



Temporal evolution of main ambient PM_{2.5} sources in Santiago, Chile, from 1998 to 2012

Francisco Barraza^{1,4}, Fabrice Lambert^{1,4}, Héctor Jorquera^{2,5}, Ana María Villalobos², and Laura Gallardo^{3,4}

¹Geography Institute, Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile

²Department of Chemical Engineering and Bioprocesses, Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile

³Department of Geophysics, Universidad de Chile, Santiago, Chile

⁴Center for Climate and Resilience Research, University of Chile, Santiago, Chile

⁵Center for Sustainable Urban Development (CEDEUS), Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile

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

Received: 6 January 2017 – Discussion started: 18 January 2017

Revised: 8 June 2017 – Accepted: 12 July 2017 – Published: 29 August 2017

Abstract. The inhabitants of Santiago, Chile have been exposed to harmful levels of air pollutants for decades. The city's poor air quality is a result of steady economic growth, and stable atmospheric conditions adverse to mixing and ventilation that favor 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. Estimating the evolution of source contributions to ambient pollution levels is also paramount to evaluating the effectiveness of pollution reduction measures that have been implemented in recent decades. Here, we quantify the main sources that have contributed to fine particulate matter (PM_{2.5}) between April 1998 and August 2012 in downtown Santiago by using two different source-receptor models (PMF 5.0 and UNMIX 6.0) that were applied to elemental measurements of 1243 24 h filter samples of ambient PM_{2.5}. PMF resolved six sources that contributed to ambient PM_{2.5}, with UNMIX producing similar results: motor vehicles (37.3 ± 1.1 %), industrial sources (18.5 ± 1.3 %), copper smelters (14.4 ± 0.8 %), wood burning (12.3 ± 1.0 %), coastal sources (9.5 ± 0.7 %) and urban dust (3.0 ± 1.2 %). Our results show that over the 15 years analyzed here, four of the resolved sources significantly decreased [95 % confidence interval]: motor vehicles 21.3 % [2.6, 36.5], industrial sources 39.3 % [28.6, 48.4], copper smelters 81.5 % [75.5, 85.9], and coastal sources 58.9 % [38.5, 72.5], while wood burning did not significantly change and urban dust increased by 72 % [48.9, 99.9]. These changes are consistent with emission reduction measures, such as im-

proved vehicle emission standards, cleaner smelting technology, introduction of low-sulfur diesel for vehicles and natural gas for industrial processes, public transport improvements, etc. However, it is also apparent that the mitigation expected from the above regulations has been partially offset by the increasing amount of private vehicle use in the city, with motor vehicles becoming the dominant source of ambient PM_{2.5} in recent years. Consequently, Santiago still experiences ambient PM_{2.5} levels above the annual and 24 h Chilean and World Health Organization standards, and further regulations are required to reach ambient air quality standards.

1 Introduction

Santiago (33.5° S, 70.5° W, 500 m above sea level; a.s.l.) is the largest metropolitan area in Chile and the seventh in South America, with a population of 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.; Fig. 1). Moreover, Santiago's climate is controlled by the quasi-permanent influence of the subtropical Pacific high (descending branch of the Hadley's cell), which results in subsidence inversions that inhibit vertical mixing. 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, especially during summer (Muñoz and Undurraga, 2010; Rutllant and Gar-

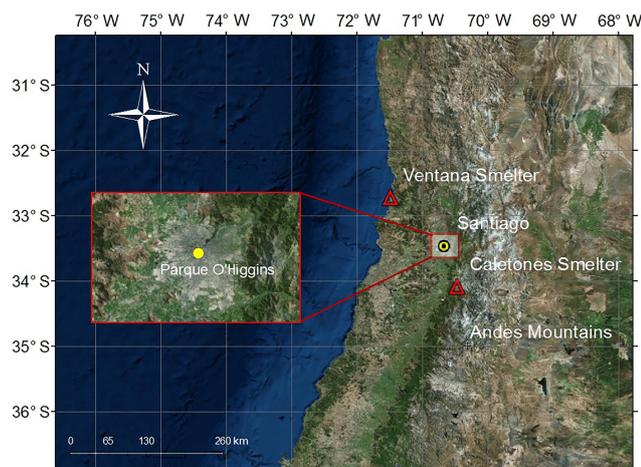


Figure 1. Map of Santiago region, Chile, with the metropolitan area indicated by the red rectangle, and the yellow circle showing the location of the monitoring site in Parque O'Higgins. The red triangles show the location of the major copper smelters close to Santiago.

reaud, 2004; Schmitz, 2005). Subsynoptic features known as coastal lows recurrently intensify the subsidence conditions (Rutllant and Garreaud, 1995), and their occurrence is linked to acute pollution episodes in winter (Gallardo et al., 2002; Saide et al., 2011). Central Chile is also characterized by significant interannual variability connected to the El Niño Southern Oscillation (ENSO) and longer-term variability associated with the Pacific Decadal Oscillation (Garreaud et al., 2009). Over the last 6 to 7 years, central and southern Chile has been affected by an extended and persistent drought, partly caused by natural variability and partly linked to a global warming trend (Boisier et al., 2016; CR2, 2015). All these conditions produce favorable conditions for the accumulation of emissions, and the generation of secondary pollutants. The Chilean Meteorological Service does not regularly launch radiosondes in Santiago, so no direct measurements of planetary boundary layer height (PBLH) are available. However, some studies have presented PBLH estimates retrieved from ceilometer readings (Muñoz and Undurraga, 2010; Muñoz and Alcañuz, 2012); the data show a distinctive seasonality with lower (higher) values for the austral winter (summer) seasons, prompted by the synoptic meteorological conditions discussed above, but the PBLH shows no significant trend between 2008 and 2015.

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; Henríquez 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 the Environment, making

it one of the longest-running PM_{2.5} air quality monitoring networks in the world (Jhun et al., 2013).

Although environmental authorities have gathered a long-term record of ambient PM_{2.5} elemental composition for Santiago, source-apportionment studies are relatively sparse, and they generally include a few months or a single year of data at most (Table S1 in the Supplement). 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. High concentration levels of PM_{2.5} have been associated with health problems in Santiago (Pino et al., 2004; Cakmak et al., 2007; Valdes et al., 2012; González et al., 2013; Leiva et al., 2013). Since 1990, Chilean authorities have implemented several air pollution abatement policies that have significantly decreased PM_{2.5} (Mena-Carrasco et al., 2014; MMA, 2015). These measures included phasing lead out of gasoline (late nineties), reducing sulfur in diesel fuel for transport and for industry (5000 ppm in 1989 to 15 ppm for vehicular and 50 ppm for industry today), stricter emission standards for mobile sources (from EURO I to EURO III since 2007, EURO IV since 2012), modernization of the public transport fleet, selective bans on private car usage during high-pollution days, a mandatory car inspection and maintenance program, street sweeping and cleaning programs, and emissions standards for industrial combustion sources (Sax et al., 2007; Moreno et al., 2010; Jhun 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 (WHO, 2005), and above the annual Chilean standard of 20 µg m⁻³ enacted in 2012 (MMA, 2012). Moreover, Santiago experiences frequent autumn and winter PM_{2.5} daily episodes with levels exceeding the WHO 24 h guideline of 25 µg m⁻³ (WHO, 2005) and the 24 h Chilean standard of 50 µg m⁻³. These episodes are recurrent and typically last several days (Saide et al., 2011).

1.1 Source-apportionment data analyses

Receptor models (see below) are state-of-the-art computational tools that allow researchers to identify and quantify the major sources that contribute to ambient PM_{2.5} concentrations in a given region and over a given period. Within the Latin American region, several source-apportionment studies have been carried out in the largest cities such as Mexico City (Mugica et al., 2002); Sao Paulo, Brazil (Andrade et al., 2012); Rio de Janeiro, Brazil (Andrade et al., 2012; Godoy et al., 2009); and Santiago, Chile (Jorquera and Barraza, 2012; Villalobos et al., 2015). However, all these studies spanned only 1–2 years, were carried out using different receptor models, and differed in the time period analyzed, so it is difficult to quantitatively compare among them.

Table 1. Comparison of source-apportionment studies in Latin American cities (WHO, 2017). Total PM_{2.5} and its sources are expressed in micrograms per cubic meter ($\mu\text{g m}^{-3}$).

