Impact of Biomass Burning on Air Quality in Temuco City, Chile

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ABSTRACT

Residential wood burning emits a complex mixture of particulate and gaseous compounds. In this article we show an in-depth chemical characterization of particulate matter evidencing the impact of biomass burning on the urban air quality in Greater Temuco, the capital city of the Araucanía Region, Chile. The measurements were carried out at two sites, Las Encinas and Padre Las Casas, in spring and winter. Extremely high fine particulate matter (PM_{2.5}) concentrations (up to 700 $\mu\text{g m}^{-3}$) were frequently observed at both stations in the wintertime, while in spring, PM_{2.5} concentrations were significantly lower (campaign-average 6.4 and 8.6 $\mu\text{g m}^{-3}$ in Las Encinas and Padre Las Casas, respectively). Chemical composition of submicron PM was dominated by organics (average 87%) followed by inorganic ions (10–30%) and a minor contribution of black carbon (< 5%). In the wintertime, atmospheric levels of biomass burning tracers, such as levoglucosan, potassium and chloride, were elevated and their diurnal profiles showed a significant concentration increase in the evening. Diurnal profiles combined with the in-depth chemical analysis clearly indicated that in the wintertime local biomass burning was the main source of air pollutants in the region. Furthermore, in winter, most of the high concentration events correlated with the periods with high surface pressure, low temperature and low wind speed. These events matched with higher temperatures at high altitude than at the surface characterizing the typical profile of a vertical inversion that prevents the dilution of air pollutants.

Keywords: Particulate matter, Residential biomass burning, Chemical composition, Elemental composition

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1 INTRODUCTION

Air pollutants have serious impact on air quality, human health, and climate (Jorquera *et al.*, 2018). Due to strict emission limits set to vehicles and industry, biomass combustion for domestic heating and cooking is nowadays often the biggest source of particulate emissions in the residential areas (e.g., Chen *et al.*, 2017; Helin *et al.*, 2018). Biomass combustion emits a complex mixture of particulate and gaseous pollutants to the atmosphere that are further oxidated and processed in the atmosphere forming secondary aerosol (Sumlin *et al.*, 2017, Kortelainen *et al.*, 2018, Fang *et al.*, 2021). The magnitude and composition of biomass combustion emissions depends strongly on the type of biomass, burning conditions as well as the burning device (Chen *et al.*, 2017, Kortelainen *et al.*, 2018). Besides residential burning, biomass combustion emissions can also be caused by other sources such as forest fires and prescribed burning. The frequency and severity of forest

fires have increased in many areas in the last decades with some fires located at the interface of wildland and urban areas directly affecting the inhabitants living in the cities (Burling *et al.*, 2011; Lindenmayer and Taylor, 2020). In some countries, the intentional agricultural burning is also widely carried out (Holder *et al.*, 2017), and the smokes from the fires often drift to the densely populated urban areas causing health and environmental issues (Mehmood *et al.*, 2018, 2020).

Biomass burning causes a serious pollution problem in southern Chile. Around 2 million people, who live in the area, are exposed annually to ambient fine particulate matter (PM_{2.5}) concentrations greater than 30 µg m⁻³ that significantly exceeds Chile's primary annual PM_{2.5} standard limit of 20 µg m⁻³ (Jorquera *et al.*, 2018). In the last decade, the ambient PM concentrations have been increasing, and the studies based on the PM chemical analyses have shown that the combustion of wood in household stoves is the main source of ambient air pollution in southern Chile (Cereceda-Balic *et al.*, 2012; Díaz-Robles *et al.*, 2014; Jorquera *et al.*, 2018). As the adverse health effects of PM have been well documented (e.g., Lelieveld *et al.*, 2015), the PM exposure is recognized as a major contributor to health impairment in the southern region of Chile (Díaz-Robles *et al.*, 2015, 2014; Sanhueza *et al.*, 2009; Schueftan and González, 2015).

The aim of this article is to show a detailed analysis of the chemical composition of PM in an urban area where residential wood combustion is widely used. By carrying out two sampling campaigns in winter and springtime, we show that in wintertime wood combustion is the main contributor to PM in the area and a major source of air pollution. State-of-the art instrumentation, in-depth real time PM characterization and meteorological endpoints were used to characterize the main chemical fractions, including organic matter, inorganic ions as well as elements, in PM_{2.5}.

2 EXPERIMENTAL

2.1 Sampling Site and Measurement Campaign

The measurement campaigns were conducted at two sites, Las Encinas (LE; 38°44'55.38"S, 72°37'14.54"W) and Padre Las Casas (PLC; 38°45'53.03"S, 72°35'55.65"W), that were both located in Greater Temuco, Chile. The Las Encinas site was located inside a sports campus representing urban background concentrations that was not exposed to the direct emission sources in the area. The Padre Las Casas site was located in an urban area close to a residential zone being directly impacted by domestic biomass combustion emissions. The locations of the LE and PLC stations are shown in Fig. 1. Measurements were conducted during two seasons. Winter campaign was conducted from 4 to 24 July, 2019 (20 days) and 24 July to 7 August, 2019 (13 days) at the LE and the PLC sites, respectively (austral winter). Spring campaign measurements were conducted from 19 November to 10 December, 2019 (22 days) and 11 to 24 December, 2019 (12 days) at the LE and the PLC sites, respectively (austral spring).

Cities of Temuco and Padre Las Casas have been declared as saturated zones for PM_{2.5} by the Chilean environmental authorities (MMA, 2015), and together they form a portion of a conurbation area called Greater Temuco having 358 541 inhabitants. In Temuco, services, tourisms, and agriculture are the main economic activities. Temuco has been ranked among the top five cities in Chile with severe air pollution problem (Díaz-Robles *et al.*, 2014). According to the environmental public agency, 94% and 82% of PM_{2.5} and PM₁₀ emissions, respectively, come from the residential wood combustion employed for cooking and heating (MMA, 2015).

