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Inhaled and inspired particulates in Metropolitan Santiago Chile exceed air quality standards

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The long-term trends and spatial variability of $PM_{2.5}$ and PM_{10} over the period between 2000 and 2012 in the Santiago Metropolitan Area, Chile are studied. The annual PM_{10} and $PM_{2.5}$ mass concentration ranged between 76 ± 5 and 52 ± 4 μg m^{-3} and between 32 ± 4 and 24 ± 3, respectively. The large levels of PM observed during the cool season (April–September) compared to the warm season (October–March) can be explained by meteorological conditions and increased emissions. $PM_{2.5}$ represents approximately 45% ± 5% and 60% ± 10% of PM_{10} in the warm and cold seasons, respectively. Reductions in PM_{10} and $PM_{2.5}$ were observed in the ranges of −2.46 to 0.31 and −3.17 to −1.80% $year^{-1}$, respectively. For the city, the comprehensive air pollution level declined gradually, illustrating that the air quality improved over the last decade. However, the air quality standards were still being exceeded, indicating the need to update and strengthen the policies to control PM pollution.

1. Introduction

In recent decades, the largest cities around the world have FACED critical environmental air quality degradation as a result of overloading the atmosphere with pollutants [11,27]. Despite technological advances and rising awareness, developed countries still continue their struggle against this tendency toward global environmental degradation. Urban centers in South America, such as Sao Paulo, Mexico City, Lima, Buenos Aires and Santiago, show significant levels of air pollution [25]; these levels may present a high risk for the population's health [1,5,27]. Faced with such risks caused by atmospheric pollution both outdoors and indoors in other countries have implemented solutions such as the building refurbishment to prevent contaminated air from entering the interior either by building cracks or leakages [14,15,21].

The long-term air quality assessment in several megacities of the world have shown the advantages of this methodological approach to study the historical exposure of the human populations and simultaneously verify the efficiency of policies and strategies for improving air quality in urban areas [5,13,28].

Fine particles (<2.5 μm in diameter; $PM_{2.5}$) and/or coarse particles (>2.5 to <10 μm in diameter; $PM_{2.5-10}$) can result in a number of health effects that are observable in broad segments of the population [7,8,23]. The damage to human health caused by $PM_{2.5}$ and PM_{10} (<10 μm in diameter) is manifested as mortality due to cardiac and respiratory causes, a decrease in lung capacity in children and asthmatic adults and an increase in chronic obstructive pulmonary diseases, among other effects [27]. To protect human health from the known effects of PM (particulate matter), organizations such as the World Health Organization (WHO) and the Environmental Ministry of Chile (Ministerio del Media Ambiente, MMA) have established safety thresholds for the environmental concentrations of PM_{10} and $PM_{2.5}$ on an annual and daily basis [9].

In 2011, the Official Environment Status Report by the Chilean Environmental Ministry emphasized that in Chile [10] at least 10 million people (approximately 60% of the population) are exposed to annual concentrations of $PM_{2.5}$ that are higher than the Chilean annual standard of 20 μg m^{-3} [9], and most of this exposure occurs

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in urban settings. The same report stated that approximately 4000 people die each year from cardiovascular diseases that are directly related to chronic exposure to $PM_{2.5}$ and that in the last decade, one of the cities with the greatest contamination by particulate matter in Chile is the Santiago Metropolitan Area (SMA), the capital of Chile.

In SMA, the levels of PM_{10} and $PM_{2.5}$ often exceed the established safety thresholds for environmental concentrations recommended by the WHO [24] and the MMA [9]. For this reason, the city was declared a non-attended area for PM in 1996 [18]. Since 1997, a Plan of Prevention and Decontamination of Atmospheric Pollution (PPDA) [18] has been employed to protect the health of the region's inhabitants. As a result of this management, a series of measures to improve air quality has been established (e.g., car-use bans; mandatory catalytic converters in new cars; the replacement of old bus fleets; reformulated gasoline; industrial emission standards; nonindustrial emissions-trading program). An Air Quality Pollution Watch Program was also implemented. Eight monitoring stations distributed throughout the city are currently measuring the concentrations of pollutant gases and atmospheric aerosols, as well as meteorological data [20]. All of these stations support the MACAM-2 network and the Air Quality Monitoring Program in SMA.

In this work, we analyzed PM_{10} and $PM_{2.5}$ measurements taken from 2000 to 2012 in SMA to characterize the spatial and temporal distribution of particulate matter concentrations on daily, monthly and yearly time scales. The air pollution trends for PM_{10} and $PM_{2.5}$ were analyzed. The effect of meteorological variables on the concentration of PM_{10} and $PM_{2.5}$ was analyzed. The data were summarized by hour of day and day of week at each location to establish differences among the zones. The results were assessed by comparing the annual average concentration and daily maximum concentration levels of PM_{10} and $PM_{2.5}$ with the corresponding MMA standards and WHO guidelines. The study sought to understand the trends in atmospheric PM pollution, to evaluate measures to improve air quality in the city and to determine the level of exposure in the population over the last 12 years.

2. Data and methodology

2.1. Study area

The Santiago Metropolitan Area (SMA, 33.5 S, 70.6 W) is the capital of Chile. The population of Santiago's urban area grew from approximately five million in 1990 to six million in 2010 and includes 40% of the total population of Chile. SMA has a fleet of more than 1.5 million motor vehicles, accounting for 42% of the motor vehicle fleet in Chile, and houses over 70% of the industrial activity at the national level [6]. The city is located in a valley in the central zone of Chile between two rivers, the Maipo and the Mapocho. The metropolitan area covers approximately 1400 km^2 and lies 500 m above sea level on average [12]. The city is bounded by the high Andes Mountains to the east (4500 m altitude on average), a lower parallel mountain range to the west (1500 m altitude on average) and two east-to-west mountain chains to the north and south of the basin; see Fig. 1.

