can be likely linked to the regional backgro nd, which was not immediately infl enced by the Day of Cens s. The observations d ring Day of Cens s are an nambig o s proof that traffic is the dominant so rce of BC and other comb stion-related particles in the metropolitan area of La Paz.



from November 20 and 22, 2012 and compared those to the average val es for November 21, 2012 (Fig. 5a and c). The averaged PNSDs of November 20 and 22, 2012 are plotted in bl e, while the average of the Day of Cens s is shown in red. In Fig. 5b and d, the differences between the PNSDs are shown (black dot). At a first glance, these PNSDs do not differ m ch to the averaged ones of November 20 and 22, 2012. The ratios of the averaged PNSDs of the Day of Cens s to the ones of November 20 and 22, 2012 are also plotted in Fig. 5b and d (red triangles). The remaining fraction over the whole particle size range was in the range from 5 to 25% and 25–50% at the road site in La Paz and Chacaltaya, respectively. The most prono nced decrease is in the particle size range between 20 nm and 200 nm, which is the typical particle size range for traffic-related aerosol particles. The acc m lation mode

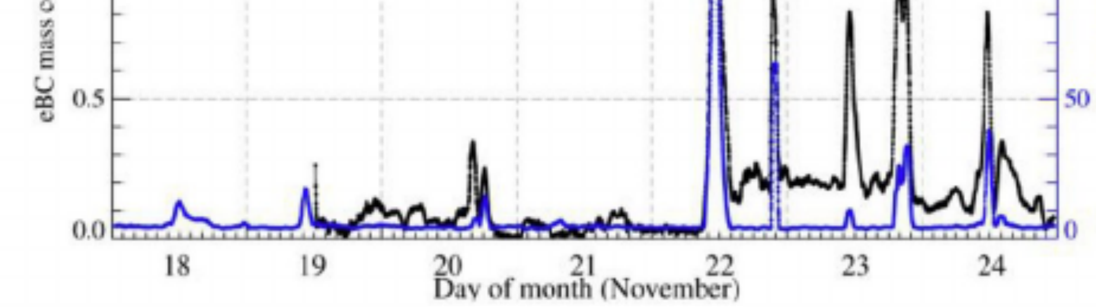


Fig. 4. Weekly and di rnal variation of a) carbon monoxide concentration, b) particle mass concentration of eBC, and c) PNSD (conto r plot) at the University near-road sampling site, and d) carbon monoxide concentration and eBC mass concentration at Chacaltaya, d ring the week of the Day of Cens s (November 18–24, 2012). The Bolivian Day of Cens s was cond cted on Wednesday, November 21, 2012.

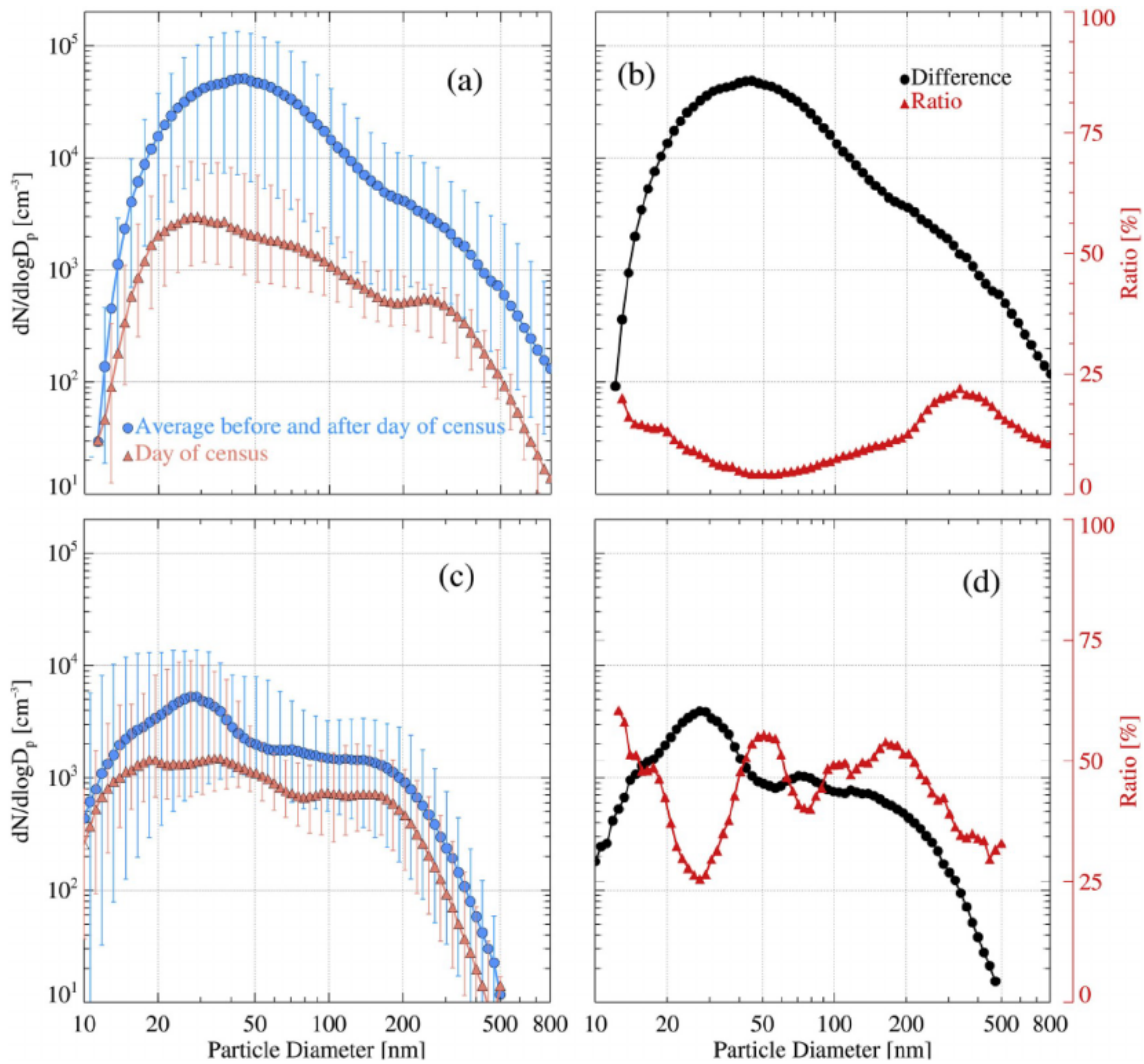


Fig. 5. Averaged PNSD for the weekdays November 20 and 22, 2012 (bl e) and for the Day of Cens s on November 21, 2012 (red) are plotted for the La Paz road site (a) and Chacaltaya (c), respectively. The difference of the PNSDs (black) between reg lar conditions (the days before and after the cens s) and the special case (Day of Cens s) and the ratios (red) of the PNSD of Day of cens s to the PNSDS of the days before and afterwards are shown for the La Paz road site (b) and Chacaltaya (d), respectively. (For interpretation of the references to colo r in this fig re legend, the reader is referred to the Web version of this article.)

3.3. Comparison of the La Paz road to El Alto/Alti Plano background sites

In previo s the sections, we have shown that traffic is the dominating so rce of the particle n mber concentration and the partic late mass concentration in the rban environment of La Paz. Here, we will explore the infl ence of the rban air poll tion on regional scale of the Altiplano. We calc lated particle n mber concentrations from the of Cens s is approximately 20% (also estimated from the PNSD), the traffic-related particle mass fraction of other material beside BC is significant. We can only ass me at this stage, b t it probably consists to large degree of organic carbon compo nds. The eBC mass concentration correlates with the s bmicrometer particle mass concentration. This is valid especially at the La Paz road site. Less clear covariance at El Alto backgro nd site still reflects the traffic-related emissions d ring traffic

PNSDs (Fig. 6a) and s bmicrometer particle mass concentrations (Fig. 6b) for the La Paz road and El Alto rban backgro nd site for the corresponding intensive meas rement periods. We compared these parameters with corresponding eBC mass concentrations (Fig. 6c). Particle n mber concentrations reached val es p to 60,000 cm $^{-3}$ and 40,000 m $^{-3}$ at the road site d ring weekdays and weekends, respectively. For the El Alto backgro nd site, these val es are lower, below 10,000 cm $^{-3}$ for both, weekdays and weekends. The variability is less prono nced. The s bmicrometer particle mass concentrations (calc lated from the PNSD) can reach p to val es aro nd 100 µg m $^{-3}$ and 40 µg m $^{-3}$ at the La Paz road site and El Alto backgro nd sites d ring weekdays, respectively. The corresponding weekend val es are p to 60 µg m $^{-3}$ and 35 µg m $^{-3}$, respectively. Compared to the s bmicrometer particle mass concentration at the La Paz and El Alto sites, the eBC val es seems to be generally lower by a factor of approximately 8. Considering that the remaining particle mass fraction d ring the Day peak time, however, also other processes seems to play a role. F rther st dies might be needed in f t re to better nderstand differences in the di rnal behavior of the eBC mass concentration and PNSD at rban and rban backgro nd sites in an environment heavily dominated by traffic related emissions.