2.2 Meteorology

Greater Temuco area is characterized by temperate rainy climate with the Mediterranean influence. The annual average temperature is approximately 12°C and rainfall close to 1000 mm per year. Fig. 2 shows the monthly variation for temperature, relative humidity, and rainfall in 2019 at the Manquehue Station (38°46'4.01"S, 72°37'54.98"W), Temuco. The lowest temperatures occur from July to September together with the relative humidity above 80% (winter season) while from October to December temperatures are above 10°C and the humidity below 80% representing the spring and summer season. During winter, successive frontal disturbances generate a large part of the rainfall registered in this zone. In the spring and summer months, the rainfall is significantly lower, approximately 10 mm per month. In 2019, when the measurements were conducted, the total precipitation was 780 mm and the highest precipitations occurred

between May and July with the total rainfall over 500 mm. Between October and December the rainfall reached almost 80 mm.

Fig. 1. Official Air Quality Network of Greater Temuco area. The locations of the air quality monitoring and meteorological sites are shown by the red dots (map extracted from Open Street Map service). Measurements presented in this article were conducted at the Las Encinas and Padre Las Casas stations.

Fig. 2. Monthly average temperature and relative humidity (a), and rainfall (b) at the Manquehue station in Temuco in 2019. Data was extracted from the Dirección Meteorológica de Chile database that belongs to Chile's Meteorological Directorate (Servicios Climáticos; meteochile.gob.cl).

2.3 On-line Instrumentation

An Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc., US) was used to measure the main non-refractory chemical species (organics, sulphate, nitrate, ammonium, chloride) of submicron PM. The ACSM is a compact aerosol mass spectrometer with a quadrupole detector described in detail by (Ng *et al.*, 2011b). Shortly, a critical orifice and aerodynamic lens are used to guide the particle flow into the instrument and focus particles into a narrow beam. Due to the restrictions of the aerodynamic lens, the size-range of the particles transmitted to the ACSM is limited to submicron particles (100% transmission approximately from 75 nm to 650 nm). After the lens system, the particles are led to the vacuum chambers that are differentially pumped by three turbo pumps. The particles are vaporized with a tungsten oven (600°C) and ionized (70 eV) prior to leading them to the residual type of quadrupole mass analyzer. Time resolution of the measurements was 30 minutes with a default collection efficiency of 0.5 applied (Ng *et al.*, 2011b).

A SIMCA (Gramsch *et al.*, 2000) was used to determinate black carbon (BC) concentrations. The SIMCA (a Spanish name for the Absorption Coefficient Measurement System) was manufactured by Santiago University, and its operation is based on the variation of the integrating plate method (Horvath, 1997) to measure the absorption coefficient of light in the air (Gramsch *et al.*, 2014b). The SIMCA contains a filter, two light-emitting diodes (LEDs), two photodetectors, an electronic amplifier, and a computer. The sample is pumped for 1 min through a 25-mm-diameter Nuclepore filter that collects particles in the air, and the intensity of light passing through the filter is measured. The filter is exchanged by a new one once the light intensity of the sampled filter decreases to a value below 30% of the initial intensity (clean original filter) in order to avoid an excessive accumulation of light absorbing particles. A second detector, placed on the side of the filter, is utilized to correct for the changes in the lamp intensity or gain in the amplifier due to the temperature changes. The performance of the SIMCA has been validated in several previous studies (Gramsch *et al.*, 2004, 2013, 2014b, 2016; Langner *et al.*, 2020; Tagle *et al.*, 2018).

PM_{2.5}, NO_x concentration and meteorological parameters were obtained from the official monitoring records (Padre Las Casas and Las Encinas stations). The hourly PM_{2.5} data were collected by a BAM-1020 Continuous Particulate Monitor, NO_x data was recorded by a Thermo Monitor 42i and the meteorological data, including temperature, relative humidity, and wind speed, was recorded by LSI LASTEM (DMA765; Environmental Monitoring Solutions - LSI Lastem Soluzioni per il monitoraggio ambientale, lsi-lastem.com) instrumentations.

2.4 Off-line Sampling and Analysis

PM_{2.5} and PM₁₀ samples were collected at the Las Encinas and Padre Las Casas sites during winter and spring campaigns. The 24-hour PM_{2.5} and PM₁₀ samples were collected to 47 mm Polytetrafluoroethylene (PTFE) filters using two Harvard impactors (Marple and Willeke, 1976). The flow rate was 16.7 L min⁻¹. The filter samples were weighed before and after the collections by using a Mettler UMT2 balance in a facility with a stable temperature (20–22°C) and relative humidity (45–55%). After the gravimetric analysis, the elemental composition was first analyzed by the energy dispersive x-ray fluorescence (XRF) analyzer, and then, the filters were split into two pieces for the subsequent ion and monosaccharide anhydride (MA) analysis.

A Panalytical Epsilon 5 XRF analyzer (Netherlands) was used for the elemental analysis of all PM₁₀ and PM_{2.5} filter samples. The analyzed elements included Al, Ba, Br, Ca, Ce, Cl, Cr, Cs, Cu, Eu, Fe, K, La, Mg, Na, P, Pb, S, Sc, Sm, Si, Tb, Ti, W and Zn. The emissions of x-ray photons from the sample are integrated over time and they yield quantitative measurements of elements ranging from sodium (Na) through lead (Pb). A spectrum of X-ray counts versus photon energy is acquired during the analysis with individual peak energies corresponding to the elements and peak areas corresponding to the elemental concentrations. A sample spectrum consists of characteristic peaks superimposed on a background caused by the scatter of x-rays from the tube into the detector. The advantages of the XRF analysis include high sensitivity for several elements, the ability to analyze small quantities of sample, and the non-destructive nature of the analysis. Regarding the elemental composition of PM_{2.5}, all the samples whose concentration value was less than or equal to their uncertainty were discarded. Only those elements that met at least 75% completeness were considered valid according to the methodology described by Kavouras *et al.* (2001).

