Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

Temporal evolution of main ambient PM2.5 sources in Santiago, Chile, from 1998 to 2012

Francisco Barraza[1,4], Fabrice Lambert[1,4], Héctor Jorquera[2,5], Ana María Villalobos[2], Laura Gallardo[3,4]

[1] Geography Institute, Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile
[2] Department of chemical engineering and bioprocesses, Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile
[3] Department of Geophysics, Universidad de Chile, Santiago, Chile
[4] Center for Climate and Resilience Research, University of Chile, Santiago, Chile
[5] Center for Sustainable Urban Development (CEDUS), Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile

Correspondence to: Francisco Barraza (fjbarraz@uc.cl)

Abstract.

The inhabitants of Santiago in Chile have been exposed to harmful levels of air pollutants for decades. The city's poor air quality is a result of sustained emissions and stable atmospheric conditions, averse to mixing and ventilation and favorable for the formation of oxidants and secondary aerosols. Identifying and quantifying the sources that contribute to the ambient levels of pollutants is key for designing adequate mitigation measures. Knowledge about the temporal evolution of the contribution of each source to ambient pollution levels is also paramount to evaluate the effectiveness of pollution reduction measures that have been implemented in the past decades. Here, we quantify the main sources that have contributed to fine particulate matter ($PM_{2.5}$) between 1998 and 2012 in Santiago's center by using two different source-receptor models (PMF 5.0 and Unmix 6.0), that re applied to elemental measurements on 1243 24-hour filter samples of ambient $PM_{2.5}$ collected between April-1998 to August-2012. Both models resolve six sources that contribute to ambient $PM_{2.5}$: motor vehicles (37%), industrial sources (19%), copper smelters (14%), wood burning (12%), coastal sources (10%), and urban dust (3%). Our results show that over the 15 years analyzed here, the emissions from motor vehicles, industrial sources, copper smelters, and coastal sources declined by about 21, 39, 81, 59, and 59% respectively, while wood burning didn't change and urban dust increase by 72%. These changes are consistent with emission reduction measures, such as improved vehicle and smelting technology, introduction of low sulfur fuel for vehicles and natural gas for industrial processes, emission controls for vehicles, public transport improvements etc.. However, it is also apparent that the mitigation expected from improved public transport, vehicle technology, and fuel has been largely nullified by the ever-rising number of private vehicle journeys in the past decade. As a consequence, Santiago still experiences $PM_{2.5}$ levels above the annual and 24-hours Chilean and World Health Organization standards

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

1 Introduction

Santiago (33.5°S, 70.5°W, 500 m a.s.l.) is the largest metropolitan area in Chile and the 7th in South America, with a population around 7 million. The city is located in a basin confined between a coastal mountain range to the west (height ~ 1000 m a.s.l.) and the Andes range to the east (average height ~ 4000 m a.s.l.), impeding horizontal air movements (Figure 1). Moreover, Santiago's climate is controlled by the quasi-permanent influence of the subtropical Pacific high, which results in a subsidence inversion that inhibits vertical mixing. Sub-synoptic features known as coastal lows recurrently intensify the subsidence conditions (Rutllant and Garreaud, 1995). The mixing layer shows a marked diurnal cycle (Saide et al., 2011). Nighttime boundary layers are usually very thin and often collapse, while vertical mixing is strongest in the afternoon hours. There is a characteristic radiatively driven circulation that defines up-slope southwesterly winds in the afternoon and down-slope northeasterly winds in the night and morning hours, more strongly so during summer (Rutllant and Garreaud, 2004 Muñoz et al., 2010;).

Particulate matter concentrations in Santiago have been recorded according to international standards since the late 1980s (http://sinca.mma.gob.cl/). The evolution of this network in terms of information content has been described elsewhere (Osses et al., 2013; Henriquez et al., 2015;), and several trend analyses have been carried out (Jorquera et al., 2004; Moreno et al., 2010; Mena-Carrasco et al., 2012; Jhun et al., 2013). $PM_{2.5}$ has been monitored in Santiago since 1989, first by the Chilean Ministry of Health, and subsequently by the Chilean Ministry of Environment, making it one of the longest running $PM_{2.5}$ air quality monitoring networks in the world (Jhun et al., 2013).The first study addressing elemental composition of particles collected in Santiago (winter and spring of 1976) identified anthropogenic sources as major contributors to the particle load (Préndez et al., 1984). These authors found anthropogenic enrichments of Cl, Cu, Zn, As, Se, Br and Sn. In the late 1980s, soil, industrial, sulfate particles, traffic, residual oil, and wood-burning were suggested as sources of fine particles collected in summer (Rojas et al., 1990). Based on this study, other authors developed new estimations for $PM_{2.5}$ source apportionment using various methods that are summarized in Table 1

Although environmental authorities have archived a continuous record of ambient $PM_{2.5}$ elemental composition for Santiago, source-apportionment studies are relatively sparse, and they generally refer to a few months or a single year of data. Moreover, they differ methodologically, which makes it hard to infer a trend in source contributions over time. In this study, we provide the first continuous 15-year source-apportionment analysis of ambient $PM_{2.5}$ for Santiago. We focus on fine particulate matter ($PM_{2.5}$) because high concentration levels are associated with significant health problems in Santiago (Pino et al., 2004; Cakmak et al., 2007; Valdes et al., 2012; González R. et al., 2013; Leiva G et al., 2013). Since 1990, Chilean authorities have implemented several air pollution abatements polices that have significantly decreased $PM_{2.5}$ – Figure 3 (Mena-Carrasco et al., 2014; MMA, 2015). These measures included removing lead from gasoline (late nineties), reducing sulfur in diesel fuel (5000 ppm in 1989 to 15 ppm today), stricter emission standards (from EURO I to EURO III since 2007) and modernization of the new public transport fleet, selective ban on car usage during emergencies, a mandatory car inspection and maintenance program, and street sweeping and cleaning programs (Sax et al., 2007; Moreno et al., 2010; Jhun

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

et al., 2013;Villalobos et al., 2015). Although these policies have collectively been successful in reducing the occurrence of extreme $PM_{2.5}$ values, annually averaged $PM_{2.5}$ remains well above the World Health Organization (WHO) yearly average guideline of 10 μg/m^3 (World Health Organization-WHO, 2005) , and the annual Chilean standard of 20 μg/m^3. Moreover, Santiago experiences frequent autumn and winter $PM_{2.5}$ daily episodes with levels exceeding the 24-hours Chilean standard of 50 μg/m3 and the WHO 24-hour guideline of 25 μg/m^3 (WHO, 2005). These episodes are recurrent and typically last several days.

In this study, we present the $PM_{2.5}$ data collected by the Chilean Ministry of the environment from April 1998 to August 2012. There are 1243 daily values collected every 4 days in central Santiago (Parque O'Higgins monitoring station). Over time, an overall decline of median and upper tail values is apparent, with the notable exception of the year 2007, which is discussed later on.

The policies and regulations implemented in Santiago were created using emission inventories that did not include regional sources, such as copper smelters, whose contributions were not explicitly acknowledged in the Air Quality Management plans originally set in the late 1990s. However, subsequent studies did show the impact of regional sources in Santiago (Gallardo et al., 2002; Olivares et al., 2002), and these industrial sources and the electrical power generation sector have been subject to increasingly stringent emission regulations at the national level in the last two decades. As a result of this, the relative chemical composition of particles has changed with time. However, no study to date has investigated the temporal evolution of particle matter source contributions. In this study, we seek to identify the major sources in Santiago using elemental characterization for ambient $PM_{2.5}$ filters collected from 1998 to 2012 (1243 samples), analyse how each source varied through time, and determine how much each contributed to total ambient $PM_{2.5}$ in Santiago.

2 Methodology

1.1 Sampling station

Environmental authorities have collected ambient $PM_{2.5}$ samples in Santiago since 1998 using Low-Vol dichotomous samplers operating at 15 L/min for 24 hours (Andersen Instrument, Inc.). The monitoring stations is located in Parque O'Higgins, in the interior area of a park in central Santiago, in a relatively flat area of the basin. (Osses et al., 2013) identified it as the most representative site of the Santiago basin. According to other statistical analyses (Gramsch et al., 2006; 2016,), this station can be characterized as an urban background station. Data collected in this station have been used for establishing trends in chemical speciation and source apportionment for particulate matter and epidemiological studies (Koutrakis et al., 2005; Sax et al., 2007; Moreno et al., 2010; Valdes et al., 2012).

