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Chemical speciation and source apportionment of fine particulate matter in Santiago, Chile, 2013

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HIGHLIGHTS

- Strong seasonal trends in $PM_{2.5}$ and source contributions, highest levels in winter
- In winter, the most important sources of $PM_{2.5}$ were wood smoke and nitrate.
- In fall and winter, wood smoke contributed around 60% of OC and 20% of $PM_{2.5}$.
- Secondary inorganic ions accounted for about 30% of $PM_{2.5}$ in fall and winter.
- Secondary organic aerosols contributed significantly to $PM_{2.5}$ in summer and spring.

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ABSTRACT

Santiago is one of the largest cities in South America and has experienced high fine particulate matter ($PM_{2.5}$) concentrations in fall and winter months for decades. To better understand the sources of fall and wintertime pollution in Santiago, $PM_{2.5}$ samples were collected for 24 h every weekday from March to October 2013 for chemical analysis. Samples were analyzed for mass, elemental carbon (EC), organic carbon (OC), water soluble organic carbon (WSOC), water soluble nitrogen (WSTN), secondary inorganic ions, and particle-phase organic tracers for source apportionment. Selected samples were analyzed as monthly composites for organic tracers. $PM_{2.5}$ concentrations were considerably higher in the coldest months (June–July), averaging (mean ± standard deviation) 62 ± 15 μg/m^3 in these two months. Average fine particle mass concentration during the study period was 40 ± 20 μg/m^3. Organic matter during the peak winter months was the major component of fine particles comprising around 70% of the particle mass. Source contributions to OC were calculated using organic molecular markers and a chemical mass balance (CMB) receptor model. The four combustion sources identified were wood smoke, diesel engine emission, gasoline vehicles, and natural gas. Wood smoke was the predominant source of OC, accounting for 58 ± 42% of OC in fall and winter. Wood smoke and nitrate were the major contributors to $PM_{2.5}$. In fall and winter, wood smoke accounted for 9.8 ± 7.1 μg/m^3 (21 ± 15%) and nitrate accounted for 9.1 ± 4.8 μg/m^3 (20 ± 10%) of fine PM. The sum of secondary inorganic ions (sulfate, nitrate, and ammonium) represented about 30% of $PM_{2.5}$ mass. Secondary organic aerosols contributed only in warm months, accounting for about 30% of fine PM during this time.

1. Introduction

Large urban cities in Latin America, like Santiago (Chile), Sao Paulo (Brazil), and Mexico City (Mexico), have been facing serious air pollution problems because of population and industry growth, as well as increasing numbers of motor vehicles (Bell et al., 2006). Numerous studies have shown the negative effects on human health resulting from high levels of particulate matter, such as respiratory problems and premature death from cardiovascular disease (Analitis et al., 2006; Dockery and Stone, 2007; Pope and Dockery, 2006; Pope et al., 2004). Due to the evidence of these adverse effects, the World Health Organization (WHO) recommends a 24-h standard of 25 μg/m^3 for $PM_{2.5}$ (WHO, 2005), which are particles with an aerodynamic diameter of less than 2.5 μm.

Santiago is the largest city in Chile and has about 6 million inhabitants (approximately 40% of the Chilean population). Santiago is located in subtropical South America (33°27′S, 70°40′W) between a coastal range to the west (height ~ 1000 m.a.s.l., meters above sea level) and the Andes mountain range to the east (heights above 3000 m.a.s.l.). Transport of pollution in Santiago's basin is controlled by the surrounding topography, persistence of subsidence conditions and associated low

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Table 1
Summary of previous source apportionment results carried out at Santiago.

Reference	Dates/location/mean $PM_{2.5}$ ($\mu g/m^3$)	Methodology	Results
Rojas et al. (1990)	West center, January–February 1987; 34 ($\mu g/m^3$)	Dichotomous sampler; XRF analysis of filters. Principal Factor Analysis for source apportionment.	Sulfates: 49%; wood burning and traffic: 26%; residual oil combustion: 13%; soil dust and metal works: 6.4%; soil dust and wood burning: 5.6%
Artaxo (1996)	Center, July–August 1996; 54.4 ($\mu g/m^3$)	SFU filter samples with PIXE analysis. Absolute Principal Factor Analysis for Source Apportionment.	Sulfates and industry: 64%; motor vehicles: 16%; soil dust: 15.5%; copper smelter: 8.7%; residual oil combustion: 1.9%
Artaxo (1998)	Center, July–August 1998; 39.7 ($\mu g/m^3$)	SFU filter samples with PIXE analysis. Absolute Principal Factor Analysis for Source Apportionment.	Motor vehicles: 35.8%; soil dust: 31.3%; residual oil combustion and industry: 23.2%; Sulfates and copper smelter: 9.7%;
Artaxo (1999)	Center, 27 June–1st December 1999; 28 ($\mu g/m^3$)	SFU filter samples with PIXE analysis and BC measurements. Absolute Principal Factor Analysis for Source Apportionment.	Motor Vehicles: 40%, Sulfates + As: 39%, Soil dust: 17%, Metal works: 4%
	East, 26 June–30 November 1999; 34 ($\mu g/m^3$)		Motor vehicles + industry: 70%, Sulfates + As: 15%, Soil dust: 7%
Gramsch (2005)	Center, July–August 2001; 61.4 ($\mu g/m^3$)	Speciation Sampler 2300 for chemical characterization, SFU samples with PIXE elemental analyses.	Nitrate: 19%; sulfate: 8%; ammonia: 12%; EC: 22%; OC: 15%; chlorine: 2%
	Center, July–August 2003; 69.4 ($\mu g/m^3$)		Nitrate: 15%; sulfate: 5%; ammonia: 7%; EC: 10%; OC: 33%; chlorine: 2%
	Center, July–August 2005;44.2 ($\mu g/m^3$)		Nitrate: 18%; sulfate: 8%; ammonia: 17%; EC: 11%; OC: 36%; chlorine: 4%
Jorquera and Barraza (2012)	East, June–December 1999 (reanalysis of Artaxo's, 1999 data set); 34 ($\mu g/m^3$)	PMF3 on filter analyses of trace elements + BC; back trajectory analyses to confirm sources.	Motor vehicles: 28%; wood burning: 25%; sulfates: 19%; marine aerosol: 13%; copper smelters: 11%; soil dust: 4%
	East, January–December 2004; 25 ($\mu g/m^3$)		Motor vehicles: 31%; wood burning: 29%; sulfates: 16%; marine aerosol: 10%; copper smelters: 10%; soil dust: 4%