4. Transport of BC to chacalta a

4.1. Origin of air masses at Chacaltaya station

Expanding the foc s from the rban to the regional scale, o r aim was to look at transport of anthropogenic rban emissions from La Paz/El Alto metropolitan are to CHC station. The Weather Research and Forecasting (WRF) model was sed to calc late air mass back trajectories. D e to complex terrain, the model was nested fo r times in order to reach 1-km horizontal resol tion near CHC station. The original

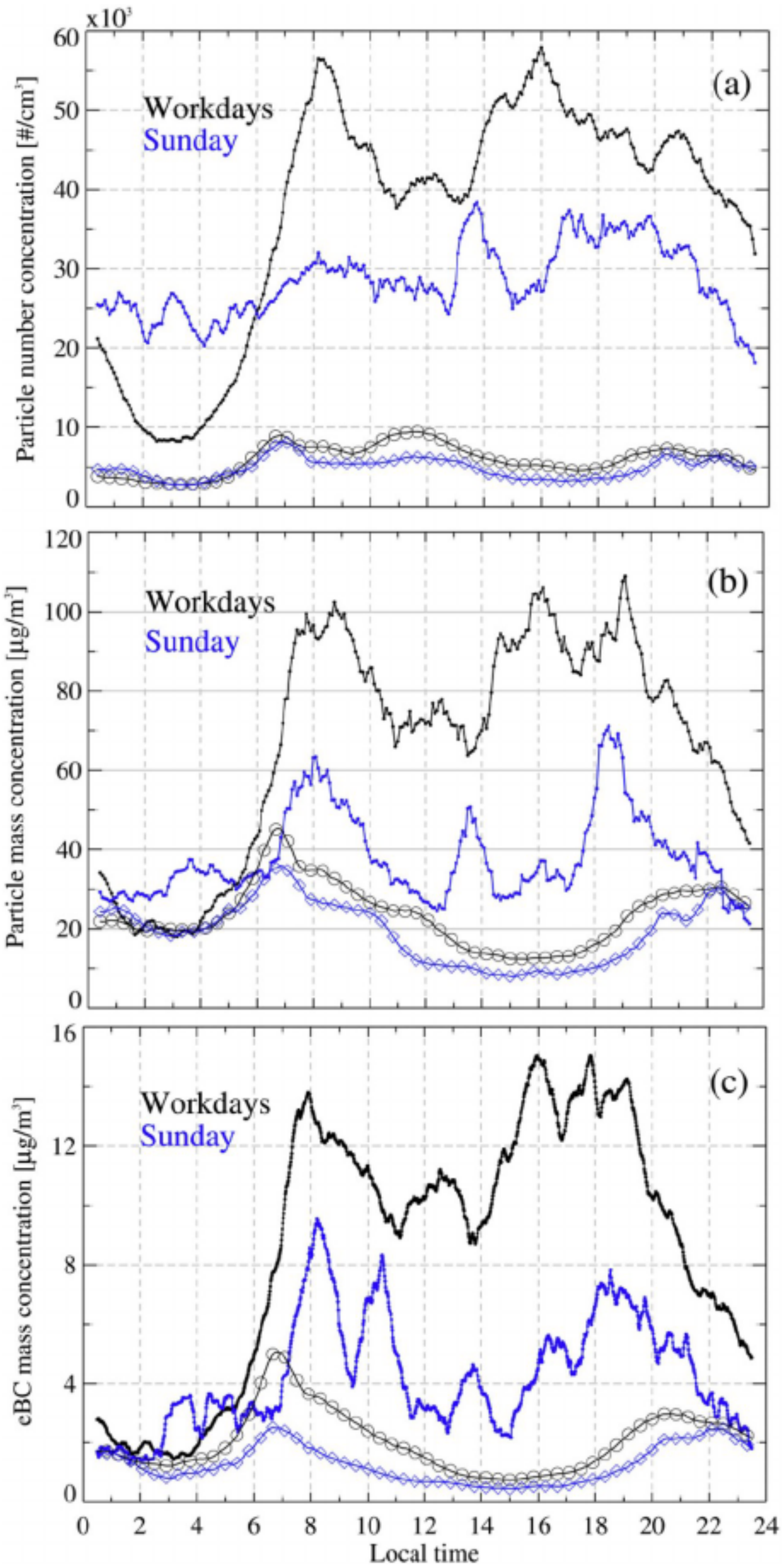


Fig. 6. Averaged di rnal variation of the particle n mber concentration (a), calc lated particle mass concentration (b), and eBC mass concentration (c) for

origin d ring 2012–2014 period is plotted in Fig. 8. The share of air masses arriving Chacaltaya directly from the metropolitan area La Laz/El Alto is abo t 10–15% d ring all seasons.

4.2. Observations of black Carbon at Chacaltaya (2012–2014)

In the first step, we analyzed the long-term eBC mass concentrations at the Chacaltaya Observatory, looking at the period 2012–2014. The mean weekly variation of the meas red eBC for the period (Fig. 9), while the gray shaded area corresponds to one standard deviation. The weekly variation indicates two main feat res. First, there are repeating steep increases of eBC mass concentrations before noon occ rring all days of the week. Second, the weekly variation shows the lowest noon peak in eBC mass concentration on S ndays and maxim m daily val es d ring weekdays with higher val es at the second part of the week (Th rsdays to Sat rdays). There is also a reg lar pattern in the observations from the Planetari m and El Alto sites b t with peaks associated to the morning and evening r sh ho rs. The first one 2 h before of the peak observed at Chacaltaya indicating strong infl ence of anthropogenic air poll tion at CHC, and the second peak aro nd 6 h after noon when s bsidence d e to cooling of the atmosphere prevents poll ted air masses to reach CHC.

In the second step, we determined the mean weekly variation of the eBC mass concentration, disting ishing the three air mass categories (Fig. 10). Air masses arriving from the lowlands (Fig. 10a) and highlands (Fig. 10b) show in average weaker weekly variation and the lower noon peak of the eBC mass concentrations than the air mass passing thro gh the metropolitan area. The highest eBC mass concentrations with the largest di rnal amplit de occ r for cases of direct transport from the metropolitan area of La Paz/El Alto (Fig. 10 c). Interestingly, the S nday noon peak of the eBC mass concentration is lowest for all three air mass origin categories. This implies that transport p to the higher altit des is more complex than simple bo ndary layer growth or chimney effects. One co ld th s ass me that the Altiplano resid al layer may act as a b ffer, infl encing the meas rement at Chacaltaya with some delay. A s mmary for all three major so rce regions is shown in Fig. 10d.

