Tropical tropospheric aerosol sources and chemical composition observed at high-altitude in the Bolivian Andes

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Abstract. The chemical composition of PM_{10} and non-overlapping $PM_{2.5}$ was studied at the summit of Mt. Chacaltaya (5380 masl, lat.-16.346950º, lon. -68.128250º) providing a unique long-term record spanning from December 2011 to March 2020. The chemical composition of aerosol at the Chacaltaya GAW site is representative of the regional background, seasonally affected by biomass burning practices and by nearby anthropogenic emissions from the metropolitan area of La Paz – El Alto. Concentration levels are clearly influenced by seasons with minim~~um~~a occurring during the wet season (December to March) and maxima occurring during the dry and transition seasons (April to November). Ions, total carbon (EC+OC) and saccharide concentrations range (IQR) between 558-1785, 384-1120 and 4.3-25.5 ng m^{-3} for bulk PM_{10} and 917-2308, 519-1175 and 3.9-24.1 ng m^{-3} for $PM_{2.5}$, respectively, with most of the aerosol seemingly present in the $PM_{2.5}$ fraction. Such concentrations are overall lower compared to other high-altitude stations around the globe, but higher than Amazonian remote sites (except for OC). For PM_{10}, there is dominance of insoluble mineral matter (33-56% of the mass), organic matter (7-34%) and secondary inorganic aerosol (15-26%). Chemical composition profiles were identified for different origins: EC, NO_3^-, NH_4^+, glucose, $C_2O_4^{-2-}$ for the nearby urban and rural areas; OC, EC, NO_3^-, K^+, acetate, form~~i~~ate, levoglucosan, some F^- and Br^- for biomass burning; $MeSO_3^-$, Na^+, Mg^{2+}, K^+, Ca^{2+} ~~Br~~ for aged marine emissions from the Pacific Ocean; arabitol, mannitol, ~~K^+~~glucose for biogenic emissions; Na^+, Ca^{2+}, Mg^{2+}~~-~~, K^+ for soil dust, and SO_4^{2-}, F^-, and some Cl^- for volcanism. Regional biomass-burning practices influence the soluble fraction of the aerosol ~~particularly~~ between Ju~~l~~yne and ~~Nov~~September. The organic fraction is present all year round and has both anthropogenic (biomass burning and other combustion sources) and natural (primary and secondary biogenic emissions) origins, with the OC/EC mass ratio being practically constant all year round (10.5±~~38.9~~5.7, IQR 8.1-13.3). Peruvian volcanism dominates the SO_4^{2-} concentration since 2014, though it presents a strong temporal variability due to the intermittence of the sources and seasonal changes on the transport patterns. These measurements represent some of the first long-term observations of aerosol chemical composition at a continental high-altitude site in the tropical Southern hemisphere.

1 Introduction

Aerosol particles are important climate-forcers. Recent estimates suggest that the impact of these aerosols on global climate falls within the range of -2.0 to –0.6 W m^{-2} (Forster et al., 2021). This impact, known as aerosol effective radiative forcing, is characterized by a high level of spatial and temporal heterogeneity (Szopa et al., 2021). Aerosol chemical composition, being key to determine climate relevant properties of aerosol particles such as hygroscopicity and refractive index, has been recently listed as an aerosol Essential Climate Variable, as defined by the Global Climate Observing System (GCOS) of the Atmosphere Ocean Panel on Climate (WMO, 2022). While aerosol chemical composition can be measured in near real time via mass spectrometry techniques or approximated through a combination of indirect observations, actual determination by chemical analysis of aerosol filters remains the simplest solution for providing a precise and quasi-exhaustive knowledge of aerosol constituents (EMEP Manual for Sampling and Analysis, 2020).

In recent decades, great progress has been made in long-term monitoring of aerosol properties, but many temporal and spatial

observational gaps remain. South America is one of the regions with under-sampled Essential Climate Variables. In this region, aerosol chemical composition is available for urban and suburban locations (e.g. Jorquera and Barraza, 2013; Barbosa, 2014; Jorquera, 2008; Olson et al., 2021; Mardoñez et al., 2022; Custodio et al., 2019) and for intensive measurement campaigns in Brazilian Amazonia (Artaxo et al., 2009; Martin et al., 2010, 2017 et references therein). For urban areas, the traffic-associated markers are unsurprisingly dominant and each location presents its specificities. However, it is noteworthy that emissions associated with agricultural practices exert a significant influence at a continental scale, influencing the air quality in urban areas located far from the sources (e.g. Longo et al., 2009; Custodio et al., 2019; Martin et al., 2010; Giglio et al., 2013; Mardoñez et al., 2022~~2~~3; Estellano et al., 2008). The studies in Amazonia permitted characterization of biomass combustion sources (e.g. Schkolnik et al., 2005; Fuzzi et al., 2007; Kundu et al., 2010b, a) and natural emissions of the Amazonian environment (e.g. Graham, 2002; Elbert et al., 2007; Claeys et al., 2004).

For the Andean region, measurements of background aerosol chemical composition are in general lacking. However, a small number of studies of certain sources of atmospheric aerosols at high-altitude are available. Some of them are based on the analysis of ice cores (Correia et al., 2003; de Angelis et al., 2003; Brugger et al., 2019; Hong et al., 2004; Magalhães et al., 2019), but these results have not been translated to an equivalent atmospheric chemical composition. Other studies focus on the characterization of atmospheric aerosols (e.g. Adams et al., 1977; Bianchi et al., 2021; Scholz et al., 2023; Chauvigné et al., 2019; Van Espen and Adams, 1983) during limited time periods.

The objective of this work is to study aerosol chemical composition based on multi-year observations at the Chacaltaya Global Atmosphere Watch (GAW) station. The aerosol at Chacaltaya exhibits influences from different provenances, including planetary boundary layer air masses influenced by the metropolitan area of La Paz and El Alto, as well as long-range transported air masses (Aliaga et al., 2021, Wiedensohler et al., 2018, Chauvigné et al., 2019). It is interesting to note that more than four decades ago it was considered a background site with very little anthropogenic influence (Adams et al., 1977; Van Espen and Adams, 1983; Cautreels et al., 1977; Adams et al., 1983). Our study presents the chemical composition of PM_{10} and $PM_{2.5}$ for major soluble ions, saccharides and EC-OC obtained at this site between December 2011 and March 2020. This nine-year record is analyzed in the light of possible source regions and transport characteristics, providing unique information on the main drivers influencing the regional aerosol composition of the Altiplano and adjacent Andes.

With this analysis, we will complement some knowledge gaps for the Andean region, particularly regarding the seasonality of the aerosol observed at high-altitude. We will also situate the Chacaltaya observations in a global and regional context. Additionally, two specific cases are included. The first, focuses on the influence of volcanism on the site. The second, emphasizes the differences between minimum and maximum planetary boundary layer influences on aerosol chemical composition at this site.

2 Methodology

2.1 Location and climatology

The Chacaltaya GAW station (lat. -16.350500º, lon. -68.131389º, 5240 m a.s.l.) is currently the highest site in the GAW network. It is ~~located at Mount Chacaltaya in the Bolivian Andes (Figures 1 and S1), where it shares facilities with the Cosmic Ray Observatory of the Instituto de Investigaciones Físicas (IIF) of the Physics Department of the Universidad Mayor de San Andrés (UMSA). Chacaltaya station is~~ located some 1400 m above the Altiplano high-plateau (mean elevation of about 3750 m a.s.l.), which is bordered to the west by the Cordillera Occidental, which includes a volcanic arc, and to the east by the Cordillera Oriental. Mt. Chacaltaya lies within the northern segment of the Cordillera Oriental, (called ~~the~~ Cordillera Real), which trends SE - NW. The semi-arid Altiplano ~~(grasslands, Puna)~~ incorporates Lake Titicaca. Mt. Chacaltaya is located about 40 km from the nearest part of the lake, and about 15 km north from the ~~metropolitan area of~~ La Paz-El Alto conurbation. El Alto (La Paz) is a fast-growing city, with its population having increased from approximately 60,000 (595,000) inhabitants in 1976 to 921,000 (782,000) inhabitants in 2012 (Censos de población y vivienda, 2021). In the Peruvian branch of the Cordillera Occidental ~~, about 350 km from the station,~~ there are two active volcanoes: Sabancaya (5976 m asl) and Ubinas (5672 m asl). ~~North and east of Mt. Chacaltaya, beyond~~ Beyond the ~~high~~ Cordillera Real, there is a lower and parallel mountain belt known as the Subandes (paramo and montane forest locally referred to as the Yungas), and beyond ~~the Subandes lie~~ them are the Amazonian lowlands. The valleys of the Cordillera Real and the Subandes are often steep and forested, and sparsely populated. General atmospheric circulation shows a pronounced annual cycle of changing dry and wet seasons, typical of the tropical zone. Regional climatological information is well described in other works (Espinoza et al., 2020 and references therein ~~; Arias et al., 2021~~). At Chacaltaya station, the mean atmospheric pressure is 534 hPa about half of the value at sea level, mean temperature around 0ºC and annual precipitation (mostly solid) 865 mm in water equivalent depth (Perry et al., 2017). Four seasons are defined for this region based on the circulation and precipitation changes: 1. Wet season (monsoon-like season) from December to March, bringing 65-70% of the annual precipitation to Chacaltaya, 2. Wet-to-dry transition season in April, 3. Dry season from May to August, with long periods without precipitation that can span more than 40 consecutive days (Andrade et al., 2017) and finally 4. Dry-to-wet ~~Wet to~~ transition season from September to November, that used to mark the onset of the rainy season that has become quite dry over the last decades (Espinoza et al., 2019). During the wet season, air masses predominantly originate from the lowlands situated northeast of the Altiplano plateau (Fig. 1). Before reaching Chacaltaya, these air masses are typically funneled through the nearby valleys to the north, resulting in a prevailing northerly influence on the short range ~~the station is influenced by air masses from the SE, E and NE (Aliaga et al., 2021), often channeled through the valleys north of the station~~ (Aliaga et al., 2021, Chauvigné et al., 2019; Perry et al., 2017; Vimeux et al., 2005). In the dry and dry-to-wet seasons, winds with a westerly component ~~predominantly~~ blow over the Altiplano towards the station bringing ~~and bring~~ mineral dust to Chacaltaya station along with biomass burning tracers (Chauvigné et al., 2019). Biomass burning emissions are transported to the Altiplano through the Subandes valleys east of the Cordillera Real (Bourgeois et al.,

2015; Magalhães et al., 2019). On an annual basis, less than 10% of air masses arrive in the region directly from the Pacific Ocean (Chauvigné et al., 2019; Perry et al., 2017).

Chacaltaya station is frequently influenced by the atmospheric boundary layer (Collaud Coen et al., 2018). During daytime, the Altiplano is subjected to intense solar radiation heating (Zaratti and Forno, 2003) resulting in a highly convective planetary boundary layer (PBL). The diurnal development of the PBL routinely brings air pollutants from the nearby metropolitan area of La Paz – El Alto conurbation to Chacaltaya (Wiedensohler et al., 2018; Chauvigné et al., 2019) all year round and without a clear seasonality (around 24% of the air masses have a PBL influence independently of the long-range origin, Aliaga et al. 2021). After sunset, the station is frequently situated within a residual layer (RL) (Figure S10S2), which acts as a barrier, trapping pollutants and keeping them confined until late in the evening. Purely free tropospheric (FT) intrusions have been observed for some very short-time periods during the night (Scholz et al., 2023; Zha et al., 2023)., and most of the time, the station is influenced by a mixture of air-masses from below and above the station (Aliaga et al., 2021).
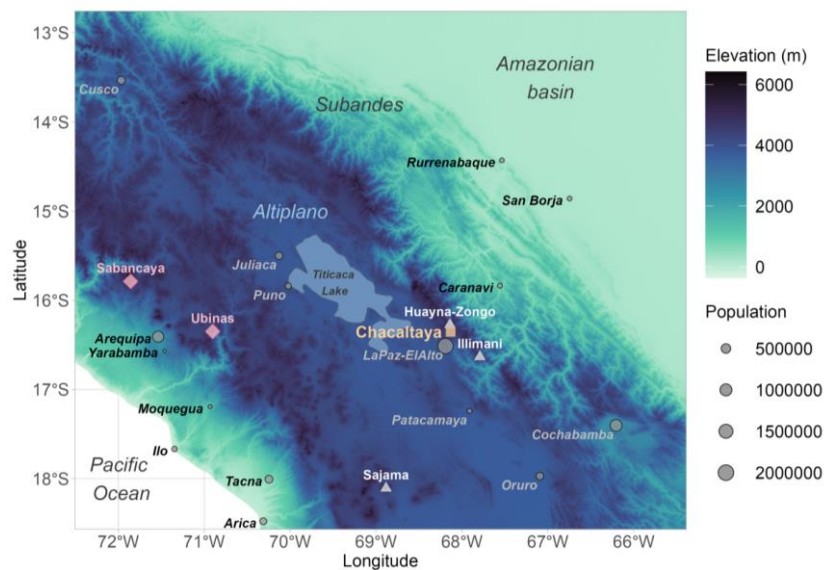
Figure 1. Location map. Square is the Chacaltaya GAW station, rhombuses are currently active volcanoes, triangles are other mountain sites where ice-core studies were performed, circles are urban sites with population higher than 40000 inhabitants (estimates for 2020 from World Population Review, 2022). Elevation from NOAA National Centers for Environmental Information (2022), Titicaca Lake shape from Natural Earth (2022).