The climate in SMA is Mediterranean; the temperatures range between −2 °C and 35 °C, with an average temperature of approximately 14 °C [3]. SMA has a persistent valley-mountain

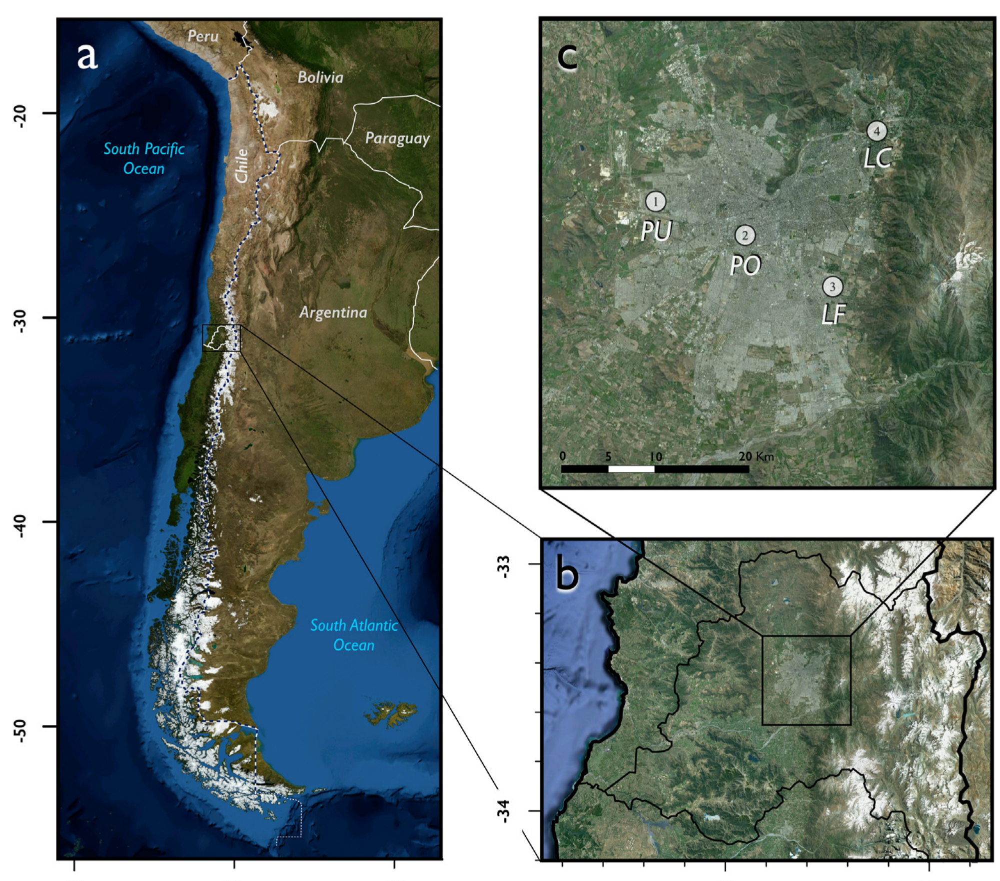

Fig. 1. Location of the monitoring stations under study for the measurement of $PM_{2.5}$ and PM_{10} concentrations in the Santiago Metropolitan area (SMA).

breeze system, with a predominant low-speed wind from the southwest that often is less than 2.0 m/s in autumn and winter, i.e., the cool season [3]. The prevailing anticyclonic meteorological conditions throughout the year lead to a permanent subsidence and thermal inversion layer [12]. Consequently, the geography and climate of the Santiago basin are generally unfavorable for dispersing air pollutants.

2.2. Pollutant concentration and meteorological measurements

Air quality data, including the concentrations of PM_{10} and $PM_{2.5}$, and meteorological data (temperature, relative humidity, wind velocity and wind direction) were analyzed over 13 years (2000–2012). The data were obtained from the National Air Quality Information system [20], which is currently run by the Environmental Ministry of Chile. The PM_{10} and $PM_{2.5}$ concentrations were determined using a tapered element oscillating microbalance (TEOM) (Thermo Scientific Air Monitoring Instruments, Franklin, MA, USA). The data had been previously validated to correct vacancies, duplicated entries and gaps.

Eight monitoring stations distributed throughout the city measure the concentrations of pollutant gases and atmospheric aerosols and determine the current meteorological data (temperature, relative humidity, wind velocity and wind direction). However, only four stations determine PM_{10} and $PM_{2.5}$ simultaneously: Las Condes (LC), La Florida (LF), Parque O'Higgins (PO) and Pudahuel (PU) stations (Fig. 1 and Table 1). The PU station is located in the western part of Santiago in a small park near a medical clinic in a residential area. The PO station is located in a large park approximately 2 km south of the city center and 1 km west of a major highway. The LF station is located in the southeast part of the city, which is mostly residential, near an urban freeway and high-traffic avenues. The LC station is located in the eastern part of Santiago. The surrounding area is primarily residential.

2.3. Data analysis

Due to the massive amounts of hourly data collected during the study period, with an average of nearly 100,000 data points for PM_{10} and $PM_{2.5}$ values alone at each monitoring station used in this study, a descriptive statistical analysis was conducted in MS-Excel© (Microsoft Corporation, Redmond, WA, USA) and the open-source statistical software programming language R [29]. The completeness of data was higher than 95%. Missing data were omitted from the analysis. Some of the analyses were conducted with the Openair software package [17] using the R programming language running under the open-source computer software RStudio: Integrated development environment for R (RStudio Boston, MA. Available from http://www.rstudio.org/). The temporal trends were estimated using the Theil–Sen approach [19,22]. The Theil–Sen test calculates slopes between all pairs of points, and the median of the slopes is selected as the Theil–Sen estimate, which is taken as the trend of the pollutant for the given period. The *deseason* option was used to deseasonalize the data. The wind rose analysis was performed using the wind plot option [17].

Table 1
Monitoring stations under study in the Santiago Metropolitan Area (SMA); see Fig. 1.

Label	Station	Latitude (S)			Longitude (W)			Altitude (m)
PU	Pudahuel	33°	26′	06″	70°	44′	52″	553
LF	La Florida	33°	30′	48″	70°	35′	09″	654
PO	Parque O'Higgins	33°	27′	40″	70°	39′	29″	562
LC	Las Condes	33°	22′	26″	70°	31′	21″	811

2.4. Assessment of standards and guidelines

The basis for judging the health impact of the data collected is the MMA [9] ambient air quality standards and the WHO [24] guidelines. The annual mobile average standards for PM_{10} are 20 μg m^{-3} (WHO) and 50 μg m^{-3} (MMA), and the annual mobile standards for $PM_{2.5}$ are 10 μg m^{-3} (WHO) and 20 μg m^{-3} (MMA); the 24-h mobile average standards are 50 μg m^{-3} (WHO) and 150 μg m^{-3} (MMA) for PM_{10} and 20 μg m^{-3} (WHO) and 50 μg m^{-3} (MMA) for $PM_{2.5}$. Note that the WHO guidelines have more stringent values because they consider only the health risks, while the other established standards also include cost-benefit considerations.