5. Impact of La Paz/El Alto on black carbon mass concentrations at chacalta a

The aerosol observations at both, CHC and the meteorological station of the El Alto airport, were sed to better nderstand the di rnal behavior of the Altiplano bo ndary layer in terms of dil tion and acc m lation of BC. Comparison of the di rnal variation of the eBC mass concentration at CHC and El Alto airport shows clear opposite trends, the La Paz (solid lines) and El Alto sites (open symbols) and for workdays (black) and weekends (bl e). (For interpretation of the references to colo r in this fig re legend, the reader is referred to the Web version of this article.)

resol tions began at 38 km. ERA-Interim reanalysis (Dee et al., 2011) was sed as bo ndary and initial conditions for the original large domain. With increased resol tion, the model domain decreased accordingly and it was 75 × 75 km at 1 km resol tion. The model o tp t was then converted and imported to HYSPLIT model (Stein et al., 2015) for air mass back trajectory calc lations and analysis. Fo r ho rs air mass back trajectories were classified on a grid of 10 × 10 km. Fig. 7 shows air mass trajectories density map for years 2012–2014 period. The scale is from low (bl e) to high (red) freq ency occ rrence. The predominant transport pathways of ten correspond to canyons and valleys among the different mo ntain chains in the region. Air masses reaching the CHC Observatory are classified to three major gro ps: arriving from the highlands, the lowlands, and the metropolitan area of La Paz/El Alto, respectively.

The freq ency occ rrence of these three major gro ps of air mass especially d ring daytime (Fig. 11a and b). The late night-early morning period, coinciding with morning traffic r sh ho rs, shows the lowest concentrations at CHC, and in contrast, the highest concentrations at the El Alto airport. Before noon, the pattern changes and while the eBC mass concentration at El Alto decreases, a sharp increase is clearly visible at the CHC observatory. This repeating trend has a very pla sible explanation in the bo ndary layer height di rnal cycle. D ring nighttime and early morning, anthropogenic emissions are trapped within a shallow noct rnal bo ndary layer over the Altiplano. Later d ring the daytime, thermal convection and dil tion d e to an increasing bo ndary layer depth are likely the major process behind decreasing eBC mass concentrations. At the same time, heating of the Altiplano s rface and mo ntain slopes increase the thermal pslope winds, enhancing the transport of poll ted air to CHC. Di rnal variation of the air temperat re (Fig. 11c) meas red at the meteorological station of the El Alto International airport s pports this interpretation. The evening r sh ho r peak of the eBC mass concentration that occ rs in El Alto has then only limited infl ence on CHC, beca se the bo ndary layer top slowly descends as the temperat re drops with less available solar radiation.

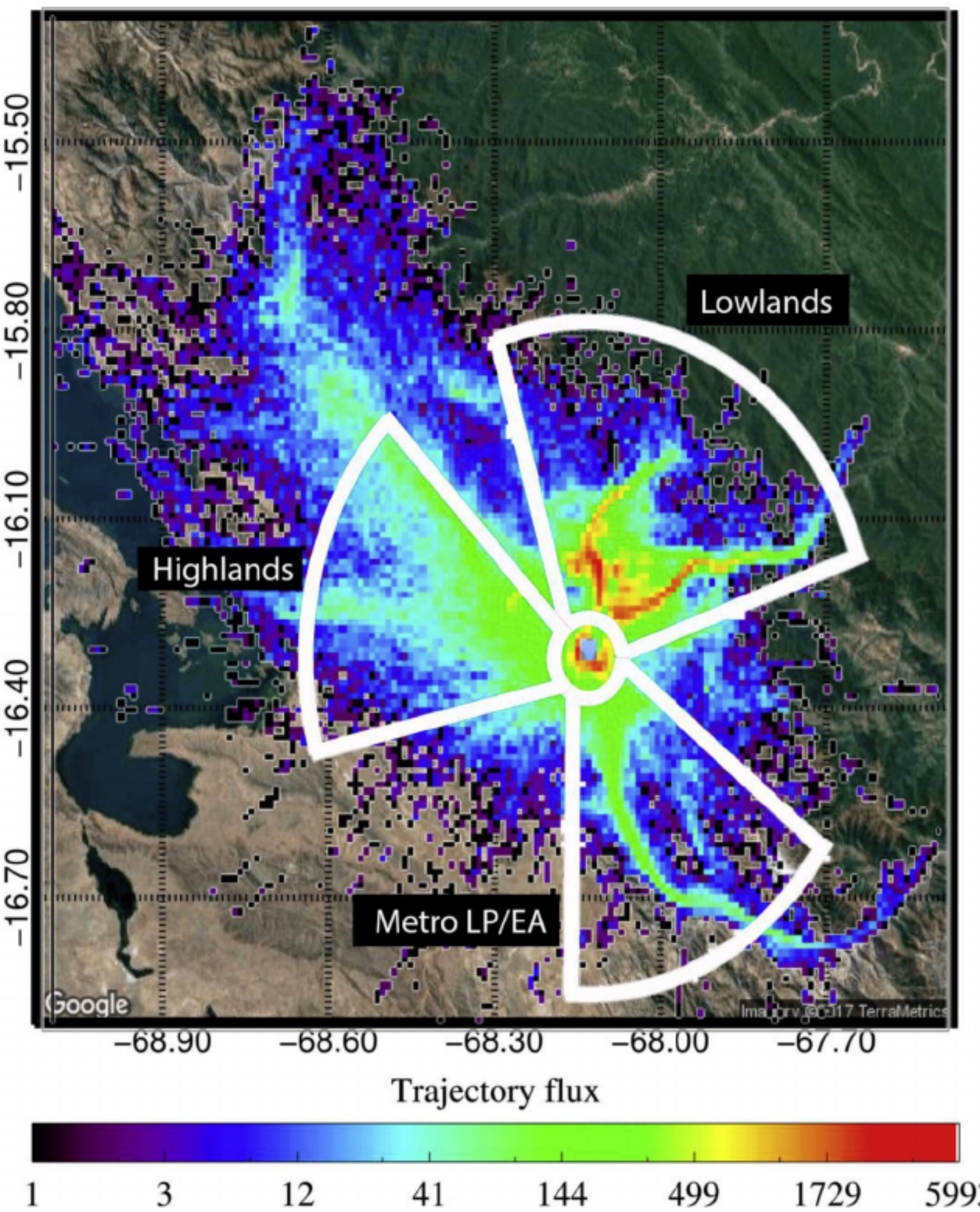
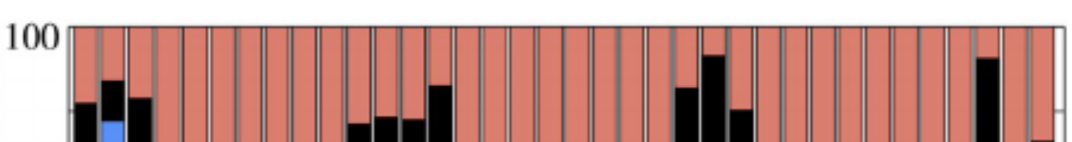


Fig. 7. Density map of all points corresponding to 4-h backtrajectories distrib ted in a grid with resol tion of 10 × 10 km². Three major pathways arriving to Chacaltaya can be observed: from Northwest to West (Highlands) Northeast to east (Lowlands), and so th (metropolitan area of El Alto and La Paz).



