General comments

We thank the reviewers for all the comments and questions that made it possible to vastly improve the manuscripts and the robustness of the results. The main changes to the new manuscript are focused in three areas: i) an appropriate description of the sampling and the quality assurance/quality control of the chemical data, ii) new comparative discussion of our results with other Latin American studies, but mostly with other cities abroad with similar multi-year data and methodology to ours, iii) more discussion about meteorological and climatic phenomena that play an important role on Santiago's air quality.

We also include a revised manuscript with track changes below the point-by-point discussion.

Response to comments by Reviewer 1

1) Overall Assessment This study involved a very large number of samples and for a long time series: 1243 24-hour filter samples of ambient PM2.5 collected between April-1998 to August-2012. It was used two different source-receptor models (PMF 5.0 and Unmix 6.0). The detailed study shows that the main aerosol sources for PM2.5 were: motor vehicles (37%), industrial sources (19%), copper smelters (14%), wood burning (12%), coastal sources (10%), and urban dust (3%).

For a very dry region, it is surprising that urban dust is only 3% of aerosol mass, even considering that the analysis is for PM2.5. Some of the dust factor must have gone in the vehicular source of other factors.

Answer and comment:

The reviewer has pointed out that our estimated urban dust is low for an arid region. However, Santiago is rather a semi-arid zone, for 1998-2012, the annual precipitation had a mean of 320 mm, a low of 110 mm (in 1998) and a high of 620 mm (in 2002). If we compare our concentrations of PMF-resolved soil factor in Santiago (average: 1.1 $\mu g/m^3$) with those estimated in several cities in California, USA (a region with a very similar climate) we find that:

a) Schauer et al (1996) have reported urban dust between 0.5 and 0.9 $\mu g/m^3$ (6.8 – 14.3%) in Pasadena, Dowtown LA, West LA and Rubidoux, CA, as an annual average for 1982, using CMB as receptor model.
b) Wang and Hopke (2013) have reported a 10-year source apportionment (PMF) at San Jose, CA and have found an average road dust of 0.58 $\mu g/m^3$ (5.1%) for 2002-2012
c) Hasheminassab et al (2014) have analyzed ambient PM2.5 at Central Los Angeles and Rubidoux, CA for the period 2002-2013. They have found, using PMF, an average soil contribution of 0.8 – 1.1 $\mu g/m^3$ at both sites (5 and 6%, respectively).
d) Kim et al (2010) have analyzed data between 2003 and 2005 at the two sites above, using PMF. They have found that the soil contribution varies between 1.5 and 2.0 $\mu g/m^3$ (6.9 and 9.8%)for Central Los Angeles and 1.6-1.9 $\mu g/m^3$ (6.0-7.6%) for Rubidoux, CA.

Furthermore, in other long term source apportionment studies carried out using PMF, the PMF resolved soil contribution (in $\mu g/m^3$) is similar in magnitude: 0.6 for the Sidney Basin between 1998 – 2009 (Cohen et al, 2011), 1.6 for Hanoi, Vietnam between 2001-2008 (Cohen et al, 2010), 0.5 and 0.8 in Detroit and Chicago for 2001-2014 (Milando et al, 2016).

Therefore, our results, on a mass basis, are within the values reported at urban sites with a similar Mediterranean climate as well as in other cities. Nonetheless, we agree with the reviewer that some urban dust may be mixed in with the motor vehicle source.

In the revised manuscript, we have added section 1.1 and two tables (1 and 2):

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. 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 below 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.

Table 1 Comparison of source apportionment studies in Latin American cities[(a)]. Total $PM_{2.5}$ and its sources are expressed in μg/m^3.