3. Results and discussion

3.1. PM_{10} and $PM_{2.5}$ annual concentration levels

Fig. 2 shows the summary statistics of the annual concentration of PM_{10} and $PM_{2.5}$ measured at the monitoring site under study. The annual PM_{10} mass concentration averages for the four monitoring stations during the sampling period (2000–2012) were 72 ± 8 μg m^{-3}, 76 ± 5 μg m^{-3}, 71 ± 4 μg m^{-3} and 52 ± 4 μg m^{-3} for PU, LF, PO and LC, respectively. The annual $PM_{2.5}$ mass concentration averages were 32 ± 3 μg m^{-3}, 33 ± 4 μg m^{-3}; 32 ± 4 μg m^{-3} and 24 ± 3 μg m^{-3} for PU, LF, PO and LC, respectively, for the same period. PU recorded higher concentrations of PM_{10} than LF, PO and LC in the first years of the study (2000–2002). In the following years, LF recorded higher concentrations, PU and PO recorded similar PM_{10} concentrations, and LC recorded lower concentrations in all periods of study. No significant differences were observed by ANOVA analysis at a 95% confident interval between the annual PM_{10} concentrations at the PU and PO stations (p-value > 0.05). In contrast, all other station pairs showed significant differences. In the case of $PM_{2.5}$, PU, LF and PO recorded similar concentrations, and LC recorded lower concentrations. The $PM_{2.5}$ annual concentrations showed no significant differences at a 95% confident interval between the pairs PU-LF and PO-LF (p-value > 0.05). These results indicate that the LC station recorded significantly different values for the PM_{10} and $PM_{2.5}$ annual concentrations. This difference is because LC is located in the northern suburbs and is the least impacted by traffic sources, while LF, PU and PO are located in an urban site that is influenced by local primary emissions from nearby vehicles, industry and residential areas.

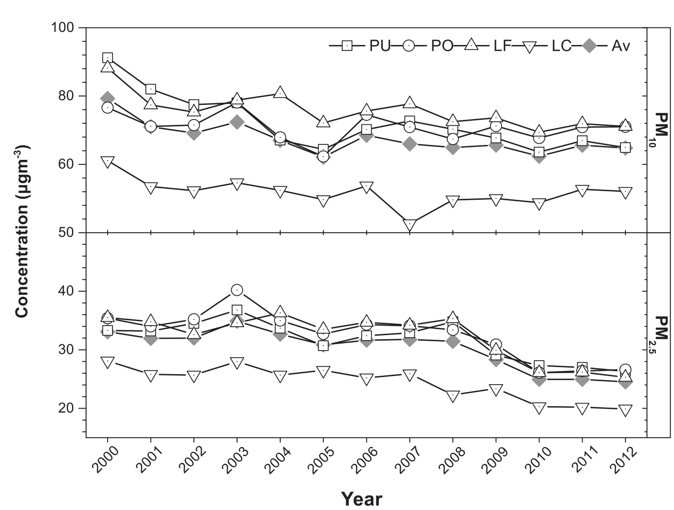

Fig. 2. Annual PM_{10} and $PM_{2.5}$ concentrations in μg m^{-3} for the stations under study (PU: Pudahuel; PO: Parque O'Higgins; LF: La Florida; LC: Las Condes and Av: Average of all stations) in the period 2000–2012.

A general decline in the $PM_{2.5}$ and PM_{10} concentrations was observed leading up to 2005, while an increase occurred from 2007 and 2008 to 2009; this behavior is due to the restriction of natural gas imports from Argentina, forcing industry to convert to other liquid fuels, such as petroleum products or diesel. This conversion increased gas emissions (NO_x and SO_2), leading to increased $PM_{2.5}$ yearly means for 2007 and 2008. Although the annual concentrations showed a downward trend, this trend turns out not to be statistically significant. ANOVA analysis of the comparison between annual records of PM_{10} (p-value > 0.05) and $PM_{2.5}$ (p-value > 0.05) found no significant differences at a 95% confident interval.

Since the implementation of the Plan of Prevention and Decontamination of Atmospheric Pollution (PPDA) for SMA, curbing measures have included the introduction of natural gas (industrial sector), a reduction in sulfur content in diesel (from 5000 ppm in 1989 to 1000 ppm in 1997, and further to 300 ppm in 2001), the introduction of emission controls for vehicles and the phasing out of old buses. These measures explain the relatively rapid reduction in PM_{10} between 1997 and 2002 [10]. A second revision of the attainment plan was released in 2004, emphasizing emission control for vehicles, a reduction in diesel sulfur content to 50 ppm and the failed introduction of an ambitious public transportation system called Transantiago. However, from 2000 to 2012, the number of cars in SMA grew by 50% to 1.5 million [6]. This growth most likely accounts for the lack of substantial reductions in pollutant levels despite the improvements in fuel and vehicle technology over the same period.

3.2. PM_{10} and $PM_{2.5}$ seasonal, monthly and daily concentration levels

The PM_{10} and $PM_{2.5}$ concentrations and the $PM_{2.5}/PM_{10}$ ratio time series measured on a monthly and daily basis at the monitoring site under study are shown in Fig. 3. Seasonal fluctuations of PM_{10} and $PM_{2.5}$ were observed at all stations studied, showing that values in the spring–summer seasons (October–March), i.e., the warm period, are lower than the values recorded in autumn–winter (April–September), i.e., the cool period. In general, the highest PM concentrations occur in the months of May, June and July. The ANOVA analysis of the data grouped into warm and cold seasons and monthly periods shows statistically significant differences, i.e., the PM_{10} and $PM_{2.5}$ p-values are higher than 0.05, suggesting that the source of variance is the differences between warm and cool seasons and months. The large levels of PM observed during both cool and warm periods can be explained by two main factors: i) the prevalence of the Pacific anticyclonic meteorological conditions with a permanent subsidence and thermal inversion layer and mixing heights of approximately 400 m in winter and 1000 m in summer [12] and ii) increasing emissions in winter due to the use of combustion sources for heating [2]. In SMA, wood burning accounts for 49% of the primary wintertime $PM_{2.5}$ emissions.

In the daily variations, during the warm period (October–March) for both PM_{10} and $PM_{2.5}$, maximum concentrations were observed after sunrise (6:00–9:00) and in the evening (18:00–21:00). The $PM_{2.5}/PM_{10}$ ratio shows a peak in the morning at all stations, while the minimum value occurs during the afternoon. In this period, $PM_{2.5}$ represents approximately 45% $\pm$ 5% of the total PM_{10}. The cold period (April–September) shows greater daily variability than the warm period. In general, the PM peaks are observed in the morning (6:00–9:00) and during the evening and night (18:00–03:00). The $PM_{2.5}/PM_{10}$ ratio exhibits similar behavior at PU, LF and PO with a maximum at approximately 6:00–9:00 and other maxima throughout the evening and night (18:00–03:00). The contribution of fine particles is above 60% $\pm$ 10% of the total PM_{10}, i.e., $PM_{2.5}/PM_{10}$ ranged from 0.6 to 0.7. This behavior can be explained by the fact that in the warm period, emissions come from vehicular sources and occur during daylight at the rush hours,