A total of 1243 daily samples (24 h filters) were collected every four days from April 1998 to August 2012. Those filters were subsequently analyzed using X-ray fluorescence (XRF) at the Desert Research Institute, Reno, NV, USA. The Ministry for the Environment provided us with the database containing the elemental analyses of the filters. In order to build statistical models based on robust chemical signals, we decided to keep only those elements for which more than 70% of the samples

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

contained valid measurements above the detection limit. Thus, out of the 49 elements reported, we only kept 17: Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Pb. The missing data in these seventeen species were treated in two separate ways. The first one consisted in leaving them blank and let the models use their internal algorithm to deal with them, which consists of replacing them with the median of the complete time-series. Since replacing missing data with the median can lead to severe distortions in the data, we also used a custom-written algorithm. This method interpolates up to three consecutive missing values using a piecewise cubic interpolation algorithm. Sections of four or more consecutive missing values are filled by summing up a mirrored copy of equal length of the data on both sides of the empty section, weighted by a cos^2 function. We ensured that only relatively small gaps were filled to fill in the missing data as best as possible without creating artificial variability in the data. Although both methods yielded comparable results, we have used the custom-written algorithm in this analysis, as it does not introduce discontinuities in the time series.

2.2 Receptor Modeling

Receptor models are mathematical procedures for identifying and quantifying the sources of ambient air pollution and their effects at a receptor site on the basis of concentration measurements, without using neither emission inventories, nor meteorological data (Willis, 2000). In mathematical terms, the general receptor modeling problem can be stated in terms of the contributions from p independent sources to n chemical species measured in a set of $\boldsymbol{m}$ samples as follows (Hopke et al., 2006):

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad (1)$$

Where X_{ij} is the j-th species mass measured in the i-th sample, g_{ik} is the PM mass concentration from the k-th source contributing to the i-th sample, f_{kj} is the j-th species mass fraction from the k-th source, e_{ij} is a model residual associated with the j-th species concentration measured in the i-th sample, and p is the total number of independent sources. In this study, we have used two different models from the US Environmental Protection Agency (EPA) to solve the equation described above. The first method is Positive Matrix Factorization (PMF) based on a multivariate factor analysis (Norris et al., 2014). The second method (Unmix), uses principal component analysis (Norris et al., 2007). The combined use of both methods increases the robustness of our results.

The Positive Matrix Factorization (PMF) method, is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices: factor contributions (G) and factor profiles (F). These factor profiles need to be interpreted by the user to identify the source types that may be contributing to the sample using measured source profile information, emission inventories or key tracer species (Norris et al., 2014). The method is a widely used receptor model for environmental samples (example: indoor and outdoor particulate matter, sediment, wet deposition and surface water) and the theoretical basis and practical implementation issues have been described elsewhere (Reff et al., 2007; Belis et al., 2013) . In this work we have used PMF version 5.0 (Norris et al., 2014) obtained from the EPA website.

The Unmix method calculates the number of source types, profiles, relative contributions, and a time-series of contributions using sample species concentrations. The species concentrations are apportioned by a principal components analysis using

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

constraints to assure non-negative and realistic source compositions and contributions (Willis, 2000). The theoretical basis and practical implementation issues have been described by Henry (Henry, 2002; 2003). In this work we have used Unmix version 6.0 (Norris et al., 2007) obtained from the EPA website.

2.3 Analysis of source contributions trends

We have used two methods for trend analyses of each source contribution to $PM_{2.5}$. The first is a robust regression to get an evaluation of the long-term change from 1998 to 2012; we used each source contribution in $\mu g/m^3$ (log transformed to achieve normal distribution) as dependent variable, and time as the independent variable. The second method detects abrupt transitions in the time series, with the aim to evaluate possible changes from specific government initiatives in a particular period. This method uses a Mann-Whitney test with sliding windows of three different lengths (320, 480 and 650 days). We compare the medians of the older and the younger half of the window, and plot the p-value of the hypothesis test result. Low p-values correspond to significant differences between the two halves and therefore a significant change in concentration between the two periods.

3 Results and Discussion

3.1 Receptor Modeling Results

We have run the two receptor models — PMF 5.0 and Unmix 6.0 — for different numbers of factors and examined source profiles looking for specific tracers and tracer ratios, as well as the seasonality of source contributions to identify potential sources. We considered 13 species that yield the best model: Al, Si, S, Cl, non-soil K (Kns), Ti, Cr, Mn, Fe, Ni, Cu, Zn and As. We note that we discarded Pb and Br in both models, because of the substantial decrease in lead (and bromine) in gasoline and diesel fuels after 2000, prompted by cleaner fuel policies. Had we included lead in the model, we would have obtained a spurious source contribution with high values in 1998-2000 and very low values afterwards. This artifact is caused because all receptor models assume constant composition in the source chemical profiles. Had we kept lead in the model we would have concluded that the motor vehicle contributions significantly decreased in a span of only one year, which is wrong. Although lead is a classical tracer of motor vehicle emissions, is still possible to identify and quantify the motor vehicles source using other species or ratios between species as we did in this work with Cr, Ni, Cu and Zn. To provide a tracer associated with wood burning we added the non-soil potassium parameter Kns calculated as Kns=(K-0.3xFe). The 0.3 coefficient was obtained from a K-Fe edge plot. This methodology has been used before by Lewis *et. al.* (Lewis et al., 2003) to remove soil contribution to the total potassium.

Both models found species regressions with coefficient (R^2) greater than 0.7. These species constitute significant identifier for the interpretation of each chemical profile and of the global model (Norris et al., 2007). Then, we applied a multiple linear regression (MLR) to the daily concentrations of $PM_{2.5}$ using the source contributions $\{g_{ik}\}$ as independent variables, and checked whether the regression coefficients were positive and statistically significant at the 95% confidence level

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

($p \leq 0.05$). This approach has been described in more detail in previous studies (Jorquera and Barraza 2012; Jorquera and Barraza 2013).

PMF 5.0 produces a six factors solution that explained 74% of the variance in ambient $PM_{2.5}$ (Figure 2). Below we discuss each source individually.

The first source was identified as "motor vehicles", as it contains more than 50% of total Cr, Cu and Zn, which are all tracers of traffic emissions (Fujiwara et al., 2011). A Zn/Fe ratio of ~ 0.31 can be found in this factor, which is similar to ratios reported in source apportionment studies in Chilean cities of Temuco, 0.34; Rancagua, 0.31; Iquique, 0.31 (Kavouras et al., 2001) and Las Condes (0.32) in Santiago (Jorquera and Barraza, 2012) for motor vehicle sources. This source has a characteristic weekly behaviour, with weekend contribution around half the working days contribution.

The second source was identified as "industrial sources". It is characterized by the high content of sulfur (65.47%) that originates from the sulfur aerosols emitted by industrial sources. This source also contains other tracer species that originate in industrial processes, such as Ni (19.5%) and Kns (non-soil potassium, 12.8%). Since this profile is dominated by sulfur, it has previously also been identified as "industrial sulfates" or "sulfates" (Artaxo et al., 1999; Jorquera and Barraza, 2012; Moreno et al., 2010). This source does not show a weekly change in contribution, as expected from sources that run continuously 7 days per week.

The third source was identified as "copper smelters". It contains almost all As measured (79%) and its S/As ratio of 23 is close to the values of 17, 15, and 18 obtained in copper smelter profiles from the cities of Rancagua (Kavouras et al., 2001), Quillota (Hedberg et al., 2005), and Las Condes (Jorquera and Barraza, 2012), respectively. Other relevant tracer species found in this source were Cu (21.4 %) and S (18.9%), which were also identified in a previous study on Santiago (Jorquera and Barraza 2012). There is no significant difference between working days and weekends ($p=0.827$), which is also consistent with the continuous operation of the smelter plants.

The fourth source was identified as "wood burning". It contains over 70% of all non-soil potassium (Kns), suggesting residential wood burning. Also, this source shows an expected seasonal and weekly trend, with winter contributions 5 times higher than during summer, and a working day/weekend ratio of 0.74 ($p=8.28X10^{-5}$).