For the ion analysis, the PM_{2.5} filter samples were extracted with 10 mL of deionized water (Milli-Q, Millipore Gradient A10) by shaking the filters for 15 minutes. Two ICS-2000 ion chromatographs (IC, Dionex, Sunnyvale, USA) were used to measure anions (Cl⁻, NO₃⁻, SO₄²⁻, oxalate) and cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺). The IC-2000 systems had 4 mm AG11/CG12A guard columns, 4 mm AS11/CS12A analytical columns, 500 µL loops, 4 mm AERS/CERS 500 suppressors and KOH and MSA eluent for the anions and cations, respectively. The uncertainty of the IC analysis of the filters was calculated based on the test samples and it was in the order of 10–15% for all the analyzed ions.

Monosaccharide anhydrides (i.e., levoglucosan, galactosan and mannosan) are water-soluble compounds that are commonly used as tracers for biomass burning since they are formed in the thermal breakdown of cellulose (Saarnio *et al.*, 2012). High-performance anion-exchange chromatography-mass spectrometry (HPAEC-MS) method was used for the determination of levoglucosan, mannosan, and galactosan concentrations from the PM_{2.5} filter samples. The analytical method was similar as described in Saarnio *et al.* (2010) except that the internal standard was methyl-β-D-arabinopyranoside. MA's were extracted from the filter using 10 mL of deionized water (with internal standard 100 ng mL⁻¹) by 15 min rotation. The HPAEC-MS system had 2 mm CarboPac™ PA10 guard and analytical columns (Dionex), KOH as an eluent, a 50 µL loop and a 2 mm AERS Ultra II suppressor. Ionization technique was electron ionization and MS was equipped with a quadrupole mass analyzer. HPAEC-MS method uses m/z 161 for MA determination.

2.5 Cluster Analysis and Heatmap

Cluster Analysis (Gramsch *et al.*, 2006) can be used as an exploratory statistical technique that seeks to reveal natural groupings in a data set. In this article, the purpose of applying cluster analysis is the segmentation of pollutant variables to a certain source, especially to identify the pollutants originating from biomass burning. It is a non-supervised technique used to identify relatively homogenous groups called clusters. The cluster must show a high degree of internal homogeneity (within the conglomerate) and a high degree of external heterogeneity (between clusters). The concept of similarity is fundamental to the analysis of conglomerates. A measure of similarity is a measure of correspondence or resemblance between objects to be grouped. Similarity can be measured in several ways, but there are three methods that are used in cluster analysis: correlation, distance, and association. These methods do not distinguish between variables dependent and independent.

Analysis of the elements and monosaccharide compounds (galactosan, levoglucosan, and mannosan) was processed as follows. Daily concentrations were considered valid if the value surpassed its associated uncertainty. For each valid daily concentration, the contribution of each element to PM_{2.5} was calculated ([element]/[PM_{2.5}]). Only those elements and chemical compounds with 75% or more valid daily data were included in the analysis. Median and standard deviation of daily contribution values for each element and chemical compound for all sites (Padre Las Casas and Las Encinas) and seasons (winter and spring) were calculated. Raw-Z score was calculated for each day as the number of standard deviations from the median. Values higher than the median were reported as positive in red while values below the median were reported as negative in green. Average linkage clustering method and Euclidean distances were employed to develop hierarchical clustering using the online visualization tool Heatmapper (Babicki *et al.*, 2016).

3 RESULTS AND DISCUSSION

3.1 On-line PM Concentrations and Chemical Composition

PM mass concentrations and the chemical composition of submicron PM were measured at the Las Encinas (LE) and Padre Las Casas (PLC) sites during winter and spring. The average PM_{2.5} concentration was higher at the urban-residential site (PLC) than at the urban background site (LE) in the wintertime (Table 1). It should be noted that the measurements were not conducted simultaneously at LE and PLC but the campaign at PLC was started immediately after that at LE and therefore they are assumed to represent similar meteorological conditions. Comparison between the periods shown in supplemental material (Figs. S1–S4, Table 1). Compared to the earlier measurements in urban areas in Chile, both sites exhibited at wintertime PM_{2.5} levels

Table 1. One hour average PM_{2.5} and submicron organics, chloride, ammonium, nitrate, sulphate and BC concentrations observed at the measurement sites (Las Encinas, Padre las Casas) during spring and winter campaigns measured with the on-line instruments (ACSM and SIMCA).

Mass concentration ($\mu\text{g m}^{-3}$)	Las Encinas (LE)		Padre Las Casas (PLC)	
	Winter (4–24 Jul)	Spring (19 Nov–10 Dec)	Winter (24 Jul–7 Aug)	Spring (11 Nov–24 Dec)
PM _{2.5} (continuous)	38.4	6.8	85.0	6.3
Organics	30.5	3.53	62.02	2.77
Chloride	0.87	0.09	1.61	0.08
Ammonium	0.62	0.37	1.26	0.34
Nitrate	1.61	0.28	2.73	0.22
Sulphate	0.51	0.86	1.07	0.83
BC	1.17	0.64	2.44	0.66

higher than those reported in Santiago during winter ($48 \mu\text{g m}^{-3}$ (Tagle *et al.*, 2018); $30 \mu\text{g m}^{-3}$ (Carbone *et al.*, 2013)). The differences between PM₁₀ levels in Temuco and Santiago have also been reported previously by Diaz-Robles *et al.* (2014, 2015). Temuco is classified as one of the most polluted cities in Latin America by the World Health Organization (Díaz-Robles *et al.*, 2015). These cities show also clear differences between the emissions sources: the main source of PM in Temuco is wood burning while in Santiago emissions originate mostly from mobile sources with a high contribution of secondary particles (Tagle *et al.*, 2018; Carbone *et al.*, 2013). This information likely explains at least partly the differences in PM levels between Santiago and Temuco.