Site location	Country	Population	Model used	Study year	PM _{2.5}	Sea salt	Dust	Traffic	Industry	Biomass burning	Other
Córdoba	Argentina	1 272 000	PMF	2009/2010	71		39.1	22.7	9.2		0.0
Curitiba	Brazil	2 751 907	APCA	2007/2008	12	0.0	0.0	6.6	1.9	0.0	3.5
Porto Alegre	Brazil	1 409 351	APCA	2007/2008	16	0.0	0.0	5.6	0.5	0.0	9.9
Belo Horizonte	Brazil	2 375 151	APCA	2007/2008	17	0.0	7.5	3.1	2.0	0.0	4.4
Recife	Brazil	1 537 704	APCA	2007/2008	18	4.3	1.4	6.7			5.6
Rio de Janeiro	Brazil	6 320 000	APCA	2007/2008	20		2.8	10.2	3.6		3.4
Sao Paulo	Brazil	11 235 503	APCA	2007/2008	28		3.6	11.2	3.6		9.5
Rio de Janeiro	Brazil	6 320 000	APFA	2003/2005	10		3.5	2.8	3.4		0.0
Santiago	Chile	5 278 000	PMF	2004	32	3.2	1.3	10.0	3.1	9.3	5.3
Santiago	Chile	6 000 000	CMB	2013	33	1.0	2.5	11.0	4.6	5.2	8.9
Moravia	Costa Rica	56 919	PMF	2010/2011	18	2.0	3.9	5.2			6.9
San José	Costa Rica	288 054	PMF	2010/2011	26	2.0	3.5	4.8	6.9		8.9
Heredia	Costa Rica	20 191	PMF	2010/2011	37	2.4	5.1	5.8	10.3		13.4
Tijuana	Mexico	1 301 000	PMF	2010	19	2.9		2.6	0.4	7.1	5.6
Mexico City	Mexico	8 851 000	CMB	2006	50		13.3	21.0	5.0		10.7
Salamanca	Mexico	152 048	PMF	2006/2007	45		7.3	5.8	8.2		23.7

Table 2. Comparison of long-term source-apportionment studies carried out in urban areas.

Location, period	PM _{2.5} mass	Motor vehicles	Sulfates + nitrates + ammonia	Biomass burning	Soil	Industry ^c
Los Angeles, CA, US, 2002–2013	17.5	3.3	9.6	1.1	1.0	–
Rubidoux, CA, US, 2002–2013	19.5	3.7	12.2	0.8	0.9	0.1
Detroit, US, 2001–2014	11.8	2.5	5.1	0.8	0.9	0.5
Chicago, US, 2006–2014	10.3	2.2	4.8	0.9	0.4	1.1
Sydney, Australia, 1998–2009	9.3	2.1	1.8 ^a	2.7	0.3	–
Hanoi, Vietnam, 2001–2008	54.0	21.6	15.7 ^a	7.0	1.8	10.3
Kuala Lumpur, Malaysia, 2002–2011	25.1	8.9	12.1 ^b	2.3	0.8	12.0

^a Only ammonium sulfate is reported. ^b Sulfate was expressed as ammonium sulfate. ^c Whenever more than one type of industrial source has been resolved, they have been lumped together in a single industrial category.

Nonetheless, traffic and industrial sources are the typical major contributors to ambient PM_{2.5}, as shown in Table 1, while biomass burning is relevant only in some cities. The “other” category source is relevant in most Latin American cities and it may be due to processes leading to organic and inorganic PM_{2.5}, plus smaller unresolved sources such as meat cooking, combustion of natural gas, coal, liquefied petroleum gas, etc. (WHO, 2017).

Although these studies provide a quantitative assessment of ambient PM_{2.5} sources, we are aware of no long-term urban source-apportionment studies in Latin America. Long-term studies provide a quantitative estimation of the temporal evolution of major contributing sources, so an evaluation of the effectiveness of sector regulations can be performed. This information is critical for policy-makers and stakeholders, to provide feedback and suggest new initiatives to further reduce pollution levels. Table 2 summarizes several long-term studies carried out in developed and developing countries

within a similar period. Motor vehicles and industrial source contributions are clearly higher in developing countries (including most Latin American cities – Table 1), whereas in developed countries those sources have been controlled and their contributions are lower.

1.2 Study objectives

Air quality policies and regulations implemented in Santiago were designed 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 up 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, the relative chemical composition

of particles in Santiago has changed with time. However, no study to date has investigated the evolution of ambient-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), analyze how each source varied through time, determine how much each contributed to total ambient PM_{2.5} in Santiago, and how effective the various regulation policies implemented over that period were.

2 Methodology

2.1 Sampling station

Environmental authorities have collected ambient PM_{2.5} samples in Santiago using a 37 mm diameter Teflon filter (Pall Flex) since 1998 using the same sampling and analysis methodology. Filters were collected using a low-volume dichotomous samplers (Anderson Instruments, Inc., Smyrna, GA, USA) operating at 15 L min⁻¹ for 24 h, with the sampler inlet located 3 m above ground. The monitoring station 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 about every 4 days (mean and median) from April 1998 to August 2012.

2.2 Laboratory and QA/QC analysis

Filters were inspected before being used, and the particles' concentration was determined gravimetrically using a microbalance, with a resolution of 0.01 mg. All filter (blank and filter samples) were stored at constant temperature (22 ± 3 °C) and relative humidity (40 % HR ± 3 %) for at least 24 h before being weighed. Those filters were analyzed using X-ray fluorescence (XRF) at the Desert Research Institute, Reno, NV, USA. The Ministry for the Environment provided the database containing the elemental analyses of those filters. In order to build statistical models based on robust chemical signals, we decided to keep only those elements selected in other studies that used the same data (CMM-MMA, 2011; Koutrakis et al., 2005; Sax et al., 2007; Valdes et al., 2012), for which more than 75 % of the samples contained valid measurements above the detection limit. The limit of detection (LOD) was calculated for each element as three times the standard deviation of the blank (blanks represented approximately 10 % of the samples). This public database

(gravimetry and elemental analysis) has been used in several studies and all of them have already described the laboratory and QA/QC methodology (CMM-MMA, 2011; Jhun et al., 2013; Koutrakis et al., 2005; Sax et al., 2007). Thus, out of the 49 elements reported, 22 agreed with the criteria described above (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As and Se, Br, Sr, Ba and Pb). Out of these, some were discarded because of large data gaps in the time series (Mg, V, Sr, Ba, Se), suspicious sources (Pb and Br, see discussion below), or because the model was not significant (Na and Ca). In the end, 12 elements were used for our analysis: Al, Si, S, Cl, K (as Kns), Ti, Cr, Fe, Ni, Cu, Zn and As. We used two separate methods to address the small missing data gaps in the time series of the selected elements. First, we let the receptor models' (PMF5, UNMIX6) internal algorithms deal with them; this process consists of replacing missing values with the median of the complete time-series for each species. Since replacing missing data with the median can lead to severe distortions in the data, we have also used a custom-written algorithm. This method interpolates up to three consecutive missing values using MATLAB's piecewise cubic interpolation algorithm. Sections of four or more consecutive missing values are filled in by summing up a mirrored copy of equal data length on both sides of the missing records, weighted by a cos² function, thus ensuring that no artificial frequencies or discontinuities are introduced in the signal – the data-filling algorithm is a MATLAB code that is available upon request to Fabrice Lambert. None of the species selected for the receptor model analysis features any data gap larger than 10 data points. Species with larger gaps were ultimately discarded from the analysis. The original and interpolated data are shown in Fig. S1 in the Supplement. Since our custom algorithm does not introduce discontinuities in the time series, we used this method for our analysis. In contrast, the receptor model results using the median-based missing data replacement can lose the seasonal signal of some species. Accordingly, the model results using the median-based filling algorithm yielded more variability in Cl, Ti, Cr, Ni and As (species with important number of blanks, see Fig. S1).

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

2.4 Analysis of source-contribution 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 micrograms per cubic meter ($\mu\text{g m}^{-3}$; log transformed to achieve normal distribution) as the 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 due to specific regulations on 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 recent 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 there-

fore a significant change in concentration between those 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 in Eq. (1) and examined the resulting source profiles, looking for specific tracers and tracer ratios, as well as the seasonality of source contributions to identify potential sources. We considered 12 species that produced the best model: Al, Si, S, Cl, nonsoil K (Kns), Ti, Cr, Fe, Ni, Cu, Zn and As. This model had the most robust regression parameter and the highest number of statistically significant source factors. We have 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 chemical composition in the source profiles. Had we kept lead in the model we would have concluded that the motor vehicle contributions significantly decreased in a span of only 1 year, which is wrong. Although lead is a classical tracer of motor vehicle emissions, it 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 have added the nonsoil potassium parameter Kns, calculated as $\text{Kns} = (\text{K} - 0.3 \cdot \text{Fe})$, and removed K from the model. The 0.3 coefficient was obtained from a K–Fe edge plot (Fig. S2). This methodology has been used before by Lewis et al. (2003) and Cohen et al. (2010) to remove soil contribution from total potassium.