2.2 Aerosol sampling

Aerosol samples were collected on Pallflex pre-baked (at 500-550ºC) quartz filters (Ø=150 mm) using a High Volume Sampler

(HiVol) that was installed in a small concrete hut at the northwestern ridge of Mt Chacaltaya some 120 meters above the main station building (5380 m a.s.l., lat.-16.346950º, lon. -68.128250º, Figure S1), with few exceptions (very few samples were taken at the main observatory). The site is accessible only by foot from the main observatory. This HiVol consisted of a DIGITEL HVS DPM10/30/00 inlet with interchangeable impactor plates for 10 and 2.5 μm aerodynamical sizes coupled to an Elmo-Rietschle G-BH7 vacuum pump, regulated to work at a nominal flow rate of 30 ± 6 m^3.h^{-1} at ambient conditions. The volume of sampled air was obtained from readings of a Honeywell Elster Quantometer QA at the start and the end of the sampling period. Note that given the low atmospheric pressure at Chacaltaya, the sampled volume almost doubles (1.89) the equivalent sampled volume at sea level. Each filter collected was folded, then wrapped in aluminum foil, sealed in a polyethylene plastic bag (sandwich Ziploc bag) and kept at -10ºC prior to shipping to the Institute des Géosciences de l'Environnement (IGE, Grenoble) where the water-soluble fractions (ions and sugars) and EC-OC were analyzed. Samples were sent once a year to the IGE and analyzed up to three years after the sample was taken. Except during transportation, filters were stored at -18ºC.

The vacuum pump was controlled by a timer to take sequentially obtain diurnal and nocturnal samples either diurnal, nocturnal or 24-hour samples, and ran for several consecutive days in order to accumulate enough mass for the analysis. When the timer was badly set, samples could still be used as 24h samples. Sampling Indeed, sampling periods shorter than 24 hours (in total) caused several species to fall below the quantification limit, especially during the core of the wet season. Therefore, later in the experiment, sampling periods of at least seven days were preferred, although some samples extended up to 10 days (intermittently) when it was impossible to access the hut due to bad weather. The night and daytime sampling was tested for several split times in the hope of capturing purely lower free troposphere air which finally proved unsuccessful (as seen in Table S7). Among all the split times tested, the samples taken between 02:00 and 09:00 BOT (UTC-4) were the more likely to capture more LFT episodes, and their complementary samples from 09:00 to 02:00 of the next day would be capturing more periods with BL and RL influence (see section 3.4). Nevertheless, Oonce the diurnal city influence was clearly identified at Chacaltaya (Wiedensohler et al., 2018), nighttime sampling (23:00 to 08:00) was preferred in order to try to better characterize regional aerosol characteristics, minimizing the city influence. Details on the sampling split times are presented resumed in Table 1.

Until July 1st 2016, the inlet lacked an inner water collection system (Figure S1). As a result, during the wet season, several filters presented marks of water runoff or were drenched. These samples were not analyzed and this led to under-sampling of the rainy season, particularly January. No vaseline was used on the impactor plate, and therefore the samples may have had an influence of particle bouncing off, especially prior to the installation of the inner water collection system which also acts as a barrier for it.

The HiVol sampler worked from December 2011 until March 2020, with PM$_{10}$ samples not overlapping with PM$_{2.5}$. Overall, sampling logistics are challenging and there are five gaps in the data set that can be gathered in three groups: 1. Gaps due to wet samples, difficult conditions to access the sampling hut due to snowfalls, and/or lightning producing power outages at the sampling hut: December 2013 to April 2014, December 2014 to January 2015, and January 2016 to April 2016, 2. Gap due to

a broken down flowmeter: August 2017 to December 2018, 3. Gap due to electric line maintenance followed by a period of social unrest that made it impossible to access the station: September 2019 to January 2020. The data series ended in March 2020 due to the Covid-19 lockdown and the theft of the pump while the station remained closed.

In total, 67 field blanks and 242 samples were collected (aside from those lost due to drenching), from which six samples were excluded from the analysis because the flow was too high (>36 m³.h⁻¹), and 13 because of specific events (San Juan bonfire festivity) or if the sampled volume was small (<300 m³). Some of the latter were helpful as study cases for particular conditions or events but are not presented here. The remaining 223 valid samples are detailed in Table 1. The number of field blanks is very large, which is essential in order to achieve a good contamination control on the data.

Table 1. Sampling characteristics for High-Volume samples at Chacaltaya station and number of samples per season. PM$_{10}$ was divided into three batches (A,B,C) following important gap periods. N stands for the number of consecutive days for sampling (intermittently for day and night samples). Sampling time (start, end, and duration) is indicated in hours and minutes. Local time (BOT) corresponds to UTC-4.

Sample group	Sampling period	N (days)	Type	Sampling hours, local time (start-end)	Wet season (DJFM)	Wet-to-dry transition (A)	Dry season (MJJA)	Dry-to-wet transition (SON)	Total
				Number of valid samples					
PM$_{10}$-A	December 2011 to July 2013	3 to 7	Day	07:00-19:00	8	1	7	7	59
			Night	19:00-07:00	7	4	12	6	
			24H	around 12:00	2	-	4	1	
PM$_{2.5}$	August 2013 to December 2015	5 to 10	Day	07:00-19:00|09:00-02:00|09:00-23:00	4	4	14	10	80
			Night	19:00-07:00|02:00-09:00|23:00-08:00	5	2	20	18	
			24H	around 12:00	2	-	1	-	
PM$_{10}$-B	April 2016 to August 2017	7 to 10	Day	09:00-23:00	-	-	2	-	52
			Night	23:00-08:00	11	5	18	9	
			24H	around 12:00	3	-	3	1	
PM$_{10}$- C	February 2019 to March 2020	7	Day	09:00-23:00	1	2	7	1	32
			Night	23:00-08:00	4	2	7	1	
			24H	around 12:00	6	0	1	0	

In total, 67 field blanks and 242 samples were collected (aside from those lost due to drenching), from which six samples were excluded from the analysis because the flow was too high (>36 m³.h⁻¹), and 13 because of specific events (San Juan bonfire festivity) or if the sampled volume was small (<300 m³). Some of the latter were helpful as study cases for particular conditions or events but are not presented here. The remaining 223 valid samples are detailed in Table 1. The number of field blanks is very large, which is essential in order to achieve a good contamination control on the data.

2.3 Mass and elemental composition

For nine PM$_{10}$ samples (taken every two months from April 2016 to August 2017), additional analyses were performed at IDAEA (Spain). Gravimetric concentrations of particulate matter were obtained by weighing the filters, prior and post-sampling, after 48h stabilization at 20°C and 50% relative humidity. After gravimetric analysis the concentrations of major and trace elements in particulate matter were determined by following the methodology described elsewhere (Querol et al., 2001; Rodríguez et al., 2011; Ripoll et al., 2015). In short, a fraction from each filter was fully acid digested using a

HNO$_3$:HF:HClO$_4$ mixture. The acidic solution obtained was analyzed by Inductively Coupled Plasma Atomic Emission

200   Spectrometry (ICP-AES) and ICP - Mass Spectrometry (ICP-MS) for the determination of major (Al, Ca, Cu, Fe, K, Mg, Mn, Na, P, and S) and trace elements (Li, Be, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, Ba, REE, W, Ti, Pb, Bi, Th, and U), respectively. Two samples were discarded due to instrumental problems (power outage, filter badly set).

The elemental composition was used to calculate the mineral matter (MM) contribution to the samples using Eq. 1:

205    $$MM = CO_3^{-2} + SiO_2 + Al_2O_3 + P_2O_5 + Fe + Ca + K + Na + Mg + Ti + Mn \ , \tag{1}$$

where SiO2 was estimated from Al and CO$_3^{2-}$ from Ca (Alastuey et al., 2016).

2.4 Ions and carbonaceous matter

Samples were analyzed for their content of soluble ions, elemental and organic carbon and sugar derivatives using sub-sampled

210   fractions of the collection filters. Carbonaceous matter was analyzed using a thermo-optical method on a Sunset Lab analyzer (Birch and Cary, 1996) as described by Aymoz et al. (2007). Carbonaceous matter is subdivided in organic carbon (OC), which is the volatile and non-light-absorbing fraction, and elementary carbon (EC), which is optically absorptive, using the EUSAAR2 protocol (Cavalli et al., 2010). For the analyses of ions and sugars, filter punches (typically of about 10 cm²) were first extracted into ultrapure water for 20 min in a vortex shaker and then filtered using a 0.22 µm Acrodisc filter. Soluble

215   anions (F$^-$, Cl$^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$) and cations (Na$^+$, Li$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}) were analyzed by ionic chromatography (IC, Thermo Fisher ICS 3000) equipped with AS/AG 11HC and CS/CG 12A columns for anion and cation analyses, respectively. Methanesulfonate (MeSO$_3^-$) and carboxylic acids were also quantified in the same anionic run (Jaffrezo et al., 1998).

Anhydrosugar, sugar alcohol, and primary saccharide analyses were achieved using an HPLC with Pulsed Amperometric Detection. A first set of equipment was used until March 2016, consisting of a Dionex DX500 equipped with three columns

220   Metrosep (Carb 1-Guard + A Supp 15-150 + Carb 1-150), the analytical run being isocratic with 70 mM sodium hydroxide eluent, followed by a gradient cleaning step with a 120 mM NaOH eluent. This analytical technique enables detection of anhydrous saccharides (levoglucosan and its stereoisomers mannosan and galactosan), polyols (arabitol, sorbitol, mannitol), and glucose. A second set of equipment was used after this date, with a Thermo-Fisher ICS 5000+ HPLC equipped with 4 mm diameter Metrosep Carb 2 × 150 mm column and 50 mm pre-column. The analytical run is isocratic with 15% of an eluent of

225   sodium hydroxide (200 mM) and sodium acetate (4 mM) and 85 % water, at 1 mL min^{-1} (Samake et al., 2018). The blank value was subtracted from the concentrations for both ions and sugars. Detection and quantification limits are presented in Table S1 of the supplementary material.

Further chemical species were determined with IC or HPLC-PAD. However, acetate, pyruvate, NO$_2^-$ and sorbitol were excluded from the database due to experimental uncertainty and possible artifacts. From 2015 onwards, aerosol concentrations

230   of inositol, glycerol, erythritol, xylitol, threalose and rhamnose were also obtained, but results are not included here due to the incompleteness of the data series and because for sorbitol, xylitol and rhamnose, most of the values were below the

quantification limit. Formate, F⁻, Cl⁻ and NO₃⁻ of PM₁₀-C were excluded from the analysis because, for this particular batch, the filters were analyzed three years after the sampling took place and acidic losses (Witz et al., 1990; Ashbaugh and Eldred, 2004) seem to have occurred.

2.5 Statistical analysis

Concentration measurements are not distributed normally and there are some outliers for individual species in certain samples. Therefore, we used non-parametric statistical methods in order to describe the data sets. The strength of the relationship between species concentrations was evaluated with the Kendall rank correlation method (τ) instead of the typical Pearson's coefficient to avoid outliers pulling the relationship. Comparison of average values between two datasets was made with Wilcoxon rank sum test (Table S4). Statistical significance was set at $p < 0.05$ unless otherwise indicated. The median is a better statistic to describe our data, hence the concentrations are reported as the median ($\tilde{x}$) $\pm$ standard deviation (σ) in the manuscript, or by their interquartile range (IQR). However, most of the literature reports mean average concentration, and therefore we will use it in the comparative figures. Mean and median concentrations and standard deviation for all species can be found in the supplementary material. (Tables S2 and S3).

In order to find a structure in the seasonality patterns, the species were grouped by two clustering methods: k-means and hierarchical clustering (Govender and Sivakumar, 2020; Abdalla, 2022). For both cases, the variable to be analyzed was the monthly median concentration based on the Euclidean distance. The hierarchical clustering was made using the Ward method (Govender and Sivakumar, 2020 and references therein).

2.6 Air-mass origin

HYSPLITv 4.8 (Hybrid Single-Particle Lagrangian Integrated Trajectory, Stein et al., 2015) back-trajectories are were used to assess the origin of the air-masses for each filtersample collected. Four-day hourly (96) back trajectories were obtained for each sample without taking into account regional precipitation data. Only the periods when the high-volume sampler was working were selected (e.g. removing power outage periods). Hysplit desktop version 4.8 was used to obtainThis produced on average 67±38 air mass backtrajectories per sample for PM₂.₅ and 94±47 for PM₁₀.

Previous studies in this site used HYSPLIT backtrajectories based on WRF model nested in three domains down to 1 km resolution, with ERA-interim data as boundary conditions (Chauvigné et al., 2019; Koenig et al., 2021). Nevertheless, this high-resolution dataset spans only until September 2016, and therefore a new set of backtrajectories covering our entire sampling period was obtained. The new backtrajectory dataset was based on ERA-5 reanalysis, which has a ~30 km horizontal resolution. The starting point of the backtrajectory was set at 1500 m a.g.l (of the ERA-5 defined topography) which corresponds to 528 hPa in the pixel containing the station coordinates. Selection of this initial pixel was done to overcome the influence of the coarse topography of the reanalysis data. This choice, however, produces a long-range biased backtrajectory due to the higher wind speed at upper levels. Moreover, the difference in the horizontal resolution (1-km vs ~30-km), and the

very complex topography of this region results in the ERA-5 backtrajectories missing some transport features in the short-range (for instance, funneling of the winds north of the station). In spite of this, there is overall agreement of both backtrajectory results at annual scale (Figure S14).

Being aware of all this, we used the ERA-5 backtrajectories for the study of volcanism origin in our record (section 3.5). We plotted each sample on a polar grid centered on Chacaltaya. We then counted for each cell of the polar grid the number of hours that each trajectory passed over it, producing a higher density of points for the most common pathways followed by the airmasses (as in Koenig et al., 2021), and then classified the samples based on their dominant air mass origins.