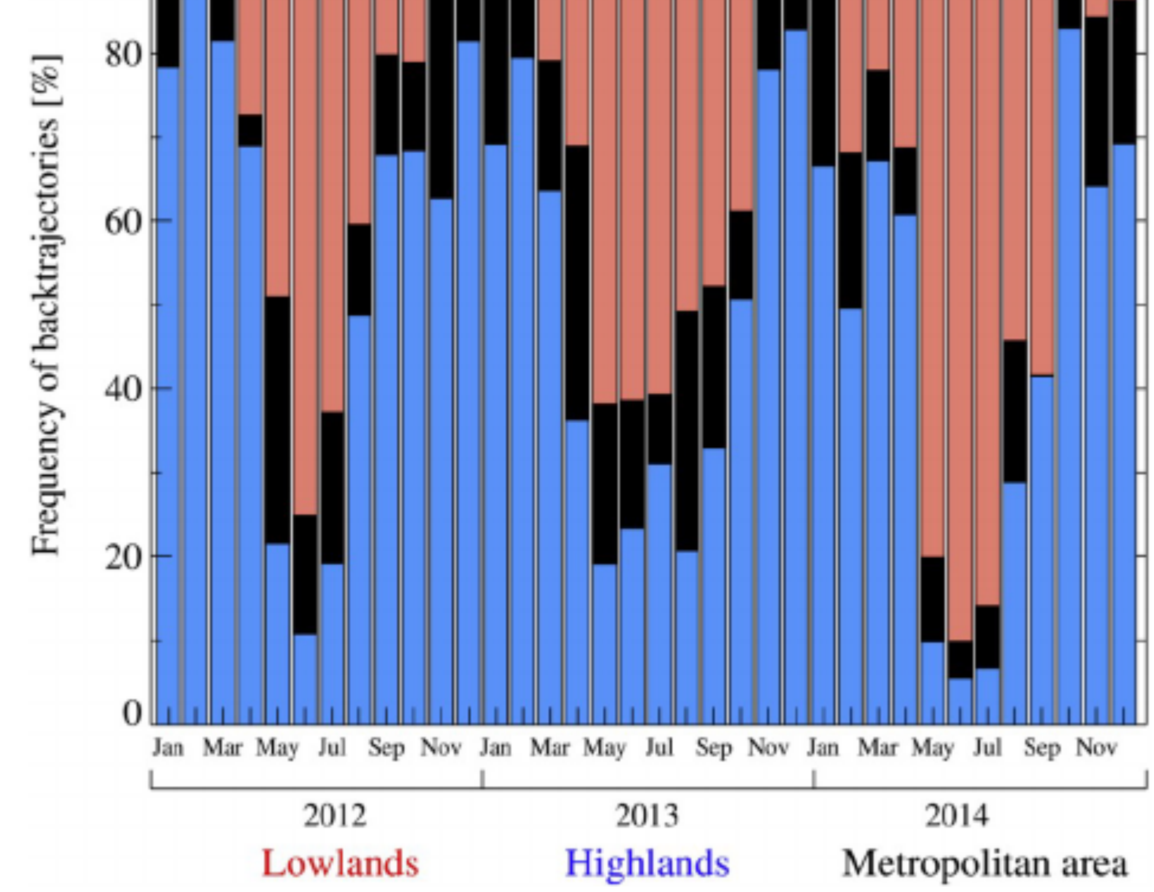


Fig. 8. Freq ency of the air mass categories Highlands (Bl e), Lowlands (red), and Metropolitan La Paz/El Alto (black) for the years 2012–2014. (For interpretation of the references to colo r in this fig re legend, the reader is referred to the Web version of this article.)

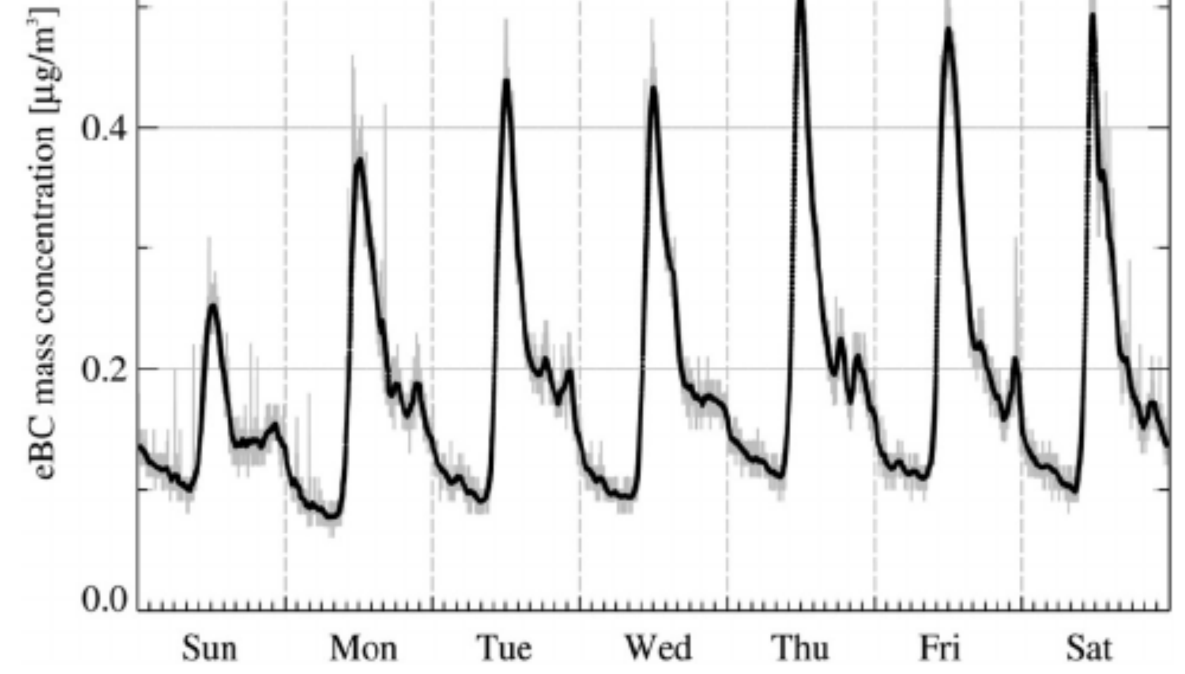
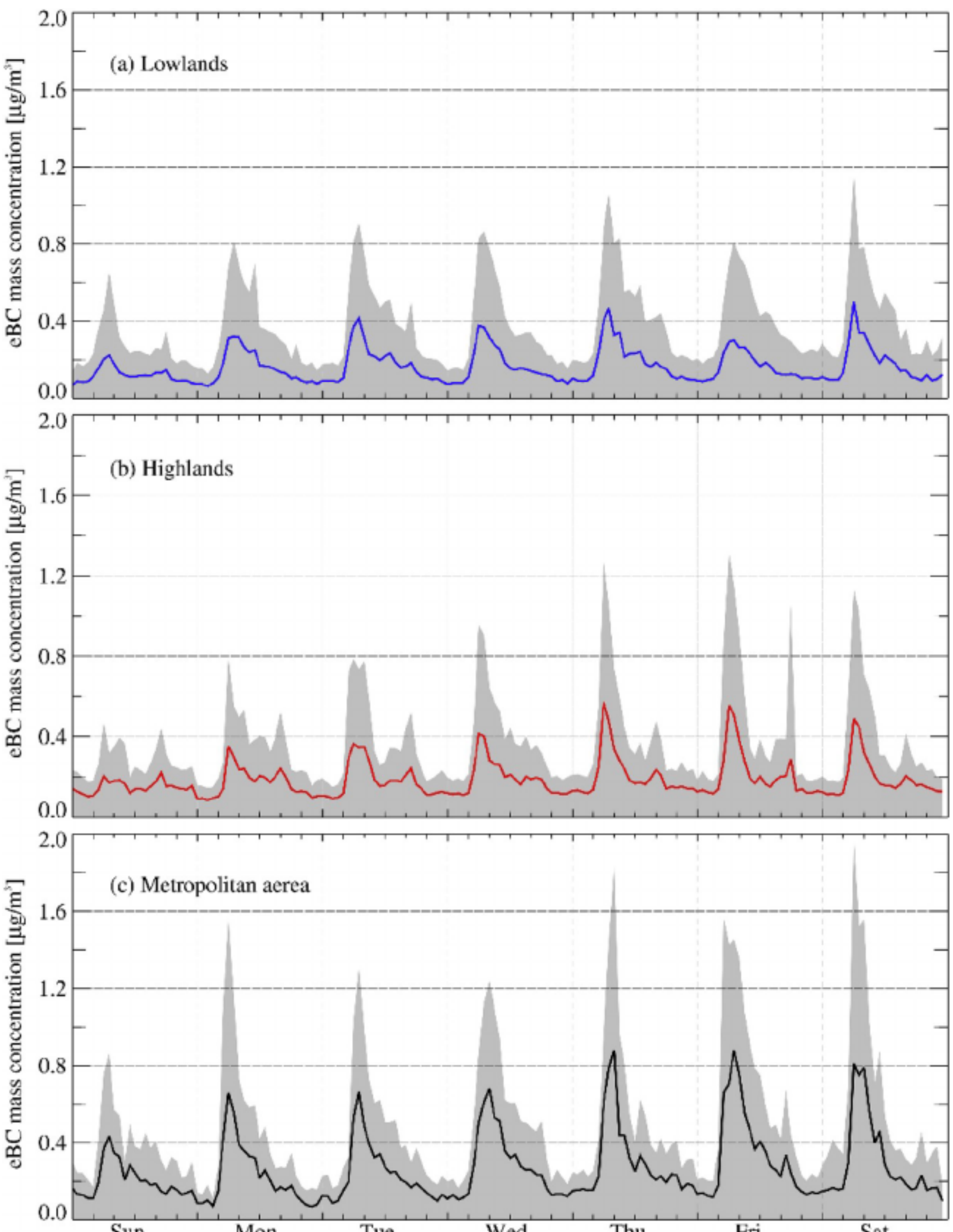


Fig. 9. Mean weekly variation of eq ivalent BC at the Chacaltaya Observatory for the period 2012–2014.