The fifth source was identified as "coastal sources". These are coastal aerosols that reach Santiago's basin. This source contains 90% of the Cl, suggesting a strong marine component. present during all seasons (Jorquera and Barraza, 2012). It also contains minor contributions of industrial sources, such as Ni (8.6%), Zn (9.9%) and As (4.7%), which suggest a contribution from anthropogenic coastal emissions. This source shows no weekly cycle ($p=0.251$).

Finally, the sixth source was identified as "urban dust". It contains most of Al, Si, and Ti and features elemental ratios that indicate soil dust emissions (Malm et al., 1994);. For example, its Si/Al ratio of 2.26 compares well with source apportionment results from other Chilean cities (Temuco, 2.17; Rancagua, 2.95; Valparaíso, 2.58 (Kavouras et al., 2001). This source shows a significant higher contribution during working days, which can be explained by the higher number of vehicles on the street during workdays that resuspend dust from the ground. (ratio working day/weekend = 1.18; $p=3.53x10^{-4}$).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

We ran UNMIX 6.0 using the same data selected for the PMF 5.0 calculations and obtained similar results (Figure 2). The main difference is that we could not identify the source "industrial sources" using Unmix 6.0 because the sulfur concentrations were distributed over the sources "urban dust", "coastal sources", "wood burning", and "copper smelters", slightly increasing their percentage contribution. Instead, UNMIX outputs a source we identified as "oil combustion" with high contribution of Ni and Cr and low values of Cu, Zn and As. This source has been also been identified in previous studies as a contributor to Santiago $PM_{2.5}$ (Rojas et al., 1990; Artaxo, 1996; 1998; Jhun et al., 2013).

The unexplained source concentration can be calculated by the intercept value in both models. For the PMF 5.0 model the unexplained fraction represents 5% of mass but it is not statistically significant (intercept estimate has a p value of 0.052) and could therefore be a statistical artefact. For the Unmix 6.0 model the unexplained fraction was statistically significant at 7% of $PM_{2.5}$ mass (intercept estimate has a p value of 0.0046). This unexplained fraction could be due to local sporadic or secondary sources. The average contributions of both models are shown in Figure 2.

3.2 Mass concentration and seasonal behavior

Over the whole study period, the daily mean (24 h) concentration of $PM_{2.5}$ was 35.60 $\mu g/m^3$ and the median 24.19 $\mu g/m^3$ (Figure 3) The highest daily levels are found during the cold seasons (autumn and winter) with a ratio close to 3 between cold seasons and warm season concentrations (Table 2). During the spring and summer seasons, boundary layer height increases along with wind speeds, and ambient $PM_{2.5}$ concentrations decrease and so do the contributions of most sources. Almost all episodes with $PM_{2.5}$ levels over the Chilean and WHO standards occur during autumn and winter.

The six identified sources have distinct seasonal contributions to $PM_{2.5}$. During winter, when $PM_{2.5}$ shows the largest number of harmful episodes, we found a distinct contribution from residential wood smoke with a 30.6% of the total amount of $PM_{2.5}$. The other five sources have their highest contributions during autumn. This is explained by the lack of rainfall during autumn, while there is more rainfall to remove $PM_{2.5}$ by wet deposition in winter.

3.3 Time series of each source contribution

3.3.1 Motor Vehicles

In Figure 4 we show temporal evolution of the source identify by PMF as motor vehicles. Over the 15 years of covered in this study, the motor vehicles contribution to $PM_{2.5}$ diminished significantly by 2.17 $\mu g/m^3$ (21.30%, p=0.0250). This is explained by several policy measures: restrictions to vehicle traffic since late 1980s (Moreno et al., 2010), mandatory catalytic converters for gasoline powered cars since 1991 (Koutrakis et al., 2005), improvement of fuel quality in 2001, and a complete overhaul of the public transportation system between 2007 and 2010 called "Transantiago" (Muñoz et al., 2014).

The reduction in the contribution of this source contribution has not been linear. Between 2000 and 2002, there was a reduction of 2.89 $\mu g/m^3$ (27.65%), which is due to the improvement of gasoline quality, highlighted by the fact that lead was entirely removed from gasoline on April 2001. (Moreno et al., 2010). These gains were partially reversed between 2003 and

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

2006 due to the steady rise of the number of motorized vehicles in Santiago since 2003 (average annual increase of 4.65% from 1998 to 2008) —Figure S1.

In February of 2007 a new fully integrated public transport system for Santiago ("Transantiago") was implemented. One of its goals was to reduce atmospheric emissions, thus improving air quality in the city. However, the motor vehicles contribution augmented by 5.68 μg/m^3 (56.64%) in 2007-2008. Unfortunately, the early days of Transantiago were plagued by design flaws, bad operation, and chaotic implementation (Muñoz et al., 2014). In addition, the bus fleet was drastically reduced from ~ 8000 to ~4500 buses in early 2007. This reduced fleet was insufficient to cope with demand and – compounded with the problems with Transantiago - this incentivized many people to buy and use private cars, which led to an 11% increase in the motorized vehicle fleet in 2007 (Figure S1 and 2). Gramsch et. al. (2013) studied the influence of Transantiago on black carbon ambient concentrations before and after Transantiago's implementation. They found that in a street without buses the black carbon concentration actually increased by 15% after the implementation, and explained the higher BC values with the increased use of private cars.

The improvement of the Transantiago public transport system in subsequent years reduced contribution of motor vehicles. The measures included i) an increase of the bus fleet by 6000 vehicles to satisfy passenger demand, ii) an extension of the subway network, and iii) the gradual implementation of EURO III emission standards (from 53% of the fleet in 2007 to 92% in May 2012 (Muñoz et al., 2014)). Comparing the period 2010-2011 with 2004-2005 we find a long-term decrease of motor vehicles contribution of 3.04 μg/m^3 (32.41%) that can be ascribed to Transantiago's implementation.

3.3.2 Industrial sources

In Figure 5 we show temporal evolution of the source identify by PMF as industrial sources. This source reduced its contributions from 1998 to 2012 by 2.63 μg/m^3 (39.23%, p=0.11x10^{-8}). This improvement can be explained by the reduction policies for sulfur in diesel fuel (Jhun et al., 2013), mandatory reductions in industrial emissions, vehicle restrictions during days of poor air quality (Mena-Carrasco et al., 2014), and a change from diesel to natural gas as industrial fuel (MMA 2015). The year 2002 showed a significant reduction of 2.52 μg/m^3 (34.33%) compared with 2001, that can be explained by a reduction on the content of sulfur in diesel, that was reduced from 1000 to 300 ppm in 2001 (Centro Mario Molina Chile, 2014; MMA, 2015).

Between 2005 and 2007 we find a significant increase of Industrial sources contributions, which was triggered by the gradual reduction of natural gas imports from Argentina. During these years, a large number of industries were forced to switch back to diesel fuel, which has a greater amount of sulfur than natural gas. Since 2008 the Chilean state imports liquefied natural gas from other countries, which is apparent in the subsequent reduction in 2009 and 2010 caused by industries changing again from diesel to natural gas (Figueroa et al., 2013; GNL-Quitero, 2016). The period 2010-2012 shows a reduction of 1.76 μg/m (31.17%) compared with the period when the natural gas imports stopped (2004-2008).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

3.3.3 Copper Smelters

In Figure 6 we show temporal evolution of the source identify by PMF as copper smelters. The contribution from copper smelters features the largest reduction of 5.24 μg/m^3 (81.46% p = 0.82x10^{-33}) between 1998 and 2012. These improvements can be attributed to technological improvements at the Caletones and Ventanas smelters near Santiago (see Figure 1). In 1998, new regulations forced Caletones to install an acid plant for SO_2 abatement, then a second one in 2002 (Minsegpres, 1998). This emission abatement technology decreased SO_2 emissions from 700,000 tons in 1999 to 100,000 tons in 2003 (CODELCO, 2015; Montezuma, 2016). The period between2002 and 2010 shows values lower by 4.13 μg/m^3 (69.04%) than those during the period 1998-2001. We find another significant reduction of 1.41 μg/m^3 (64.66 %) between 2009 and 2012 explained by further reductions in SO_2 emissions at both smelters. The Ventanas smelter reduced its SO_2 emissions from 20.3 kton/year in 2009 to 4.7 kton/year in 2012, while the Caletones smelter's SO_2 emissions were reduced from 141 kton/year in 2009 to 50 kton/year in 2012 (Montezuma, 2016). Chagres is small private copper smelter for which no data are available.