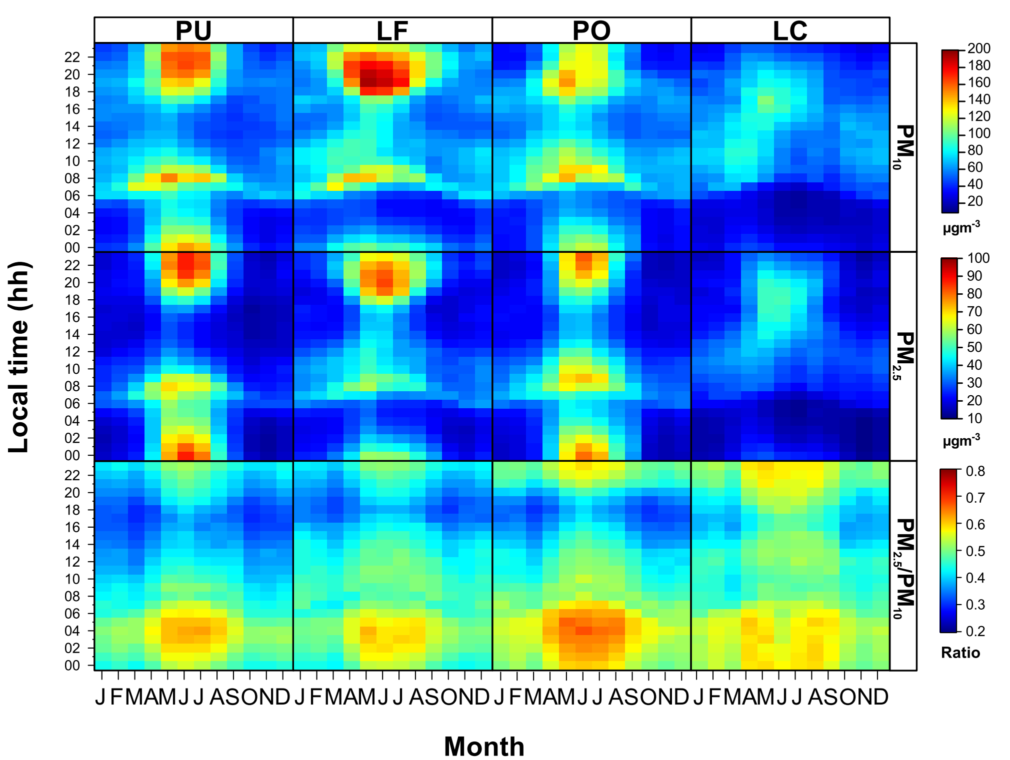

Fig. 3. Hourly and monthly time series of PM_{10} and $PM_{2.5}$ concentrations in µg m^{-3}, for the stations under study (PU: Pudahuel; PO: Parque O'Higgins; LF: La Florida; LC: Las Condes) during 2000–2012. The plots show average concentrations on the hour, beginning at the hour.

i.e., the morning (6:00–9:00) and afternoon (17:00–21:00), and good atmospheric conditions allow the dispersion of pollutants. In contrast, during the cold periods, in addition to vehicle exhaust emissions, the burning of biomass for heating produces emissions that are an important source of PM, and commonly occurring unfavorable atmospheric dispersion conditions allow the increase of PM concentrations in this period.

3.3. PM_{10} and $PM_{2.5}$ correlations for paired sites

Table 2 shows the inter-site Pearson correlation coefficients of PM_{10i} vs. PM_{10j}, $PM_{2.5i}$ vs. $PM_{2.5j}$ and $PM_{2.5i}$ vs. PM_{10j} (hourly data) concentrations. In general, the concentrations for each particle fraction (PM_{10i} vs. $PM_{2.5i}$) at the same site are all significantly correlated ($0.89 \geq r \geq 0.79$), indicating that the PM_{10} and $PM_{2.5}$ concentrations should come from similar emission sources. The concentrations for each particle fraction (PM_{10i} vs. PM_{10j} and $PM_{2.5i}$ vs. $PM_{2.5j}$) between paired type-sites are correlated by height for PU-LF, PU-PO, LF-PO and LF-LC (PM_{10i} vs. PM_{10j}: $0.89 \geq r \geq 0.79$; $PM_{2.5i}$ vs. $PM_{2.5j}$: $0.73 \geq r \geq 0.55$), which implies that a common factor affects the PM concentration whether the location is a roadside, residential or industrial site. The exception is the paired LC-PU and LC-PO stations ($0.21 \geq r \geq 0.40$); in these cases, the pollution appears to be substantially affected by local factors, and the LC station recorded lower $PM_{2.5}$ and PM_{10} concentrations in relation to the other stations. These results indicate that the $PM_{2.5}$ and PM_{10} concentrations are not uniform throughout the city.

Coefficients of divergence (COD) were calculated to describe the relative interurban concentration heterogeneity between sites. The COD is defined mathematically as follows:

$$COD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{x_{ij}-x_{ik}}{x_{ij}+x_{ik}}\right)^2}$$

where x_{ij} and x_{ik} represent the 1-h average particulate concentration for sampling day i at sampling sites j and k, and p is the number of observations [26]. The COD values range between 0 and 1, with zero values indicating the same concentrations at both sites and 1 indicating different concentrations. The results of the statistical summary of COD for the paired sites appear in Fig. 4 for PM_{10} and $PM_{2.5}$ 1-h concentrations for all periods under study and for both the cool and warm seasons.

Table 2
Site and inter-site Pearson correlation coefficients of PM_{10} vs. PM_{10}, $PM_{2.5}$ vs. $PM_{2.5}$ and $PM_{2.5}$ vs. PM_{10} (hourly data) between paired monitoring stations (PU: Pudahuel; PO: Parque O'Higgins; LF: La Florida; LC: Las Condes).

Variable	Station	PM_{10}			
		PU	LF	PO	LC
PM_{10}	PU	1.00	0.59	0.71	0.24
	LF	–	1.00	0.67	0.52
	PO	–	–	1.00	0.40
	LC	–	–	–	1.00
$PM_{2.5}$	PU	0.89	–	–	–
	LF	–	0.85	–	–
	PO	–	–	0.82	–
	LC	–	–	–	0.79
Variable	Station	$PM_{2.5}$			
		PU	LF	PO	LC
$PM_{2.5}$	PU	1.00	0.55	0.73	0.21
	LF	–	1.00	0.65	0.60
	PO	–	–	1.00	0.36
	LC	–	–	–	1.00

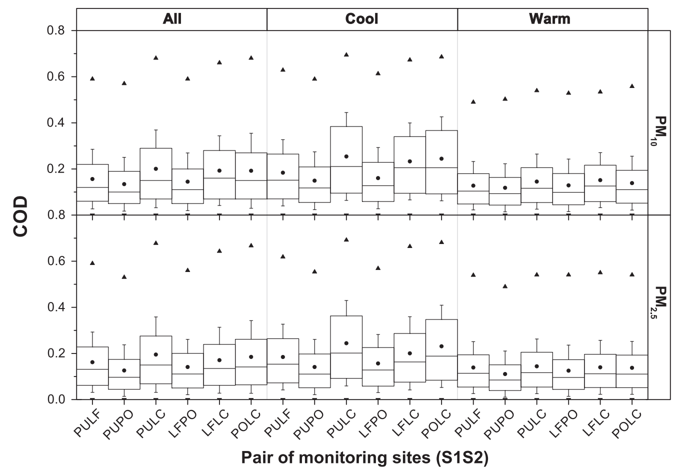

Fig. 4. Inter-site coefficients of divergence (CODs) calculated for PM_{10} and $PM_{2.5}$ 1-h concentrations.