Both models found species regressions with a coefficient (R^2) greater than 0.7. These species are tracers for the interpretation of each source profile and of the global model as well (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 ($p \leq 0.05$). This approach has been already described in previous studies (Jorquera and Barraza, 2012, 2013).

Both models produced a similar six-factor solution that explained 74 % of the variance in ambient PM_{2.5} (Fig. 2). This 74 % figure is a good result if we bear in mind that sources' profiles may not stay constant over the 15-year modeling period, adding uncertainty to model results. In addition, there are no available data for either organic carbon (OC), elemental carbon (EC), or secondary organic aerosols (SOA). The addition of these two components would have reduced

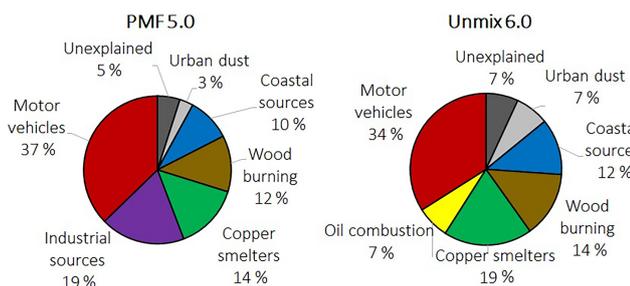


Figure 2. Source apportionment of fine particulate matter in Santiago, Chile, over the whole period 1998–2012 using two different models. The PM_{2.5} median over 15 years was 24.19 $\mu\text{g m}^{-3}$.

the uncertainty in the resolved source profiles. For instance, the addition of OC and EC would help the model discriminate between motor vehicle and wood-burning emissions. SOA may be relevant in the warm season (October–April), as shown by Villalobos et al. (2015) for Santiago in 2013; these authors estimated that up to 30 % of summertime PM_{2.5} may correspond to SOA. Below we discuss each source individually.

The main difference between PMF and UNMIX average results (Fig. 2) was that UNMIX resolved the oil combustion as a unique source, apportioning 85 % of Ni to that source profile, similar to one found in Santiago by Artaxo (1998). Although vanadium and nickel are good tracers for oil industrial combustion, we had to remove vanadium from the models, because the high number of missing data in that species precluded a PMF solution. The PMF solution apportions 56.5 and 19.5 % of Ni concentration within the motor vehicles and industrial source profiles, likely because vanadium was excluded from PMF input. This is a consequence of the different methodologies used by PMF and UNMIX to compute source profiles.

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 in Santiago (0.32) (Jorquera and Barraza, 2012) for motor vehicle sources. This source has a characteristic weekly behavior, with weekend contributions around half the working days’ contributions.

The second source was identified as “industrial sources”. It is characterized by the high content of sulfur (65.47 %) that originates from SO₂ emitted by industrial sources. This source also contains other tracer species that originate in industrial processes, such as Ni (19.5 %). Since this profile is dominated by sulfur, it has previously also been identified as “industrial sulfates” or “sulfates” (Jorquera and Barraza, 2012; Moreno et al., 2010). This source does not show a

weekly change in contribution, as expected from sources that run 24/7.

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 resolved by PMF with ambient data from the cities of Rancagua (Kavouras et al., 2001), Quillota (Hedberg et al., 2005), and Las Condes (Santiago; 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 smelters’ continuous operation.

The fourth source was identified as “wood burning”. It contains over 70 % of nonsoil potassium, 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 ($p = 8.28 \times 10^{-5}$).

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 sea salt component, present all year long (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 as well. This source shows no weekly cycle ($p = 0.251$), as expected for natural or continuous anthropogenic sources.

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 contribution (Malm et al., 1994). For example, its Si / Al ratio of 2.26 is close to source-apportionment results from other Chilean cities (Temuco, 2.17; Valparaíso, 2.58; Kavouras et al., 2001). Also, this source did not present any contribution of the pseudo-species of Kns as expected; this validates that using Kns was a good choice to discriminate soil from wood burning. 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 street dust (ratio working day / weekend = 1.18; $p = 3.53 \times 10^{-4}$).

We ran UNMIX 6.0 using the same data selected for the PMF 5.0 calculations and obtained similar results (Fig. 2). The main difference is that we could not identify the source “industrial sources” using UNMIX 6.0, because the PMF solution apportions sulfur among the sources “urban dust”, “coastal sources”, “wood burning” and “copper smelters”. Instead, UNMIX resolves a source that we identified as “oil combustion”, with a high contribution of Ni and Cr and low values of Cu, Zn and As. This source has been identified in previous studies as a contributor to Santiago’s ambient PM_{2.5} (Rojas et al., 1990; Artaxo, 1996, 1998; Jhun et al., 2013). This “oil combustion” source was not resolved by PMF, as discussed above.

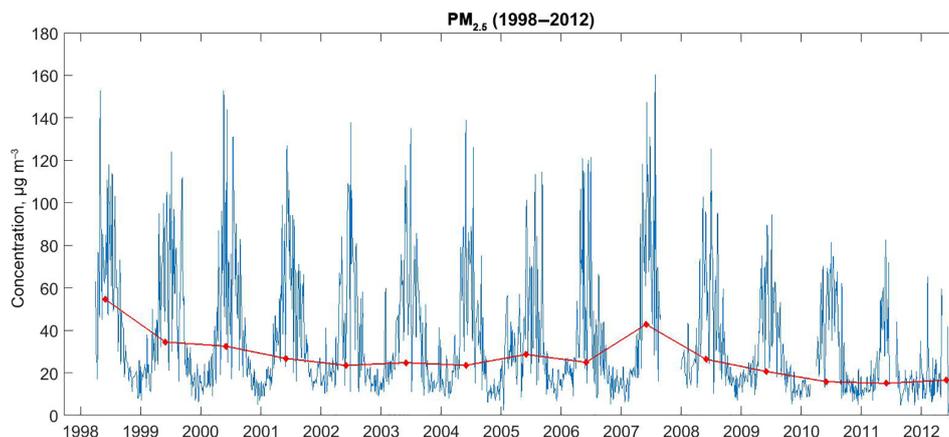


Figure 3. Temporal evolution of PM_{2.5} concentrations in Parque O'Higgins monitoring station in central Santiago. The red line shows the annual median.

Table 3. Seasonal PM_{2.5} and source contribution identified by a stratified regression of the contributions obtained by PMF 5.0. The concentration values are given in micrograms per cubic meter ($\mu\text{g m}^{-3}$) for each season and source, with corresponding standard errors at 95 % confidence level within the brackets. The 24 h Chilean standard for PM_{2.5} is $50 \mu\text{g m}^{-3}$ and the WHO guidelines is $25 \mu\text{g m}^{-3}$.

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 smelters	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 daily samples	343	315	292	294

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 artifact. 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 such as secondary organic aerosols (Villalobos et al., 2015). The average contributions of both models are shown in Fig. 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 (standard deviation 27.89) $\mu\text{g m}^{-3}$ and the median $24.19 \mu\text{g m}^{-3}$ (median absolute deviation of 11.81), as show in Fig. 3. Over the 15 years of the analyzed time period, there were 599 and 293 days when daily PM_{2.5} concentrations were above WHO and Chilean standards, respectively. The highest daily levels are found during the cold

seasons (autumn and winter) with a ratio close to 3 between cold-season and warm-season concentrations (Table 3). During the spring and summer seasons, boundary layer height increases (Muñoz and Undurraga, 2010; Muñoz and Alcañiz, 2012) along with wind speeds. The seasonal signal in most sources is strongly linked with the reduction of air volume below the boundary layer during the cold season, and does not necessarily imply seasonal variability in the emissions. The contribution of all sources to PM_{2.5} air concentrations increases during the cold season, with almost all episodes with PM_{2.5} levels over the Chilean and WHO standards occurring during autumn and winter.