3.3.4 Wood Burning

In Figure 7 we show temporal evolution of the source identify by PMF as wood burning. It is the only identified source with no net significant change in the period 1998-2012 (p=0.1390). Nevertheless, we find two significant changes during this period that canceled each other out: i) an increase in 2007-2009 of 1.17 μg/m^3 (43.39%), compared with 2004-2006, and ii) a reduction in 2010-2012 of 1.16 μg/m^3 (30.13%) compared with 2007-2009.

To curb wood burning emissions, Chilean authorities have prohibited open chimneys since 1997, only certified woodstoves can be used, and residential wood burning is completely banned during bad air quality episodes (Mena-Carrasco et al., 2012). Our results show that these measures have not been effective (at least during the studied period) to reduce wood burning emissions. Mena-Carrasco at al., 2012 suggested the replacement of current wood stoves in Santiago with stoves using cleaner fuels as a cost-effective way of reducing air pollution. They estimated a reduction of 2.07 μg/m^3 in $PM_{2.5}$ concentrations if all wood stoves were changed to natural gas stoves. This estimate represents ~ 50% of the current wood burning contribution to Santiago $PM_{2.5}$.

3.3.5 Coastal sources

In Figure 8 we show temporal evolution of the source identify by PMF as coastal sources. This source contribution shows a significant reduction of 1.48 μg/m^3 (58.66% p=0.88x10^{-5}). We find a significant reduction of 1.62 μg/m^3 (77.46%) from 2000 to 2002 compared with the period 1998-1999 that can be explained in same the availability of cleaner industrial fuel explained for the Industrial sources. On the coastal aerosol trajectory to Santiago are many industries that in the 90's use to used Natural or the Diesel reduced in sulfur. However, those coastal industries were also affected by the stopping of natural gas imports from Argentina, increasing from 2004 – 2008 due to a temporary switch to diesel and then reducing again after

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

2009 after the second conversion to LNG. Since 2010 coastal sources have reduced their contribution by 1.05 μg/m^3 (76.17%) compared with the period 2007-2008.

3.3.6 Urban Dust

In Figure 9 we show temporal evolution of the source identify by PMF as urban dust. It is the only identified source that has increased its contributions significantly by 0.49 μg/m^3 (72.19% p = 0.26x10^{-12}) from 1998 to 2012. Three significant changes are apparent. The first is a reduction of 0.42 μg/m^3 (48.84%) between 2001 and 2002, which can be explained by the improvement of the fuel quality in 2001, when lead was removed from gasoline (Jhun et al., 2013). Ayrault et al., 2013 showed that lead particles emitted by gasoline can be deposited on surface soil and remain for a long time.

A second change was an increase of 0.67 μg/m^3 (171.78%) from 2004 to 2010, which can be explained by the significant increase of the number of cars in the city (Instituto Nacional de Estadísticas, 2016). The third significant change was in 2011, with an increase of 0.48 μg/m^3 (51.61%). Two factors may explain this rise: i) an annual increase of 7% in the number of cars (Instituto Nacional de Estadísticas, 2016), and ii) since 2010 central Chile has experienced an extended drought ((CR2), 2015; Boisier et al., 2016), which leads to drier conditions and promotes aeolian aerosol resuspension.

In Table 3 we summarize of the main shifts in concentration levels for each source and the corresponding air quality measure or other events that provoked these changes.

3.3.7 Source percentage change

From 1998 to 2012 total $PM_{2.5}$ concentrations have been reduced as a consequence of the measures described above. However, individual sources did not vary in the same proportion and their relative contribution changed over the 15 years (Figure 10). The main reduction was obtained from copper smelter emissions that lowered their relative contribution from 33% in 1998-1999 to 5% in 2011-2012. On the other hand, the impact of motorized vehicles increased significantly, with this source becoming the largest contributor in since 2003-2005. In connection with the rise in motor vehicle numbers after 2005, urban dust also increased from 3 to 7%.

4. Conclusions

We applied two different receptor models (PMF 5.0 and Unmix 6.0) to a multiyear database of $PM_{2.5}$ concentrations measured on air filter samples collected in Santiago, Chile. Both models identify six major sources of ambient $PM_{2.5}$ (motor vehicles, industrial sources, copper smelters, wood burning, coastal sources, urban dust) and show the temporal evolution of each source from 1998 to 2012. Five of the six identified sources show a pronounced seasonal trend, increasing their contribution significantly during autumn and winter, which together with inadequate ventilation triggers a high number of episodes with harmful concentrations of $PM_{2.5}$.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

During the 15 years investigated in this study (1998-2012), several government regulations have been implemented, with the aim to reduce ambient $PM_{2.5}$ levels in Santiago. The most successful measures were on industrial emissions, particularly the regulation of copper smelter emissions and the shift to cleaner fuels. The copper smelters, coastal sources and industrial sources reduces their contribution by 5.24, 1.48 and 2.63 µg/m^3, respectively (81.46, 39.23 and 58.66%).

The motor vehicles source also reduced its contribution by 2.17 µg/m^3 (21.30%) over the whole period. However, the fast growth in the number of private cars has cancelled out a significant part of the gains from more stringent vehicle emission standards implemented so far. The main challenge for the future therefore seems to be the implementation of behavioral changes in the population to prefer public transportation over private cars.

Urban dust (a mixture of crustal and road dust) is the only identified source that has increased its contribution significantly by 0.49 µg/m^3 (72.49%). This might be due to the increase in private vehicle trips over the years leading to road dust suspension or perhaps to drier conditions in central Chile as experienced since 2010. Its overall contribution to $PM_{2.5}$ was nevertheless minor (< 1.41 µg/m^3 or < 10 % of total $PM_{2.5}$) in 2012.

We did not find any significant long-term change in residential wood burning contributions. This source is particularly important in the cold season when it explains roughly 30.6 % of $PM_{2.5}$. Measures to reduce this source's contribution are urgently needed and may greatly improve winter air quality in Santiago at relatively little cost.

Although government measures have been partially successful at improving air quality, the inhabitants of Santiago are still exposed to harmful $PM_{2.5}$ concentrations that stay above Chilean ambient standards and WHO guidelines for a significant amount of time. Based on this study it is apparent that industry emissions have already been capped significantly. Without calling for a halt to further industrial emission reductions we suggest to shift the focus on policies to reduce residential and motor vehicles emission as there is a large reduction potential in these sources.

5 Acknowledgments

Financial support for this work was provided by grants FONDECYT 3160639 and 1151427, FONDAP 15110009 and 15110020, and Anillo ACT1410. We thank the Chilean Ministry of Environment for providing $PM_{2.5}$ filter analysis data.

References

(CR2), C. for C. and R.R., 2015. Mega Drought (2010-2015): a lesson to the future. Report for policymakers (in Spanish).

Artaxo, 1999. Aerosol characterization study in Santiago de Chile 1999. Caracterización Físicoquimica del Material Particulado Inorgánico Primario. Distribución por Tamaño y Modelo Receptor — 1999. technical report for the National Commission of the Environment.

Artaxo, P., 1998. Aerosol characterization study in Santiago de Chile Wintertime 1998: Technical report for the National Commission of the Environment. Santiago.

Artaxo, P., 1996. Aerosol source apportionment at Santiago Chile Winter 1996: technical report for the National Commission of the Environment.

Artaxo, P., Oyola, P., Martinez, R., 1999. Aerosol composition and source apportionment in Santiago de Chile. Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 150, 409–416. doi:10.1016/S0168-583X(98)01078-7

Ayrault, S., Catinon, M., Boudouma, O., Bordier, L., Agnello, G., Reynaud, S., Tissut, M., 2013. Street Dust : Source and Sink of Heavy Metals To Urban Environment, in: Pirrone, N. (Ed.), Proceedingd of the 16th International Conference on Heavy Metals in the Environment. Rome, Italy, pp. 1998–2001.