Site Location	Country	Population	Model used	Reference	Study year	$PM_{2.5}$	Sea salt	Dust	Traffic	Industry	Biomass burning	Other
Cordoba	Argentina	1,272,000	PMF	Lopez[66]	2009/2010	71		39.1	22.7	9.2		0.0
Curitiba	Brazil	2,751,907	APCA	Andrade[1]	2007/2008	12	0.0	0.0	6.6	1.9	0.0	3.5
Porto Alegre	Brazil	1,409,351	APCA	Andrade[1]	2007/2008	16	0.0	0.0	5.6	0.5	0.0	9.9
Belo Horizonte	Brazil	2,375,151	APCA	Andrade[1]	2007/2008	17	0.0	7.5	3.1	2.0	0.0	4.4
Recife	Brazil	1,537,704	APCA	Andrade[1]	2007/2008	18	4.3	1.4	6.7			5.6
Rio de Jainero	Brazil	6,320,000	APCA	Andrade[1]	2007/2008	20		2.8	10.2	3.6		3.4
Sao Paulo	Brazil	11,235,503	APCA	Andrade[1]	2007/2008	28		3.6	11.2	3.6		9.5
Rio de Janeiro	Brazil	6,320,000	APFA	Godoy[5]	2003/2005	10		3.5	2.8	3.4		0.0
Santiago	Chile	5,278,000	PMF	Jorquera[63–65]	2004	32	3.2	1.3	10.0	3.1	9.3	5.3
Santiago	Chile	6,000,000	CMB	Villalobos	2013	33	1.0	2.5	11.0	4.6	5.2	8.9
Moravia	Costa Rica	56,919	PMF	Murillo[67]	2010/2011	18	2.0	3.9	5.2			6.9
San Jose	Costa Rica	288,054	PMF	Murillo[67]	2010/2011	26	2.0	3.5	4.8	6.9		8.9
Heredia	Costa Rica	20,191	PMF	Murillo[67]	2010/2011	37	2.4	5.1	5.8	10.3		13.4
Tijuana	Mexico	1,301,000	PMF	Minguillon[50]	2010	19	2.9		2.6	0.4	7.1	5.6
Mexico City	Mexico	8,851,000	CMB	Mugica[51]	2006	50		13.3	21.0	5.0		10.7
Salamanca	Mexico	152,048	PMF	Murillo[52]	2006/2007	45		7.3	5.8	8.2		23.7

(a) Adapted from WHO, http://www.who.int/quantifying_ehimpacts/global/source_apport/en/.

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

Location, period	PM2.5 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
Sidney, 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.

2) After analyzing the 15 years time series, the results show that over the 15 years, 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%. Do you have an estimate for the standard deviation of this important result? The significance of these values depends on the standard deviations that are not reported. Are these reduction numbers all statistically significant at the 95% confidence interval?
Another point is that it is not correct you say that the EMISSIONS were reduced, because you have not measure the emissions, but atmospheric concentrations. I think the best term would be: "The reduction of the impact of the different sources to atmospheric concentrations were". Also important is that there is a lack overall in the whole manuscript of standard deviation for the reported values. Even mean concentrations for PM2.5 do not report their standard deviation. The standard deviation is as important as the average value.

Answer and comment:

We certainly agree with the reviewer on this, so now we quote uncertainties for all reported results. Likewise, the trends that come from robust linear regression of model source contributions against time are now reported with their 95% confidence intervals; in this way, we can conclude about the significance of each one. On the other hand, the standard deviation is not the best parameter to describe dispersion of non-normally distributed data, so we have used the MAD (median absolute deviations) in the revised manuscript. In discussing our results, we now refer to 'impacts' or contributions rather than to 'emissions'.

For example, the following paragraph is from the abstract in the revised manuscript:

PMF resolved six sources that contributed to ambient PM2.5, 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 didn't significantly change, and urban dust increased by 72% [48.9, 99.9].

3) I feel that in the overall manuscript and also in the reference list, there are very few references to similar studies in other cities. It looks as the study has no connections to other urban areas in Latin America and other places. It looks too isolated in the context on urban aerosol source apportionment. It is important to set the manuscript in a broader context of similar studies done in other urban areas, such as Mexico City, Sao Paulo, La Paz, Quito, etc, as well as some Indian cities that could share similar sources. There is an excess of Chilean studies reported, and a lack of other studies worldwide.