The results showed a relative spatial uniformity for both fractions of PM at the paired sites. It may also be observed that the COD for the cold season is higher than for the warm season. The pairs PU-LC, LF-LC and PO-LC show higher COD values, indicating that there are greater differences among PU, PO and LF with respect to LC.

3.4. Theil–Sen estimated trends

Estimates of long-term trends based on the Theil–Sen estimator were performed for the averages of time series data for all seasons and for subsets of the data, including the cool and warm season time series for each station and the average of all stations under study. The estimated de-seasoned trends are summarized in Table 3. In general, the results show a decreasing trend for PM_{10} mass concentrations when all years are considered, ranging from -0.47 to -1.89% year^{-1}. No significant trends are identified at the 95% confidence level for PO in the cool or warm periods; note that the 95% confidence intervals include zero slope. On the other hand, no differences in the trends are identified at the 95% confidence level for the warm and cool season time series. The $PM_{2.5}$ concentrations show similar trends to PM_{10}, i.e., a decreasing trend, but are more pronounced, ranging from -1.82 to -2.31% year^{-1}. A significant trend was identified at the 95% confidence level for the $PM_{2.5}$ concentration time series for all stations.

3.5. Effects of meteorological variables

Table 4 shows the meteorological parameters recorded in SMA during warm and cold periods between 2000 and 2012. SMA has registered an average temperature of 12.4 °C in cool period and 19.9 °C in warm period. Lower temperatures in cool periods are crucial to produce thermal inversions by surface cooling, which prevent the vertical mixing and promote the occurrence of air pollution episodes.

Relative humidity recorded an average of 67.8% and 54.8% in warm and cold periods, respectively. The wind speed reaches a maximum average in PU station during warm periods (2.3 m/s). However, at the other stations remains at average values of 1.4 m/s in warm periods and 1.1 m/s in cold periods. In general, parameters studied showed no significant differences between sites, except for wind direction in the LC site, which by its altitude and proximity to the Andes Mountain exhibit a particular behavior.

Table 3
Summary of the time trend analysis using the de-seasoned Theil–Sen method. The table shows the median slope in % year^{-1}. The 95% confidence interval of the slope and p trend indicate statistically significant results (PU: Pudahuel; PO: Parque O'Higgins; LF: La Florida; LC: Las Condes).

Season	Station	PM_{10}			$PM_{2.5}$		
		Slope (% year^{-1})	95 CI (% year^{-1})	p	Slope (% year^{-1})	95 CI (% year^{-1})	p
Overall	PU	−1.89	−2.29 to −1.41	0.001	−1.82	−2.19 to −1.45	0.001
	LF	−1.24	−1.59 to −0.79	0.001	−2.16	−2.54 to −1.70	0.001
	PO	−0.47	−0.89 to 0.05	0.05	−2.05	−2.53 to −1.52	0.001
	LC	−0.97	−1.38 to −0.48	0.001	−2.31	−2.74 to −1.90	0.001
Warm	PU	−2.46	−2.82 to −2.11	0.001	−1.96	−2.36 to −1.53	0.001
	LF	−1.58	−1.89 to −1.31	0.001	−1.80	−2.21 to −1.33	0.001
	PO	−0.31	−0.76 to 0.10	0.05	−2.09	−2.50 to −1.54	0.001
	LC	−1.06	−1.46 to −0.65	0.001	−2.01	−2.4 to −1.72	0.001
Cool	PU	−1.74	−2.22 to −1.29	0.001	−2.13	−2.51 to −1.85	0.001
	LF	−1.05	−1.59 to −0.54	0.001	−2.79	−3.03 to −2.39	0.001
	PO	−0.55	−1.07 to 0.00	0.05	−2.61	−3.04 to −2.18	0.001
	LC	−0.98	−1.65 to −0.33	0.001	−3.17	−3.43 to −2.68	0.001

Table 5 shows the correlation coefficient between $PM_{2.5}/PM_{10}$ and the meteorological variables (temperature, relative humidity, wind speed and velocity). A negative correlation was found between $PM_{2.5}/PM_{10}$ and atmospheric temperature. In general, the correlation is stronger in the cool season compared to the warm season (the correlation coefficient ranges from −0.53 to −0.34 and from −0.34 to −0.15 for the cool and warm seasons, respectively). In the case of the relationship with relative humidity, a positive correlation was observed. Similar to temperature, the correlation with RH is stronger in the cool season compared to the warm season (the correlation coefficient ranges from −0.57 to −0.39 and from −0.42 to −0.34 for the cool and warm seasons, respectively). These correlations are thought to be due to the effects of temperature and relativity humidity on the formation of new particles with an aerodynamic diameter less than 2.5 μm through gas-to-particle conversion processes. In this sense, the meteorological conditions in the cool seasons are more favorable to the formation of new particles than the warm season.

Two environmental factors that reduce the effects of air pollution are generated: wet deposition by rain and dry deposition achieved by dew [16]. Santiago has a frequency of rain 20 days/year, occurring mainly between the months of May to September. The oscillation of drought and abundance is about four years alternately. The last study year (2012) has proved to be rather dry characteristics, with 150.3 mm of rainfall, with its deficit of −40 mm relative to a normal year. Its annual average of rainfall in the last decade, found to be 263.1 mm [4].

Fig. 5 shows the bivariate polar plot for the mean concentrations of PM_{10} and $PM_{2.5}$ for the sites under study during the warm and cold periods. The polarPlot option in Openair was used [17]. High concentrations of PM_{10} and $PM_{2.5}$ were observed during the cool period and in calm wind conditions for PU, PO and LF, indicating that local emissions are a significant contributor to the concentration of PM during critical events. The LC site presents a unique behavior in which the concentration peaks of PM for both fractions occur at high wind speed (>2 m/s) during the cool season, which could be explained by the transport of polluted air masses from the city center. In contrast, during the warm season, for all stations under study, the transport of polluted air masses is the most important contributor to PM during critical events, as the warm season presents the best conditions for pollution dispersion.