The six identified sources have distinct seasonal contributions to PM_{2.5}. During winter, when PM_{2.5} reaches its largest concentrations and ambient temperatures are lowest, we find a maximum contribution from residential wood smoke to total PM_{2.5} because of the widespread use of fire wood for heating purposes. However, the other five sources have their highest contributions during autumn. Unlike wood burning, the emissions from these sources are more constant through the seasons and their contribution to PM_{2.5} concen-

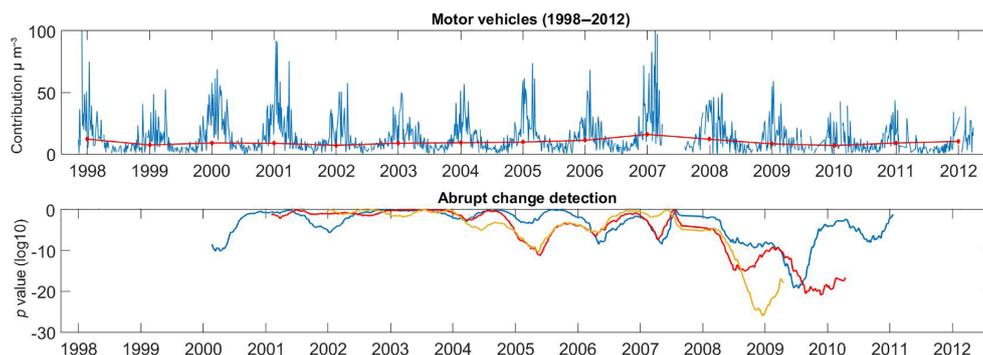


Figure 4. Top panel: time series of motor vehicles’ contribution to PM_{2.5} and the annual median in red. Bottom panel: p value from a Mann–Whitney hypothesis test comparing the medians of both halves of a sliding window, repeated for three different window lengths (320, 480 and 640 days for blue, red and yellow, respectively).

trations more strongly modulated by meteorological conditions. Their peak during the latter half of the cold season is explained by the rainy season that takes place during winter and washed out a large fraction of the contaminants from the air. The lack of rainfall and low boundary layer height during autumn produces the maximum contributions in these sources.

3.3 Time series of each source contribution

3.3.1 Motor vehicles

In Fig. 4 we show the temporal evolution of the source identified by PMF as motor vehicles. Over the 15 years analyzed in this study, the motor vehicles’ contribution to PM_{2.5} decreased significantly by $2.17 (\pm 1.91) \mu\text{g m}^{-3}$, $p = 0.0250$ (21.3 %, 95 % CI [2.6 %, 36.5 %]). This is explained by several policy measures: restrictions to vehicle traffic since the late 1980s (Moreno et al., 2010), mandatory catalytic converters for gasoline-powered cars since 1991 (Koutrakis et al., 2005), reduction of sulfur in gasoline and diesel, operation of new urban highways and the implementation of a new public transportation system between 2007 and 2010 called “Transantiago” (Muñoz et al., 2014).

The reduction in motor vehicles’ contributions has not been constant. In 2002 there was a reduction of $1.53 \mu\text{g m}^{-3}$ (15.6 %), which is due to the improvement of gasoline and diesel quality, highlighted by the fact that lead was entirely removed from gasoline on April 2001 (Moreno et al., 2010). Between 2005 and 2006, four new urban highways opened, and one of these is only 2.4 km from the sampling site. During this period, the vehicles contribution increased in $1.6 \mu\text{g m}^{-3}$ (18.9 %). We ascribe this rise to the proximity of the new highways to the sampling site as well as the increase in the traffic there. Brugge et al. (2007) concluded over several studies in several cities that proximity to highways increases the exposition to air particles.

In February 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 increased by $1.34 \mu\text{g m}^{-3}$ (13.4 %) during 2007–2008. Unfortunately, the beginning of Transantiago included 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 above problems with Transantiago – induced people to buy and use private cars, which led to an 11 % increase in the motorized vehicle fleet in 2007 (Figs. S3 and S4).

Subsequent improvements in the Transantiago public transport system after 2007 led to a reduced contribution of motor vehicles. The measures included (i) a renewed increase of the bus fleet to 6000 vehicles to satisfy passenger demand, (ii) an extension of the subway network and (iii) the gradual implementation of EURO III emission standards for buses (from 53 % of the fleet in 2007 to 92 % in May 2012; Muñoz et al., 2014). Comparing the period 2010–2011 with 2005–2006 we found a long-term decrease of motor vehicles’ contribution of $2.78 \mu\text{g m}^{-3}$ (27.7 %) that can be ascribed to Transantiago’s full implementation.

3.3.2 Industrial sources

In Fig. 5 we show the temporal evolution of the source identified as industrial sources. This source reduced its contributions from 1998 to 2012 by $2.63 (\pm 0.71) \mu\text{g m}^{-3}$, $p = 1.1 \times 10^{-9}$ (39.3 %, 95 % CI [28.6, 48.4 %]). This improvement can be explained by abatement policies for sulfur in industrial diesel fuel (Jhun et al., 2013), mandatory reductions in industrial emissions (Mena-Carrasco et al., 2014), and a change from diesel to natural gas as industrial fuel (MMA 2015). We found a significant reduction of $2.52 \mu\text{g m}^{-3}$ (34.3 %) in 2002 compared with 2001 that can be explained by a reduction of sulfur in industrial diesel, which was re-

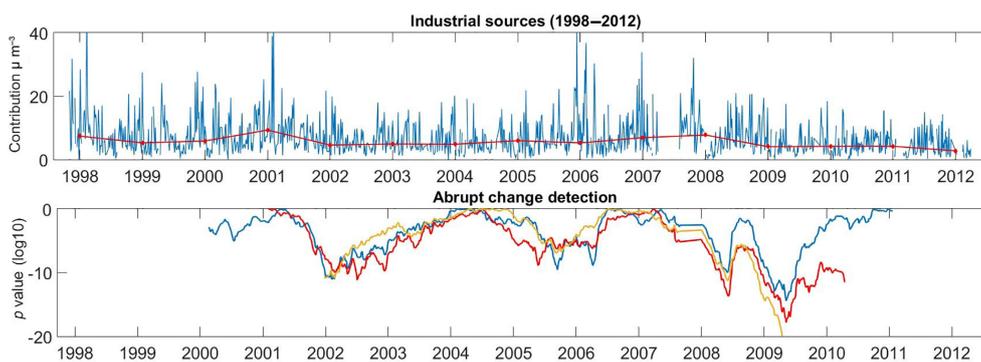


Figure 5. Top panel: time series of industrial sources contribution to PM_{2.5} and the annual median in red. Bottom panel: p value from a Mann–Whitney hypothesis test comparing the median of both halves of a sliding window, repeated for three different window lengths (320, 480 and 640 days for blue, red and yellow, respectively).

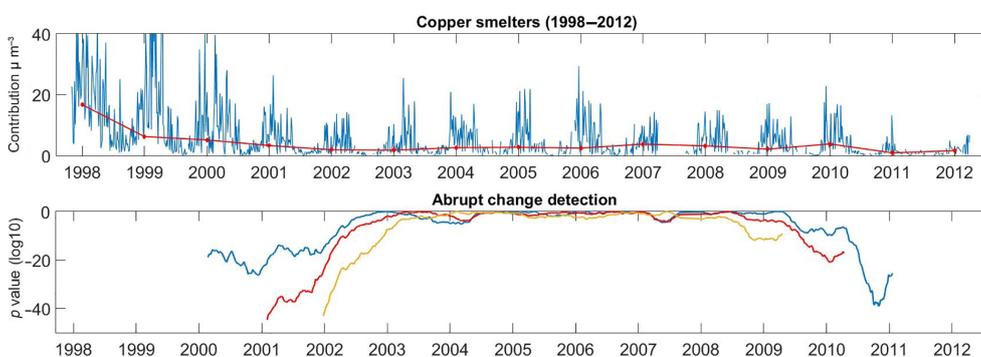


Figure 6. Top panel: time series of copper smelters' contribution to PM_{2.5} and the annual median in red. Bottom panel: p value from a Mann–Whitney hypothesis test comparing the median of both halves of a sliding window, repeated for three different window lengths (320, 480 and 640 days for blue, red and yellow, respectively).

duced from 1000 to 300 ppm in 2001 (CMM, 2014; MMA, 2015).

Between 2005 and 2007 we find a significant increase of industrial sources contributions, which was triggered by the phasing out of natural gas imports from Argentina. During those years, a large number of industries were forced to switch back to diesel fuel or fuel oil. Since 2008, the Chilean government imports liquefied natural gas from other countries, which explains the reduction between 2009 and 2010 caused by industries switching back to natural gas (Figuerola et al., 2013; GNL-Quitero, 2016). The period 2010–2012 shows a reduction of $1.76 \mu\text{g m}^{-1}$ (31.2 %) compared with the period without natural gas imports (2004–2008).