Answer and comment:

We agree with the reviewer. We have now included a revised Table 1 that summarizes source apportionment studies conducted in Latin American cities (WHO, 2017). We have commented on the similarities among them in the introductory section.

We did not find any long-term source apportionment studies in Latin American cities. Therefore, we have summarized long-term source apportionment studies carried out abroad, with an emphasis on California because of the similarities with Santiago's climate. We have added a new Table 2 with comparisons with the following long-term $PM_{2.5}$ source apportionment studies (all carried out using PMF) that we have found in the literature:

a) 2002-2012 in San Jose, CA (Wang and Hopke, 2013)
b) 2002-2013 in Central Los Angeles and Rubidoux, CA (Hasheminassab et al., 2014)
c) 2002-2011 in Detroit and Chicago (Milando et al., 2016)
d) 1998-2009 in Sidney, Australia (Cohen et al., 2011)
e) 2002-2011 in Kuala Lumpur, Malasya (Rahman et al., 2015)
f) 2001-2008 in Hanoi, Vietnam (Cohen et al., 2010)

We have also commented upon these studies in the introduction section (see answer to question 1 above).

4) Figure 2 shows that PMF has not separated residual oil combustion that UNIMIX attributes 7%. There is no discussion on why the two models provided such different results. Of course residual oil combustion must be present in Santiago. In PMF, where Vanadium and Nickel was attributed? This is an important issue that was not discussed in the manuscript.

Answer and comment:

UNMIX resolved the oil combustion as a unique source, apportioning 85% of Ni concentration to that source profile. The PMF solution apportions 56.5 and 19.5% of Ni concentration to the motor vehicles and industrial source profiles, respectively; in other words, PMF mixes sources that come together at the receptor site, transported by winds. This is a consequence of the different methodologies used by PMF and UNMIX to compute source profiles.

We acknowledge that vanadium and nickel are good tracers for oil industrial combustion, but we removed vanadium from the model, because we couldn't obtain a PMF solution using this element. This was due to prolonged periods with vanadium values below LOD between 2002 and 2006. During that period, Santiago's industry used natural gas as industrial fuel, explaining those low vanadium records.

We have added the above two paragraphs in the discussion section.

5) Figures 3 to 9 shows boxplots that are difficult to read, and provide limited information with the outliners. I suggest only shows 50, 75 and 25 percentile, and forget about the outliers, to improve the readability of the figures.

Answer and comment:

We agree with the reviewer. We have improved those figures. As an example, we show below two of those figures.

Figure 1 Temporal evolution of PM2.5 concentrations in Parque O'Higgins monitoring station in central Santiago. The red line shows the annual median.