Belis, C.A.A., Karagulian, F., Larsen, B.R.R., Hopke, P.K.K., 2013. Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe. Atmos. Environ. 69, 94–108. doi:10.1016/j.atmosenv.2012.11.009

Boisier, J.P., Rondanelli, R., Garreaud, R.D., Mu????oz, F., 2016. Anthropogenic and natural contributions to the Southeast Pacific precipitation decline and recent megadrought in central Chile. Geophys. Res. Lett. 43, 413–421. doi:10.1002/2015GL067265

Cakmak, S., Dales, R., Blanco, C., 2007. Air Pollution and Mortality in Chile : Susceptibility among the Elderly. Environ. Health Perspect. 155, 524–527. doi:10.1289/ehp.9567

Centro Mario Molina Chile, 2014. Propuesta de regulaciones para la reducción del MP2,5, sus cambios precursores y contaminantes que afecten al cambio climático, para las distintas fuentes estacionarias de la Región Metropolitana.

CODELCO, 2015. Memoria anual 2014.

Figueroa, E., Gómez-Lobo, A., Jorquera, P., Labrín, F., 2013. Develando econométricamente los impactos sobre la concentración atmosférica de material particulado de un proyecto de remodelación del transporte urbano: El caso del Transantiago en Chile. Estud. Econ. 40, 53–79. doi:10.4067/S0718-52862013000100003

Fujiwara, F., Rebagliati, R.J., Dawidowski, L., Gómez, D., Polla, G., Pereyra, V., Smichowski, P., 2011. Spatial and chemical patterns of size fractionated road dust collected in a megacitiy. Atmos. Environ. 45, 1497–1505.

Gallardo, L., Olivares, G., Langner, J., Arrhus, B., 2002. Coastal lows and sulphur air pollution in Central Chile. Atmos. Environ. 36, 3829–3841.

GNL-Quitero, 2016. No Title [WWW Document]. URL http://www.gnlquintero.com/

González R., N., Torres-Avilés, F., Carrasco P., E., Salas P., F., Pérez B., F., 2013. Estudio temporal de diabetes mellitus tipo 1 en Chile: Asociación con factores ambientales durante el período 2000-2007. Rev. Med. Chil. 141, 595–601. doi:10.4067/S0034-98872013000500007

Gramsch, E., Cereceda-Balic, F., Oyola, P., Vonbaer, D., 2006. Examination of pollution trends in Santiago de Chile with cluster analysis of PM10 and Ozone data. Atmos. Environ. 40, 5464–5475. doi:10.1016/j.atmosenv.2006.03.062

Gramsch, E., Reyes, F., Vásquez, Y., Oyola, P., Rubio, A.M., 2016. Prevalence of Freshly Generated Particles during Pollution Episodes in Santiago de Chile. Aerosol Air Qual. Res. 16, 2172-2185. doi:10.4209/aaqr.2015.12.0691

Hedberg, E., Gidhagen, L., Johansson, C., 2005. Source contributions to PM10 and arsenic concentrations in Central Chile using positive matrix factorization. Atmos. Environ. 39, 549–561. doi:10.1016/j.atmosenv.2004.11.001

Henriquez, A., Osses, A., Gallardo, L., Diaz, M., 2015. Analysis and optimal design of air quality monitoring networks using a variational approach. Tellus Ser. B-Chemical Phys. Meteorol. 67, 1–13. doi:10.3402/tellusb.v67.25385

Henry, R.C., 2003. Multivariate receptor modeling by N -dimensional edge detection. Chemom. Intell. Lab. Syst. 65, 179–189.

Henry, R.C., 2002. Multivariate receptor models — current practice and future trends. Chemom. Intell. Lab. Syst. 60, 43–48.

Hopke, P.K., Ito, K., Mar, T., Christensen, W.F., Eatough, D.J., Henry, R.C., Kim, E., Laden, F., Lall, R., Larson, T. V, Liu, H., Neas, L., Pinto, J., Stolzel, M., Suh, H., Paatero, P., Thurston, G.D., 2006. PM source apportionment and health effects: 1. Intercomparison of source apportionment results. J. Expo. Sci. Environ. Epidemiol. 16, 275–286.

Instituto Nacional de Estadísticas, 2016. Anuarios parque de vehículos en circulación 2001-2013 [WWW Document]. URL http://www.ine.cl/canales/chile_estadistico/estadisticas_economicas/transporte_y_comunicaciones/parquevehiculos.php

Jhun, I., Oyola, P., Moreno, F., Castillo, M.A., Koutrakis, P., 2013. PM2.5 mass and species trends in Santiago, Chile, 1998 to 2010: The impact of fuel-related interventions and fuel sales The impact of fuel-related interventions and fuel sales. J. Air Waste Manage. Assoc. 63, 161–169. doi:10.1080/10962247.2012.742027

Jorquera, H., Barraza, F., 2013. Source apportionment of PM10 and PM2.5 in a desert region in northern Chile. Sci. Total Environ. 444, 327–335. doi:10.1016/j.scitotenv.2012.12.007

Jorquera, H., Barraza, F., 2012. Source apportionment of ambient PM2.5 in Santiago, Chile: 1999 and 2004 results. Sci. Total Environ. 435–436, 418–429. doi:10.1016/j.scitotenv.2012.07.049

Jorquera, H., Orrego, G., Castro, J., Vesovic, V., 2004. Trends in air quality and population exposure in Santiago, Chile, 1989-2001. Int. J. Environ. Pollut. 22, 507–530. doi:10.1504/IJEP.2004.005684

Kavouras, I.G., Koutrakis, P., Cereceda-Balic, F., Oyola, P., 2001. Source apportionment of PM10 and PM2.5 in five Chilean cities using factor analysis. J. Air Waste Manag. Assoc. 51, 451–464.

Koutrakis, P., Sax, S.N., Sarnat, J. a, Coull, B., Demokritou, P., Oyola, P., Garcia, J., Gramsch, E., 2005. Analysis of PM10, PM2.5, and PM2 5-10 concentrations in Santiago, Chile, from 1989 to 2001. J. Air Waste Manag. Assoc. 55, 342–351. doi:10.1080/10473289.2005.10464627

Leiva G, M.A., Santibañez, D.A., Ibarra E, S., Matus C, P., Seguel, R., 2013. A five-year study of particulate matter (PM2.5) and cerebrovascular diseases. Environ. Pollut. 181, 1–6. doi:10.1016/j.envpol.2013.05.057

Lewis, C.W., Norris, G. a, Conner, T.L., Henry, R.C., 2003. Source apportionment of Phoenix PM2.5 aerosol with the Unmix receptor model. J. Air Waste Manag. Assoc. 53, 325–338. doi:10.1080/10473289.2003.10466155

Malm, W.C., Sisler, J.F., Huffman, D., Eldred, R.A., Cahill, T.A., Malm, C Sisler, James F Cahill, A., 1994. Spatial and seasonal trends in particle concentration and optical extinction in the United States. J. Geophys. Res. 99, 1347–1370. doi:10.1029/93JD02916

Mena-Carrasco, M., Oliva, E., Saide, P., Spak, S.N., de la Maza, C., Osses, M., Tolvett, S., Campbell, J.E., Tsao, T. es C.C., Molina, L.T., 2012. Estimating the health benefits from natural gas use in transport and heating in Santiago, Chile. Sci. Total Environ. 429, 257–265. doi:10.1016/j.scitotenv.2012.04.037

Mena-Carrasco, M., Saide, P., Delgado, R., Hernandez, P., Spak, S., Molina, L., Carmichael, G., Jiang, X., 2014. Regional climate feedbacks in Central Chile and their effect on air quality episodes and meteorology. Urban Clim. 10, 771–781. doi:10.1016/j.uclim.2014.06.006

Minsegpres, 1998. Plan de descontaminación para el área circundante a la fundición de Caletones de la división el teniente de Codelco Chile.

MMA, 2015. Ministerio del Medio Ambiente - Anteproyecto del plan de prevención y descontaminación atmosférica para la región metropolitana de Santaigo.

Montezuma, A.I., 2016. Inversiones y exigencias ambientales en las fundiciones estatales de cobre chilenas: 1990-2014 - Master thesis. Pontificia Universidad Católica de Chile.