3.6. Air pollution assessment

Fig. 6 shows the ranking of the PM_{10} and $PM_{2.5}$ concentrations in different cities around the world according to the 2011 WHO Urban outdoor air pollution database [25], the average PM concentrations in SMA during the study period and a statistical summary of the PM concentrations (maximum, minimum, mean and standard deviation). SMA is one of the most polluted cities in terms of PM in South America and throughout the world. SMA is ranked at 135 ± 25 of 1100 cities and 14 ± 5 of 577 cities for PM_{10} and $PM_{2.5}$, respectively.

PM_{10} levels in SMA (68 ± 11 μg m^{-3}, average 2000–2012) are approximately twice the average concentration (36 μg m^{-3}) of all the cities listed in the WHO database and are similar to the values in Guangzhou (70 μg m^{-3}), Hohhot (74 μg m^{-3}) and Guiyang (74 μg m^{-3}), China; Lima (78 μg m^{-3}), Peru; Bogota (77 μg m^{-3}), Colombia; Zona Metropolitana de Monterrey (76 μg m^{-3}) and Zona Metropolitana del Valle de Toluca (66 μg m^{-3}), México; Shiraz (70 μg m^{-3}), Iran and Seoul (64 μg m^{-3}), Republic of Korea. SMA's concentrations are approximately twice as high as Moscow (33 μg m^{-3}), Russia; Lisbon (30 μg m^{-3}), Portugal; London

Table 4
Meteorological parameters recorded in the four stations in study during cool and warm periods (2000–2012). Values expressed as Mean ± SD for temperature (T°), relative humidity (RH), wind speed (WS) and wind direction (WD).

Season	Station	T° (°C)	RH (%)	WS (m/s)	WD (degrees)
Overall	PU	16.4 ± 6.8	62.7 ± 21.7	1.8 ± 1.4	204.4 ± 69.3
	LF	16.1 ± 7.1	59.8 ± 22.1	1.0 ± 0.6	200.7 ± 80.8
	PO	16.1 ± 6.9	62.2 ± 21.1	1.3 ± 0.9	206.2 ± 61.1
	LC	15.5 ± 6.8	60.7 ± 21.2	1.3 ± 0.7	157.0 ± 87.0
Warm	PU	20.3 ± 5.9	55.1 ± 20.4	2.3 ± 1.5	207.7 ± 47.3
	LF	20.1 ± 6.2	52.2 ± 20.4	1.1 ± 0.7	213.4 ± 78.1
	PO	20.0 ± 6.1	54.8 ± 19.7	1.6 ± 1.0	221.0 ± 39.3
	LC	19.1 ± 6.1	57.0 ± 20.3	1.4 ± 0.7	171.2 ± 79.2
Cool	PU	12.7 ± 5.4	70.2 ± 20.4	1.3 ± 1.0	201.3 ± 85.0
	LF	12.4 ± 5.8	67.3 ± 21.0	0.9 ± 0.5	188.6 ± 81.5
	PO	12.3 ± 5.5	69.4 ± 20.0	1.0 ± 0.7	192.2 ± 73.4
	LC	12.0 ± 5.6	64.4 ± 21.4	1.3 ± 0.7	143.5 ± 91.8

Table 5
Pearson's correlation analysis between the $PM_{2.5}/PM_{10}$ ratio, T and RH during cool and warm periods (2000–2012) (PU: Pudahuel; PO: Parque O'Higgins; LF: La Florida; LC: Las Condes).

Station	Parameter	$PM_{2.5}/PM_{10}$	
		Cool	Warm
PU	T°	−0.53	−0.34
	RH	0.57	0.40
LF	T°	−0.38	−0.15
	RH	0.44	0.21
PO	T°	−0.47	−0.34
	RH	0.52	0.42
LC	T°	−0.36	−0.29
	RH	0.39	0.34

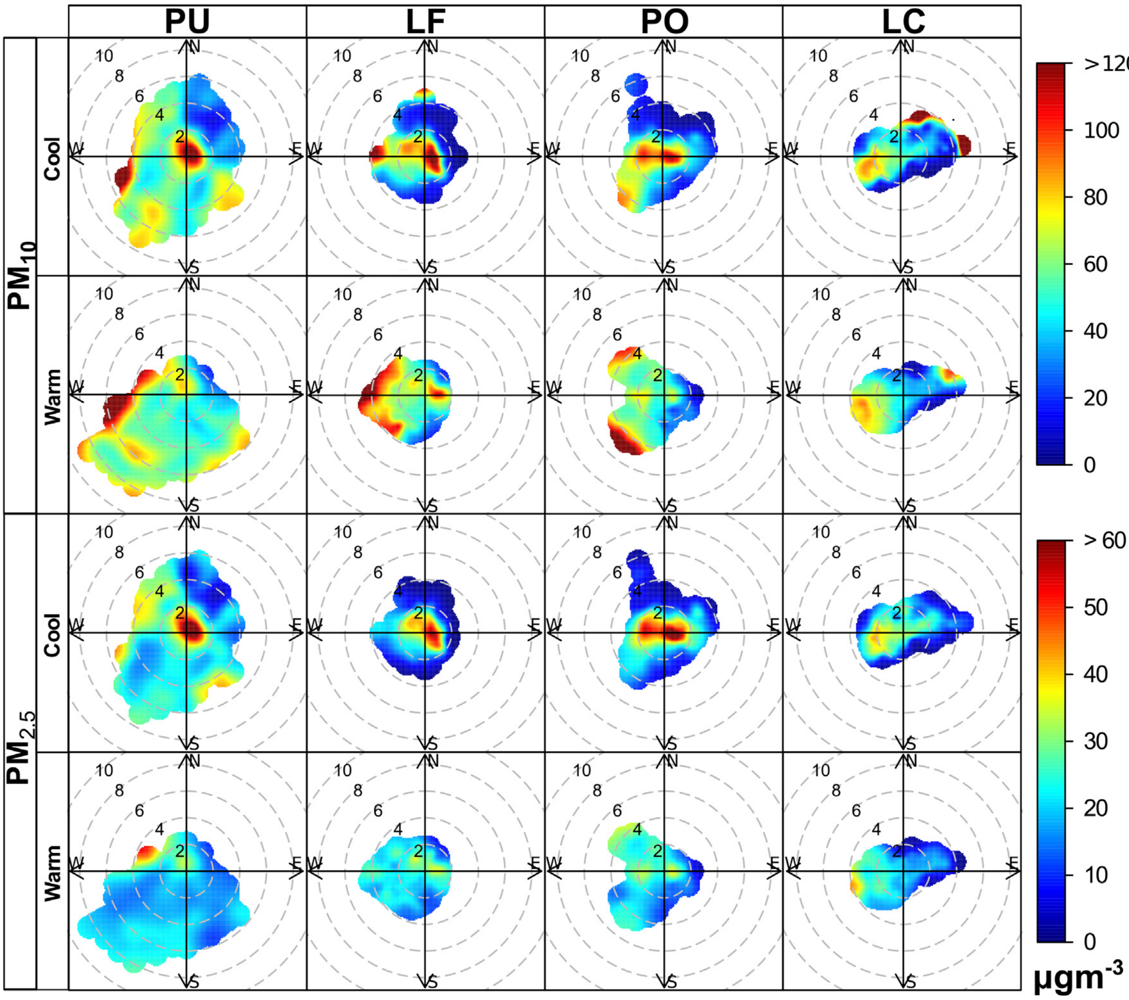

Fig. 5. Bivariate polar plot for the 1-h mean mass concentrations of PM_{10} and $PM_{2.5}$ in µg m^{-3} for the sites under study in the cold and warm seasons (PU: Pudahuel; PO: Parque O'Higgins; LF: La Florida; LC: Las Condes).