96-hour back trajectories (without taking into account regional precipitation), run every hour. Only the periods when the high-volume sampler was working were selected. The working time of each filter was corrected if there was a reason for a change in the pre-defined schedule (power outage, mistake in programming the timer, etc.). This produced on average 67±38 air mass back trajectories per filter for $PM_{2.5}$ and 94±47 for PM_{10}. The back trajectories corresponding to each sample were then plotted on a polar grid centered on Chacaltaya. We then counted for each cell of the polar grid, the number of hours that each trajectory passed over it, producing a higher density of points for the most common pathways followed by the airmasses (see more details of this representation in Koenig et al., 2021).

Two different meteorological inputs were used to drive the backtrajectory analysis:

High resolution dataset from January 2012 to September 2016: based on WRF model nested in three domains (Figures S5, S6 and Table S5) down to 1 km resolution, with ERA-interim data as boundary conditions. Nine starting points at 500 m a.g.l. were used in a 3x3 grid over Chacaltaya, with the station coordinates as the central point. This dataset has a topography better represented than the coarse resolution dataset described below, and represents well the transport over the complex terrain of the region (e.g., uplift of Amazonian air masses through valleys). It was used in previous works (Chauvigné et al., 2019; Koenig et al., 2021) and we use it for both individual sample-to-sample and grouped analysis. For the 143 samples covered by this dataset, only 15% of the samples had air masses being brought from a single dominant direction (W, NW, N, NE), 29% for two dominant directions (W, NW, N, NE, SW, SSW, S) and 49% of very mixed origins (no information for 7% of the samples).

Coarse resolution dataset from January 2012 to April 2021: based on data from ERA-5, which has 30 km resolution and a more smoothed topography. This dataset cover the entire sampling period. The starting point of the backtrajectory was set at 1500 m a.g.l (of the ERA-5 defined topography) which corresponds to 528 hPa in the pixel containing the station coordinates. Selection of this initial pixel was done to overcome the influence of the coarse topography of the reanalysis data. This choice, however, produces a long-range biased backtrajectory due to the higher wind speed at upper levels. This dataset covers all samples, but sample to sample comparison with the nested-WRF backtrajectories shows only 43% of coincidences in transport patterns, although for long-range grouped back trajectories, there is overall agreement (Figure S8). We thus use this dataset for the interpretation of the entire record, using grouped samples (section 3.5).

2.7 Source apportionment

Source apportionment was performed with the software EPA PMF v.5.0.14 following the recommendations of Belis et al. (2019). Fifteen species were used: OC, EC, $C_2O_4^{2-}$, $MeSO_3^-$, SO_4^{2-}, NH_4^+, Br^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, levoglucosan, arabitol, mannitol, glucose. Organic carbon is adjusted for the carbon contribution of organic species using Equation 2. Nitrate, Cl^-, F^- were not used because they are pulled into a factor that only represents their absence in batch PM_{10}-C.

$$OC^* = OC - \frac{oxalate}{3.67} - \frac{methanesulfonate}{7.92} - \frac{levoglucosan}{2.25} - \frac{arabitol}{2.53} - \frac{mannitol}{2.53} - \frac{glucose}{2.50} \qquad (2)$$

Given the characteristics of our sampling schedule and the high-altitude, the measured species present a low range of concentrations. Plus, they are quite mixed during transport, making general variability low and co-linearity high. Complete information on the source apportionment setup can be found in the supplementary material.

3 Results and discussion

Mass concentrations were transformed to standard cubic meters (1013hPa, 0ºC, see supplementary material) for all the sites used in this work (presented in Table 4. For Chacaltaya, ambient concentrations can be found in Table S2 in the supplementary material). Concentrations are reported by pooling day, and night and 24-hour samples (Table 2) because day and nighttime concentrations were statistically similar for the majority of the species (Table 5, section 3.5 S7). Although $PM_{2.5}$ and PM_{10} measurements were not simultaneous, we have compared the average mass concentrations for major species considering that the two fractions were sampled during long enough periods (>1yr). For the three PM_{10} groups, there was variability from group to group and season to season, indicating highly variable environmental controls. The species Nevertheless, concentrations in three PM_{10} batches and the $PM_{2.5}$ batch were statistically similar for most of the species (Table S4), particularly in the wet season (DJFM). This hints to a predominant concentration of most species in $PM_{2.5}$ fraction, long-range transport of small particles, less emission of coarse material in the wet months, and in some cases co-emitting or co-located sources. For the three PM_{10} groups, there was variability from group to group and season to season (Table S4), indicating highly variable environmental controls.

Table 2. Bulk mass concentration (ng m^{-3}) of EC, OC, and species measured in Mt. Chacaltaya aerosol. Mean ($\bar{x}$), median ($\tilde{x}$), standard deviation (σ) and number of samples above the quantification limit (N) reported. Volume taken to standard cubic meters (1013hPa, 0ºC). Data segregated by seasons and also at ambient conditions can be found in Tables S2 and S3.

Species	PM$_{10}$-A				PM$_{2.5}$				PM$_{10}$-B				PM$_{10}$-C			
	December 2011 to July 2013				August 2013 to Dec. 2015				April 2016 to August 2017				February 2019 to March 2020			
ng m^{-3}	$\bar{x}$	$\tilde{x}$	σ	N	$\bar{x}$	$\tilde{x}$	σ	N	$\bar{x}$	$\tilde{x}$	σ	N	$\bar{x}$	$\tilde{x}$	σ	N
OC	913	**703**	(648)	56	881	**669**	(729)	77	801	**605**	(604)	49	607	**529**	(449)	32
EC	92.8	**68.2**	(90.8)	36	80.7	**69.7**	(48.6)	74	77.7	**56.5**	(68.7)	49	65.8	**51.3**	(48.5)	32
Li$^+$	0.05	**0.04**	(0.07)	48	0.02	**0.03**	(0.03)	52	0.012	**0.005**	(0.023)	19	0.015	**0.013**	(0.012)	27
Na$^+$	25.2	**21.9**	(20.8)	54	25.2	**20.1**	(15.4)	71	29.9	**22.7**	(26.8)	41	12.05	**9.17**	(10.3)	31
NH$_4^+$	158	**145**	(106)	58	305	**295**	(192)	78	316	**306**	(196)	49	281	**248**	(161)	32
K$^+$	24.2	**17.7**	(22.8)	54	26.4	**23.3**	(17.8)	77	34.1	**15.5**	(34.0)	47	25.7	**19.9**	(26.3)	31

Con formato: Superíndice

Con formato: Superíndice

	val			n	val			n	val			n	val			n
Mg+2	7.28	**6.83**	(4.51)	56	8.62	**7.87**	(5.51)	75	6.86	**5.04**	(6.66)	49	6.66	**5.76**	(4.89)	32
Ca+2	72.4	**66.4**	(43.0)	55	90.8	**74.5**	(78.4)	79	57.4	**51.3**	(43.0)	48	51.4	**36.2**	(42.0)	32
F-	2.05	**1.48**	(2.31)	49	2.80	**1.79**	(2.49)	76	1.49	**1.13**	(1.17)	42		*Lost*		14
Cl-	8.72	**6.17**	(7.08)	47	13.3	**9.79**	(11.0)	45	10.85	**7.73**	(11.91)	34		*Lost*		25
Br-	1.45	**1.27**	(0.92)	50	1.18	**0.91**	(0.79)	69	1.63	**1.09**	(1.54)	38	0.96	**0.78**	(0.80)	28
NO3-	149	**128**	(114.2)	58	84.9	**65.6**	(79.2)	76	110	**71.1**	(115.8)	45		*Lost*		29
SO4-2	451	**399**	(327)	58	1121	**1047**	(795)	79	991	**920**	(761)	52	905	**889**	(499)	32
MeSO3-	6.58	**6.67**	(3.56)	54	7.86	**7.45**	(4.41)	76	6.73	**6.22**	(3.45)	48	4.52	**4.83**	(2.48)	32
HCO3-	12.3	**8.78**	(10.7)	48	13.8	**12.0**	(6.99)	50	27.6	**9.80**	(68.9)	16		*Lost*		27
C2O4-2	32.8	**22.6**	(40.8)	57	44.0	**40.3**	(30.5)	76	38.0	**30.3**	(37.4)	45	53.2	**43.6**	(31.7)	32
Glucose	3.29	**2.64**	(2.10)	54	3.69	**3.04**	(2.64)	48	2.91	**2.46**	(1.75)	44	1.81	**1.59**	(1.12)	23
Levoglucosan	12.6	**5.3**	(22.7)	56	14.3	**8.47**	(18.9)	70	36.6	**26.5**	(41.1)	32	11.0	**6.77**	(10.6)	19
Mannosan	2.92	**0.99**	(5.5)	17	2.06	**0.80**	(3.7)	50	6.93	**4.07**	(9.51)	25	1.38	**1.10**	(1.32)	14
Galactosan	1.99	**0.76**	(4.92)	23	1.38	**0.57**	(2.26)	48	5.01	**2.35**	(8.09)	26	1.09	**1.04**	(0.94)	14
Arabitol	3.76	**2.63**	(4.31)	58	1.67	**1.45**	(0.88)	44	1.04	**0.96**	(0.32)	31	0.56	**0.51**	(0.38)	22
Mannitol	1.38	**1.09**	(1.10)	49	1.69	**1.37**	(1.24)	43	1.85	**1.63**	(1.04)	40	1.17	**0.92**	(0.87)	13

3.1 General composition of particulate matter and comparison to other sites

3.1.1 Dominant ions and carbonaceous species

PM$_{10}$ and PM$_{2.5}$ samples were collected during non-overlapping periods. Mass concentrations determined at Chacaltaya for ions, total carbon (EC+OC) and saccharides present an interquartile range of 917 to 2308, 519 to 1175, and 3.9 to 24.1 ng m^{-3} for PM$_{2.5}$ respectively; and 558 to 1785, 384 to 1120, and 4.3 to 25.5 ng m^{-3} for bulk PM$_{10}$. Chacaltaya PM$_{10}$ is compared to other available high-altitude sites (Northern Hemisphere) and other selected sites in South America listed on Table 4 and presented in Figure 2.

Table 4. Sites used in the comparative Figures 2 and 3. The ABL-TopoIndex classifies high-altitude sites according to the influence of the atmospheric boundary layer on them (the lowest the value, the less influenced by the convective planetary boundary layer, Collaud Coen et al., 2018), which is available for some of the sites.

	Acronym and location	Lat.	Lon.	Alt. m.a.s.l	ABL Topo Index	Type	References
High-altitude	CHC Chacaltaya, Andes, western Bolivia	-16.3470	-68.1283	5380	1.34	High altitude, regional background	This work
	NCO Nepal Climate Observatory, Mt. Everest, Nepal	27.9578	86.8149	5079	3.43	High altitude, regional background	Decesari et al., 2010
	IZO Izaña, Canary Islands, Spain	28.3090	16.4994	2373	0.57	High altitude, island mountain top, background	García et al., 2017a,b
	RUN Maïdo Observatory, Reunion Island	-21.0795	55.3831	2160	0.79	High altitude, island mountain top, background	Dominutti et al., 2022
	AMV Atlas Mohamed V Observatory, Middle Atla,s, Morocco	33.4062	-5.1033	2100	-	High altitude, regional background	Deabji et al., 2021
	MSC Montsec, Spain	42.0500	0.7333	1570	2.07	High altitude, continental background	Ripoll et al., 2015
	PDD Pûy de Dôme, Massif Centrale, France	45.7723	2.9658	1465	2.72	High altitude, continental background	Bourcier et al., 2012
	EA El Alto city, Bolivia	-16.5100	-68.1987	4025	-	Urban near Chacaltaya, high altitude but not mountain sites	Mardoñez et al., 2023
	LP La Paz city, Bolivia	-16.5013	-68.1259	3600	-		
Forest and rural	RBJ Jaru natural reserve, Rondônia state, Brazil	-10.0819	-61.9300	110		Forest, background	Graham, 2002
	ZF2 Cuieiras ZF2 natural reserve (TT34), Amazonas state, Brazil (+54m tower)	-2.6091	-60.2092	110		Forest, background	Custodio et al., 2019
	ATTO Amazonian Tall Tower Observatory (+80m tower), Amazonas state, Brazil	-2.1465	-59.0218	120	Not applicable	Forest, background	Barbosa, 2014
	BAL-01 Balbina, Amazonas state, Brazil	-1.9166	-59.4000	174		Forest, background	Claeys et al., 2004 Elbert et al., 2007
	FNS Fazenda Nossa Señora Aparecida, Rondônia state, Brazil	-10.7622	-62.3575	315		Rural (biomass burning campaign)	Kundu et al., 2010a
	SHU Shuara 9, Sucumbíos, Ecuador	-0.0592	-76.5603	250		Rural background	Barraza et al., 2020
	Auca Sur, Orellana, Ecuador	-0.7046	-76.8878	277		Rural background	Barraza et al., 2020

| FLO | La Florida, Esmeraldas, Ecuador | -0.9317 | -79.6780 | 72 | | Rural background | Barraza et al., 2020 |

335 Ions and EC-OC concentrations at Chacaltaya station are lower than other high-altitudes sites, with the exception of EC-OC for the sub-tropical station of Izaña and the tropical station of Maïdo, for which concentration levels are similar to Chacaltaya. For Izaña, nitrate and stands out as a long-range pollutant transported to the observatory (Rodríguez et al., 2011) while for Chacaltaya its concentration is proportionally lower. In Chacaltaya, nitrate is likely related to both long-range transport to the region (Mardoñez et al., 2023) that includes biomass burning, and short-range influence of traffic emissions from below the 340 station (diurnal cycle of PM_1 NO_3^- related to transport through the convective boundary layer, Bianchi et al., 2021).