Moreno, F., Gramsch, E., Oyola, P., Rubio, M.A., 2010. Modification in the soil and traffic-related sources of particle matter between 1998 and 2007 in Santiago de Chile. J. Air Waste Manage. Assoc. 60, 1410–1421. doi:10.3155/1047-3289.60.12.1410

Muñoz, J.C., Batarce, M., Hidalgo, D., 2014. Transantiago, five years after its launch. Res. Transp. Econ. 48, 184–193. doi:10.1016/j.retrec.2014.09.041

Muñoz, R.C., Undurraga, A. a., Munoz, R.C., Undurraga, A. a., Muñoz, R.C., Undurraga, A. a., 2010. Daytime mixed layer over the Santiago Basin: Description of two years of observations with a lidar ceilometer. J. Appl. Meteorol. Climatol. 49, 1728–1741. doi:10.1175/2010JAMC2347.1

Norris, G., Duvall, R., Brown, S., Bai, S., 2014. EPA-Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide.

Norris, G., Vendantham, R., Duvall, R., Henry, R.C., 2007. EPA Unmix 6 . 0 Fundamentals & User Guide.

Olivares, G., Gallardo, L., Langner, J., Aarhus, B., 2002. Regional dispersion of oxidized sulfur in Central Chile. Atmos. Environ. 36, 3819–3828. doi:10.1016/S1352-2310(02)00286-8

Osses, A., Gallardo, L., Faundez, T., 2013. Analysis and evolution of air quality monitoring networks using combined statistical information indexes. Tellus Ser. B-Chemical Phys. Meteorol. 65, 1–17. doi:10.3402/tellusb.v65i0.19822

Pino, P., Walter, T., Oyarzun, M., Villegas, R., Romieu, I., 2004. Fine particulate matter and wheezing illnesses in the first year of life. Epidemiology 15, 702–708.

Préndez, M., Ortiz, J.L., Cortés, E., Cassorla, V., 1984. Elemental Composition of Airborne Particulate Elemental Composition of Airborne Particulate Matter from Santiago City , Chile , 1976. J. Air Pollut. Control Assoc. 34, 54–56. doi:10.1080/00022470.1984.10465726

Reff, A., Eberly, S.I., Bhave, P. V, 2007. Receptor modeling of ambient particulate matter data using positive matrix factorization: review of existing methods. J. Air Waste Manage. Assoc. 57, 146–154. doi:10.1080/10473289.2007.10465319

Rojas, C.M., Artaxo, P., Van Grieken, R., Grieken, R. Van, 1990. Aerosols in Santiago de Chile: A study using receptor modeling with X-ray fluorescence and single particle analysis. Atmos. Environ. B.Urban Atmos. 24, 227–241. doi:10.1016/0957-1272(90)90028-S

Rutllant, J., Garreaud, R., 2004. Episodes of Strong Flow down the Western Slope of the Subtropical Andes. Mon. Weather Rev. 132, 611–622. doi:10.1175/1520-0493(2004)132<0611:EOSFDT>2.0.CO;2

Rutllant, J., Garreaud, R., 1995. Meteorological air pollution potential for Santiago, Chile: Towards an objective episode forecasting. Environ. Monit. Assess. 34, 223–244. doi:10.1007/BF00554796

Saide, P.E., Carmichael, G.R., Spak, S.N., Gallardo, L., Osses, A.E., Mena-Carrasco, M.A., Pagowski, M., 2011. Forecasting urban PM10 and PM2.5 pollution episodes in very stable nocturnal conditions and complex terrain using WRF–Chem CO tracer model. Atmos. Environ. 45, 2769–2780. doi:10.1016/j.atmosenv.2011.02.001

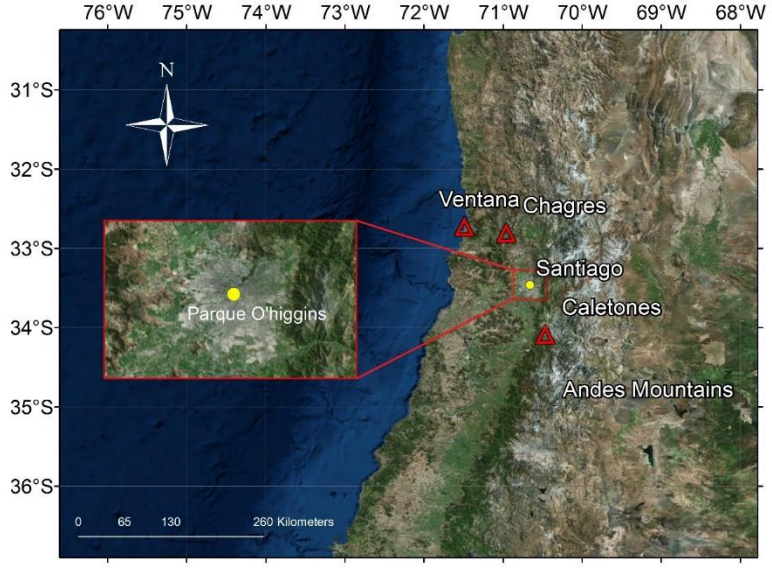
Sax, S.N., Koutrakis, P., Rudolph, P.A.R., Cereceda-Balic, F., Grarnsch, E., Oyola, P., 2007. Trends in the elemental composition of fine particulate matter in Santiago, Chile, from 1998 to 2003. J. Air Waste Manage. Assoc. 57, 845–855.

Valdes, A., Zanobetti, A., Halonen, J.I., Cifuentes, L.A., Morata, D., Schwartz, J., Valdés, A., Zanobetti, A., Halonen, J.I., Cifuentes, L.A., Morata, D., Schwartz, J., 2012. Elemental concentrations of ambient particles and cause specific mortality in Santiago, Chile: a time series study. Environ. Heal. 11, 82. doi:10.1186/1476-069X-11-82

Villalobos, A.M., Barraza, F., Jorquera, H., Schauer, J.J., 2015. Chemical speciation and source apportionment of fine particulate matter in Santiago, Chile, 2013. Sci. Total Environ. 512–513, 133–142. doi:10.1016/j.scitotenv.2015.01.006

Willis, R.D., 2000. Workshop on UNMIX and PMF as applied to PM2.5. U.S. EPA, Report No. EPA/600/A-00/048.

World Health Organization-WHO, 2005. Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide - Global update 2005.



Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

Figure 1 Map of Santiago region, Chile, with the metropolitan area indicated by the red rectangle, and the yellow circle showing the location of the monitoring site in Parque O'Higgins. The red triangles show the location of the major copper smelters close to Santiago.

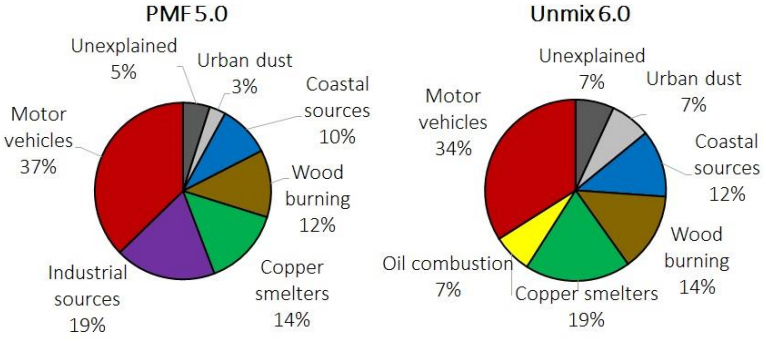


Figure 2 Global percentage of source apportionment to fine particulate matter in Santiago, Chile, 1998-2012. The $PM_{2.5}$ median over 15 years was 24.19 µg/m³.

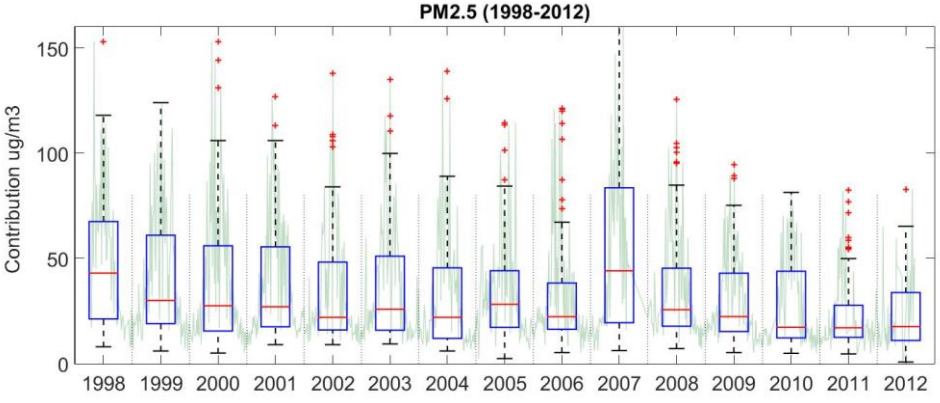


Figure 3 Temporal evolution of PM2.5 concentrations in Parque O'Higgins monitoring station in central Santiago.