3.3.3 Copper smelters

In Fig. 6 we show the temporal evolution of the source identified as copper smelters. This contribution features the largest reduction of $5.24 (\pm 1.38) \mu\text{g m}^{-3}$, $p = 0.82 \times 10^{-33}$ (81.5 %, 95 % CI [75.8 %, 85.9 %]) between 1998 and 2012. This decrease can be attributed to technological improvements at the Caletones and Ventanas smelters near Santiago (see Fig. 1). In 1998, new regulations forced Caletones to install an acid

plant for SO₂ abatement, followed by a second one in 2002 (Minsegres, 1998). This emission abatement technology decreased SO₂ emissions from 700 000 t in 1999 to 100 000 t in 2003 (CODELCO, 2015; Montezuma, 2016). The period between 2002 and 2010 shows a reduction of $4.13 \mu\text{g m}^{-3}$ (69.0 %) compared to the period 1998–2001. We find another significant reduction of $1.41 \mu\text{g m}^{-3}$ (64.7 %) between 2009 and 2012, explained by further reductions in SO₂ emissions at both smelters. The Ventanas smelter reduced its SO₂ emissions from $20.3 \text{ kton yr}^{-1}$ in 2009 to 4.7 kton yr^{-1} in 2012, while the Caletones smelter's SO₂ emissions were reduced from 141 kton yr^{-1} in 2009 to 50 kton yr^{-1} in 2012 (Montezuma, 2016).

3.3.4 Wood burning

In Fig. 7 we show the temporal evolution of the source identified as wood burning. It is the only resolved source with no net significant change in the period 1998–2012: $0.43 (\pm 0.60) \mu\text{g m}^{-3}$, $p = 0.139$ (12.8 %, 95 % CI [−4.9 %, 27.6 %]). Nevertheless, we find two significant changes during this period that canceled each other out: (i) an increase in 2007–2009 of $1.17 \mu\text{g m}^{-3}$ (43.4 %) compared with 2004–

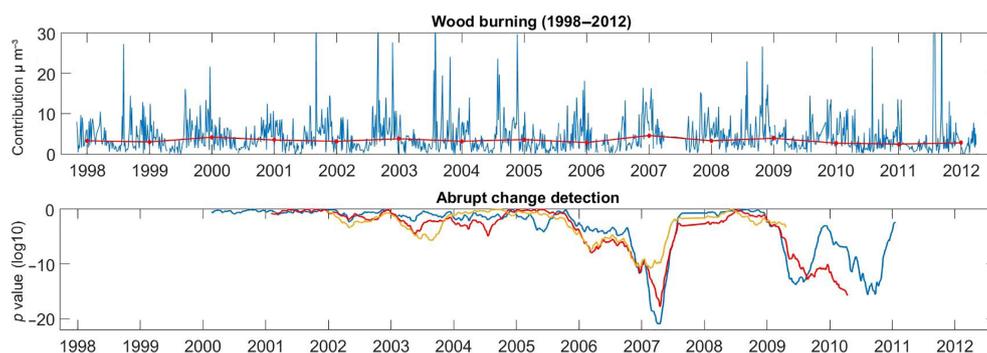


Figure 7. Top panel: time series of wood-burning contribution to PM_{2.5} and the annual median in red. Bottom panel: p value from a Mann–Whitney hypothesis test comparing the median of both halves of a sliding window, repeated for three different window lengths (320, 480 and 640 days for blue, red and yellow, respectively).

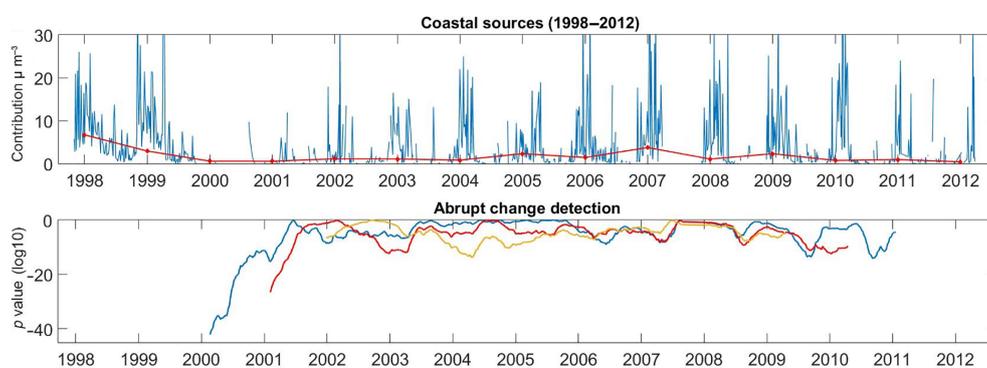


Figure 8. Top panel: time series of coastal sources contributions to PM_{2.5} and the annual median in red. Bottom panel: p value from a Mann–Whitney hypothesis test comparing the median of both halves of a sliding window, repeated for three different window lengths (320, 480 and 640 days for blue, red and yellow, respectively).

2006 and (ii) a reduction in 2010–2012 of $1.16 \mu\text{g m}^{-3}$ (30.1 %) compared with 2007–2009.

To curb wood-burning emissions, Chilean authorities have forbidden open chimneys since 1997, only allowing the use of certified woodstoves. In addition, 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) in reducing the wood-burning contribution to PM_{2.5}. Mena-Carrasco et 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 $2.07 \mu\text{g m}^{-3}$ in PM_{2.5} concentrations if all wood stoves were changed to natural gas stoves. This would represent about 50 % of our estimate of current wood-burning contributions to Santiago’s ambient PM_{2.5}.

3.3.5 Coastal sources

In Fig. 8 we show the temporal evolution of the source identified by PMF as coastal sources. This source is a mixture of marine aerosols and coastal industry emission. Its contribution shows a significant reduction of $1.48 (\pm 0.51) \mu\text{g m}^{-3}$,

$p = 0.88 \times 10^{-5}$ (58.9 %, 95 % CI [38.5 %, 72.5 %]), which we attribute to changes in the coastal industry, while we assume that marine aerosols remained constant. We find a significant reduction of $1.62 \mu\text{g m}^{-3}$ (77.5 %) from 2000 to 2002 compared with the period 1998–1999 that can be explained by cleaner industrial fuel, as explained for the industrial source contribution case. Likewise, those coastal industries were also affected by the shortage of natural gas imports from Argentina, increasing their contributions from 2004–2008 due to a temporary switch to diesel, and then reducing contributions after 2009 following LNG imports. Since 2010, coastal sources have reduced their contribution by $1.05 \mu\text{g m}^{-3}$ (76.2 %) compared with the period 2007–2008.

3.3.6 Urban dust

In Fig. 9 we show the temporal evolution of the source identified as urban dust. It is the only resolved source that has increased its contributions significantly by $0.49 (\pm 0.18) \mu\text{g m}^{-3}$, $p = 0.26 \times 10^{-12}$ (72.6 %, 95 % CI [48.9 %, 99.9 %]) from 1998 to 2012. Three significant changes are apparent. The first is a reduction of $0.42 \mu\text{g m}^{-3}$ (48.8 %) be-

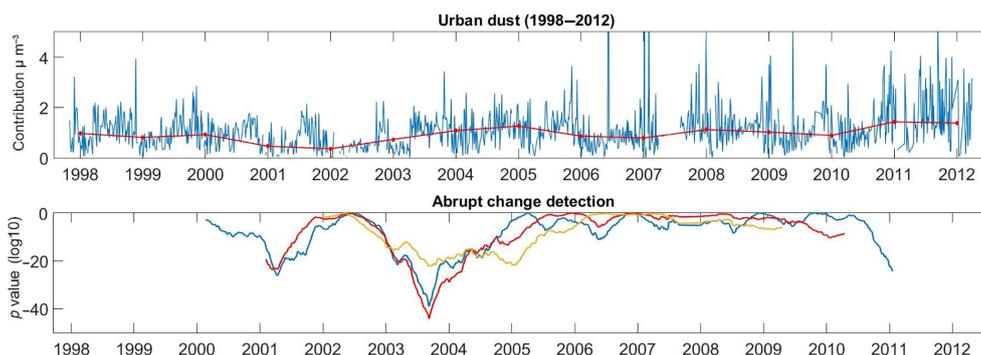


Figure 9. Top panel: time series of urban dust contribution to PM_{2.5} and the annual median in red. Bottom panel: p value from a Mann–Whitney hypothesis test comparing the median of both halves of a sliding window, repeated for three different window lengths (320, 480 and 640 days for blue, red and yellow, respectively).

tween 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 there for a long time.

A second change was an increase of $0.67 \mu\text{g m}^{-3}$ (171.8 %) 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 $0.48 \mu\text{g m}^{-3}$ (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 (Boisier et al., 2016; CR2, 2015), which leads to drier conditions and promotes eolian aerosol resuspension.

In Table 4 we summarize the main changes in each source contribution and the corresponding air quality regulation or other events that caused these changes.