Mt. Atlas presents a higher load of anions and cations relative to Mt. Chacaltaya, mostly related to important dust and urban influences at a broad regional scale. Pûy de Dôme, Montsec, and Mt. Everest present a higher influence of pollution (SO_4^{-2}, NO_3^-, EC, OC) compared to Mt. Chacaltaya, because the former lie in the populated western Europe and are influenced by regional pollution (Bourcier et al., 2012; Ripoll et al., 2015; Querol et al., 2013), and because the latter is influenced by long-345 range north Asiatic pollution in spite of its remote location (Bonasoni et al., 2010; Decesari et al., 2010). EC, OC and chloride concentrations at Chacaltaya can be more than five times lower than urban sites in the region, and Cl^- is also lower than sites influenced by relatively fresh and unchanged marine aerosol (such as ATTO, Barbosa 2014). Combustion tracers (OC, EC, K^+, section 3.3) at Chacaltaya are lower compared to sites showed in Figure 2. Chacaltaya concentrations are similar to the

tropical broadleaf forest site of Cuieras ZF2, with the exception of a significantly higher OC, K$^+$, Na$^+$ contribution in ZF2 due

350   to the important influence of both biomass burning and biogenic emissions at the forest site.
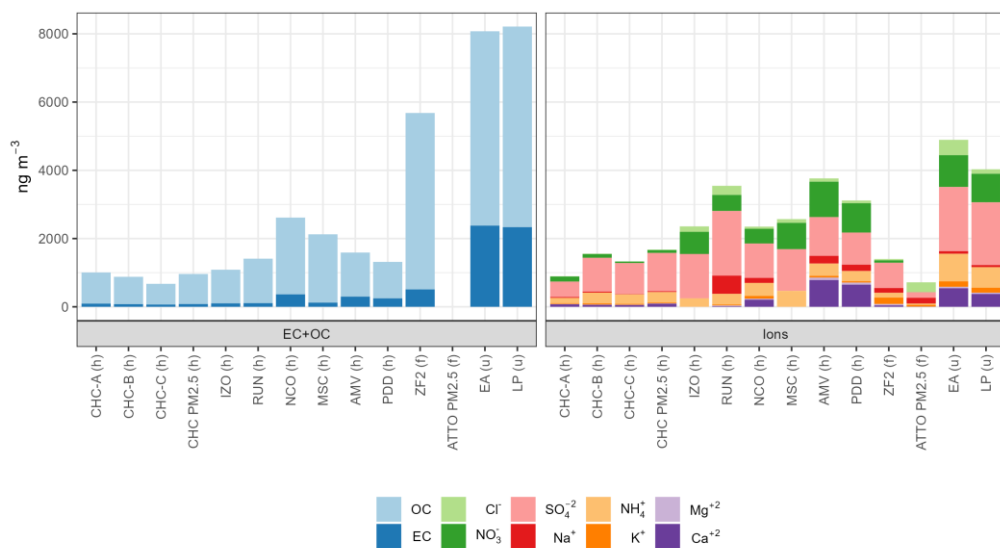
Figure 2. Aerosol chemical composition at standard conditions of several sites compared to Chacaltaya. PM$_{10}$ is reported for all the sites, except for ATTO which has only PM$_{2.5}$ information. Note that Na$^+$, K$^+$, Mg^{+2}, Ca^{+2} are not available for IZO, MSC; and EC,
355   **OC for ATTO.**

For Chacaltaya, OC and SO$_4^{2-}$ are the two dominant components identified, both adding up to 70% of the measured mass of each size fraction, followed by NH$_4^+$ (which neutralizes sulfate) and NO$_3^-$, which together contribute 17% to the aerosol mass. The dominance of OC and sulfate is similar to most of the other sites shown in Figure 2, but sources are different. For instance, for the Cuieras forest site, OC represents alone 70% due natural and biomass burning influences. At Izaña, sulfate is mainly
360   related to long-range transport of anthropogenic emissions (Rodríguez et al., 2011; García et al., 2017a) and at Mt. Everest, OC and sulfate emissions are heavily influenced by coal burning (Bonasoni et al., 2010; Decesari et al., 2010). At Chacaltaya, sulfate can have a variety of sources: sea salt, soil dust (Surkyn et al., 1983), ~~fossil fuel combustion (diel cycle observed in Chacaltaya for PM$_1$, Bianchi et al., 2021),~~ marine secondary aerosol (Scholtz et al., 2023), and volcanism (Aliaga et al., 2021). Impact of coal combustion in Chacaltaya is discarded given that coal is not used in the tropical Andes (EANET, 2019) as
365   corroborated by the absence of lignite markers in the samples (Figure S411). Sea-salt sulfate contributions account only for 3% for PM$_{10}$-A and 1% for PM$_{10}$-B, C and PM$_{2.5}$ (calculated as [seaSO$_4^{2-}$]=2.06 [Mg^{2+}] ng m^{-3} based on Keene (1986) ratios with Mg^{2+} chosen because of fewer missing values than for Na$^+$). Soil dust contribution to sulfate is 8% and volcanism accounts

for at least 80% on average in our record (section 3.2). ~~Nitrate and~~ Or~~r~~g~~a~~ic ~~C~~carbon ~~are~~is notably related to regional biomass burning (section 3.3), ~~and urban~~ emissions from the ~~metropolitan area~~ nearby ~~(Bianchi et al., 2021),~~urban area and long-range transport (section 3.2), though in the wet season, part of ~~the organic fraction~~it has been related to natural sources (Zha et al., 2023). NH_4^+ is discussed in section 3.~~5~~3. Although Chacaltaya ion concentrations are lower than northern hemisphere stations, this Andean site doubles the total soluble fraction (Σ_{ions}=1.7 µg m^{-3} in PM$_{2.5}$) measured at the pristine Amazonian Tall Tower Observatory (Σ_{ions}=0.7 µg m^{-3} in PM$_{2.5}$ from Barbosa, 2014).

In summary, the Chacaltaya GAW station is a regional background site with relatively low ion and EC-OC concentrations when compared to other high-altitude stations in the world and low-altitude background stations in the region (with the notable exception of the Amazonian Tall Tower Observatory).

3.1.2   Organic and elemental carbon

Elemental carbon (EC) is related to fine particles directly emitted by combustion processes (typically traffic and biomass burning) and organic carbon (OC) to both primary and secondary organic aerosol (SOA). The OC/EC ratio is used as a proxy for the nature of carboneous primary sources (Salma et al., 2004) but also of the aging of aerosols (Waked et al., 2014). The OC/EC mass ratio in Chacaltaya was 10.~~9~~4±4.5 (IQR 8.0-12.3) for bulk PM$_{10}$ and 11.0±7.2 (IQR 8.1-15.0) for PM$_{2.5}$, similar to sites classified as «rural» (8-11 Querol et al., 2013), but the interquartile range also encompasses the «remote site» classification (12-15 Querol et al., 2013). This mass ratio is much higher than the observed for urban areas in South America (e.g. El Alto 2.6±1.1 from Mardoñez et. al 202~~2~~3; Jaciara 2.0 ±1.2, Campo Novo dos Parecis 3.0±1.9, from Custodio et al., 2019) and closer to the natural environment of Cuieiras forest (12.2±2.2 for PM$_{10}$ and 6.6±1.0 for PM$_{2.5}$ Custodio et al., 2019). It is lower than for remote locations where aerosol arrives quite aged (13 in Siberia, Mikhailov et al., 2017; 12 in remote China, Zhang et al., 2008; 12-15 for Izaña and Montsec, Querol et al., 2013) and forest burning emissions near the source (14.5 Watson and Chow, 2001).

In Chacaltaya, the OC/EC ratio is quite similar over the year: median value is 10.5±7.0 for DJFM, 8.6±2.7 for April,10.4±6.0 for MJJA, and 10.9±4.5 for SON. Not even the outstanding biomass burning season (JAS) produces a ratio (10.4±4.4) different from the rest of the year. This is contrasting with what has been observed in other sites such as Mt. Atlas, where OC/EC ratio showed marked seasonality (summer: 11.2, winter: 2.2, Deabji et al., 2021). The measured ratios and their uniformity over the year seem to be influenced by two factors: First, air-masses that are relatively aged during long-range transport, and second, the quick transformation (in ca. two hours) of short-range urban emissions such as observed over other urban areas (DeCarlo et al., 2008). According to the source apportionment study (section 3.2), 71%~~We hypothesize that the high UV of the tropical atmosphere over the Altiplano could play a role in the impressively fast aging of the organic matter at this site when transported from the nearby urban area.~~
 of the organic carbon is related to long-range transport and 29% to nearby urban emissions.

400 Secondary organic aerosol was estimated for bulk PM_{10} using the Castro et al. (1999) approximation ($OC_{secondary} = OC_{total} -$ [levoglucosan]*$[OC/levoglucosan]_{min} - EC*[OC/EC]_{min}$) and it was found that SOA contributes approximately 50% of the OC mass during the dry season and 69% during the wet season for the entire dataseries. During the wet season, other organic markers such as formate, oxalate, arabitol, mannitol and glucose are present, suggesting that important SOA formation processes are not only due to anthropogenic but also to natural precursors.

405 ### 3.1.3   Saccharides

In Figure 3 we present a comparison of arabitol, mannitol and glucose, which are tracers of primary biogenic aerosol, at for several sites. Arabitol and mannitol are emitted along with fungal and fern spores (Bauer et al., 2008, Elbert et al., Graham et al., 2003), but also found in leaves, pollens and green algal lichens (Medeiros et al., 2006; Jia et al., 2010). Glucose is the most abundant sugar in vascular plants (Opsahl and Benner, 1999) and consequently, it is found inrelated to plant fragments

410 (Pietrogrande et al., 2014; Graham et al., 2003), suspended soil from cultivated land (Rogge et al., 2007), biomass burning products and pollen (Elbert et al., 2007; Kundu et al., 2010a; Claeys et al., 2010). Indeed, pollen is transported to the Chacaltaya region mostly from Puna herbaceous vegetation (Altiplano) and Yungas (Subandes) trees, with a marginal evergreen Amazonian contribution (Brugger et al., 2019). Arabitol and mannitol are emitted along with fungal (Bauer et al., 2008) and fern spores (Graham et al., 2003), but also found in leaves, pollens and green algal lichens (Medeiros et al., 2006; Jia et al.,

415 2010). In Balbina, Amazonia, mannitol has been linked to nocturnal Basydiomycota emissions (Elbert et al., 2007). ChacaltayaThe concentrations of these primary biogenic aerosols in Chacaltaya are highly variable, as can be seen in PM_{10} A, B and C barplots in Figure 3. Saccharide data for high-altitude sites are scarce, but for what areis available, Chacaltaya bulk PM_{10} concentrations (glucose 2.9 ± 1.9 ng m^{-3}, arabitol 1.4 ± 3.4 ng m^{-3}, mannitol 1.5 ± 1.1 ng m^{-3}) are similar to other semi-arid environments such as Mt. Everest and Mt. Atlas, but lower than Maïdo observatory in the tropical Southern Ocean, and rural

420 sites either from tropical (Brazil, Ecuador; Figure 3) and extra tropical regions (e.g. France form Samake et al., 2018). This difference is more pronounced for PM_{10}, depicting an important influence of a region where vegetation is scarce (Altiplano), in agreement with other studies (Brugger et. al., 2019). This is interesting, because even if the highly productive Amazonian forest is in the windward side (Figure 1) of the observatory it does not seem to have a big influence at our site in terms of saccharides, probably due to dilution, loss of coarse primary biogenic aerosol in the transport and/or unstudied degradation

425 mechanisms of sugars along the way.
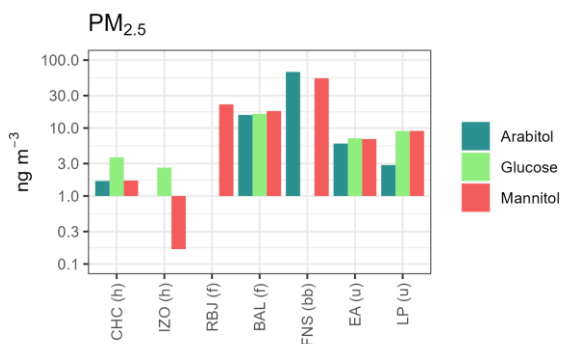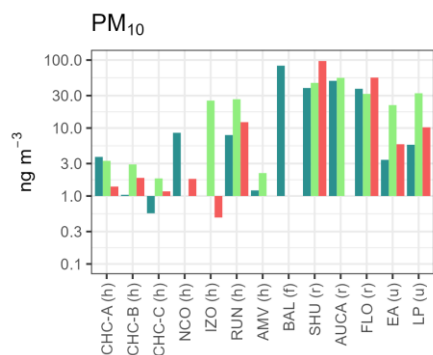
Figure 3. Comparison of biogenic markers (mean concentrations) among different sites taken to standard cubic meters for PM$_{10}$ (upper panel) and PM$_{2.5}$ (lower panel). Mind the logarithmic scale. For AMV, only cases without Saharan dust influences were

In general, polyols tend to be more concentrated in PM_{10} than in $PM_{2.5}$ (Yttri et al., 2007; Samake et al., 2018; Elbert et al., 2007; Brighty et al., 2021; Zhang et al., 2015), especially in dry conditions (Rathnayake et al., 2017), but they are shifted to $PM_{2.5}$ when the cells rupture under moist conditions (Rathnayake et al., 2017; Yttri et al., 2007) and therefore they are not very affected by rainout. This difference between PM_{10} and $PM_{2.5}$ is not pronounced at Chacaltaya, likely indicating fragmented biogenic material that is present mostly in $PM_{2.5}$ and/or loss of coarse material during long range transport. The loss of coarse material even for short distances seems supported by the difference with measurements in the nearby conurbation. In fact, glucose in LP-EA shows a pronounced difference between PM_{10} and $PM_{2.5}$, but this difference is not translated to Chacaltaya Chacaltaya concentrations are highly variable, as can be seen in PM_{10}-A, B and C barplots in Figure 3. Saccharide data for high-altitude sites are scarce, but for what are available, Chacaltaya bulk PM_{10} concentrations (glucose 2.9±1.9 ng m⁻³, arabitol 1.4±3.4 ng m⁻³, mannitol 1.5±1.1 ng m⁻³) are similar to other semi-arid environments such as Mt. Everest and Mt. Atlas, but lower than Maïdo observatory in the tropical Southern Ocean, and rural sites either from tropical (Brazil, Ecuador; Figure 3) and extra tropical regions (e.g. France form Samake et al., 2018). This difference is more pronounced for PM_{10}, depicting an important influence of a region where vegetation is scarce (Altiplano), in agreement with other studies (Brugger et. al., 2019). This is interesting, because even if the highly productive Amazonian forest is in the windward side (Figure 1) of the observatory it does not to have a big influence at our site in terms of saccharides, probably due to dilution, loss of coarse primary biogenic aerosol in the transport and/or unstudied degradation mechanisms of sugars along the way.