On the other hand, the peak hourly PM_{2.5} concentrations (up to $700 \mu\text{g m}^{-3}$) measured at Las Encinas and Padre Las Casas are comparable to the concentrations typically observed in the world's most polluted cities (Gani *et al.*, 2019; Huang *et al.*, 2010). In the springtime, significantly lower average PM_{2.5} concentrations (PLC $6.3 \mu\text{g m}^{-3}$, LE $6.8 \mu\text{g m}^{-3}$) were measured. In spring, the PM_{2.5} concentrations at Las Encinas and Padre Las Casas were comparable to those reported elsewhere in the world (Lorelei de Jesus *et al.*, 2020). In terms of chemical species, the average concentrations of organics, inorganic compounds (nitrate, sulphate, ammonium, and chloride) and BC were similar at both sites in spring, however, in winter the concentrations at Padre Las Casas were double the values observed at Las Encinas. In general, the concentrations were significantly higher in winter for all the compounds at both sites, except for sulphate at Las Encinas (Table 1).

Figs. 3 and 4. show the time series for the concentrations of the main chemical components of submicron particles i.e., organics, BC, nitrate, sulphate, ammonium and chloride measured by the ACSM and SIMCA whereas Figs. 5 and 6. show the corresponding mass fractions of the chemical components at both sites in spring and winter, respectively. The sum of the main chemical components in submicron particles follows the time trend of the PM_{2.5} concentration (Pearson $r = 0.82$ and $r = 0.48$ for winter and spring, respectively) at both stations. In the springtime, the variation in the measured concentrations was smaller (between $5\text{--}35 \mu\text{g m}^{-3}$), whereas in winter, a number of large spikes for the PM_{2.5} concentrations between 200 and $700 \mu\text{g m}^{-3}$ were observed. Higher Pearson correlation values in winter compared to the spring campaign can be related to the changes in the strengths of the predominant emission sources. PM_{2.5} concentrations in winter were 5.6–13.5 times higher than those reported during the spring campaign. Winter/spring difference was especially large at the PLC station. Regarding chemical composition, organics and chloride shows the biggest changes among the season, mostly related to wood burning. Based on the high Pearson correlation in the winter campaign, it can be assumed that the temporal variation of PM_{2.5} in winter is mainly due to wood combustion sources. In the springtime, the strength of these emission sources decreased significantly because of lower demand for heating. Therefore, in spring, other PM_{2.5} sources were more important, like dust components, which are not measured by real time instrumentation used here (because dust is mostly refractory material, i.e., carbonates). The increase of the relative contribution of refractory material in PM_{2.5} could also explain the lower person coefficient recorded in the spring campaign.

Submicron particle mass was dominated by organic compounds in winter and spring periods. During spring, the average contribution of organics was 61 and 57% of the total analyzed mass

Fig. 3. The timeseries of submicron organics, nitrate (NO_3^-), sulphate (SO_4^{2-}), ammonium (NH_4^+) and chloride (Cl^-) measured with the ACSM, BC measured with the SIMCA and $\text{PM}_{2.5}$ concentration measured with the BAM-1020 at Las Encinas Temuco and Padre las Casas in winter.

Fig. 4. The timeseries of submicron organics (Org), nitrate (NO_3^-), sulphate (SO_4^{2-}), ammonium (NH_4^+) and chloride (Cl^-) measured with the ACSM, BC measured with the SIMCA and $\text{PM}_{2.5}$ concentration measured with the BAM-1020 at Las Encinas Temuco and Padre las Casas in spring.

at Las Encinas and Padre Las Casas, respectively, whereas during winter, the average contribution of organics was larger reaching 86 and 87% at Las Encinas and Padre Las Casas, respectively. The average contribution of inorganic ions was 28 and 30% during spring, and it decreased to 10 and 9% during winter at Las Encinas and Padre Las Casas, respectively. Similarly, the BC contribution was smaller during winter (3.3 and 3.4%) than during spring (11 and 13%) at Las Encinas and Padre Las Casas, respectively. It should be noted that the mass fraction (Fig. 5) does not change substantially between the sites, indicating that the average chemical composition reflects a rather regional influence. However, the contribution of inorganic ions and BC was significantly smaller in the winter season whereas the concentrations of organics was larger. In-depth analysis of inorganic compounds is presented in a later section. The higher concentrations of BC found at Padre Las Casas were mainly attributed to the impact of local emissions from the sources located in the surroundings of the station, especially residential biomass burning (discussed later).

The composition of submicron PM with prevailing organic fraction, relatively large inorganic fraction (9–30%) and a small fraction of BC (< 13%) was similar to the composition observed in the polluted areas in Asia (Gani *et al.*, 2019; Huang *et al.*, 2019). In a study conducted in India

Fig. 5. Mass fractions of submicron organics, nitrate (NO_3^-), sulphate (SO_4^{2-}), ammonium (NH_4^+) and chloride (Cl^-) measured with the ACSM and BC measured with the SIMCA at Las Encinas Temuco and Padre las Casas in winter.

Fig. 6. Mass fractions of submicron organics, nitrate (NO_3^-), sulphate (SO_4^{2-}), ammonium (NH_4^+) and chloride (Cl^-) measured with the ACSM and BC measured with the SIMCA at Las Encinas Temuco and Padre las Casas in spring.

(Gani *et al.*, 2019), they found a BC contribution of only 5%, and in another study conducted in Beijing, the BC contribution reached 3.1% (Huang *et al.* 2010), similar to the BC contribution obtained in this study.