3.3.7 Relative changes in source contributions

From 1998 to 2012 total PM_{2.5} concentrations have been reduced as a consequence of the air quality regulations described above. However, individual sources did not vary in the same proportion, and their relative contributions changed over the 15 years (Fig. 10). On the one hand, the main reduction was effected for copper smelters' contributions that reduced their relative contribution to total PM_{2.5} from 33 % in 1998–1999 to 5 % in 2011–2012. On the other hand, the impact of motor vehicles increased significantly in relative terms, to the point that this source has become the largest PM_{2.5} contributor since 2003–2005. In connection with the rise in motor vehicle numbers after 2005, the 73% increase in urban dust raised its contribution to PM_{2.5} from 3 to 7 %.

One should note that during the time period discussed here, precipitation decreased in central Chile (Fig. S5), leading to a worsening of dispersion conditions in Santiago's basin during autumn and winter. Therefore, the estimated changes for the four sources that decreased their contribu-

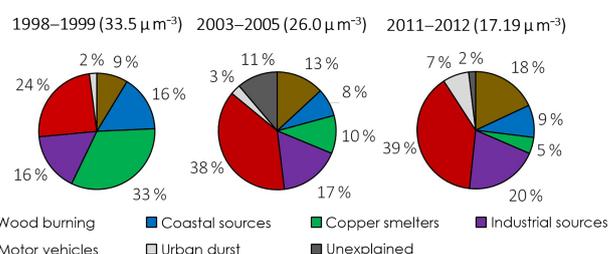


Figure 10. Relative contribution of each source at the beginning, middle, and end of the period investigated in this study. Median levels of total PM_{2.5} are given in brackets next to the corresponding time period.

tions are a lower-bound estimate of the reductions in the respective source emissions. Likewise, the relative increase in urban dust estimated is an upper bound of actual dust emission changes.

4 Conclusions

We have applied two different receptor models (PMF 5.0 and UNMIX 6.0) to a multiyear database of ambient PM_{2.5} concentrations measured in air filters (1243 samples) collected in a central site in Santiago, Chile. Both models resolve six major sources of ambient PM_{2.5} (motor vehicles, industrial sources, copper smelters, wood burning, coastal sources and urban dust) and show the temporal evolution of each source from 1998 to 2012. Five of the six identified sources feature significant seasonal variability, increasing their contributions during autumn and winter, and triggering a high number of episodes with harmful concentrations of PM_{2.5}.

During the 15 years analyzed in this study (1998–2012) several air quality regulations were implemented by regional authorities, with the aim of reducing ambient particle levels in Santiago. The most successful measures were those that targeted industrial sources, particularly the regulation of copper smelter emissions and the introduction of cleaner fuels.

Table 4. Significant changes in PM_{2.5} sources in context with Santiago air quality improvement measures taken at that time.

Source	Date	Impact on source contribution	Explanation and comments
Motor vehicles	2002	Reduction of 1.53 $\mu\text{g m}^{-3}$ (15.59 %)	Fuel quality improvement. Lead removed from gasoline.
Motor vehicles	2005 and 2006	Increase of 1.60 $\mu\text{g m}^{-3}$ (18.92 %).	Operation of urban highways.
Motor vehicles	2007	Increase of 1.34 $\mu\text{g m}^{-3}$ (13.42 %).	Increase in number of private motorized vehicles due to poor implementation of Transantiago.
Motor vehicles	late 2008–2010	Reduction of 5.69 $\mu\text{g m}^{-3}$ (43.97 %)	Improvement to Transantiago.
Industrial sources	2002	Reduction of 2.52 $\mu\text{g m}^{-3}$ (34.33 %)	Diesel fuel sulfur content reduction in 2001.
Industrial sources	2005–2007	Increase of 1.86 $\mu\text{g m}^{-3}$ (45.04 %).	Argentinean natural gas import reduction.
Industrial sources	2009–2010	Reduction of 1.76 $\mu\text{g m}^{-3}$ (31.17 %)	Opening of Quintero terminal for LNG import through marine port.
Copper smelter	1998–2002	Reduction of 4.13 $\mu\text{g m}^{-3}$ (69.04 %)	Implementation of emission abatement technology in Caletones smelter.
Copper smelter	2010–2011	Reduction of 1.41 $\mu\text{g m}^{-3}$ (64.66 %)	Reduction of SO ₂ and PM emissions in Caletones and Ventana smelters.
Wood burning	2007–2008	Increase of 1.16 $\mu\text{g m}^{-3}$ (43.39 %)	Unknown.
Wood burning	2009–2010	Reduction of 0.55 $\mu\text{g m}^{-3}$ (16.98 %)	Unknown.
Coastal sources	2002–2005	Reduction of 1.62 $\mu\text{g m}^{-3}$ (77.46 %)	Diesel sulfur-content reduction.
Coastal sources	Since 2010	Reduction of 1.05 $\mu\text{g m}^{-3}$ (76.17 %)	Opening of Quintero terminal for LNG import through marine port.
Urban dust	2001–2002	Reduction of 0.42 $\mu\text{g m}^{-3}$ (48.84 %)	Lead-free gasoline introduction.
Urban dust	Since 2004	Increase of 0.67 $\mu\text{g m}^{-3}$ (171.78 %).	Increase in the number of motorized cars (annual growth rate of 4 %).
Urban dust	Since 2011	Increase of 0.48 $\mu\text{g m}^{-3}$ (51.61 %).	Increase in the number of motorized cars (annual growth rate of 7 %), extended drought since 2010.

Copper smelters, coastal sources and industrial sources reduced their contribution by 5.24 (± 1.38), 1.48 (± 0.51) and 2.63 (± 0.71) $\mu\text{g m}^{-3}$, respectively, or 81.5, 39.3 and 58.9 %, respectively, from 1998 to 2012. These estimates are lower bounds of the respective changes in emissions sources, because of a steady decrease in precipitation during this time period (Fig. S5).

Motor vehicles' contribution was reduced by 2.17 (± 1.91) $\mu\text{g m}^{-3}$ (21.3 %) over the whole period, again a lower-bound estimate in traffic emissions changes. Although

vehicle fleets have moved to cleaner technologies, the fast growth in the number of private cars has offset part of the gains achieved from tighter vehicle emission standards. Thus, a big challenge for the future is the promotion of behavioral changes in commuters to choose public transportation or nonmotorized travel over private cars.

Urban dust (a mixture of crustal and road dust) is the only identified source that has significantly increased its contribution to total PM_{2.5}. Our estimated 0.49 (± 0.18) $\mu\text{g m}^{-3}$ (72.6 %) increase since 1998 is likely an upper bound in dust

emissions changes. It might be due to the rise in private vehicle trips over the years, leading to road dust suspension, combined with drier conditions in central Chile as experienced since 2010 (Fig. S5). Its overall contribution to PM_{2.5} was nevertheless minor ($< 1.41 \mu\text{g m}^{-3}$ or $< 10\%$ of total PM_{2.5}) in 2012, in agreement with long-term source-apportionment studies elsewhere (Table 2).

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 account for roughly 30.6% of PM_{2.5}. Measures to reduce this source's contribution are urgently needed to improve winter air quality in Santiago. However, the road to achieve such reduction is not an easy one: cultural tradition and risk misperception are barriers for change in household practices (Hine et al., 2007; Reeve et al., 2013).

Although government measures have been successful at improving air quality in recent decades, 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. It is apparent that industrial sources have been capped significantly. Besides further industrial emission reductions, our study suggests that policies aimed at reducing traffic and residential emissions should be emphasized, as there is still a large reduction potential for these two sources. Table 2 shows that in developed countries with similar climates it is feasible to achieve source contributions that are substantially lower than the current estimates for Santiago.

Code availability. The data-filling algorithm is a MATLAB code that is available upon request to Fabrice Lambert.

The Supplement related to this article is available online at <https://doi.org/10.5194/acp-17-10093-2017-supplement>.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. 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. The authors thank Paulo Artaxo and an anonymous reviewer for their constructive comments and suggestions.