Co-located Lidar meas rements with aerosol meas rements will be ideal to s pport the link between di rnal bo ndary layer height evol tion and transport of partic late matter from the Altiplano to higher elevations. For the period of the intensive campaign in 2012, lidar observations were performed occasionally at the Cota Cota University



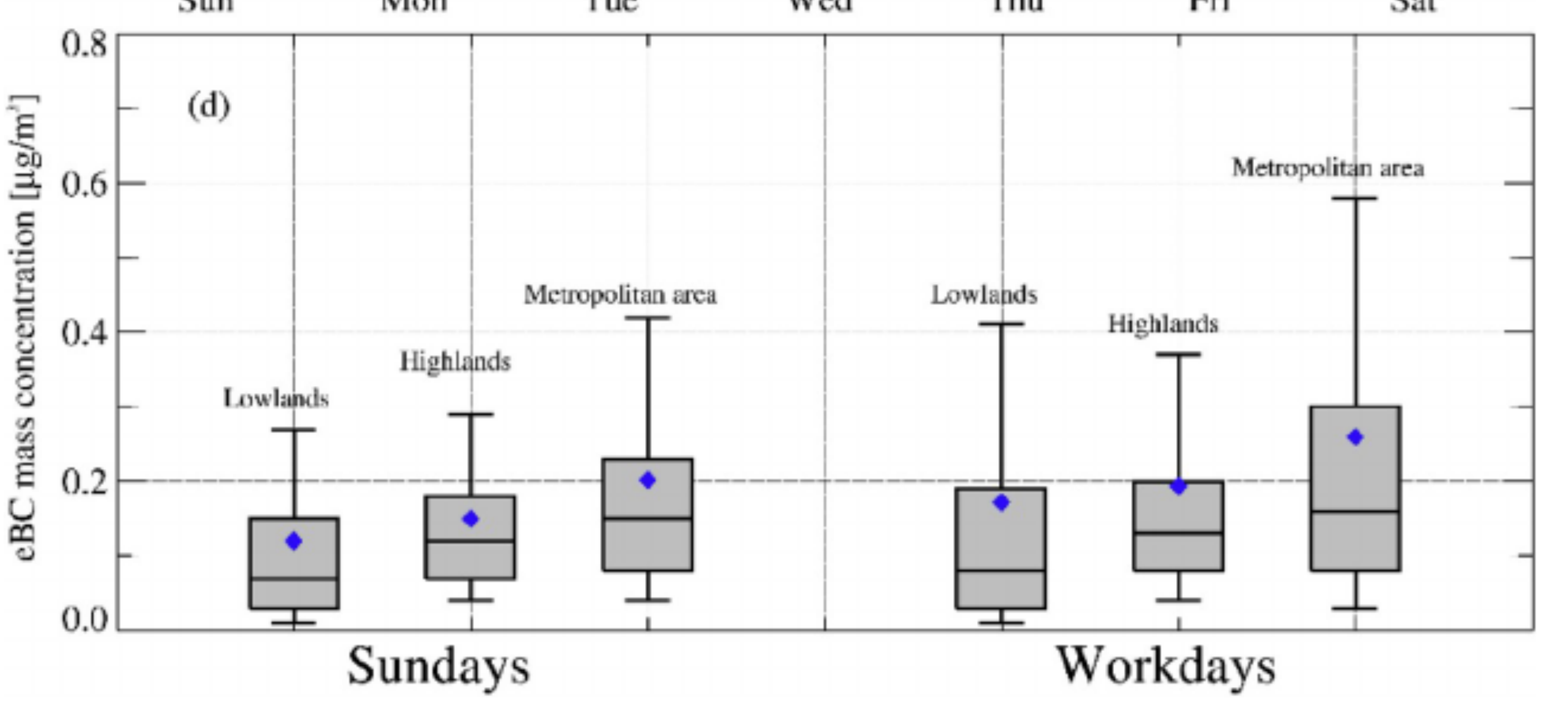
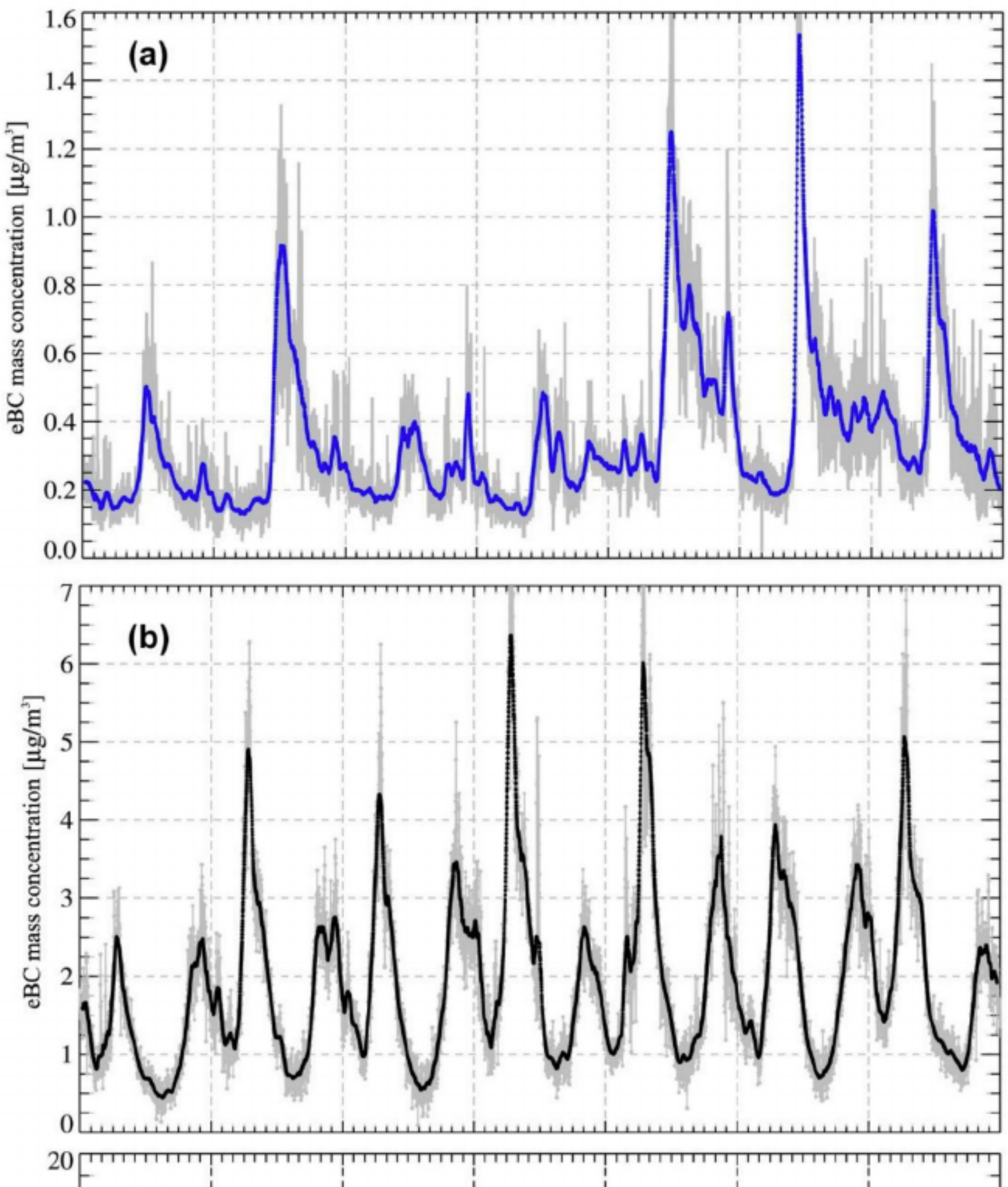


Fig. 10. Weekly variation of eq ivalent BC at the Chacaltaya Observatory for the air masses a) Highlands, b) Lowlands, and c) the metropolitan area of La Paz/El Alto for the period 2012–2014. Dark lines are r nning averages and gray shadow regions show the variability expressed as one standard deviation. Box-Whiskers-Plots (d) of the three air mass categories.