(29 µg m^{-3}), United Kingdom; Osaka (27 µg m^{-3}), Japan and Berlin (26 µg m^{-3}), Germany. The $PM_{2.5}$ levels in SMA (30 ± 5 µg m^{-3}, average 2000–2012) are approximately three times the average concentration (11 µg m^{-3}) of all cities listed in the database and are similar to concentrations observed in the cities of Lima (34.2 µg m^{-3}), Peru; Milan (31.7 µg m^{-3}), Italy; Beirut (31.0 µg m^{-3}), Lebanon; and Athens (27.4 µg m^{-3}), Greece; and these values are about twice as high as in the cities of Stuttgart (15.5 µg m^{-3}), Germany; Região Metropolitana Sao Paulo (15.0 µg m^{-3}), Brazil; Los Angeles-Long Beach-Santa Ana (14.8 µg m^{-3}), CA, USA; Toledo

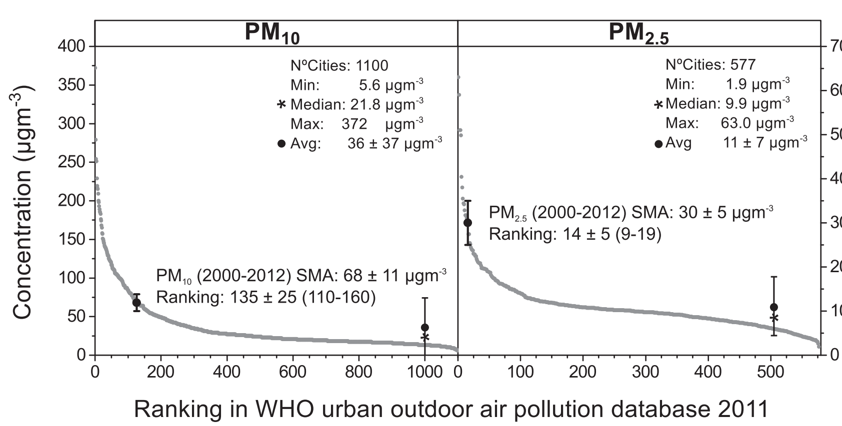

Fig. 6. Ranking of concentrations of particulate matter (PM_{10} and $PM_{2.5}$) in different cities around the world [25].

(14.0 μg m^{-3}), Spain; London (13.5 μg m^{-3}), UK; Madrid (13.1 μg m^{-3}), Spain and New York – Northern New Jersey – Long Island (12.7 μg m^{-3}), NY – NJ – PA, USA.

According to the WHO guidelines and Chilean regulations, the annual mean PM_{10} concentrations in SMA exceed the limits of 20 μg m^{-3} [24] and 50 μg m^{-3} [9]. The threshold concentration was exceeded by 3.6 and 1.4 times at the stations of PU, PO and LF and by 2.6 and 1.4 times at LC, respectively, for the WHO and MMA standards. For $PM_{2.5}$, the WHO guidelines (10 μg m^{-3}) and MMA regulations (20 μg m^{-3}) were exceeded for all stations during the period of study. The $PM_{2.5}$ WHO guideline was exceeded by a factor of 3.3 at PU, PO and LF and by 2.4 times at LC. The $PM_{2.5}$ MMA regulation was exceeded by a factor of 1.6 at PU, PO and LF and by 1.2 times at LC.

Table 6 shows the percentages of days when the daily mean of PM_{10} and $PM_{2.5}$ concentrations exceeded the daily threshold, according to the WHO guidelines and MMA regulations. The results listed in the table show that the limits established by the WHO guidelines and MMA regulations are routinely exceeded at all reported stations. In general, the percentage of exceeded days per year for the PM_{10} and $PM_{2.5}$ WHO guidelines is above 50%; the greatest exceedances are observed in LF, followed by PU and PO, while the lowest are observed in LC. For the PM_{10} and $PM_{2.5}$ MMA regulations, the percentage of the exceeded days per year ranges from 0.2% to 10.1% for PM_{10} and from 5.6% to 23.2% for $PM_{2.5}$. Similar to the WHO guideline, the maximum rate of exceedances for both fractions of PM with respect to MMA regulations is observed at PO, PU and LF, while the lowest percentage of exceedances occurs at LC. A decrease in exceedances from 2000 to 2012 was observed for all stations and for both fractions of PM, but the recorded values still exceeded the limits established in the MMA regulations and WHO guidelines.

The largest number of days that exceeded the WHO guidelines and MMA regulations for both fractions was registered during the coldest part of the year (Fig. 3), i.e., April–September. The smallest concentrations were registered from October to March, i.e., the warm season. The elevated concentrations of PM observed during the cool season are related mainly to domestic heating and fossil fuel combustion. Meteorological conditions such as a stable boundary layer and low wind speeds during winter anticyclone systems favor particulate matter accumulation during its increased production (Fig. 5).

4. Conclusions

The urban atmosphere of SMA is severely polluted by PM_{10} and $PM_{2.5}$. The annual PM_{10} mass concentration averages range between 76 ± 5 μg m^{-3} and 32 ± 4 μg m^{-3}. The largest PM_{10} concentrations were observed at LF (76 ± 5 μg m^{-3}), PU (72 ± 8 μg m^{-3}) and PO (71 ± 5 μg m^{-3}), and the lowest concentration was observed at LC (52 ± 4 μg m^{-3}). For $PM_{2.5}$, the annual concentrations range between 33 ± 4 μg m^{-3} and 24 ± 3 μg m^{-3}. The largest $PM_{2.5}$ concentrations were observed at PU, PO and LF (≈33 ± 4 μg m^{-3}), and the lowest was observed at LC (24 ± 3 μg m^{-3}). The LC station has significantly different values from the other stations for the annual concentrations of both PM fractions.