3.2 Diurnal Variation of PM and Chemical Components

Fig. 7 shows the average diurnal variation for organics, BC, sulphate, nitrate, ammonium, and chloride at both sites, LE and PLC, in the winter and spring seasons. The data from both sites were combined. In the wintertime, the compounds measured by the ACSM increased in the morning between 08:00 and 10:00 AM, and again at the evening between 4:00 and 10:00 PM, except sulphate which had no clear diurnal trend. Besides that, for nitrate, ammonium, organics and chloride a third (small) peak was observed at 11:00 AM that was probably associated with photochemical activity and the formation of secondary ammonium nitrate (Wang *et al.*, 2015).

Fig. 8 shows the average diurnal profiles for NO_x measured at the PLC station. NO and NO_2 had similar diurnal trends to organics and chloride (Fig. 7), although they were peaking approximately one hour later. The evening peaks for the chemical species (excluding sulphate) and NO_x were dominating over the morning peaks. In the springtime, the diurnal profile for the species was not

Fig.7. Average diurnal variation of the main particulate chemical species in the winter (a) and spring (b) campaign.

so profound. Lowest concentrations for the species were measured typically during the midday and relatively higher concentrations during nights indicating poor mixing during the night.

The diurnal profile for the NO_2/NO_x ratio at the Padre Las Casas station shows a clear decrease during the rush-hour in the spring morning indicating a clear impact from traffic emissions at that time of the day. NO_2/NO_x ratio values between 0.1 and 0.3 have been reported for biomass burning emissions while significantly lower values have been attributed to the vehicle exhaust emissions (Burling *et al.*, 2010; Yokelson *et al.*, 1996). Rapid conversion from NO to NO_2 can also be affecting the NO_2/NO_x ratio, which can be in seconds scale under normal conditions (1 atm, 298 K, 50 ppbv O_3) due to the NO reaction with O_3 that increases the NO_2/NO_x ratio (Wild *et al.*, 2017). Probably, the NO_2/NO_x increase is also reflecting the ozone production during afternoon hours.

To explore the day-to-night variation in more detail, Table 2 shows the average concentrations of organics, sulphate, ammonium, nitrate, chloride, BC, and the meteorological data during day (average between 7 AM and 7 PM) and night (average between 7 PM and 7 AM) in Temuco in winter and spring. In the wintertime, the daytime concentration was significantly lower than the nighttime averages. High concentrations in winter nights were observed for all the analyzed components (Table 2). For instance, the concentrations of organics were 25 and 9 times higher during the winter nights than the average concentrations during the spring nights in Padre las Casas and Las Encinas, respectively. Low temperatures in winter increased the need for heating the homes, especially at night, which likely caused an increase in pollutant levels. However, temperatures were not that different between the day and night in winter which indicates that the boundary layer depth had a stronger influence than temperature changes. This trend may also be due to the fact that during the night people stay in their homes, after returning from work

Fig. 8. Diurnal variation of NO_2 (lowest panel), NO , (middle panel), and NO_2/NO_x ratio (upper panel) in Temuco in winter (asterisk) and spring (circle).

Table 2. Average concentrations of organics, chloride, ammonium, nitrate, sulphate, BC, $\text{PM}_{2.5}$, temperature, relative humidity, and wind speed during day (7 AM–7 PM) and night (7 PM–7 AM) in the winter and spring campaigns at both stations (LE and PLC). LE station has no RH records for the measurement period.

Measured parameter/time	Padre las Casas				Las Encinas			
	Winter Day	Winter Night	Spring Day	Spring Night	Winter Day	Winter Night	Spring Day	Spring Night
Organics ($\mu\text{g m}^{-3}$)	10.88	22.21	0.78	0.87	6.99	16.57	1.39	1.76
Chloride ($\mu\text{g m}^{-3}$)	0.30	0.57	0.02	0.03	0.20	0.47	0.03	0.04
Ammonium ($\mu\text{g m}^{-3}$)	0.29	0.35	0.08	0.09	0.19	0.27	0.12	0.15
Nitrate ($\mu\text{g m}^{-3}$)	0.60	0.83	0.06	0.07	0.53	0.71	0.09	0.15
Sulphate ($\mu\text{g m}^{-3}$)	0.21	0.24	0.20	0.22	0.15	0.21	0.29	0.35
Black Carbon ($\mu\text{g m}^{-3}$)	1.88	4.13	0.46	0.64	0.81	1.53	0.50	0.66
$\text{PM}_{2.5}$ ($\mu\text{g m}^{-3}$)	63.40	107.58	5.44	7.15	26.14	50.96	5.87	7.78
Temperature ($^{\circ}\text{C}$)	9.15	7.63	17.56	12.64	9.20	7.08	17.35	12.10
Relative humidity (%)	82.41	89.85	60.97	80.03	–	–	–	–
Wind speed (m s^{-1})	1.79	1.22	1.90	0.93	2.03	1.51	2.42	1.27

and educational places, so there is a need to keep the houses warm. Besides more intensive sources in nighttime, it can be observed from the meteorological data that Padre Las Casas had the most unfavorable mixing conditions at night due to the low wind speed, high relative humidity, and low temperature. In the case of Las Encinas, higher wind speed during the day favored an increased aerosol dispersion.

3.3 Influence of Biomass Burning and Local Meteorology during Pollution Episodes

The contribution of biomass combustion to the organic fraction and the aging of organic compounds were estimated based on the ACSM tracers' signals. The fraction f_{44} ($f_{44} = \frac{m/z = 44}{OA}$) was used as a tracer for secondary organic aerosol (SOA) (Jimenez *et al.*, 2009; Ng *et al.*, 2011a) and f_{60} ($f_{60} = \frac{m/z = 60}{OA}$) as a tracer for primary organic aerosol (POA) emitted by biomass burning (Cubison *et al.*, 2011; Ortega *et al.*, 2013).