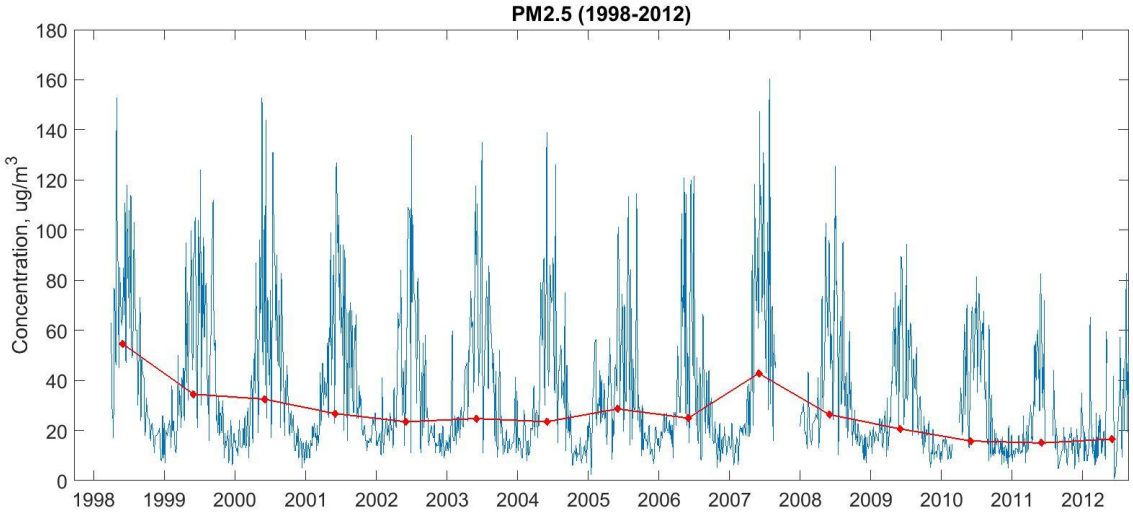
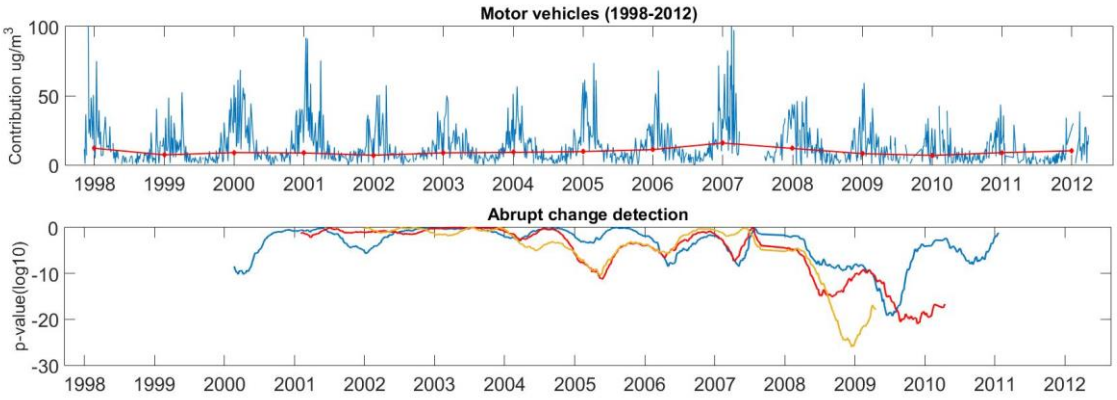


Figure 2 Top panel: Time series of motor vehicles contribution to PM2.5 and the annual median in red. Bottom panel: p-value from a Mann-Whitney hypothesis test comparing the medians of both halves of a sliding window, repeated for 3 different windows lengths (320, 480 and 640 days for blue, red and yellow, respectively).