At Chacaltaya, mannitol concentrations are similar for PM_{10} and $PM_{2.5}$, while for arabitol this is not so clear (Table S4). Their correlation is poor to moderate (τ=0.54, 0.29, 0.47, 0.54 for $PM_{2.5}$, PM_{10}-A,B,C, respectively), contrary to what was found for a significant number of sites (Marynowski and Simoneit, 2022 and references therein), indicating emissions of endemic fungal species. Maximum values of arabitol were found in the PM_{10}-A fraction, but later on (Figure S3) concentrations show a significant decrease. Glucose correlates moderately well with mannitol except for PM_{10}-C (τ = 0.67, 0.51, 0.67, and 0.27) where it correlates with arabitol (τ = 0.36, 0.30, 0.43, 0.67), the explanation for which remains unclear.

3.2 Source apportionment

Tests were made for 4 to 6 factors and different species and constraints. The results were statistically sound for four constrained factors, but a single source per factor was not achieved (with the exception of the « Biomass burning » factor). The concentration of the species in each factor is presented in Table 5, and more details of the source apportionment results can be found in the supplementary material. Briefly, the obtained factors are:

1. « Westward » containing volcanic (SO_4^{2+}), ammonium and marine ($MeSO_3^-$, cations) contributions
2. « Soil dust and bromide » containing soil dust tracers, bromide and OC
3. « Biomass burning » defined by levoglucosan, K^+, and OC, being the only factor fully resolved for a single source
4. « Combustion » characterized by EC, oxalate and OC, that seems to represent both urban and biomass burning

Table 5. Concentrations of each species per factor in ng m^{-3} at STP.

Factors	OC*	EC	Br⁻	SO_4^{2-}	Na⁺	NH_4^+	K⁺	Mg^{2+}	Ca^{2+}	$MeSO_3^-$	Oxalate	Levoglucosan	Arabitol	Mannitol	Glucose
Westward	18.3	1.3	-	618	3.6	176	3.8	2.4	16.2	2.7	-	-	0.1	0.3	0.1
Soil dust and bromide	243	-	0.7	60.8	10.2	8.1	4.0	2.8	28.6	0.5	0.2	-	0.4	0.2	0.8
Biomass burning	205	2.4	-	-	0.4	10.7	12.7	0.4	5.3	1.6	1.7	9.6	0.1	0.2	0.3
Combustion	186	42.4	0.1	98.5	0.7	45.5	-	-	1.6	-	29.7	0.2	-	0.04	0.1

The first two factors are related to species whose seasonality is defined by atmospheric circulation changes, with lowest concentrations during the wet months (section 3.3.1). The last two factors also have a common seasonality, characterized by the regional influence of biomass burning (section 3.3.2). The mixed « Westward » factor appeared almost unchanged in every test made and it seems to represent transport through the low free troposphere.

Some caveats must be taken into account. For instance, $MeSO_3^-$ 57% was assigned to the « Westward » factor, 34% to « Biomass burning » and the rest was divided in the other two factors. However, the « Westward » factor is defined by the step increase of SO_4^{2-} after 2013 (section 3.5), and this is pulling along $MeSO_3^-$. We know that $MeSO_3^-$ contributions did not change along with sulfate after 2013 (Table 7, Figure S16). Therefore, we are aware that the division of this species in several factors is not necessarily due to a geochemical reason, but to the lack of other species (that were not measured) to help better constrain the solutions.

This said, even if the source apportionment gives valuable results, it cannot fully resolve the sources at this site, and in consequence we use it in combination with the next section.

3.3 Observed seasonality of the atmospheric species

Long-term series (Figure S3) show clear seasonality for most of the species, and seasonal patterns were obtained from monthly boxplots. The number of samples available per month are presented in Figure 4, which shows that at least 10 samples per month were available. In Figures 5, 6, and 7, monthly boxplots for each species are presented. The boxplots were made by aggregating all the sampled periods. Seasonal patterns can be classified in three principal groups based on clustering of their normalized median monthly concentrations (Figure S15). These groups are: 1. Species with high concentration during the dry months, 2. Species with maxima concentration between June and November, 3. Species with unclear seasonality patterns. However, there are nuances within this classification and they will be discussed in the text.
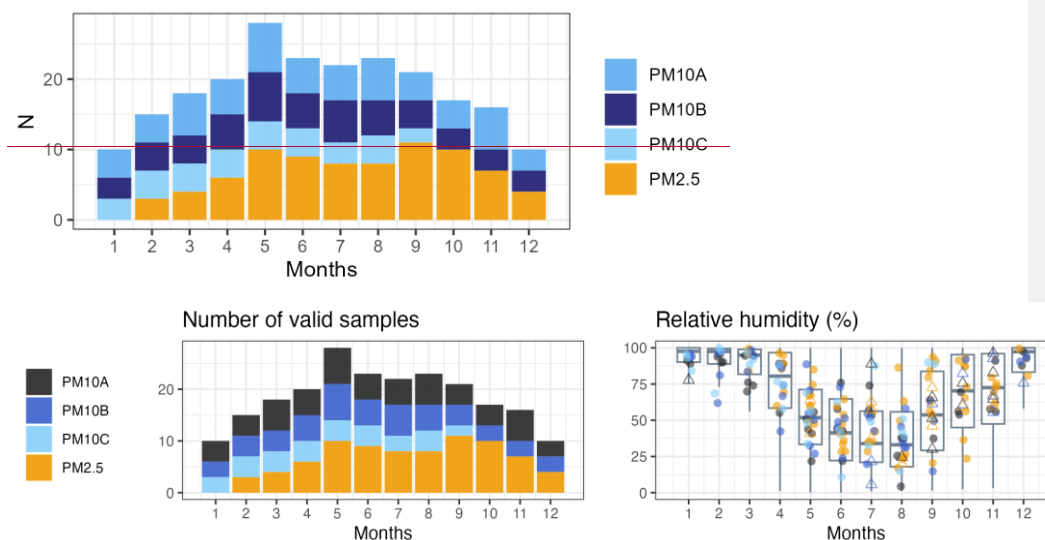
Figure 4. The number of valid samples per month used in this study. The color represents the sampling period (see Table 1 for details).

~~3.2.1~~3.3.1 Species with ~~high~~ low concentration during the ~~dry~~ wet months

The ions $MeSO_3^-$, SO_4^{2-}, NH_4^+, Na^+, Mg^{2+}, and Ca^{2+} present a seasonality opposed to the seasonality of moisture (Figure ~~S1~~34, right panel) and related to the seasonal increase of westerlies at the station (Scholz et al., 2023), having the lowest values in the wet-season (DJFM), and higher values during the dry months of the year, with an abrupt transition between November and December (Figure 4). In the wet-season, air masses arrive mostly from Amazonia (N, NE, Figure S7.), typically along with precipitation, and these species can be affected by rainout or simply not be emitted (such as mineral dust from wet soils). For the rest of the year, air resides more over the Altiplano, arriving to the station from three main directions as identified by Chauvigné et al (2019) and shown in Figure S7: east-south east (Amazonia and Chaco), northwest (Manu, Madidi, national parcs) and west (eastern Bolivia, southern Peru). The further away the air mass is coming, the lower the influence from the surface (Aliaga et al., 2021). All these species arrive together to the station due to the large-scale atmospheric circulation seasonality, but have different sources.

Sulfate and ammonia correlate well (τ =0.81), likely because of the formation of HNH_4SO_4 and $(NH_4)_2SO_4$ that can be transported over long distances. Sulfate sources were mentioned in section ~~3.2.1~~3.1. ~~A and a~~mmoni~~um~~a ~~sources are discussed in section 3.5~~ is produced by letter or wood burning in the nearby conurbation (Mardoñez et al., 2023), but it can also be produced by the decomposition of animal excreta and fertilizers in nearby rural environments. It presents a pronounced diurnal

cycle in Chacaltaya for PM_1 related to transport from below the station through the convective boundary layer (Bianchi et al., 2021). Methanesulfonate is a well-known tracer of phytoplankton emissions (Finlayson-Pitts and Pitts Jr, 1999), as biogenic dimethyl sulfide is transformed into $MeSO_3^-$ in the atmosphere. Median $MeSO_3^-$ concentrations in Chacaltaya (bulk PM_{10}: 6.03±3.40, $PM_{2.5}$ 7.45±4.41 ng m^{-3}) are twice the concentration at La Paz-El Alto. It has been shown that $MeSO_3^-$ is transported to Chacaltaya from the Pacific Ocean (at least 330 km from the station but as far as >1600 km) through the low free troposphere with a negligible contribution from Titicaca Lake (Scholz et al., 2023). Most of $MeSO_3^-$ is associated with the factor named « Westward » that represents both volcanic and marine influences that tend to arrive through the low free troposphere.