A f_{44} vs. f_{60} scatter plot proposed by (Cubison *et al.*, 2011) was created using the combined data from both sites (Las Encinas and Padre Las Casas), separately for the winter and spring campaign (Fig. 9 and Fig. 10, respectively). These graphs reveal the impact of biomass burning as a function of the level of atmospheric oxidation. Higher f_{44} values indicate strongly oxidized OA. Size and color of the points are proportional to the $PM_{2.5}$ concentration and ambient temperature, respectively. In the wintertime, the f_{44} values measured at the Las Encinas and Padre Las Casas stations indicate that the OA oxidation reached an intermediate state with most of the f_{44} values in the region of $0.05 < f_{44} < 0.13$ – 0.15 , like typically observed for semi-volatile oxygenated organic aerosol (SV-OOA) (Ng, *et al.*, 2011). A strong biomass burning impact was observed in the winter campaign since the f_{60} values were significantly higher than the background values. By the size and color of the points (Fig. 9), the higher $PM_{2.5}$ concentrations and lower temperatures are located at larger f_{60} values indicating that high $PM_{2.5}$ concentrations were mostly related to POA

Fig. 9. Scatter graph of f_{44} vs. f_{60} for the winter campaigns at Las Encinas and Padre las Casas. The sizes of the points are proportional to the $PM_{2.5}$ concentration.

Fig. 10. Scatter graph of f_{44} vs. f_{60} for the spring campaigns in Las Encinas and Padre las Casas. The sizes of the points are proportional to the $PM_{2.5}$ concentration.

coming from the biomass burning emissions. Since atmospheric stability and thermal inversion at very low altitudes predominate during the episodes with the high $PM_{2.5}$ concentration, it can be concluded that local biomass burning emissions contribute significantly to the observed $PM_{2.5}$ mass during the episodes. The observed f_{44} and f_{60} values were increased and reduced respectively during the spring campaign when compared to the winter campaign. However, f_{60} levels remained above the reference level also in spring indicating that the firewood combustion emissions from non-heating purposes probably impact the air quality during spring.

Meteorological conditions are the most important factors determining the impact of biomass burning on air quality at both monitoring sites. Gramsch *et al.* (2014a) argue that in Chile the days with high pollution typically present the following characteristics: (1) clear sky, (2) low wind speed, (3) large temperature variation during the day, and (4) frequent surface thermal inversion at night and early in the morning that further restricts the vertical air movements. In this study, different meteorological parameters for the winter and spring campaigns were compared, among them, precipitation levels, pressure, wind speed, surface temperature (10 m), and temperature registered at 344 m, to analyze the trend and to define a criterion for the identification of these high concentration events. Mehmood *et al.* (2020) have presented model results how surface weather patterns influence on the temporal and spatial variation of $PM_{2.5}$ concentrations over central and eastern China.

During the winter campaign, several pollution episodes with elevated PM concentrations were observed (Fig. 11). Most of these events (4–5, 14–16, 18–19 and 22–25 July, 2019 in Las Encinas, and 27–28 July and 2–6 August, 2019 in Padre las Casas) were characterized by the periods with high surface pressure, low temperatures, and low wind speed (marked with orange areas in Fig. 11). Also, the events matched with higher temperatures at high altitude than in the surface, identifying the typical profile of a vertical inversion. Additionally, these days had a high variation in day-to-night temperature, indicating frequent radiative thermal inversions in the Temuco region. As shown previously in Fig. 4, during the high pollution events (in the winter campaign), the concentrations of all the chemical species were observed to significantly increase and the organic fraction was prevailing. During the spring season (Fig. 12), no significant episode periods

were identified. Therefore, it is possible to conclude that the nights with the highest levels of air-pollution were determined both by the increased biomass combustion due to cold temperatures and by the meteorological conditions that hinder the dispersion of pollutants (lower temperatures, development of very low altitude thermal inversions, and low wind speeds), which enhance the impact of local emissions at the Las Encinas and Padre las Casas sites.

Fig. 11. Time series of $PM_{2.5}$ concentration and meteorological parameters for the winter campaign in 2019. Periods with the high concentration events (episode days) are qualitatively illustrated in orange areas. LE: Las Encinas station. PLC: Padre Las Casas station. P: Ambient pressure. WS: Wind speed. T: Temperature. Pp: Precipitation.

Fig. 12. Time series of $PM_{2.5}$ concentration and meteorological parameters for the spring campaign in 2019. LE: Las Encinas station. PLC: Padre Las Casas station. P: Ambient pressure. WS: Wind direction. T: Temperature. Pp: Precipitation.

3.4 PM_{2.5} Elemental Composition and Monosaccharides

In addition to real-time instruments that measured the main chemical species in PM₁, the concentrations of several elements and MA's were analyzed from the PM_{2.5} filter samples. Significantly elevated MA concentrations were observed during wintertime (Table 3) at both PLC and LE. Elevated MA concentrations are typically observed in areas where biomass burning is a prevailing source (e.g., Wang *et al.*, 2011; Saarnio *et al.*, 2012). The largest elemental concentrations were measured for P, S, Cl, K and Ca (Table 3). Note that elemental chlorine is marked differently (Cl) from ionic chloride measured by the ACSM (Chloride). Most of the elements had higher concentrations in winter than in spring, especially K, Cl, Zn, and Br at both sites. Only Al had higher concentrations in spring than in winter at both measurement locations. When comparing the sites, the concentrations of the elements were mostly higher at Padre las Casas.