mixing heights (Muñoz and Undurraga, 2010), and thermally driven winds that peak in the warmer months. Southwesterly winds occur during daytime both in winter (Rutllant and Garreaud, 2004) and summer (Schmitz, 2005; Viale and Garreaud, 2013). In summertime conditions, pollutants from Santiago are transported towards the northeast out of the basin by up-slope winds reaching up to 4000 m (Schmitz, 2005). The climate is Mediterranean with dry spring and summer seasons and wet fall and winter seasons as shown in Supplementary Table 1 for year 2013.

The city has been facing air pollution problems for more than three decades. The poor air quality is believed to be the result of the growing industrial sector, fast growing population, and increased number of motor vehicles (Ministerio de Transporte, 2014), worsened by the aforementioned geophysical constraints for pollutant dispersion in Santiago's basin: in fall and winter seasons subsidence conditions induce thermal inversion layers that increase ambient levels of pollutant concentrations and produce a characteristic seasonality of air quality in the city (Didyk et al., 2000; Jorquera et al., 2000; Sax et al., 2007; Tsapakis et al., 2002).

The Chilean government has been implementing regulations in recent decades to control air pollution in Santiago (Jorquera et al., 2000; Mena-Carrasco et al., in press). Efforts have been directed at modernizing the public transport system by replacing old buses with lower-emission buses, using cleaner fuels (including the removal of lead from gasoline in 2001), and reducing the sulfur level in diesel fuel. Policies for emissions reduction from industrial sources were also promulgated, along with street sweeping and cleaning programs to reduce fugitive dust emissions. Contingency measures are implemented every year from April 1 to August 31 (fall and winter) for high pollution events that include activity restrictions on vehicles, industries, residential wood stoves, and exclusive lanes for public buses (MMA, 2014). Restrictions applied during critical days have been effective in reducing levels of particulate matter and NO_X (Troncoso et al., 2012). These regulations have decreased the average concentrations of PM_{10} and $PM_{2.5}$ in Santiago; however, levels in winter are still significantly above WHO guidelines (Barraza et al., in press; Jorquera and Barraza, 2012; Koutrakis et al., 2005; Sax et al., 2007).

In this work we focus on $PM_{2.5}$ because its health impacts are greater than those of coarse particles, and currently the particulate matter problems for $PM_{2.5}$ concentrations in Santiago are more complex to manage. This is because secondary $PM_{2.5}$ has become more relevant as primary emissions have been reduced with the aforementioned policies. Hence new pollution abatement strategies ought to include abatement of gaseous precursors and primary $PM_{2.5}$ emissions as well.

Policies and regulations implemented in Santiago during recent decades have not only decreased the concentration of particulate matter, they also have changed the relative chemical composition of particles. Table 1 summarizes previous studies in Santiago that have used the chemical composition of $PM_{2.5}$ to determine its sources; the most relevant sources identified between 1987 and 2005 were motor vehicles, wood burning, secondary aerosols, industrial sources and soil dust. In that period, sulfate concentrations were decreasing while organic carbon concentrations were increasing. However, none of those studies used a chemical mass balance (CMB) receptor model with organic molecular tracers. This method has been applied in other cities around the world (Daher et al., 2011, 2012; Heo et al., 2013; Stone et al., 2008, 2010), but not in Chile.

The goal of this work is to characterize the chemical composition of $PM_{2.5}$ in Santiago through elemental and organic carbon (ECOC), water soluble organic carbon (WSOC), water soluble total nitrogen (WSTN), ionic, elemental, and organic tracer analyses, and to use organic tracers in the CMB model to better identify sources of fine particles and estimate their apportionment. Santiago still needs to reduce the levels of fine particles, so it is expected that the results of this research will better direct control strategies to reduce particulate matter concentrations.