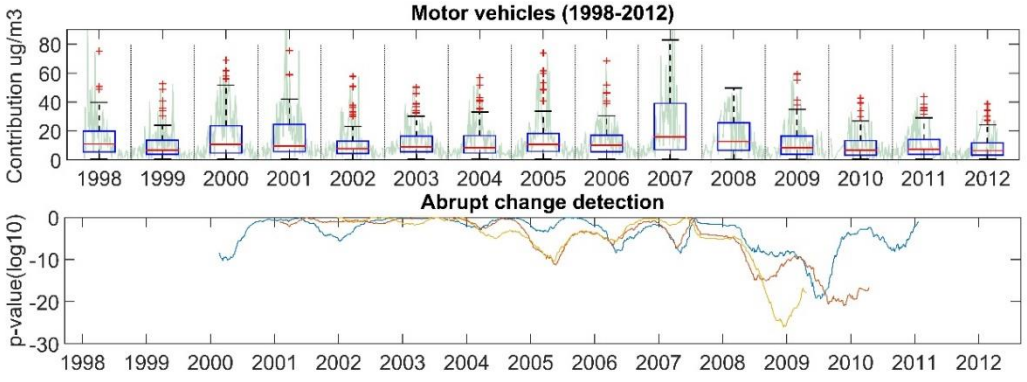


Figure 4 Top panel: Time series (green) and boxplot of the motor vehicles contribution to PM2.5. Bottom panel: p-value from a hypothesis test comparing the median of both halves of a sliding window, repeated for 3 different windows lengths (320, 480 and 640 days for blue, red and yellow, respectively).

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

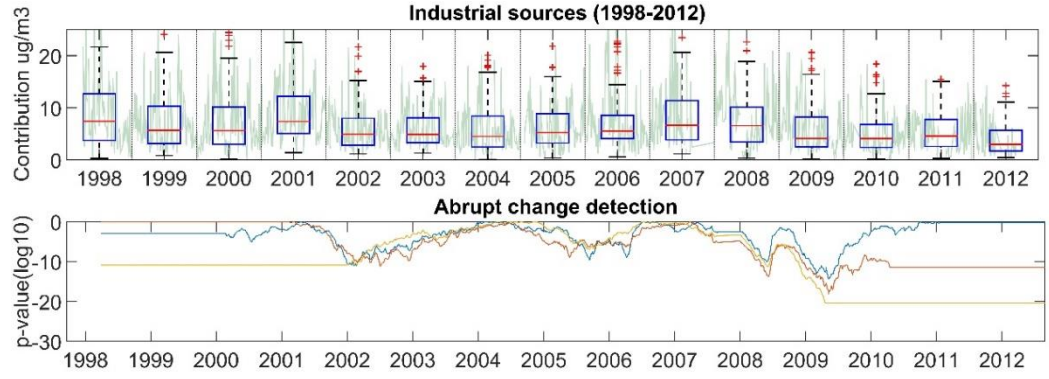


Figure 5 Top panel: Time series (green) and boxplot of the Industrial sources contribution to PM2.5. Bottom panel: p-value from a hypothesis test comparing the median of both halves of a sliding window, repeated for 3 different windows lengths (320, 480 and 640 days for blue, red and yellow, respectively).

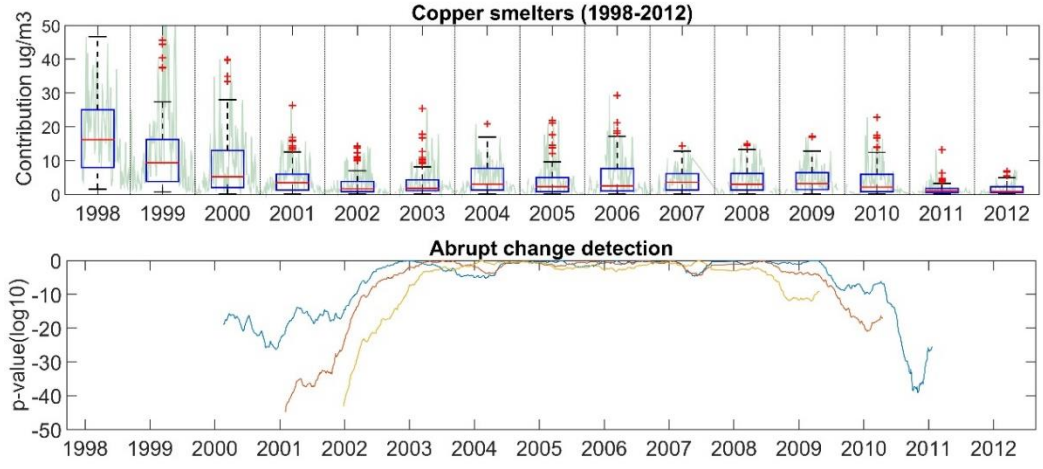
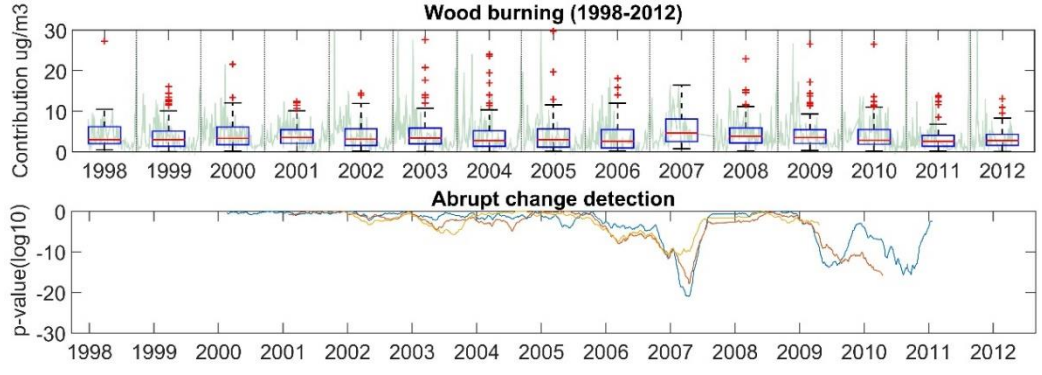


Figure 6 Top panel: Time series (green) and boxplot of the Industrial sources contribution to PM2.5. Bottom panel: p-value from a hypothesis test comparing the median of both halves of a sliding window, repeated for 3 different windows lengths (320, 480 and 640 days for blue, red and yellow, respectively).



Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

Figure 7 Top panel: Time series (green) and boxplot of the Wood burning contribution to PM2.5. Bottom panel: p-value from a hypothesis test comparing the median of both halves of a sliding window, repeated for 3 different windows lengths (320, 480 and 640 days for blue, red and yellow, respectively).

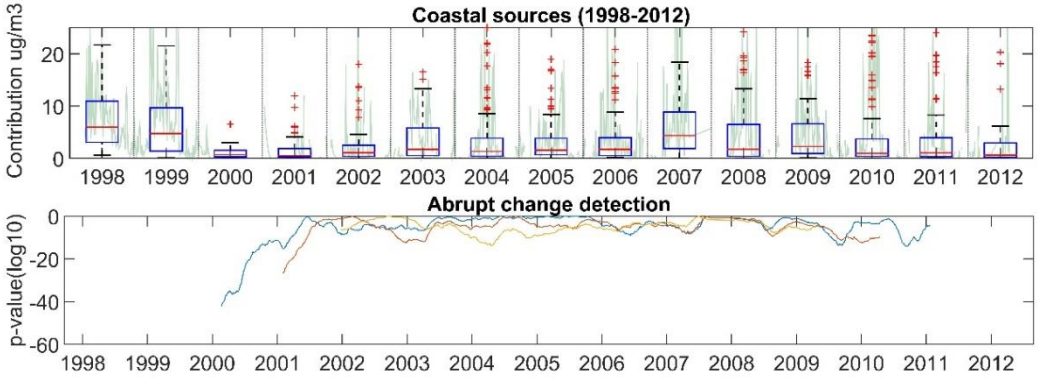


Figure 8 Top panel: Time series (green) and boxplot of the Coastal sources to PM2.5. Bottom panel: p-value from a hypothesis test comparing the median of both halves of a sliding window, repeated for 3 different windows lengths (320, 480 and 640 days for blue, red and yellow, respectively).