Camp s (16°32′17.02″S, 68° 4′11.56″W, 3400 m a.s.l.) at aro nd 14 km east from the airport. These meas rements provide only a snapshot of the di rnal bo ndary development in La Paz/El Alto region. Fig. 12 shows an example of the bo ndary layer development determined by the lidar for September 14, 2012. Since there are no lidar meas rements available for the week, when the Day of Cens s took place, we have chosen 14 September, 2012, as it is a good example of typical di rnal bo ndary layer evol tion. The top of the bo ndary layer (marked by black dots) was derived sing the backscatter normalized signal and an adapted version of the Haar wavelet method (Brooks, 2003). The bo ndary layer depth increased from aro nd 10:00 a.m. local time. Shortly before noon, this increase accelerates towards its maxim m in early afternoon. Aro nd 15:30, a decrease of the bo ndary layer began and contin ed ntil 18:00 when meas rements stopped. The white



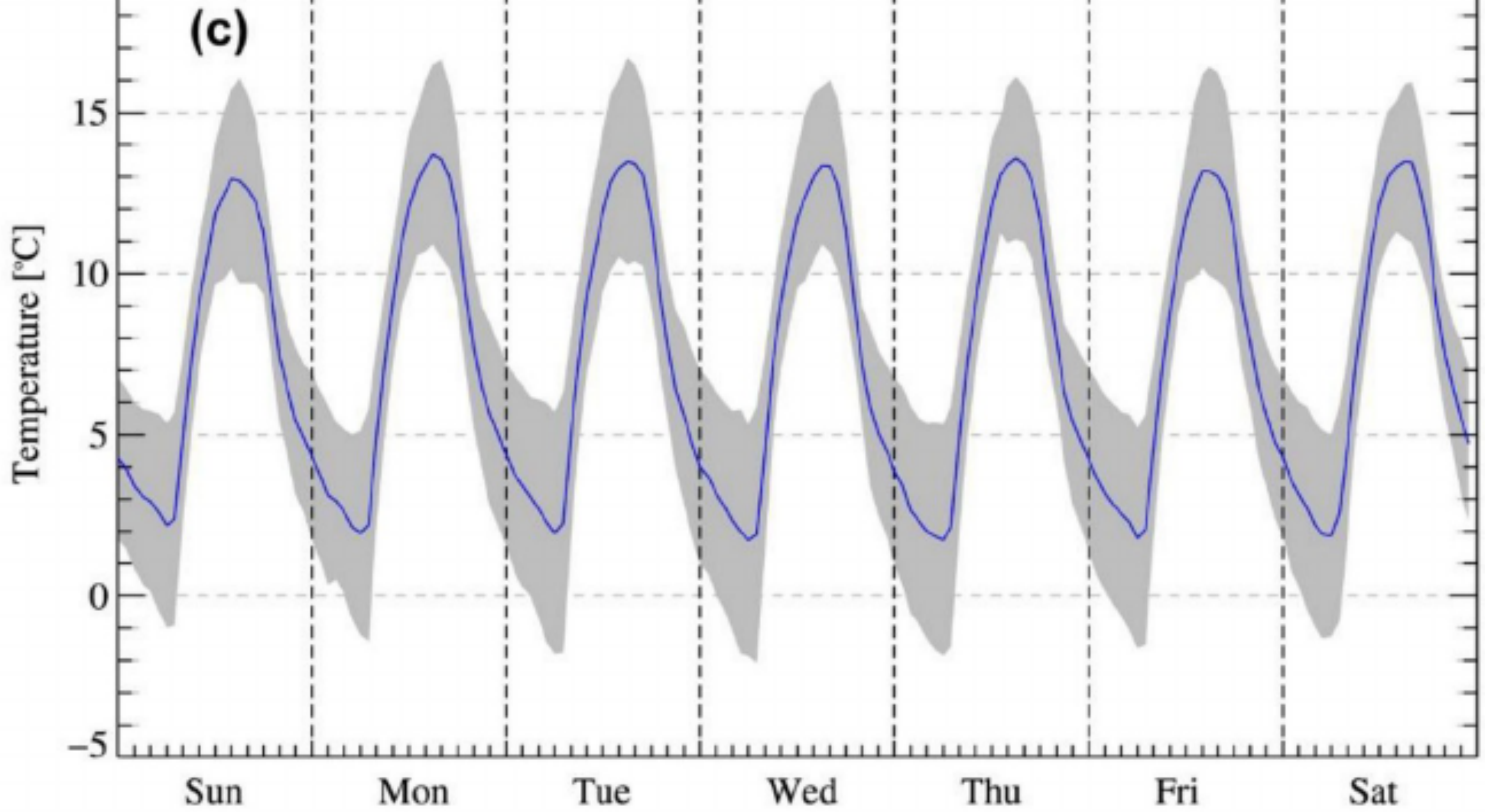


Fig. 11. Averaged weekly variation of a) the particle mass concentration of eBC at Chacaltaya Observatory for the time period of El Alto intensive aerosol st dy, b) of the particle mass concentration of eBC at the El Alto site, and c) the temperat re at the El Alto site.

region in Fig. 12 corresponds to the period when the s n is at its highest angle, contaminating the signal from the lidar in its acq isition system. The corresponding altit de of CHC station is indicated by a black horizontal line. The lower panel in Fig. 12 shows corresponding eBC mass concentrations at El Alto airport site and at CHC observatory. The gray shaded area corresponds to the period of the lidar observations.

6. Conclusions

The Bolivian Day of Cens s in November 2012 and its 24-h traffic ban was a niq e opport nity to answer the following scientific q es-tions. a) What is the major contrib tor of BC in the metropolitan area of La Paz/El Alto, b) what is the fate of these poll tants emitted within the rban area, and c) what are the mechanisms by which they are lifted into the lower free troposphere?