The high daily concentrations of both fractions of PM observed during both cool and warm periods can be explained by two main factors: i) the prevalence of the Pacific anticyclonic meteorological conditions with a permanent subsidence and thermal inversion layer and ii) increased emissions in winter due to the use of combustion sources for heating. The daily variability shows that the maximum hourly concentration occurs during the nights and early mornings because of the low temperatures and the daily previous accumulation of primary particles and secondary particulate precursors. $PM_{2.5}$ represents approximately 45% ± 5% and 60% ± 10% of PM_{10} during the warm and cold periods, respectively.

Estimates of long-term trends based on the Theil–Sen estimator show a decreasing trend for PM_{10} mass concentrations when all years are considered, ranging from −0.47 to −1.89% year^{-1}. The $PM_{2.5}$ concentrations show a similar trend to PM_{10}, i.e., a decreasing trend, but are more pronounced, ranging from −1.82 to −2.31% year^{-1}. For the city, the comprehensive air pollution level has declined gradually, illustrating that the air quality in Santiago, Chile improved in the last decade. However, despite this historical decline in PM concentrations, the national air quality standards were still exceeded in 2012, indicating the need to update and strengthen the policies and strategies to control particulate matter pollution and its precursors in the city of Santiago.

SMA is one of the cities most heavily polluted by PM in South America and worldwide. SMA is ranked 135 ± 25 of 1100 cities and 14 ± 5 of 577 cities for PM_{10} and $PM_{2.5}$, respectively. The PM_{10} levels in SMA (68 ± 11 μg m^{-3}, average 2000–2012) are approximately twice the average concentration (36 μg m^{-3}) in all the cities listed

Table 6
Annual exceedances (in % of days per year) of the 24-h Chilean air quality standards (MMA) and World Health Organization guidelines (WHO) at the monitoring sites under study (PU: Pudahuel; PO: Parque O'Higgins; LF: La Florida; LC: Las Condes), for the period 2000–2012.

Year	PM_{10}								$PM_{2.5}$							
	WHO (50 μg m^{-3})				MMA (150 μg m^{-3})				WHO (25 μg m^{-3})				MMA (50 μg m^{-3})			
	PU	LF	PO	LC	PU	LF	PO	LC	PU	LF	PO	LC	PU	LF	PO	LC
2000	94.3	94.5	86.1	77.3	17.2	12.6	11.7	1.4	64.5	79.5	70.5	60.7	25.4	28.4	29.2	14.8
2001	89.9	94.0	88.2	75.9	11.5	3.6	7.4	0.3	63.0	88.2	71.5	60.3	25.8	21.4	26.6	6.3
2002	87.9	92.3	86.0	73.7	14.2	6.0	9.0	0.0	61.1	72.9	70.1	58.4	27.1	20.8	28.5	7.7
2003	87.9	96.7	91.8	70.4	12.3	3.8	11.5	0.5	68.2	72.9	74.2	62.7	32.6	25.5	35.1	11.5
2004	81.7	91.5	79.8	67.2	5.7	7.9	4.9	0.3	64.2	82.2	68.9	56.0	24.6	29.0	27.9	7.7
2005	73.4	91.0	72.1	67.1	7.1	4.1	4.1	0.0	64.7	82.7	73.7	69.6	20.0	23.0	20.5	6.0
2006	74.2	89.6	87.7	71.5	10.4	8.5	9.0	0.0	61.4	79.2	73.4	55.9	23.3	21.1	23.6	5.8
2007	77.8	91.5	81.1	46.6	14.8	9.9	10.4	0.0	57.8	78.6	66.6	54.0	26.8	21.6	26.0	8.8
2008	76.5	90.2	80.6	56.8	10.1	3.3	5.5	0.3	68.6	85.5	70.5	38.0	24.3	24.6	24.0	0.3
2009	77.8	90.7	87.9	59.2	8.5	2.5	4.4	0.0	57.8	74.2	70.4	52.3	18.4	9.6	18.4	3.8
2010	65.2	87.4	81.6	61.9	5.2	1.6	2.2	0.0	47.7	55.1	48.8	32.9	16.7	8.2	14.0	0.3
2011	76.4	89.3	86.3	71.5	7.1	2.2	6.3	0.0	45.8	53.2	53.7	31.8	16.7	10.4	13.2	0.3
2012	69.4	85.5	83.6	67.8	7.7	4.6	6.3	0.0	48.4	53.6	54.1	36.6	16.7	6.8	14.5	1.1
Average	79.4	91.1	84.1	66.7	10.1	5.4	7.1	0.2	59.5	73.7	66.6	51.5	23.0	19.3	23.2	5.7
SD	8.5	3.0	5.1	8.6	3.7	3.3	3.0	0.4	7.7	12.1	8.6	12.4	4.9	7.8	6.7	4.5

in the WHO database. The $PM_{2.5}$ levels in SMA ($30 \pm 5\ \mu g\ m^{-3}$, average 2000–2012) are approximately three times the average concentration ($11\ \mu g\ m^{-3}$) in all the cities listed in the WHO database.

According to both the WHO guidelines and the Chilean regulations, the threshold annual and daily concentrations for both fractions of PM were exceeded systematically at all monitoring stations. The exceeded days per year for PM_{10} and $PM_{2.5}$ were above 50% according to WHO guidelines. Similarly, the maximum rate of exceedances for both fractions of PM with respect to MMA regulations was 23%. A decrease in exceedances from 2000 to 2012 was observed for all stations and for both fractions of PM, but the values still exceeded the limits established in the MMA regulations and WHO guidelines.

Improving air quality obeys rather to mitigation measures implemented in the last decade in SMA and the response – often late – to the problem of air pollution that suffer its inhabitants. Such measures include the renewal of the public transport system, updating the euro emission standards from mobile sources, the implementation of regulations to certify emissions from stationary sources, mobile sources and vehicular restriction during critical episodes of contamination, that have been effective in the past decade. However, extrapolating into the future the percentages per year obtained for each fraction of particles, it can project that SMA will comply within 20 years the annual standards for $PM_{2.5}$ and MMA for 25 years corresponding to the PM_{10} fraction. The same projection for annual WHO standards indicates that SMA meet on 35 and 60 years such standards for $PM_{2.5}$ and PM_{10}, respectively.

We think that these periods show the existence of local policies and responses to crisis events, rather than national or regional policies being completely and permanently associated to health impacts. Moreover, in this work it is presented results collected in 4 monitoring stations, which represent a very small surface area of Santiago. Therefore it is required to strengthen and to extend the application of the policies and strategies of air quality management, including, strategic planning construction, the design of sustainable urban areas, periodic evaluation of past policies and fortify the association with health impact and many others. They have argued that the extension of these local policies cannot be profitable. However, recent studies also reported that the cost of health impact in European cities has been estimated at 23 billion euros. So in this area also need to incorporate a more complete model of the associated economic impacts, in order to make more broadly applicable air quality policies. We believe these measures will significantly accelerate time to comply with the above standards.

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