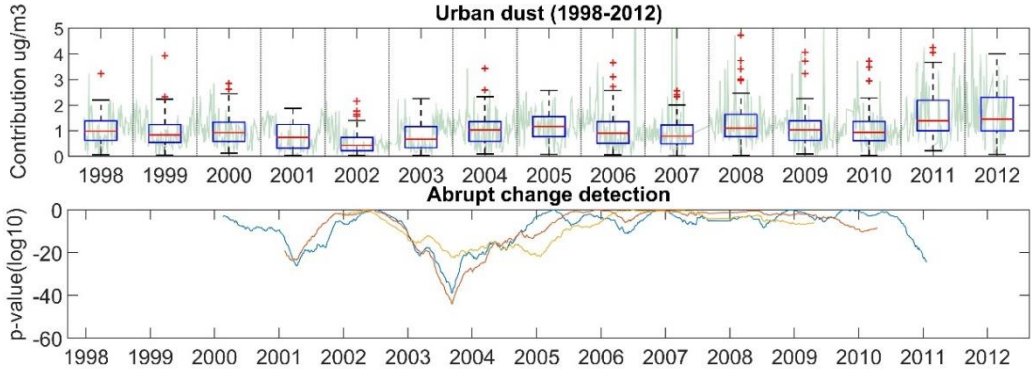


Figure 9 Top panel: Time series (green) and boxplot of the Coastal sources to PM2.5. Bottom panel: p-value from a hypothesis test comparing the median of both halves of a sliding window, repeated for 3 different windows lengths (320, 480 and 640 days for blue, red and yellow, respectively).

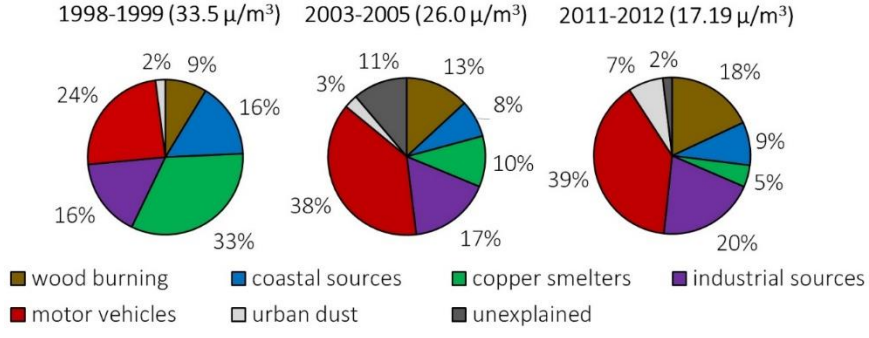


Figure 10 Relative contribution change of each source in the beginning, middle, and end of the period investigated in this study. Median levels of total PM2.5 are given in brackets next to the corresponding time period.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

Reference	(Rojas et al., 1990)	(Artaxo, 1996)	(Artaxo, 1998)	(Artaxo, 1999)	(Artaxo, 1999)	(Moreno et al., 2010)	(Jorquera and Barraza, 2012)	(Jorquera and Barraza, 2012)	(Villalobos et al., 2015)
Location in Santiago	Downtown	Downtown	Downtown	Downtown	East	Downtown	Las Condes	Las Condes	San Joaquin
Time period considered	January-February 1987	July-august 1996	July-august 1998	June-December 1999	June-December, 1999	1998-2007	1999	2004	2013
Sulfates	49					13.6	19	16	
Sulfates + As				39	15				
Sulfates + copper smelters			9.7						
Copper smelters		8.7					11	10	
Sulfates + industry		64							
Residual oil combustion + industry			23.2						
Residual oil combustion	13	1.9				13.6			
Motor vehicles + industry					70				
Motor vehicles		16	35.8	40		12.3	28	31	
Wood burning							25	29	19
Wood burning + car exhausts	5.6								
Solid dust + wood	26								

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

burning									
Solid dust		15.5	31.3	17	7	24.6	4	4	
Solid dust + metallurgical	6.4			4					
Marine aerosol							13	10	
Diesel emission									8
Gasoline vehicles									9
Ion nitrate									18
Ion sulfates									5
Ion ammonium									8
Secondary organic aerosol									7

Table 1 Summary of previous Santiago source apportionment studies (each column shows percentage contribution to PM2.5).

Source	*Autumn*	*Winter*	*Spring*	*Summer*
$PM_{2.5}$	43.9 (±19.3)	48.8 (±18.8)	16.0 (4.0)	16.7 (±4.7)
Wood burning	5.27 (±0.82)	14.95 (±1.77)	3.94 ± 0.48	2.85 ± 0.24
coastal sources	3.21 (±0.43)	1.86 (±0.44)	1.12 ± 0.42	not *significant*
Copper Smelter	5.67 (±0.62)	3.62±(0.52)	3.57 ± 0.24	3.20 ± 0.84
Industrial Sources	7.89 (±0.88)	5.39 ±(1.04)	6.10 ± 0.37	5.28 ± 0.59
Vehicles	11.70 (±0.74)	10.84 ±(0.83)	7.85 ± 0.64	7.72 ± 1.34
Urban Dust	2.57 (±0.60)	*not significant*	*not significant*	2.34 ± 0.66
Days over Chilean standard	138	149	2	4
Days over WHO guidelines	265	257	32	45
No of Samples	343	315	292	294

Table 2 Seasonal PM2.5 and source contribution identified by a stratified regression to the contribution obtained by PMF 5.0. The concentration values are given in µg/m3 for each season and source with corresponding standard errors within the brackets. Maximum values are highlighted in bold. The 24-hour Chilean standard for PM2.5 is 50 µg/m3 and the WHO guidelines is 25 µg/m3.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-18, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Published: 18 January 2017

Atmospheric Chemistry and Physics Discussions

Source	Date Change event	Impact over source contributions	Explanation and comments
Motor vehicles	2000-2002	Reduction of 2.98 µg/m3 (27.65%)	Improvement of fuel quality. Lead was removed from gasoline
Motor vehicles	2007-2008	Increase of 5.68 µg/m^3 (56.64%).	Increase in number of private motorized vehicles due to poor implementation of Transantiago
Motor vehicles	late 2008-2010	Reduction of 3.04 µg/m3 (32.41%)	Improvement to Transantiago
Industrial sources	2002	Reduction of 2.52 µg/m3 (34.33%)	Diesel fuel sulfur content reduction in 2001.
Industrial sources	2005-2007	Increase of 1.86 µg/m3 (45.04%).	Argentinean Natural Gas import reduction
Industrial sources	2009-2010	Reduction of 1.76 µg/m (31.17%)	Opening of Quintero Terminal for LNG import from other countries
Cooper smelter	1998-2002	Reduction of 4.13 µg/m3 (69.04%)	Implementation of emission abatement technology in Caletones smelter
Cooper smelter	2010-2011	Reduction of 1.41 µg/m3 (64.66%)	Reduction of SO_2 and PM emissions in Caletones and Ventana smelters
Wood burning	2007-2008	Increase of 1.16 µg/m3 (43.39%).	Unknow
Wood burning	2009-2010	Reduction of 0.55 µg/m3 (16.98%)	Unknow
coastal sources	2002-2005	Reduction of 1.62 µg/m3 (77.46%)	Diesel sulfur content reduction
coastal sources	Since 2010	Reduction of 1.05 µg/m3 (76.17%)	Opening of Quintero Terminal for import LNG import from other countries
Urban dust	2001-2002	Reduction of 0.42 µg/m3 (48.84%)	Lead-free gasoline introduction
Urban dust	Since 2004	Increase of 0.67 µg/m^3 (171.78%).	Increase in the number of motorized car (annual growth rate of 4%)
Urban dust	Since 2011	Increase of 0.48 µg/m^3 (51.61%).	Increase in the number of motorized car (annual growth rate of 7%), extended drought since 2010

Table 3 Measurements who increased or reduced each source contribution to apportionment to ambient PM2.5 levels in Santiago.