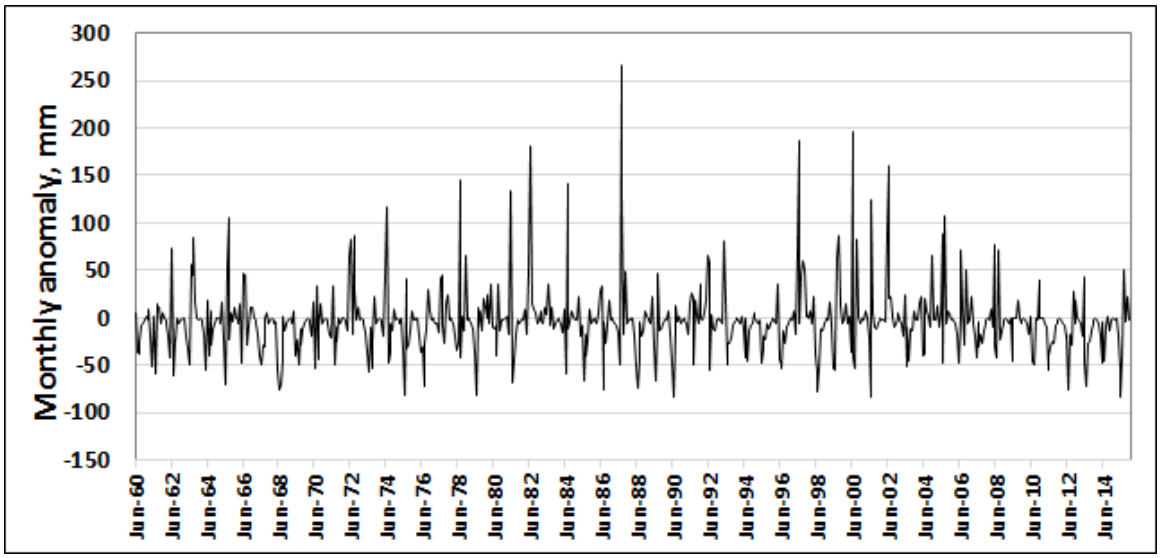


6) You discussed the impact of sources to $PM_{2.5}$. What about the meteorology? Did it rain less? more? Cloud cover has changed? Wind direction has changed? Inversions got stronger? Since aerosol concentrations are a function of sources and meteorology, you need to discuss the possible changes in meteorology in detail. I think that the study needs important improvements before it could be considered for publication in ACP. There are several important specific comments that needs to be addressed as well as the general comments discussed above.

Answer and comment:

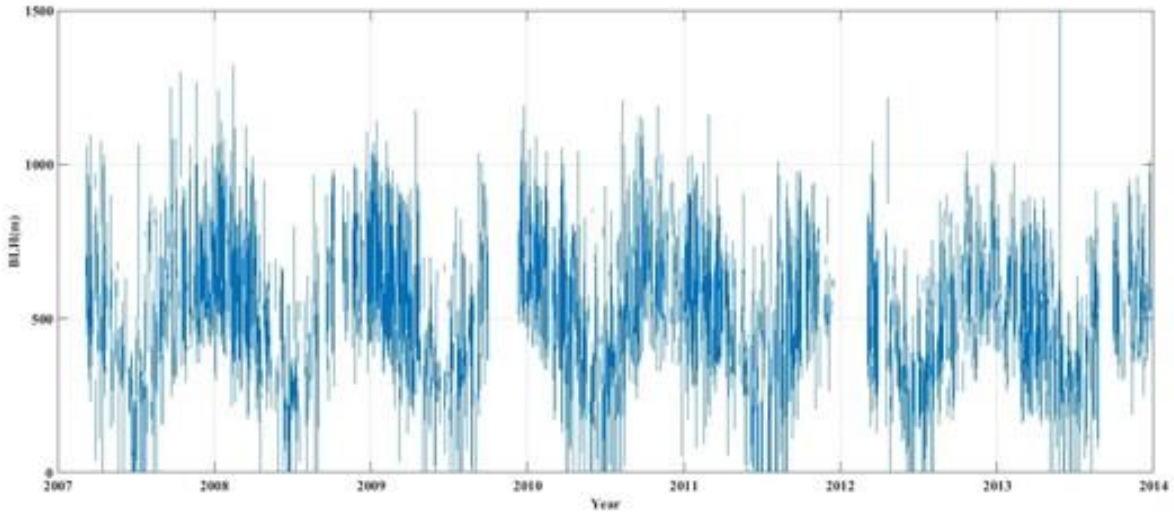
We do agree, and we have completed the discussion on meteorology. In fact, Central Chile is characterized by significant inter-annual variability in connection with El Niño Southern Oscillation (ENSO) (Garreaud et al., 2009) This characteristic inter-annual variability is illustrated in Supplementary figure 5 below that shows monthly anomalies in precipitation (mm) registered in Santiago downtown since 1960 (Data available at http://explorador.cr2.cl/).