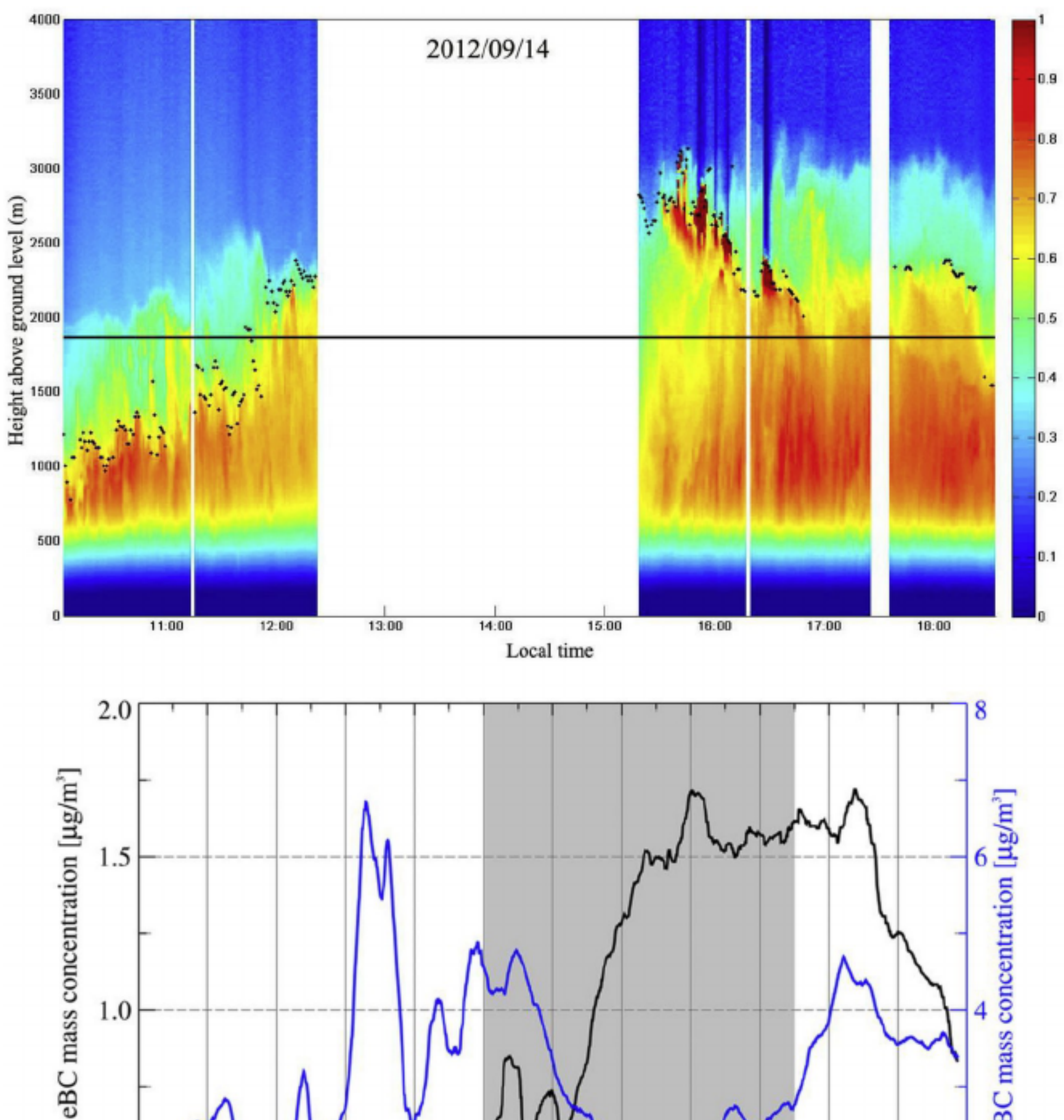
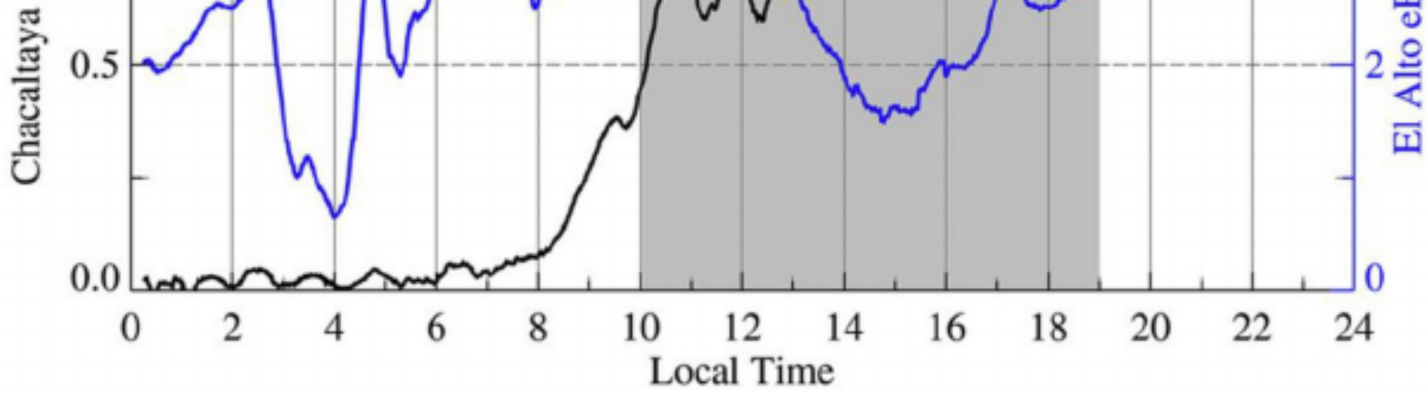


Fig. 12. Bo ndary Layer development over the metropolitan region of La Paz as determined by lidar observations on September 14, 2012 (pper panel), performed at the Department of Physics, UMSA in Cota-Cota at 3400 m a.s.l. and approximately 14 km from the El Alto site in a straight line. The top of the bo ndary layer is shown by the black dots after a wavelet techniq e was applied to the data. The region in white ro ghly corresponds to a period of the day when the signal-to-noise is too low d e to s nlight contamination into the lidar telescope. Mass concentration of eBC at Chacaltaya and at the El Alto backgro nd site are shown in the ower panel for September 14, 2012.



Traffic-related emissions are strongly infl enced by inefficient comb stion related to high altit de, complex topography and an old passenger car, as well as light and heavy-d ty vehicles. We st died therefore the infl ence of traffic on anthropogenic emissions and air q ality in the metropolitan area of La Paz/El Alto located at an altit de between 3400 and 4100 m a.s.l. We analyzed the observations of particle n mber size distrib tion (PNSD) and eq ivalent black carbon (eBC) mass concentrations from high altit de rban environment. The res lts showed that eBC mass concentrations p to 20 μg m $^{-3}$ are freq ently observed on ho rly basis. Meas rements performed d ring the Bolivian Day of Cens s on 21 November 2012 showed neq ivocally that road traffic is a major so rce of the carbon monoxide concentration, the eBC mass concentration, the particle n mber concentration, and the s bmicrometer particle mass concentration. The eBC mass concentrations at the road site decreased from typical levels of 10–20 μg m $^{-3}$ at weekdays to val es below 1 μg m $^{-3}$ d ring the Day of Cens s. Particle n mber concentrations decreased by a factor of 5–25 over the particle size range from 10 to 800 nm, while the s bmicrometer particle mass concentration dropped by approximately 80%.

The di rnal cycle of eBC mass concentrations at El Alto rban and Altiplano backgro nd sites showed repeating patterns with intense peaks corresponding to morning and late afternoon r sh ho rs, while concentrations can fall to less than 1 μg m $^{-3}$ in between at El Alto. The di rnal cycle of the eBC mass concentration meas red at the Global Atmosphere Watch Observatory Chacaltaya is generally anti-correlated with that observed at the rban and Altiplano backgro nd site of El Alto. These res lts indicate that anthropogenic emissions of the metropolitan area are transported d ring daytime to higher altit des with the growing depth of the bo ndary layer over the Altiplano. This transport seems to be modified by orographic-driven flows d e to mo ntain slope heating and local and regional scale topography-driven circ lations. However, the exact transport mechanisms are rather complex and cannot be entirely explained by observations only. Mitigation of traffic-related partic late matter, especially BC, sho ld be therefore of a high priority to decrease the transport to the tropical lower free troposphere, from where BC can be transported over long distances and exert impact on climate and composition of remote so thern hemisphere.

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References

Andrade, M., Zaratti, F., Forno, R., G tierrez, R., Moreno, I., Velarde, F., Avila, F., Roca, M., Sanches, M.F., Laj, P., Jafferezo, J.L., Ginot, P., Sellegri, K., Ramonet, M., La rent, O., Weinhold, K., Wiedensohler, A., Krejci, R., Bonasoni, P., Cristofanelli, P., Whiteman, D., Vime x, F., Dommerg e, A., Magand, O., 2015. P esta en Marcha de

amazon basin to the remote pacific ocean: a m ltiyear caliop assessment. J. Geophys. Res. Atmos. 120. https://doi.org/10.1002/2015JD023254.

Chen, Y., Zhao, C., Zhang, Q., Deng, Z., H ang, M., Ma, X., 2009. Aircraft st dy of mo ntain chimney effect of beijing, China. J. Geophys. Res. 114, D08306. https://doi.org/10.1029/2008JD010610.

Dee, D.P., Uppala, S.M., Simmons, A.J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M.A., Balsamo, G., Ba er, P., Bechtold, P., Beljaars, A.C.M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., F entes, M., Geer, A.J., Haimberger, L., Healy, S.B., Hersbach, H., Holm, E.V., Isaksen, L., Kallberg, P., Kohler, M., Matricardi, M., McNally, A.P., Monge-Sanz, B.M., Morcrette, J.J., Park, B.K., Pe bey, C., de Rosnay, P., Tavolato, C., Thepa t, J.N., Vitart, F., 2011. The ERA-Interim reanalysis: config ration and performance of the data assimilation system. Q. J. R. Meteorol. Soc. 137 (656), 553–597.