The ions Ca^{2+}, Mg^{2+}, and Na^+ seem to have both a ~~dominant~~ continental and a marine origin. ~~Non-sea-salt Ca^{2+} accounts for 97% of Ca^{2+}.~~ Median Ca^{2+}/ Mg^{2+} mass ratio is 8.8±4.1 and 10.6±4.7 for bulk PM_{10} and $PM_{2.5}$, respectively, with slightly higher values in the dry season (12.1±3.6 and 11.2±3.6), in agreement with very dry soils and strong winds typical of that time of the year. Indeed, Ca^{2+}/ Mg^{2+} mass ratio is closer to continental stations values (PM_{10}: Mt. Atlas 10.8, El Alto 10.3, $PM_{2.5}$: Arequipa 8.8, El Alto 9.5) than to sea salt (0.31 Keene, William C. et al., 1986). Non-sea-salt Ca^{2+} accounts for 97% of Ca^2, and ~~f~~For PM_{10}-B, the median soluble fraction for Ca^{2+}, Mg^{2+}, and Na^+ was 30±25%, 10±8% and 10±18%, respectively, indicating an important crustal influence. This is confirmed by the source apportionment study in which the « Soil dust and bromide » factor contains 55 % of the Ca^{2+}, 50% Mg^{2+} and 69% Na^+ (and 20% of K^+) and a marine source accounts for 31% Ca^{2+}, 43% Mg^{2+} and 24% Na^+ (« Westward» factor, which also includes 18% of K^+). ~~However,~~The a marine contribution was also hinted by the clustering of~~seems also possible especially for a fraction of~~ Mg^{2+} and Na^+~~, hinted by their clustering together~~ (Figure S1~~1~~5), and it is ~~in~~ agreement with a marine source composed by Br, Cl, I, Mg and Na affecting this site as hypothesized by Adams et al. (1977). Finally, and in agreement with our findings, SO_4^{-2}, Ca^{2+}, Mg^{2+}, and Na^+ were identified as a group of species influencing the region from the long-range (Mardoñez et al., 202~~2~~3).
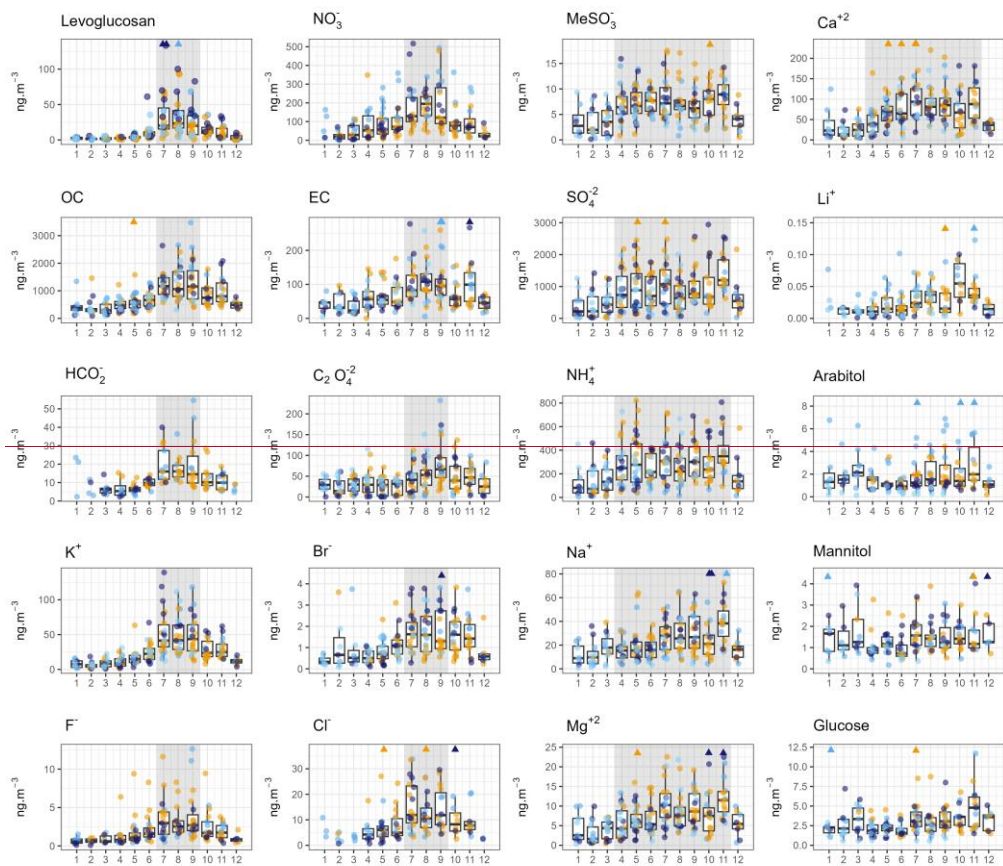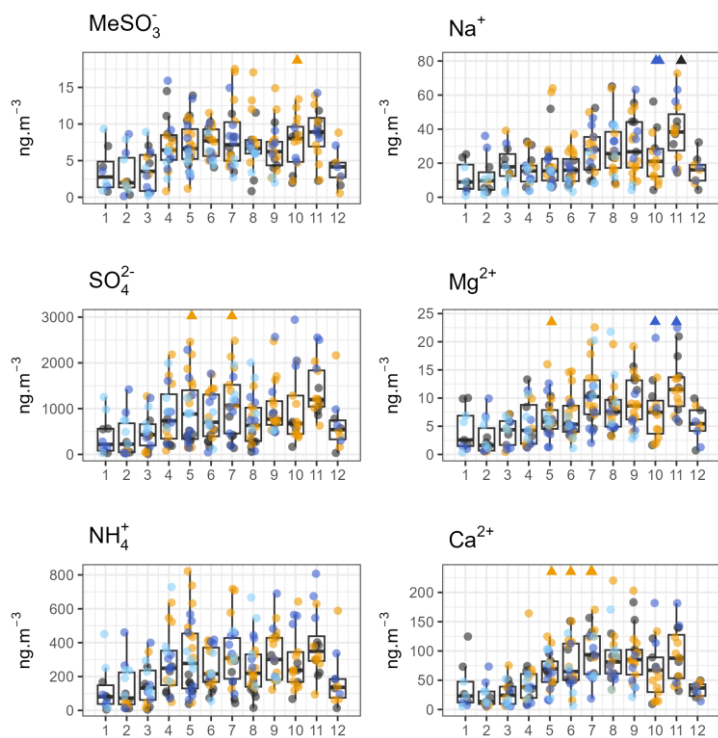
Figure 5. Monthly boxplots for Chacaltaya, all samples together (same color scale as Figure 4). F⁻, Cl⁻, formate and NO₃⁻ ~~were~~ not included for PM₁₀-C due to suspected losses. Boxplots were produced with at least five points, with top, middle and bottom lines for the 75th, median and 25th percentiles, respectively and the whiskers for the 5% and 95% confidence intervals. Extreme outliers are plotted as triangles, and their values are in the supplementary material. ~~Species are ordered according to their seasonality pattern. Shading highlights maximum input of biomass burning products in July, August and September (section 3.3.2.), and April to November (section 3.3.1). Plots with no shading are the group of species without a clear seasonal pattern (section 3.3.1)~~

~~3.2.2~~ Species with maxima concentration between Ju~~ly~~ne and ~~Sept~~November

Levoglucosan, K⁺, NO₃⁻, EC, OC, formate, oxalate, F⁻, Cl⁻, and Br⁻ constitute another group that is presented in Figure 6. They follow the same seasonality as levoglucosan[1]*, a proxy of biomass burning emissions, which shows concentrations above the annual average between June and November, with ~~notorious~~ maxima concentrations between July and September. For this group, the transport conditions are essentially the same as in the previously described group. However, the main difference is

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[1] Levoglucosan* = levoglucosan + mannosan + galactosan

540 that this group is heavily influenced by the seasonal activity of a dominant source, namely human-induced fires related to agriculture and deforestation. The regions active in terms of burning for June to November (within the range of four-day backtrajectories) are located in the Amazonian (Bolivia east of the Andes, and Brazilian states neighboring Bolivia, particularly those part of the "deforestation arc") and Gran Chaco (southern Bolivia, northern Argentina and Paraguay) basins (Carmona-Moreno et al., 2005; Giglio et al., 2013; Dutra et al., 2022; Pereira et al., 2022). Southern Peru and Altiplano grassland fires

545 have a very small influence compared to the aforementioned regions (Bradley and Millington, 2006).

Levoglucosan stereoisomer ratios can be used to assess the substrate that was burned (Marynowski & Simoneit 2022; Xu et al. 2019). For the entire dataseries, the interquartile range of the mass ratio levoglucosan/mannosan is 9.3-21.5 and mannosan/galactosan is 0.94-1.67, depicting a wide variety of sources, with grass, duff/litter and hardwood being the main burning substrates, and a few events of peat fires (Figure S114). All this includes agricultural waste burning and also probably

550 land clearing due to the hardwood fingerprint (forests being changed to pasture sites). Note however, that mannosan and galactosan are usually below the quantification limit in the wet months and therefore, ratios between December and April cannot be calculated even if levoglucosan is present. For the wet season the burning source is hypothesized to be nearby small-scale fires (such as those observed in the close urban area, Mardoñez et al., 20223).

Fluoride and bromide are not important constituents of vegetation, but plants can bio accumulate halogens in polluted

555 environments (Jayarathne et al., 2014), so for the burning season the species may release agrochemicals to the atmosphere. Indeed, F$^-$ was observed in rainwater samples affected by agrochemicals (Zunckel et al., 2003), and in high concentrations ≥100 ng m^{-3} near anthropized burning sources (Kundu et al., 2010a).

The transport mechanism of smoke to this site is complex. Burning emissions, along with other organic pollutants, are transported to the Andes (Magalhães et al., 2019; Estellano et al., 2008) through what would be the free troposphere from an

560 Amazonian point of view (1-4 km a.s.l, Andreae et al., 1988; Kundu et al., 2010b), and a regional residual layer from the Altiplano point of view (> 5 km a.s.l., Figure S12). Additionally, smoke goes upslope in the valleys (Bourgeois et al., 2015), as observed on higher influence of smoke in aerosol mass in La Paz valley (17% in mass) than at the Altiplano (13%, Mardoñez et al., 20223). Once the smoke arrives to the Altiplano, it is picked up by convection and it is transported with the PBL development to the station (along with urban pollutants, natural emissions, etc.). Hence, although the smoke primarily travels

 from east to west towards the Andes, it also reaches the mountains through a bottom-up flow originating from the western side of the Cordillera Real.
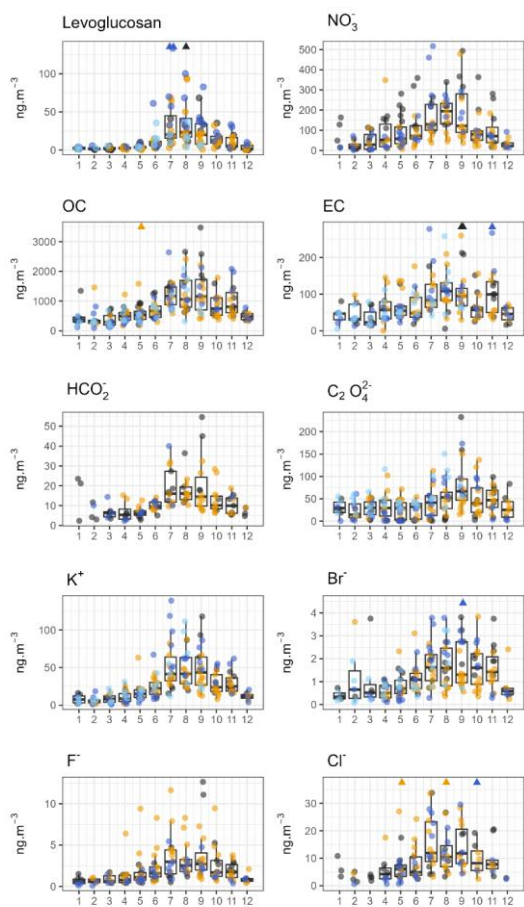
Figure 6. Same as figure 5 for species whose seasonality is marked by biomass burning

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Finally, the source apportionment study (section 3.2) is able to divide the species of this group in three factors:

- o « Biomass burning », which has a classical signature of burned vegetation containing 98% of the total levoglucosan burden, 62% of K^+, 31% of OC*, 5% of EC, and 5% of $C_2O_4^{2-}$, along with a marginal contribution of cations (3% Na^+, 5% of NH_4^+, 7% Mg^{2+} and 10% Ca^{2+})

- o « Combustion », which does follow the biomass burning seasonality (figure S8) but that seems to have a dominant urban origin. It is composed by 92% of the EC burden, 94% of $C_2O_4^{2-}$, 29% of OC*, 15 % of Br^- and 2% of levoglucosan (along with 13% SO_4^{2-}, 4% Na^+, 19% NH_4^+, 3% Ca^{2+}) . Given that EC is a typical traffic marker (Jorquera and Barraza, 2013; Mardoñez et al., 2023) and oxalate, another urban pollution marker (Kawamura and Kaplan, 1987) is clustered with it (Figure S15), we assign this factor to the nearby urban area. Nevertheless, biogenic emissions of oxalate (Kundu et al., 2010b), oxidation of different carboxylic acids (Yang et al., 2014), and in-cloud formation of $C_2O_4^{-2}$ (Zhang et al., 2017) are also probably involved in the formation of oxalate.

- o the « Soil dust and bromide » factor, which includes 85% of the Br^- burden, 37% of OC*, 20% of K^+, and cations. The assignment of K^+ to this factor seems correct as it can also have a mineral origin such as silico aluminates (clay minerals and feldspars), but it is unclear why bromide and OC* are ascribed to it.

All this contrasts with a study performed more than 40 years ago, when biomass burning contributed only marginally to the aerosol composition at Chacaltaya (Adams et al., 1977; Van Espen and Adams, 1983)

The species in this group can have other origins than solely biomass burning, as they are also observed throughout the rest of the year. Potassium seems to also have a biogenic influence. Its correlation with levoglucosan is good (τ=0.63), but lower than near the source (r^2=0.8, Schkolnik et al., 2005; r^2=0.92 at pasture site, r^2=0.64 at forest site Graham, 2002), indicating the input of other sources of K^+ between the emission location and Chacaltaya, such as silico aluminates (clay minerals and feldspars), aged marine aerosols and/or primary forest emissions (Ascomycota spore discharge Elbert et al., 2007; Webster et al., 1995), the latter in agreement with other studies (Correia et al., 2003). Fluoride and bromide are not important constituents of vegetation, but plants can bio-accumulate halogens in polluted environments (Jayarathne et al., 2014), so for the burning season the species may release agrochemicals to the atmosphere. Indeed, F^- was observed in rainwater samples affected by agrochemicals (Zunckel et al., 2003), and in high concentrations >100 ng m^{-3} near anthropized burning sources (Kundu et al., 2010a). Additionally, F^- can have a volcanic source (Aiuppa, 2009; Aiuppa et al., 2009) that is active all year round, as it was detected in 81% the samples and more frequently in the 2014-2015 time period (yellow dots in Figure 4). For Br^- a volcanic origin seems unlikely because of the very low values of HBr measured in emissions from Sabancaya volcano in 2015 (Moussallam, personnal communication). Instead, bromide seems to have a marine origin (along with Cl, I, Mg and Na; Adams et al., 1977), its concentrations in Chacaltaya (1.3±1.0 ng m^{-3}) being in the lower range of those reported in a coastal site (1 to 8 ng m^{-3} in Cape Verde, Müller et al., 2010). Chloride can also have marine, volcanic and urban origins. The Na^+/Cl^- ratio is 2.9±9.3, higher than marine ratio (0.56 Keene, 1986), but it is well established that Cl^- can be lost to gaseous phase in the presence of atmospheric acids (Laskin et al., 2012 and references therein). A hint for a volcanic origin of chloride is found in some samples with high Cl^- content coinciding with the onset of eruptive activity of Peruvian volcanoes (Table S6). The

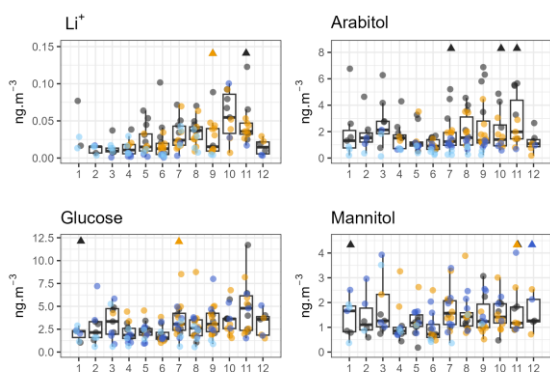
influence of an urban source (seen in Mardoñez et al., 2022 as litter burning) seems small, as Cl⁻ was <1% in PM₁ mass (Bianchi et al 2021). Nitrate has permanent urban influence as a secondary inorganic aerosol (section 3.5), long-range transport to the region (Mardoñez et al., 2022) and probably some lightning (Wang et al., 2021) in the wet season. Finally, formate (12.0 ± 7.0 ng m⁻³ for PM₂.₅, 6.0 ± 30.4 ng m⁻³ for bulk PM₁₀) and oxalate concentrations (40.3 ± 30.5; 32.4 ± 38.3 ng m⁻³) are in the lower end of those measured in continental environments (HCO_2^-: 9-239 ng m⁻³ Yu, 2000; $C_2O_4^{-2}$: 20-400 ng m⁻³ Golly et al., 2019). Oxalate seems to have an urban origin (Kawamura and Kaplan, 1987) because it clusters with EC (Figure S11). However, other processes (such as biogenic emissions Kundu et al., 2010b; Yamasoe et al., 2000; oxidation of different carboxylic acids Yang et al., 2014, in cloud formation of $C_2O_4^{-2}$ Zhang et al., 2017) are most probably involved.