Edited by: Maria Cristina Facchini

Reviewed by: Paulo Artaxo and one anonymous referee

References

- Andrade, M. de F., de Miranda, R. M., Fornaro, A., Kerr, A., Oyama, B., de Andre, P. A., and Saldiva, P.: Vehicle emissions and PM_{2.5} mass concentrations in six Brazilian cities, *Air Qual. Atmos. Heal.*, 5, 79–88, <https://doi.org/10.1007/s11869-010-0104-5>, 2012.
- Artaxo, P.: Aerosol source apportionment at Santiago Chile Winter 1996, Technical report for the National Commission of the Environment, Santiago, Chile, 1996.
- Artaxo, P.: Aerosol characterization study in Santiago de Chile Wintertime 1998: Technical report for the National Commission of the Environment, Santiago, Chile, 1998.
- Ayrault, S., Catinon, M., Boudouma, O., Bordier, L., Agnello, G., Reynaud, S., and Tissut, M.: Street Dust?: Source and Sink of Heavy Metals To Urban Environment, in: *Proceeding of the 16th International Conference on Heavy Metals in the Environment*, Vol. 1, edited by: Pirrone, N., 1998–2001, Rome, Italy, 2013.
- Belis, C. A. A., Karagulian, F., Larsen, B. R. R., and Hopke, P. K. K.: Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe, *Atmos. Environ.*, 69, 94–108, <https://doi.org/10.1016/j.atmosenv.2012.11.009>, 2013.
- Boisier, J. P., Rondanelli, R., Garreaud, R. D., and Muñoz, F.: Anthropogenic and natural contributions to the Southeast Pacific precipitation decline and recent megadrought in central Chile, *Geophys. Res. Lett.*, 43, 413–421, <https://doi.org/10.1002/2015GL067265>, 2016.
- Brugge, D., Durant, J. L., and Rioux, C.: Near-highway pollutants in motor vehicle exhaust: A review of epidemiologic evidence of cardiac and pulmonary health risks, *Environ. Health*, 6, 23, <https://doi.org/10.1186/1476-069X-6-23>, 2007.
- Cakmak, S., Dales, R., and Blanco, C.: Air Pollution and Mortality in Chile?: Susceptibility among the Elderly, *Environ. Health Persp.*, 155, 524–527, <https://doi.org/10.1289/ehp.9567>, 2007.
- CMM: Propuesta de regulaciones para la reducción del MP2,5, sus cambios precursores y contaminantes que afectan al cambio climático, para las distintas fuentes estacionarias de la Región Metropolitana, Santiago, Chile, 2014.
- CMM-MMA: Análisis de Tendencia Para Material Particulado en la Región Metropolitana (2008–2010), Santiago, Chile, 2011.
- CODELCO: Memoria anual 2014, Corporación Nacional del Cobre Chileno, Chile, 2015.
- Cohen, D. D., Crawford, J., Stelcer, E., and Bac, V. T.: Characterisation and source apportionment of fine particulate sources at Hanoi from 2001 to 2008, *Atmos. Environ.*, 44, 320–328, <https://doi.org/10.1016/j.atmosenv.2009.10.037>, 2010.
- CR2: Informe a la Nación La megasequía 2010–2015: Una lección para el futuro, Rep., 28 pp., Center for Climate and Resilience Research (CR2), Santiago, Chile, 2015 (in Spanish).
- Figueroa, E., Gómez-Lobo, A., Jorquera, P., and Labrín, F.: Develando económicamente 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, <https://doi.org/10.4067/S0718-52862013000100003>, 2013.
- Fujiwara, F., Rebagliati, R. J., Dawidowski, L., Gómez, D., Polla, G., Pereyra, V., and Smichowski, P.: Spatial and chemical pat-

- terns of size fractionated road dust collected in a megacity, *Atmos. Environ.*, 45, 1497–1505, 2011.
- Gallardo, L., Olivares, G., Langner, J., and Arrhus, B.: Coastal lows and sulphur air pollution in Central Chile, *Atmos. Environ.*, 36, 3829–3841, 2002.
- Garreaud, R. D., Vuille, M., Compagnucci, R., and Marengo, J.: Present-day South American climate, *Palaeogeogr. Palaeoclimatol.*, 281, 180–195, <https://doi.org/10.1016/j.palaeo.2007.10.032>, 2009.
- GNL-Quintero: available at: <http://www.gnlquintero.com/> (last access: January 2017), 2016.
- Godoy, M. L. D. P., Godoy, J. M., Roldão, L. A., Soluri, D. S., and Donagemma, R. A.: Coarse and fine aerosol source apportionment in Rio de Janeiro, Brazil, *Atmos. Environ.*, 43, 2366–2374, <https://doi.org/10.1016/j.atmosenv.2008.12.046>, 2009.
- González, R. N., Torres-Avilés, F., Carrasco, P. E., Salas, P. F., and Pérez, B. F.: Estudio temporal de diabetes mellitus tipo 1 en Chile: Asociación con factores ambientales durante el período 2000–2007, *Rev. Med. Chil.*, 141, 595–601, <https://doi.org/10.4067/S0034-98872013000500007>, 2013.
- Gramsch, E., Cereceda-Balic, F., Oyola, P., and Vonbaer, D.: Examination of pollution trends in Santiago de Chile with cluster analysis of PM₁₀ and Ozone data, *Atmos. Environ.*, 40, 5464–5475, <https://doi.org/10.1016/j.atmosenv.2006.03.062>, 2006.
- Gramsch, E., Reyes, F., Vásquez, Y., Oyola, P., and Rubio, A. M.: Prevalence of Freshly Generated Particles during Pollution Episodes in Santiago de Chile, *Aerosol Air Qual. Res.*, 16, 2172–2185, <https://doi.org/10.4209/aaqr.2015.12.0691>, 2016.
- Hedberg, E., Gidhagen, L., and Johansson, C.: Source contributions to PM₁₀ and arsenic concentrations in Central Chile using positive matrix factorization, *Atmos. Environ.*, 39, 549–561, <https://doi.org/10.1016/j.atmosenv.2004.11.001>, 2005.
- Henriquez, A., Osses, A., Gallardo, L., and Diaz, M.: Analysis and optimal design of air quality monitoring networks using a variational approach, *Tellus B*, 67, 1–13, <https://doi.org/10.3402/tellusb.v67.25385>, 2015.
- Henry, R. C.: Multivariate receptor models – current practice and future trends, *Chemom. Intell. Lab. Syst.*, 60, 43–48, 2002.
- Henry, R. C.: Multivariate receptor modeling by N-dimensional edge detection, *Chemom. Intell. Lab. Syst.*, 65, 179–189, 2003.
- Hine, D. W., Marks, A. D. G., Nachreiner, M., Gifford, R., and Heath, Y.: Keeping the home fires burning: The affect heuristic and wood smoke pollution, *J. Environ. Psychol.*, 27, 26–32, <https://doi.org/10.1016/j.jenvp.2007.01.001>, 2007.
- 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., and Thurston, G. D.: PM source apportionment and health effects: 1. Intercomparison of source apportionment results, *J. Expo. Sci. Env. Epidemiol.*, 16, 275–286, 2006.
- Instituto Nacional de Estadísticas: Anuarios parque de vehículos en circulación 2001–2013, available at: http://www.ine.cl/canales/chile_estadistico/estadisticas_economicas/transporte_y_comunicaciones/parquevehiculos.php (accessed: January 2017), 2016.
- Jhun, I., Oyola, P., Moreno, F., Castillo, M. A., and Koutrakis, P.: PM_{2.5} 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.*, 63, 161–169, <https://doi.org/10.1080/10962247.2012.742027>, 2013.
- Jorquera, H. and Barraza, F.: Source apportionment of ambient PM_{2.5} in Santiago, Chile: 1999 and 2004 results, *Sci. Total Environ.*, 435–436, 418–429, <https://doi.org/10.1016/j.scitotenv.2012.07.049>, 2012.
- Jorquera, H. and Barraza, F.: Source apportionment of PM₁₀ and PM_{2.5} in a desert region in northern Chile, *Sci. Total Environ.*, 444, 327–335, <https://doi.org/10.1016/j.scitotenv.2012.12.007>, 2013.
- Jorquera, H., Orrego, G., Castro, J., and Vesovic, V.: Trends in air quality and population exposure in Santiago, Chile, 1989–2001, *Int. J. Environ. Pollut.*, 22, 507–530, <https://doi.org/10.1504/IJEP.2004.005684>, 2004.
- Kavouras, I. G., Koutrakis, P., Cereceda-Balic, F., and Oyola, P.: Source apportionment of PM₁₀ and PM_{2.5} in five Chilean cities using factor analysis, *J. Air Waste Manage.*, 51, 451–464, 2001.
- Koutrakis, P., Sax, S. N., Sarnat, J. A., Coull, B., Demokritou, P., Oyola, P., Garcia, J., and Gramsch, E.: Analysis of PM₁₀, PM_{2.5}, and PM_{2.5–10} concentrations in Santiago, Chile, from 1989 to 2001, *J. Air Waste Manage.*, 55, 342–351, <https://doi.org/10.1080/10473289.2005.10464627>, 2005.
- Leiva, G. M. A., Santibañez, D. A., Ibarra, E. S., Matus, C. P., and Seguel, R.: A five-year study of particulate matter (PM_{2.5}) and cerebrovascular diseases, *Environ. Pollut.*, 181, 1–6, <https://doi.org/10.1016/j.envpol.2013.05.057>, 2013.
- Lewis, C. W., Norris, G. A., Conner, T. L., and Henry, R. C.: Source apportionment of Phoenix PM_{2.5} aerosol with the Unmix receptor model, *J. Air Waste Manage.*, 53, 325–338, <https://doi.org/10.1080/10473289.2003.10466155>, 2003.
- Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A., Cahill, T. A., Malm, C., Sisler, J. F., and Cahill, A.: Spatial and seasonal trends in particle concentration and optical extinction in the United States, *J. Geophys. Res.*, 99, 1347–1370, <https://doi.org/10.1029/93JD02916>, 1994.
- Mena-Carrasco, M., Oliva, E., Saide, P., Spak, S. N., De la Maza, C., Osses, M., Tolvet, S., Campbell, J. E., Tsao, T. C., and Molina, L. T.: Estimating the health benefits from natural gas use in transport and heating in Santiago, Chile, *Sci. Total Environ.*, 429, 257–265, <https://doi.org/10.1016/j.scitotenv.2012.04.037>, 2012.
- Mena-Carrasco, M., Saide, P., Delgado, R., Hernandez, P., Spak, S., Molina, L., Carmichael, G., and Jiang, X.: Regional climate feedbacks in Central Chile and their effect on air quality episodes and meteorology, *Urban Clim.*, 10, 771–781, <https://doi.org/10.1016/j.uclim.2014.06.006>, 2014.
- Minsepres: Ministerio Secretaria General de la Presidencia – Plan de descontaminación para el área circundante a la fundición de Caletones de la división el teniente de Codelco Chile, Chile, available at: <http://www.sinia.cl/1292/w3-articulo-26084.html> (last access: 21 August 2017), 1998.
- MMA: Norma primaria de calidad ambiental para el material particulado fino respirable, Chile, 2012.
- MMA: Ministerio del Medio Ambiente – Anteproyecto del plan de prevención y descontaminación atmosférica para la región metropolitana de Santiago, Santiago, Chile, 2015.
- Montezuma, A. I.: Inversiones y exigencias ambientales en las fundiciones estatales de cobre chilenas: 1990–2014 – Master thesis. Pontificia Universidad Católica de Chile, Santiago, Chile, 2016.