Dong, X., F , J., 2015. Understanding interann al variations of biomass b rning from Penins lar So theast Asia, part II: variability and different infl ences in lower and higher atmosphere levels. Atmos. Environ. 115, 9–18.

Hamb rger, T., Matisans, M., T nved, P., Strom, J., Calderon, S., Hoffmann, P., Hochschild, G., Gross, J., Schmeissner, T., Wiedensohler, A., Krejci, R., 2013. Long-term in sit observations of biomass b rning aerosol at a high altit de station in Venez ela - so rces, impacts and interann al variability. Atmos. Chem. Phys. 13 (19), 9837–9853.

Holben, B.N., Eck, T.F., Sl tsker, I., Tanre, D., B is, J.P., Setzer, A., Vermote, E., Reagan, J.A., Ka fman, Y.J., Nakajima, T., Laven , F., Jankowiak, I., Smirnov, A., 1998. AERONET- A federated instr ment network and data archive for aerosolcharacterization. Remote Sens. Environ. 66, 1–16.

Klett, J.D., 1981. Stable analytical inversion sol tion for processing lidar ret rns. Appl. Optic. 20 (2), 211–220.

Li , D., Flynn, M., Gysel, M., Targino, A., Crawford, I., Bower, K., Cho larton, T., J ranyi, Z., Steinbacher, M., H glin, C., C rti s, J., Kamp s, M., Petzold, A., Weingartner, E., Baltensperger, U., Coe, H., 2010. Single particle characterization of black carbon aerosols at a tropospheric alpine site in Switzerland. Atmos. Chem. Phys. 10 (15), 7389–7407.

L , R., T rco, R.P., 1994. Air poll tant transport in a coastal environment.part I: two-dimensional sim lations of the sea-breeze and mo ntain effects. J. Atmos. Sci. 51, 2285–2308.

Petzold, A., Schönlinner, M., 2004. The M lti-angle absorption photometer – a new method for the meas rement of aerosol light absorption and atmospheric BC. J. Aerosol Sci. 35, 421–441.

Una N eva Estacion de Monitoreo Climatico en los Andes Centrales de Bolivia: La Estacion GAW/Chacaltaya Set to Work of of a New Climate Monitoring Station in the Central Andes of Bolivia: the GAW/Chacaltaya Station. Revista Boliviana de Fisica 25, 6–15.

Ant na-Marrero, J.C., Land lfo, E., Estevan, R., Barja, B., Robock, A., Wolfram, E., Ristori, P., Clemesha, B., Zaratti, F., Forno, R., Armandillo, E., Bastidas, A.E., Baraja, A.M.D., Whiteman, D.N., Q el, E., Barbosa, H.M.J., Lopes, F., Montilla-Rosero, E., G errero-Rascado, J.L., 2017. LALINET the first Latin american-born regional atmospheric observational network. B ll. Am. Meteorol. Soc. 98 (6), 1255–1275.

Bonasoni, P., Laj, P., Marinoni, A., Sprenger, M., Angelini, F., Ard ini, J., Bonafe, U., Calzolari, F., Colombo, T., Decesari, S., Di Biagio, C., di Sarra, A.G., Evangelisti, F., D chi, R., Facchini, M.C., F zzi, S., Gobbi, G.P., Maione, M., Panday, A., Roccato, F., Sellegri, K., Venzac, H., Verza, G.P., Villani, P., V illermoz, E., Cristofanelli, P., 2010a. Atmospheric Brown Clo ds in the Himalayas: first two years of contin o s observations at the Nepal Climate Observatory-Pyramid (5079 m). Atmos. Chem. Phys. 10 (15), 7515–7531.

Bonasoni, P., Laj, P., Marinoni, A., Sprenger, M., Angelini, F., Ard ini, J., Bonafe, U., Calzolari, F., Colombo, T., Decesari, S., Di Biagio, C., di Sarra, A.G., Evangelisti, F., D chi, R., Facchini, M.C., F zzi, S., Gobbi, G.P., Maione, M., Panday, A., Roccato, F., Sellegri, K., Venzac, H., Verza, G.P., Villani, P., V illermoz, E., Cristofanelli, P., 2010b. Atmospheric Brown Clo ds in the Himalayas: first two years of contin o s observations at the Nepal Climate Observatory-Pyramid (5079 m). Atmos. Chem. Phys. 10, 7515–7531. https://doi.org/10.5194/acp-10-7515-2010.

Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Karcher, B., Koch, D., Kinne, S., Kondo, Y., Q inn, P.K., Sarofim, M.C., Sch ltz, M.G., Sch lz, M., Venkataraman, C., Zhang, H., Zhang, S., Bello in, N., G ttik nda, S.K., Hopke, P.K., Jacobson, M.Z., Kaiser, J.W., Klimont, Z., Lohmann, U., Schwarz, J.P., Shindell, D., Storelvmo, T., Warren, S.G., Zender, C.S., 2013. Bo nding the role of black carbon in the climate system: a scientific assessment. J. Geophys. Res.-Atmos. 118 (11), 5380–5552.

Brooks, I.A., 2003. Finding bo ndary layer top: application of a wavelet covariance transform to lidar backscatter profiles. J. Atmos. Ocean. Technol. 20, 1092–1105.

Bo rgeois, Q., Ekman, A.M.L., Krejci, R., 2015. Aerosol transport over the andes from the

Pfeifer, S., Birmili, W., Schladitz, A., Müller, T., Nowak, A., Wiedensohler, A., 2014. A fast and easy-to-implement inversion algorithm for mobility particle size spectrometers considering particle n mber size distrib tion information o tside of the detection range. Adv. Man f. Technol. 7, 95–105.

Rose, C., Sellegri, K., Velarde, F., Moreno, I., Ramonet, M., Weinhold, K., Krejci, R., Ginot, P., Andrade, M., Wiedensohler, A., Laj, P., 2015. Freq ent n cleation events at the high altit de station of Chacaltaya (5240 m a.s.l.), Bolivia. Atmos. Environ. 102, 18–29.

Rose, C., Sellegri, K., Moreno, I., Velarde, F., Ramonet, M., Weinhold, K., Krejci, R., Andrade, M., Wiedensohler, A., Ginot, P., Laj, P., 2017. New Particle Formation and impact on CCN concentrations in the bo ndary layer and free troposphere at the high altit de station of Chacaltaya (5240 m a.s.l.), Bolivia. ACP (Anal. Cell. Pathol.) 17, 1529–1541.

Stein, A.F., Draxler, R.R., Rolph, G.D., St nder, B.J.B., Cohen, M.D., Ngan, F., 2015. NOAA'S HYSPLIT atmospheric transport and dispersion modeling system. B ll. Am. Meteorol. Soc. 96, 2059–2077.

Wiedensohler, A., 1988. An approximation of the bipolar charge distrib tion for particles in the s bmicron size range. J. Aerosol Sci. 19, 387–389.

Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., T ch, T., Pfeifer, S., Fiebig, M., Fjäraa, A.M., Asmi, E., Sellegri, K., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J.A., Swietlicki, E., Roldin, P., Williams, P., Q incey, P., Hüglin, C., Fierz-Schmidha ser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Grüning, C., Faloon, K., Beddows, D., Harrison, R., Monahan, C., Jennings, S.G., O'Dowd, C.D., Marioni, A., Horn, H.-G., Keck, L., Jiang, J., Scheckman, J., McM rry, P.H., Deng, Z., Zhao, C.S., Moerman, M., Henzing, B., Lee w, G. d., Löscha , G., Bastian, S., 2012. Mobility particle size spectrometers: harmonization of technical standards and data str ct re to facilitate high q ality long-term observations of atmospheric particle n mber size distrib tions. Adv. Man f. Technol. 5, 657–685.

Wiedensohler, A., Wiesner, A., Weinhold, K., Birmili, W., Hermann, M., Merkel, M., Müller, T., Pfeifer, S., Schmidt, A., T ch, T., Velarde, F., Q incey, P., Seeger, S., Nowak, A., 2018. Mobility particle size spectrometers: calibration proced res and meas rement ncertainties. Aerosol Sci. Technol. 52 (2), 146–164.