Several elements and monosaccharides determined in this study have been used as tracers of specific sources in other Chilean cities, such as biomass burning (K, MA's, Cl), vehicular emissions (Zn and Cr) and secondary components (S in sulphate) (Barraza *et al.*, 2017; Jhun *et al.*, 2013; Kavouras *et al.*, 2001; Villalobos *et al.*, 2017). In this study, Cl and K correlated strongly with MA's ($R > 0.8$), indicating that they are related mostly to biomass burning emissions (Hedberg *et al.*, 2002; McDonald *et al.*, 2000). Zn showed a positive correlation with MA's ($R = 0.75$) and weak correlation with Cr ($R = 0.22$) indicating that the vehicular emissions, previously characterized by Zn and Cr, were altered probably by a significant Zn contribution from wood burning emissions (Dilger *et al.*, 2016; Molnár *et al.*, 2005). At both sites, the PM_{2.5} concentration correlated strongly

Table 3. Seasonal average (average $\pm$ standard deviation) of PM_{2.5} concentration and elements for the Padre Las Casas and Las Encinas sites. Cells marked with “–” were not considered representative for the site/campaign as they had less than 75% of filter results available.

Species		Padre Las Casas		Las Encinas	
		Winter	Spring	Winter	Spring
PM _{2.5}	($\mu\text{g m}^{-3}$)	77.3 $\pm$ 80.9	8.6 $\pm$ 3.8	56.1 $\pm$ 50.4	6.7 $\pm$ 2.4
Levogluconan	(ng m ⁻³)	8446 $\pm$ 7406	313.9 $\pm$ 447.3	8041.9 $\pm$ 8118.1	148.3 $\pm$ 233.3
Mannosan	(ng m ⁻³)	694.9 $\pm$ 665	29 $\pm$ 42.7	562.6 $\pm$ 567	11.9 $\pm$ 18.9
Galactosan	(ng m ⁻³)	596 $\pm$ 529.2	21.4 $\pm$ 29	641.6 $\pm$ 698.1	9.6 $\pm$ 13.2
Na	(ng m ⁻³)	–	68.3 $\pm$ 27.8	72.4 $\pm$ 31.8	66 $\pm$ 29.1
Mg	(ng m ⁻³)	86.7 $\pm$ 34.9	–	47.9 $\pm$ 21.9	–
Al	(ng m ⁻³)	86.2 $\pm$ 30.4	50.7 $\pm$ 16.1	46.6 $\pm$ 21.7	49.5 $\pm$ 12.5
Si	(ng m ⁻³)	26.5 $\pm$ 24.4	33.8 $\pm$ 25.7	19.8 $\pm$ 16.6	25.5 $\pm$ 20
P	(ng m ⁻³)	170.9 $\pm$ 17.2	75 $\pm$ 14.6	77.3 $\pm$ 13.7	72.2 $\pm$ 15.1
S	(ng m ⁻³)	244.2 $\pm$ 155	110.4 $\pm$ 40.3	162.1 $\pm$ 105.6	100.6 $\pm$ 38.8
Cl	(ng m ⁻³)	833.3 $\pm$ 708.4	166.3 $\pm$ 97.5	540.1 $\pm$ 487.2	147.3 $\pm$ 78.5
K	(ng m ⁻³)	945 $\pm$ 640.8	106.5 $\pm$ 44.9	634.6 $\pm$ 540.8	73.8 $\pm$ 31.9
Ca	(ng m ⁻³)	180.5 $\pm$ 69.4	115.5 $\pm$ 16.3	102.7 $\pm$ 23.7	104.7 $\pm$ 12.6
Sc	(ng m ⁻³)	73.3 $\pm$ 10.5	20 $\pm$ 3.8	33.4 $\pm$ 6.5	19.3 $\pm$ 4.2
Ti	(ng m ⁻³)	23.2 $\pm$ 6.3	17.7 $\pm$ 3.9	13.4 $\pm$ 3.5	16.1 $\pm$ 3
Cr	(ng m ⁻³)	5.8 $\pm$ 2.4	2.8 $\pm$ 0.9	2.8 $\pm$ 1.2	2.8 $\pm$ 1.1
Fe	(ng m ⁻³)	76.2 $\pm$ 47	63.4 $\pm$ 30.3	57.1 $\pm$ 46.3	49 $\pm$ 22.9
Cu	(ng m ⁻³)	19.3 $\pm$ 6.4	6.5 $\pm$ 2.1	10.6 $\pm$ 4.2	5.9 $\pm$ 1.7
Zn	(ng m ⁻³)	51.1 $\pm$ 18.4	12.4 $\pm$ 3.7	30.6 $\pm$ 19.7	10 $\pm$ 3.5
Br	(ng m ⁻³)	13.5 $\pm$ 9	4.2 $\pm$ 2.1	7.1 $\pm$ 4.7	3.2 $\pm$ 1.1
Cs	(ng m ⁻³)	–	–	32.5 $\pm$ 14.8	–
La	(ng m ⁻³)	136.9 $\pm$ 51.4	–	63.9 $\pm$ 30	–
Ce	(ng m ⁻³)	–	43.3 $\pm$ 22.2	52 $\pm$ 26.9	40 $\pm$ 25.8
Sm	(ng m ⁻³)	235.5 $\pm$ 90.1	–	110.9 $\pm$ 44.5	–
Eu	(ng m ⁻³)	318.2 $\pm$ 162.8	171.5 $\pm$ 65.7	166.4 $\pm$ 62.8	157.2 $\pm$ 73.7
Tb	(ng m ⁻³)	–	–	–	116.6 $\pm$ 45.9
W	(ng m ⁻³)	27.4 $\pm$ 13.7	13.1 $\pm$ 9.9	12.7 $\pm$ 8.1	11.3 $\pm$ 8.7
Pb	(ng m ⁻³)	20.4 $\pm$ 8.7	5.3 $\pm$ 1.7	8.4 $\pm$ 4.9	–

with MA's, Cl and K ($R^2 > 0.43$) in the wintertime suggesting that biomass burning is the most important emission source in the zone. In spring, MA's showed lower R^2 values with $PM_{2.5}$ at both sites indicating a reduced impact of wood combustion sources. The role of biomass burning is comparable to the results from other places, e.g., China (Mehmood *et al.*, 2018). In addition, elevated concentrations of several Lanthanide elements (i.e., La, Sm, Eu) were observed. The lanthanides are likely originating from the mining activities. Previous studies have observed elevated rare earth element concentrations in Chile in mine tailings as well as in atmospheric and environmental samples (Goecke *et al.*, 2017, Mesías Monsalve *et al.*, 2018, Rodríguez *et al.*, 2021).