3.2.33.3.2 Species with unclear individual seasonality patterns

No straight seasonal pattern can be inferred for Li⁺, arabitol, mannitol, and glucose from Figure 74. Hence, for these species, it seems that there are other drivers of their climatology, as they do not completely fit into the narrative of a clear emission source (such as the levoglucosan group) nor the circulation pattern change (MeSO₃⁻ group).

Soluble lithium contributions (0.03 ± 0.05 ng m⁻³) are barely higher than the quantification limit, and present relative maxima between September and November, probably in relation to biomass burning. Additionally, the semi-arid environment where Chacaltaya is located, along with salt flats located south (ca. 400 km) can have an influence as elemental Li at this site. It was observed that backtrajectories dominated by Amazonian airmasses (N, NNE) present markedly different concentrations of elemental Li (0.04 to 0.05 ng m⁻³) compared to the rest of the origins (0.18 to 0.38 ng m⁻³).

Glucose, mannitol, and arabitol present high variability, even during the wet season, when and they seem to have a relative maximum in March, at the end of the wet season. This is consistent with increased biogenic (such as fungal) activity is enhanced with rain, high atmospheric moisture content and warm conditions during the summer. All this suggests that the biogenic sources from the nearby Amazonian basin have a continuous influence on this site throughout the year.

These poylols have not been resolved in a single source origin (section 3.2). What we know, is that glucose tends to be transported within the planetary boundary layer to the station (Table S7) and its sources seem to be dominated by emissions below the station as fragmented vegetation and pollen. Arabitol and glucose are mostly found in the « Soil dust » factor (67% and 62%, respectively), in line with a pollen origin in the Chacaltaya region from the Altiplano grasslands within a radius of 200-300 km (Brugger et. al., 2019). They also have an influence of biomass burning (23% and 22%, respectively). Mannitol, in contrast, seems to be influenced by several sources: « biomass burning » (27%), « Soil dust » (28%) and « Westward » (38%) factors, but these results need to be confirmed with other studies.

~~S~~Average ~~s~~oluble lithium contributions (0.03±0.05 ng m^{-3}) are barely higher than the quantification limit. ~~H,~~oweve~~rand~~ ~~present relative maxima between September and November, probably in relation to biomass burning. Additionally, the semi-arid environment where Chacaltaya is located, along with salt flats located south (ca. 400 km) can have an influence as~~ elemental Li concentrations ~~at this site.~~are higher (0.18 to 0.38 ng m^{-3}) from airmasses other than ~~It was observed that backtrajectories dominated by~~ Amazonian origin airmasses (N, NNE) ~~present markedly different concentrations of elemental Li (,~~0.04 to 0.05 ng m^{-3}). ~~compared to the rest of the origins (0.18 to 0.38 ng m^{-3}).~~

~~3.3~~3.4 Special case: increased sulfate contribution after 2013

The increased concentration of SO$_4^{-2}$ in PM$_{2.5}$, PM$_{10}$-B and PM$_{10}$-C compared to PM$_{10}$-A (Table 2 ~~and Table 5~~) calls for more in-depth analysis. In Table 6, we detected that the sulfate increase in our data series was statistically significant. In fact, PM$_{2.5}$ sampling (2013-2015) coincides with the onset of degassing volcanic activity in the upwind Arequipa and Moquegua regions in 2014 (Global Volcanism Program, 2023). Volcanoes are known sources of SO$_2$, which is transformed into SO$_4^{2-}$ in the atmosphere (Eatough et al., 1994), though they can also directly emit SO$_4^{2-}$ (Allen et al., 2002).   This increase in regional volcanic activity is the main hypothesis for mass concentrations of sulfate in PM$_{2.5}$ being higher than those of PM$_{10}$ ~~(2011-2013 and 2016-2020, and Figure 2). .~~ Before the onset of volcanic degassing in the region, mean sulfate concentration in Chacaltaya was 451 ng m^{-3}, and after it started, Chacaltaya concentrations become > 900 ng m^{-3} (Table 2).   Frequent tropospheric volcanic activity has been documented in the region through ice-core analysis, though the sources were not identified at the time (de Angelis et al., 2003). Recently one source has been identified as the Sabancaya volcano, with sulfate being dominantly from volcanic origin in PM$_1$ when the station is under westerly air influence (Aliaga et al., 2021). However,

Ubinas ~~volcano~~ has also been in an active phase since 2006 (Moussallam et al., 2017 and references therein). Both volcanoes are located upwind of Chacaltaya, and therefore their emissions can arrive together when transport conditions are favorable (section 3.3.~~1~~). Indeed, F^- a typical volcanic marker (Aiuppa et al., 2009, de Angelis et al., 2003) was detected in 81% the samples and more frequently (94%) and with higher concentrations in the early eruptive period (2014-2015, yellow dots in Figure 4). Moreover, ~~A~~a hint for a volcanic origin of chloride is found in some samples with high Cl^- content coinciding with the onset of eruptive activity of Peruvian volcanoes (Table S~~6~~2). For Br^-, a volcanic origin seems unlikely because of the very low values of HBr measured in emissions from Sabancaya volcano in 2015 (Moussallam, personnal communication)

Table 6~~5~~. Results of the two-sided Mann-Kendall test merging all sampling periods. Values statistically significant are in *italic*

Species	Probable sources	p value
SO_4^{2-}	Dominated by volcanism	*<0.05*
NH_4^+	Emissions close to the ground neutralizing most sulfate	*<0.05*
$MeSO_3^-$ (control)	Phytoplankton emissions transformed in the atmosphere	0.09
EC (control)	Urban + biomass burning	0.13

To assess the influence of Peruvian volcanism in the sulfate burden at the station, we group up all samples that have a west (W) or northwest (NW) origin based on ERA-5 backtrajectories and compare them with SO_2 emissions for both Sabancaya (400 km away from Chacaltaya) and Ubinas (300 km), which are available on an annual basis (Carn et al., 2017; Fioletov et al., 2023). Chacaltaya SO_4^{2-} data from filter sampling were added up, using years with at least nine months of data, to obtain the annual accumulated value and also the annual mean. The results are presented in Figure 6~~8~~.

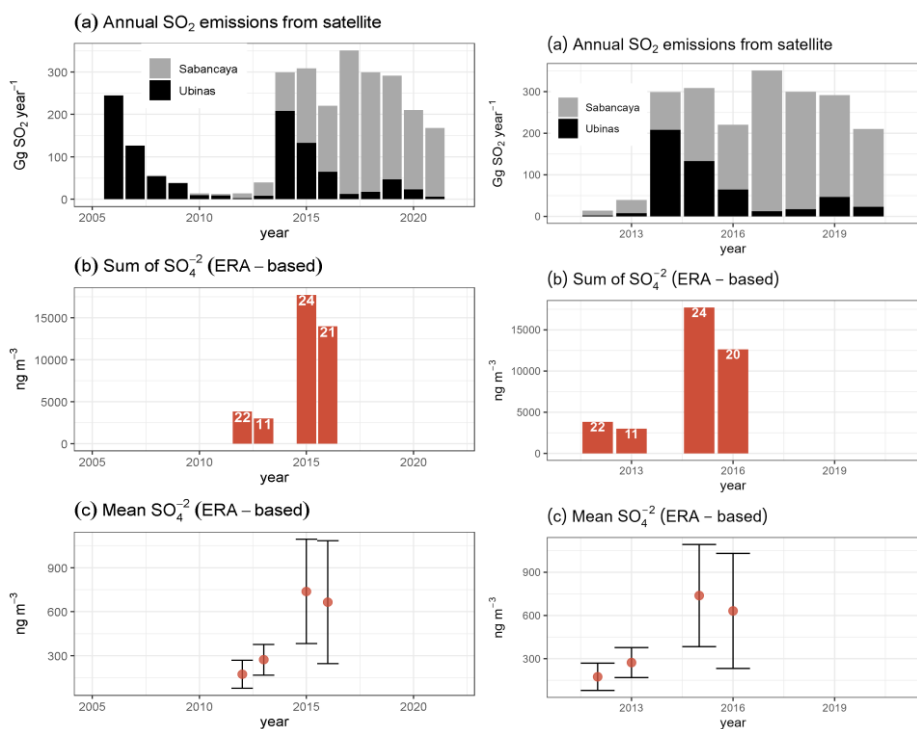



Figure 86. Study case for volcanic transport. Only years with at least 9 months of filter data were used. (a) Annual SO$_2$ emissions for Sabancaya (grey) and Ubinas (black) from the global catalog of SO$_2$ emissions (Fioletov et al., 2023) (b) Accumulated SO$_4^{-2}$ measured in the filters taken under W and/or NW influence grouped per year based on ERA-5 backtrajectories. The number of samples used is in white letters inside the bars (c) Mean concentration and standard deviation for the selected samples.

As observed from satellite detection, (Figure 6a) the aforementioned volcanoes were in an active degassing phase since 2014 and the total sulfate detected at the station (Figure 6bsum of sulfate) is in agreement with the sharp increase in SO$_2$ emissions. Even the mean sulfate concentration per sample (Figure 6c) is significantly higher after 2014. Note that 2012-2013 are statistically different from 2015-2016. As a control case, MeSO$_3^-$ transport was also calculated (Figure S106), indicating a relatively constant marine source with little circulation changes over the studied period. Moreover, as pointed out by Olson et. al. (2021), Sabancaya emissions do not seem to subside and influence nearby locations below the vent (volcanism contributes only to 9% of the measured sulfate in the city of Arequipa), which seems to be the case too at La Paz and El Alto, where the long-range secondary sulfate contributes only to 8% of the aerosol mass (Mardoñez et al., 20223). Therefore, we hypothesize that volcanic emissions are readily transported aloft, directly influencing high-altitude sites downwind such as Chacaltaya, as

Con formato: Resaltar

detected by the « Westward » factor of the source apportionment study. . In consequence, the statistically significant increase in SO_4^{-2} of our samples from 2014 onwards seems to be mostly related to an intensified degassing process of Peruvian volcanoes leading to a regional increase in H_2SO_4.

3.5 Short-term study: Mass and mass closure

Most of the samples were not weighted, but a subset of them does have information on aerosol mass for PM_{10}. This is presented on Table 7. PM_{10}. mass ranges from 2.4 to 22.6 µg m^{-3} (at ambient conditions: 1.1-12.0 µg m^{-3}). Even though this dataset is limited in temporal extent, it is consistent with measurements made on mountain sites, like Pûy de Dôme in France (5.6±4.6 µg m^{-3}, Bourcier et. al., 2012), Mt. Atlas in Morocco (11.8-14.5 µg m^{-3}, Deabji et al., 2021), Mt. Everest in Nepal (10 µg m^{-3}, Decesari et al., 2010); Montsec in Spain (2.9-20.6 µg m^{-3}; Ripoll et al., 2015), and Izaña at the Canary Islands (10.9-50.5 µg m^{-3}; García et al., 2017a, b). The highest measured mass coincides with a dry month and the start of the eruptions of Sabancaya volcano in November 2016 (Moussallam et al., 2017).

For mass closure estimation, organic matter (OM) was calculated based on OC concentrations. As source contributions vary with the seasons, it is not possible to assign a single conversion factor between OC and OM. Therefore, it was estimated for two cases: a minimum value using a factor of 1.8 as for other mountain sites and a maximum value using a factor of 2.6 as for aged aerosol (Cozic et al., 2008; Chow et al., 2015 and references therein), so organic contributions were estimated to range from 7 to 34% for the available series.

The contribution of mineral dust is very important, especially for the dry season, accounting for 33-56% of PM_{10}. This fraction is higher than in La Paz – El Alto, where mineral dust contributes to 20-35% of the mass (Mardoñez et al., 2023). Secondary inorganic aerosol (SIA= $NH_4^+ + NO_3^- + SO_4^{-2}$) ranged from 15 to 26%, with all sulfur found in soluble form. The unaccounted fraction (ND) is related to heteroatoms and water content, and it usually ranges from 20 to 40% (Tsyro, 2005; Hueglin et al., 2005). For our case, the non-determined fraction ranged from 2 to 35%, being lower particularly in the wet season. This may be due to wash out of hygroscopic species and maybe also to less heteroatoms present in the organic fraction, though this is still under study.