- Moreno, F., Gramsch, E., Oyola, P., and Rubio, M. A.: Modification in the soil and traffic-related sources of particle matter between 1998 and 2007 in Santiago de Chile, *J. Air Waste Manage.*, 60, 1410–1421, <https://doi.org/10.3155/1047-3289.60.12.1410>, 2010.
- Mugica, V., Watson, J., Vega, E., Reyes, E., Ruiz, M. E., and Chow, J.: Receptor model source apportionment of nonmethane hydrocarbons in Mexico City, *Scientific World Journal*, 2, 844–860, <https://doi.org/10.1100/tsw.2002.147>, 2002.
- Muñoz, J. C., Batarce, M., and Hidalgo, D.: Transantiago, five years after its launch, *Res. Trans. E.*, 48, 184–193, <https://doi.org/10.1016/j.retrec.2014.09.041>, 2014.
- Muñoz, R. C. and Alcañal, R. I.: Variability of urban aerosols over Santiago, Chile: Comparison of surface PM₁₀ concentrations and remote sensing with ceilometer and lidar, *Aerosol Air Qual. Res.*, 12, 8–14, <https://doi.org/10.4209/aaqr.2011.08.0133>, 2012.
- Muñoz, R. C. and Undurraga, A. A.: Daytime mixed layer over the Santiago Basin: Description of two years of observations with a lidar ceilometer, *J. Appl. Meteorol. Clim.*, 49, 1728–1741, <https://doi.org/10.1175/2010JAMC2347.1>, 2010.
- Norris, G., Vendantham, R., Duvall, R., and Henry, R. C.: EPA Unmix 6.0 Fundamentals & User Guide, U.S. Environmental Protection Agency, Washington, DC, 2007.
- Norris, G., Duvall, R., Brown, S., and Bai, S.: EPA-Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide, U.S. Environmental Protection Agency, Washington, DC, 2014.
- Olivares, G., Gallardo, L., Langner, J., and Aarhus, B.: Regional dispersion of oxidized sulfur in Central Chile, *Atmos. Environ.*, 36, 3819–3828, [https://doi.org/10.1016/S1352-2310\(02\)00286-8](https://doi.org/10.1016/S1352-2310(02)00286-8), 2002.
- Osses, A., Gallardo, L., and Faundez, T.: Analysis and evolution of air quality monitoring networks using combined statistical information indexes, *Tellus B*, 65, 1–17, <https://doi.org/10.3402/tellusb.v65i0.19822>, 2013.
- Pino, P., Walter, T., Oyarzun, M., Villegas, R., and Romieu, I.: Fine particulate matter and wheezing illnesses in the first year of life, *Epidemiology*, 15, 702–708, 2004.
- Reeve, I., Scott, J., Hine, D. W., and Bhullar, N.: “This is not a burning issue for me”: How citizens justify their use of wood heaters in a city with a severe air pollution problem, *Energy Policy*, 57, 204–211, <https://doi.org/10.1016/j.enpol.2013.01.042>, 2013.
- Reff, A., Eberly, S. I., and Bhave, P. V.: Receptor modeling of ambient particulate matter data using positive matrix factorization: review of existing methods, *J. Air Waste Manage.*, 57, 146–154, <https://doi.org/10.1080/10473289.2007.10465319>, 2007.
- Rojas, C. M., Artaxo, P., Van Grieken, R., and Van Grieken, R.: Aerosols in Santiago de Chile: A study using receptor modeling with X-ray fluorescence and single particle analysis, *Atmos. Environ. B-Urb.*, 24, 227–241, [https://doi.org/10.1016/0957-1272\(90\)90028-S](https://doi.org/10.1016/0957-1272(90)90028-S), 1990.
- Rutllant, J. and Garreaud, R.: Meteorological air pollution potential for Santiago, Chile: Towards an objective episode forecasting, *Environ. Monit. Assess.*, 34, 223–244, <https://doi.org/10.1007/BF00554796>, 1995.
- Rutllant, J. and Garreaud, R.: Episodes of Strong Flow down the Western Slope of the Subtropical Andes, *Mon. Weather Rev.*, 132, 611–622, [https://doi.org/10.1175/1520-0493\(2004\)132<0611:EOSFDT>2.0.CO;2](https://doi.org/10.1175/1520-0493(2004)132<0611:EOSFDT>2.0.CO;2), 2004.
- Saide, P. E., Carmichael, G. R., Spak, S. N., Gallardo, L., Osses, A. E., Mena-Carrasco, M. A., and Pagowski, M.: Forecasting urban PM₁₀ and PM_{2.5} pollution episodes in very stable nocturnal conditions and complex terrain using WRF-Chem CO tracer model, *Atmos. Environ.*, 45, 2769–2780, <https://doi.org/10.1016/j.atmosenv.2011.02.001>, 2011.
- Sax, S. N., Koutrakis, P., Rudolph, P. A. R., Cereceda-Balic, F., Gramsch, E., and Oyola, P.: Trends in the elemental composition of fine particulate matter in Santiago, Chile, from 1998 to 2003, *J. Air Waste Manage.*, 57, 845–855, 2007.
- Schmitz, R.: Modelling of air pollution dispersion in Santiago de Chile, *Atmos. Environ.*, 39, 2035–2047, <https://doi.org/10.1016/j.atmosenv.2004.12.033>, 2005.
- 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., and Schwartz, J.: Elemental concentrations of ambient particles and cause specific mortality in Santiago, Chile: a time series study, *Environ. Heal.*, 11, 82, <https://doi.org/10.1186/1476-069X-11-82>, 2012.
- Villalobos, A. M., Barraza, F., Jorquera, H., and Schauer, J. J.: Chemical speciation and source apportionment of fine particulate matter in Santiago, Chile, 2013, *Sci. Total Environ.*, 512–513, 133–142, <https://doi.org/10.1016/j.scitotenv.2015.01.006>, 2015.
- WHO (World Health Organization): Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide, Global update, 2005.
- WHO (World Health Organization): Database on source apportionment studies for particulate matter in the air (PM₁₀ and PM_{2.5}), available at: http://www.who.int/quantifying_ehimpacts/global_source_apport/en/ (last access: January 2017), 2017.
- Willis, R. D.: Workshop on UNMIX and PMF as applied to PM_{2.5}, U.S. EPA, Report No. EPA/600/A-00/048, 2000.