The levoglucosan/mannosan (L/M) ratio has been established as an indication of the type of wood used in the combustion (Gonçalves *et al.*, 2010; Schmidl *et al.*, 2011). In this study the ratio varied between 12 and 17 in winter without any clear difference between the sites. During the spring, the ratio was slightly smaller. The ratio obtained in this study has been typically observed for combustion of mostly Mediterranean species of hardwood (Schmidl *et al.*, 2008). However, recent studies e.g., May *et al.* (2012) have reported levoglucosan volatilization at temperatures above 30°C, limiting its tracer applicability in some field measurements. Considering that this study was conducted in the cold season with monthly average temperatures below 10°C (Fig. 2), the partitioning of levoglucosan into the gas phase can be considered negligible.

Previous studies have indicated that elements in atmospheric PM in Chile may originate e.g., from mining activities, traffic, industrial activities or resuspended dust (e.g., Sax *et al.*, 2007, Mesías Monsalve *et al.*, 2018, Saarikoski *et al.*, 2019). The Cluster Heatmap analysis (Fig. S5 in the supplemental material) groups elements depending on their similarity during the campaign period. Attributable source(s) for these elements can be inferred and, generally some elements tend to cluster together depending on the method employed to group them. In our approach, we evaluated the daily behavior of the elemental contribution to $PM_{2.5}$ as the number of standard deviations from the median for each element or compound. The patterns of the contribution of different elements and compounds to $PM_{2.5}$ were clearly segregated by the season when they were collected (winter and spring represented by blue and yellow colours respectively in the y-axis). During winter, but not in spring, PLC and LE sites were mildly segregated, but generally a clear separation among the monitoring sites was not observed indicating a similar impact of common emissions sources at both sites. Elements and compounds (x-axis) were grouped in two clear clusters. Galactosan, levoglucosan and mannosan were grouped with K, indicating a strong influence of biomass burning (Jorquera and Barraza, 2012) for that cluster. In contrast to all elements analysed, the contribution of the MA's to $PM_{2.5}$ was higher during winter. The other distinctive cluster grouped all remaining elements. Although clear groups were not distinguished for this cluster, crustal elements such as (Ca, Al, Si, Fe) (Sax *et al.*, 2007) were closely related but not forming a distinctive cluster. Similarly, Pb and Br (generally related to vehicular combustion, Gramsch *et al.*, 2021) were close to each other but not in a distinctive cluster. In summary, the only source-identifiable cluster was biomass combustion, while additional sources were not cluster-defined and elements enriched in emissions from certain sources behaved similarly during the campaign period.

4 SUMMARY AND CONCLUSIONS

The results obtained from two measurement campaigns, carried out in winter and spring at the stations located at Temuco, Las Encinas and Padre las Casas, showed clearly that in winter the daily $PM_{2.5}$ levels frequently exceeded the Chile's primary annual $PM_{2.5}$ standard limit. To better understand the reasons for this non-compliance with the PM standard, advanced air quality measurement techniques and equipment, such as the ACSM, were implemented, which allows the real-time measurement of organics, sulphate, ammonium, nitrate and chloride together with the SIMCA monitor that measured black carbon. During the measurement campaigns, the samples of PM_{10} and $PM_{2.5}$ were collected in Teflon filters with Harvard impactors, creating an important database of elements and monosaccharides, which together with the PM composition, concentration, and meteorological data, allowed the identification of the main sources of pollutants impacting the air quality in Las Encinas and Padre las Casas.

The main component in submicron particles was organic matter that contributed almost 90% of

the analyzed PM₁ components in winter with the mean winter concentrations of 30 and 62 $\mu\text{g m}^{-3}$ at LE and PLC, respectively. In spring, the concentrations of organics were 10–20 times smaller. The average contribution of inorganic ions to the analyzed PM₁ components varied from 9 to 30% being larger in spring than in winter. Similarly, the contribution of BC was smaller during winter (~3%) than during spring (11–13%) at both sites.

Biomass combustion had high impact on PM_{2.5} in wintertime at both sites. The biomass burning tracers, monosaccharides, potassium and chloride, were elevated in the wintertime and their diurnal profiles showed an increase in concentrations in the evening. The contribution of MA's to PM_{2.5} was 11 and 20% at PLC and LE, respectively, in winter, while the contribution was 3–4% in the springtime pointing out a significant influence of biomass burning on PM_{2.5} in winter. Also, the contribution of biomass combustion to organic fraction and the aging of organic compounds was estimated based on the ACSM tracers' signals. The fraction of ion m/z 60, which is used as a tracer ion in biomass combustion, to organics in total organic mass spectra (f₆₀), showed higher values during winter and especially during colder temperatures. Diurnal profiles combined with the in-depth chemical analysis clearly showed that in the wintertime local biomass burning is the main source of air pollutants in the region. Furthermore, in winter, most of the high concentration events correlated with the periods with high surface pressure, low temperature, and low wind speed. These events matched with higher temperatures at high altitude than at the surface, characterizing the typical profile of a vertical inversion preventing the dilution of air pollutants.

In summary, the use of firewood as fuel in the studied area together with the unfavorable local meteorological parameters were observed to contribute to the development of poor air quality episodes in Temuco causing exceedances of the Chilean PM_{2.5} standard. To achieve and comply with the PM₁₀ and PM_{2.5} standard, the Chilean environmental authority must massively reduce the emissions from firewood combustion by prioritizing the use of non-polluting energy, control the quality of firewood, and inspect the correct use of the heaters together with educating the population in the efficient way to use wood as a fuel.

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SUPPLEMENTARY MATERIAL

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