Table 7. Chacaltaya STP concentrations of PM_{10} total mass, mineral matter (MM), secondary inorganic aerosol (SIA), elemental carbon (EC), the sum of trace and rare elements (TE), organic matter minimum and maximum estimations, and the fraction of non-determined (ND) aerosol, its range defined by the OM variation. No ion data for B49 and B50. For ambient conditions, divide concentrations by 1.88

Sample	Start and end date	PM_{10} µg m^{-3}	MM µg m^{-3}	SIA µg m^{-3}	EC µg m^{-3}	TE µg m^{-3}	OM µg m^{-3}	ND %	Measured PM_{10}/Σions
B42	04/11 – 11/11/2016	22.58	7.43	3.41	0.16	0.12	3.56-5.14	35-28%	5.7
B44	30/12/2016 – 06/01/2017	2.78	0.98	0.42	0.04	0.02	0.66-0.96	24-13%	6.3
B45	03/02 – 10/02/2017	8.04	3.60	1.98	0.08	0.05	1.48-2.13	11-2%	3.7
B46	03/03 – 10/03/2017	2.44	1.02	0.63	0.02	0.02	0.41-0.59	14-7%	3.8
B48	12/05 – 19/05/2017	15.12	8.41	2.29	0.06	0.11	1.09-1.57	21-18%	6.1
B49	23/06 – 30/06/2017	12.44	6.97	-	-	0.09	-	-	-
B50	04/08 – 11/08/2017	21.87	10.34	-	-	0.14	-	-	-

3.1 Species transported under maximum/minimum influence of the convective planetary boundary layer to the station

A subset of PM$_{2.5}$ samples was studied with two objectives: first, to identify if there are differences between daytime and nighttime concentrations of the measured species at Chacaltaya, and second, to identify if the species are transported from nearby locations (or from long distances), all this in relation to the influence of the convective planetary boundary layer at the station. These 20 samples span from November 2013 to December 2014 (gap from January to March 2014), and they were obtained under maximum and minimum influence of the convective planetary boundary layer at the station. Samples obtained under maximum PBL influence (*maxPBL*) correspond to 17 hours continuously sampled (09:00-02:00 BOT) than include the diurnal development of the convective boundary layer and a nocturnal stable boundary layer that may be capped by a residual layer (Collaud Coen et. al., 2018). Samples obtained under minimum PBL influence (*minPBL*) correspond to seven consecutive hours that include nighttime and early morning, before the arrival of the convective boundary layer to Chacaltaya (02:00-09:00 BOT). This is a period when there can be an influence of a reminiscent residual layer but it also corresponds to the time when we expect to capture more low-free-troposphere events.

Concentration and variability of concentration (represented by σ) for all species is higher during *maxPBL* than during *minPBL* influence (Table 6). However, only for EC, NH$_4^+$, NO$_2^-$ and glucose the significance level (α) is <10%. In practical terms, most of the species present statistically similar concentrations for day and nighttime sampling, and this is the justification to have pooled all types of samples (Table 2) in the previous sections of this work.

Nevertheless, the different significance levels reported (Table 6) present a structure that can provide hints for short- or long-range transport. With a significance level <10%, it is clear that for EC, NH$_4^+$, NO$_2^-$ and glucose transport under *maxPBL* influence (mostly daytime and residual layer) dominates over the transport under *minPBL* influence (nighttime and early morning). Therefore, this points to dominant sources nearby, in line with previous findings about the short-range influence of urban pollution at the station (Wiedensohler et al., 2018; Bianchi et al., 2021). EC and NO$_3^-$ are typical traffic tracers that have a marked diurnal cycle (Jorquera and Barraza, 2013; Bianchi et al., 2021; Mardoñez et al., 2022); and NH$_4^+$ and EC are produced by litter or wood burning in the La Paz – El Alto urban area (Mardoñez et al., 2022). Ammonium can also be produced by the decomposition of human and animal excreta, synthetic fertilizers, and biomass burning (Trebs et al., 2004; Nowak et al., 2012; Behera et al., 2013) in nearby urban and sub-urban environments. Assigning a source below Chacaltaya for these species agrees with PM$_1$ data obtained during an intensive campaign (Bianchi et al., 2021) where NH$_4^+$ and NO$_2^-$, showed a diurnal cycle in Chacaltaya related to transport through the convective boundary layer. Finally, glucose is known to present a marked daily cycle (Claeys et al., 2004; Wang et al., 2008) and its sources, as previously discussed, seem to be dominated by emissions below the station (Altiplano, valleys) as fragmented vegetation and pollen from a radius of 200-300 km according to Brugger et. al. (2019).

For the rest of the species, we speculate that even if the defined significance level of 10% is not reached, we can infer an increased influence of long-range transport under *minPBL* conditions based on the varying degree of significance levels. A subgroup of species, namely SO_4^{2-}, OC, F^-, Cl^-, Br^-, $C_2O_4^{-2}$, K^+, Ca^{+2} and mannitol, present a significance level between 14 and 35%. This may indicate that even if they tend to be transported under *maxPBL* (hence, with sources near the station), they may not have very pronounced diurnal cycle and/or they may also be influenced by long-range transport. The complex transport mechanism described in section 3.3.2 may explain this. Finally, for Li^+, Na^+, $MeSO_2^-$, arabitol, Mg^{+2} and levoglucosan, there is no significance level reached to find a difference between *maxPBL* and *minPBL*, their concentrations being statistically similar. This similarity points to a preferential long-range transport for those species that overwhelms local emissions. This is interesting because even if the Chacaltaya observatory is under stable atmospheric conditions between 02:00 and 09:00 BOT, low free tropospheric intrusions are difficult to observe with high-volume sampling because they are not long enough (Scholz et. al 2023 reported free tropospheric episodes lasting less than 8 hours) to leave a marked fingerprint in our dataset. In this regard, high frequency (on-line) measurements of the aerosol chemical composition at the station prove their value as complementary to the long-term observations (Bianchi et al., 2021; Scholz et al., 2023; Zha et al., 2023).

Table 6. Chemical composition for PM$_{2.5}$ samples obtained during maximum (Mixing/Boundary Layer + Residual Layer) and minimum (Residual Layer + Low Free Troposphere) influence of the atmospheric boundary layer at the station Mean ($\bar{x}$), median ($\tilde{x}$), standard deviation (σ) and number of samples above quantification limit (N) are presented. Levoglucosan * includes its stereoisomers. Two-tailed Wilcoxon Rank sum test results as α (significance level in %).

Ambient concentrations ng m^{-3}	Maximum influence ABL (ML+RL) 0900 to 0200 of next day				Minimum influence ABL (RL+LFT) 0200 to 0900				$\dfrac{\sigma_{maxPBL}}{\sigma_{minPBL}}$	$\dfrac{\tilde{x}_{maxPBL}}{\tilde{x}_{minPBL}}$	Significance level α (%)
	$\bar{x}$	$\tilde{x}$	σ	N	$\bar{x}$	$\tilde{x}$	σ	N			
NH_4^+	215	185	(122)	8	120	122	(49.7)	12	2.5	1.5	1.5
NO_3^-	61.5	62.0	(28.4)	8	32.8	35.4	(14.0)	12	2.0	1.8	2.3
Glucose	1.78	1.36	(0.94)	7	1.12	1.03	(0.41)	11	2.3	1.3	5.6
EC	42.6	39.0	(24.3)	8	23.0	22.4	(4.68)	11	5.2	1.7	7.5
SO_4^{-2}	824	655	(615)	8	520	490	(262)	12	2.3	1.3	14
OC	549	569	(277)	8	357	313	(95.5)	11	2.9	1.8	16
Mannitol	0.84	0.72	(0.46)	7	0.55	0.59	(0.14)	11	3.2	1.2	18
Br^-	1.12	1.24	(0.57)	7	0.82	0.78	(0.28)	10	2.0	1.6	23
F^-	1.86	1.86	(1.55)	8	0.97	0.71	(0.54)	11	2.8	2.6	24
K^+	17.9	19.4	(10.2)	7	12.0	10.1	(4.61)	11	2.2	1.9	29
Cl^-	8.10	8.36	(5.05)	6	4.84	3.51	(2.46)	7	2.1	2.4	30
$C_2O_4^{-2}$	21.1	20.0	(12.4)	7	15.1	13.5	(9.77)	10	1.3	1.5	32

~~Ca+2~~	~~77.0~~	~~55.0~~	~~(76.3)~~	~~8~~	~~52.6~~	~~42.5~~	~~(51.4)~~	~~12~~	~~1.5~~ ~~1.3~~	~~34~~
~~Levoglucosan *~~	~~6.79~~	~~4.37~~	~~(6.51)~~	~~8~~	~~4.1~~	~~3.81~~	~~(2.73)~~	~~12~~	~~2.4~~ ~~1.1~~	~~47~~
~~Mg+2~~	~~6.31~~	~~4.67~~	~~(4.46)~~	~~7~~	~~4.74~~	~~3.96~~	~~(2.92)~~	~~11~~	~~1.5~~ ~~1.2~~	~~48~~
~~Arabitol~~	~~0.92~~	~~0.81~~	~~(0.61)~~	~~8~~	~~0.73~~	~~0.78~~	~~(0.22)~~	~~11~~	~~2.8~~ ~~1.0~~	~~60~~
~~Li+~~	~~0.02~~	~~0.01~~	~~(0.02)~~	~~7~~	~~0.01~~	~~0.01~~	~~(0.01)~~	~~10~~	~~1.8~~ ~~1.1~~	~~-~~
~~Na+~~	~~13.1~~	~~10.1~~	~~(10.3)~~	~~8~~	~~13.4~~	~~12.4~~	~~(8.16)~~	~~12~~	~~1.3~~ ~~0.8~~	~~-~~
~~MeSO3-~~	~~4.65~~	~~3.30~~	~~(4.45)~~	~~8~~	~~3.64~~	~~3.27~~	~~(1.87)~~	~~12~~	~~2.4~~ ~~1.0~~	~~-~~

4 Summary and conclusions

In this study, we present a unique long-term record of the chemical composition of aerosol sampled at the Chacaltaya station, the highest in the GAW network. The information is valuable in a region otherwise poorly characterized, documenting the variability of an essential climate variable in the tropical Andes.

Concentration levels of PM_{10} range from 2.4 to 22.6 µg m^{-3} STP confirming that the site is regularly influenced by nearby sources such as rural emissions and urban pollution, and that the air sampled at 5380 m a.s.l. is not purely free-tropospheric. The station is representative of the regional background in a radius of 200-1600 km, with the distance from the site depending on the transport conditions. Loss of coarse particles along the way seems important.

The seasonality of several species has been described for the first time in the region, showing lowest concentrations for most species during the wet months (December to March) and maximum concentrations during the dry months (April to November). This is due to the marked seasonality of both the transport conditions and intensity of source emissions.

Between Ju~~ly~~ne and ~~Nov~~Sept~~ember~~ (though ~~extending~~ with absolute maxima from Ju~~ne~~ly to ~~Nov~~Sept~~ember~~), the high concentrations of an important number of species (EC, OC, K^+, Br^-, F^-, Cl^-, NO_3^-, formate, oxalate and levoglucosan) are related to agricultural practices, which include biomass burning. Biomass burning practices clearly influence regional aerosol composition, contrary to what was found at this site four decades ago, when deforestation (and subsequent land use change) was just beginning in Amazonia and therefore the Andean aerosol was only marginally influenced by biomass burning emissions.

This study also reports key organic compounds emitted by direct biogenic emissions. The sugar alcohols arabitol and mannitol are not strongly correlated, which marks a different behavior compared to other documented sites. Other biogenic sources (K^+) are also detected during the wet season, but additional studies are needed to fully understand the behavior of primary biogenic aerosols in the Amazonian and Andean regions. All this gains relevance in a period when the deforestation advances rapidly in the region, and therefore documentation on its effects on the aerosol chemical composition is needed.

The cities of La Paz and El Alto ~~and the surrounding activities over the Altiplano~~ clearly affect the aerosol chemical composition with EC, NO_3^- and ~~probably~~ oxalate as traffic indicators, and 29% of the total OC* burden. The surrounding

activities over the Altiplano include; NH_4^+ from both urban and agricultural activities and litter burning; and glucose likely related to vascular vegetation debris (grasslands, agriculture). Additionally, insoluble mineral matter represents an important fraction (33-56%) of the aerosol, originating from dry soils. All these are transported from below the station along with the development of the convective planetary boundary layer and are likely to have an impact at a wide scale high-altitude in the region.

The OC/EC ratio encompasses a range is similar to rural and remote background sites, and does not have a marked seasonality, likely due to the permanent dominant influence of long-range transport (accounting for 71% of OC*), and the constant aging processes that take place in thisat high-altitude in the tropical altitude region all year round in spite of the change in circulation patterns and source activity.

Sustained volcanic degassing from Sabancaya and Ubinas is hypothesized to influence the regional background of sulfate especially at high altitude, as emissions are directly vented out above 5000 masl, where conditions for long-range transport are met. Interestingly, as active volcanoes lie on the path between the Pacific Ocean and Chacaltaya, their emissions arrive along with aged marine air masses. The recent unveiling of those volcanic sources can help reinterpret paleorecords, in the light of the current knowledge of transport conditions to the tropical Andes. These measurements constitute one of the first long-term observations of aerosol chemical composition at a high-altitude site in the tropical Southern Hemisphere. The high altitude poses numerous challenges when it comes to maintain sample collection and analysis. However, these efforts have yielded valuable insights into this specific region, allowing us to effectively track and comprehend the natural and anthropogenic influences at play.

Contributions

IM, FV, LT performed the fieldwork. FV generated the back-trajectory data and LT, MAK, DA contributed to their treatment. AA made possible the mass and elemental measurements; JLJ supervised the chemical analyses and provided most of the funding for doing them. IM, RK, GU, AA and PL conceptualized the manuscript. IM curated and analyzed the data, and prepared the manuscript with contribution from all co-authors.

Open access data

Data are available through the WMO/GAW WDCA monitoring database (EBAS) currently hosted at the Norwegian Institute for Air Research (NILU) at https://ebas.nilu.no/

Competing interests

R. Krejcji is editor in ACP

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