Figure S5 Monthly precipitation anomalies from the mean in downtown Santiago, 1960-2015. Source: http://explorador.cr2.cl/



We can see from the above figure that there was a downward trend in annual precipitation between 1998 and 2012. Furthermore, since 2007, 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 ((CR2), 2015; Boisier et al., 2016). We think this drought is a contributing factor in explaining the increase in soil dust contribution in our PMF solution. Likewise, the above downward trend in precipitation implies a worsening of ventilation in Santiago's basin along the period analyzed. However, our trend analysis shows four major $PM_{2.5}$ sources decreasing their contributions in the same period. The fact that all our trend estimates for those four sources were negative and significant means that they are conservative estimates, because we did not adjust them for meteorological conditions. The latter computation is beyond the scope of this study because it would require inverse modeling to estimate source strengths.

Regarding mixing height observations, the Chilean Meteorological Service does not launch radiosondes in Santiago, except for limited, short-term campaigns. The only data available are collected with a ceilometer since 2008 (Muñoz et al., 2010; Muñoz and Alcafuz, 2012); these data have significant diurnal, day-to-day, seasonal and possibly inter-annual variability. The following figure illustrates boundary layer height (BLH) retrieved at the Geophysics Department in downtown Santiago between January 1st, 2007 and December 31st 2013 (data kindly provided by Prof. Muñoz). The methodology for the retrievals is described in Muñoz and Undurraga (2010), and considers cloud-free data between 10 and 15 local time (UTC-4). The figure shows a clear seasonality in BLH, with peak values in the austral summer season and lowest values during the austral winter. We see no apparent temporal trend on BLH, so we think this meteorological variable played no role in the temporal trends estimated for all sources resolved by the receptor model analysis.



We added these new comments to the introduction and discussion sections.

7) Specific comments

Page 1 – line 18: the word WERE was missing

Answer: This has been corrected in the revised manuscript

Page 2 line 4 – instead of "impeding horizontal air movements", maybe it is better making it difficult the air mass transport over the metropolitan region.

Answer: This has been corrected in the revised manuscript

Page 2 Line 7 – It would be great to have more information on mixing layer heights than only the expression: The mixing layer shows a marked diurnal cycle (Saide et al., 2011).””. How much is the mixing layer height over winter and summer at midday? Frequency of thermal inversions? Etc. . .

Answer: This has been corrected in the revised manuscript. Please see the above response regarding meteorological variables in Santiago.

Page 3 line 5 –upperscript for ug/m3.

Answer: This has been corrected in the revised manuscript

Page 4 – Line 33: The detection limit is an important variable, because of the phrase: "We decided to keep only those elements for which more than 70% of the samples contained valid measurements above the detection limit.". There are many ways to derive detection limits in XRF analysis. How were these derived? Blank variability was included? It was derived using 3 sigma? It was derived using multiple analysis of the same filter? How much was the average detection limit in ng/m3 for each element?.

Answer: A new section on Laboratory and QA/QC analysis was added with this information (section 2.2). For each species LOD was calculated as 3 times the standard deviation of field blanks.

Page 4 – Which filter were used? I guess were 37 mm Teflon filters, but this needs to be explicitly mentioned. The same filter was used over the 12 years of sampling?

Answer: A new section on Laboratory and QA/QC analysis was added with this information (section 2.2). 37 mm Teflon filter were used and the methodology was the same throughout the 15 years.

Page 4 The XRF methodology is described under the sampling station section, which is not correct. Suggestion: Open a new section to describe the XRF methodology.

Answer: A new section on Laboratory and QA/QC analysis was added with this information (section 2.2).

Below we present the section on QA/QC included in the revised manuscript that answers the above three specific comments.

2.2 Laboratory and QA/QC analysis

Filters were inspected before being used, and the particles' concentration were 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 a least 24-hours 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, 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, 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, which 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 $\cos^2$ 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 F. 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 Supplementary figure S1. 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 Supplementary figure S1).

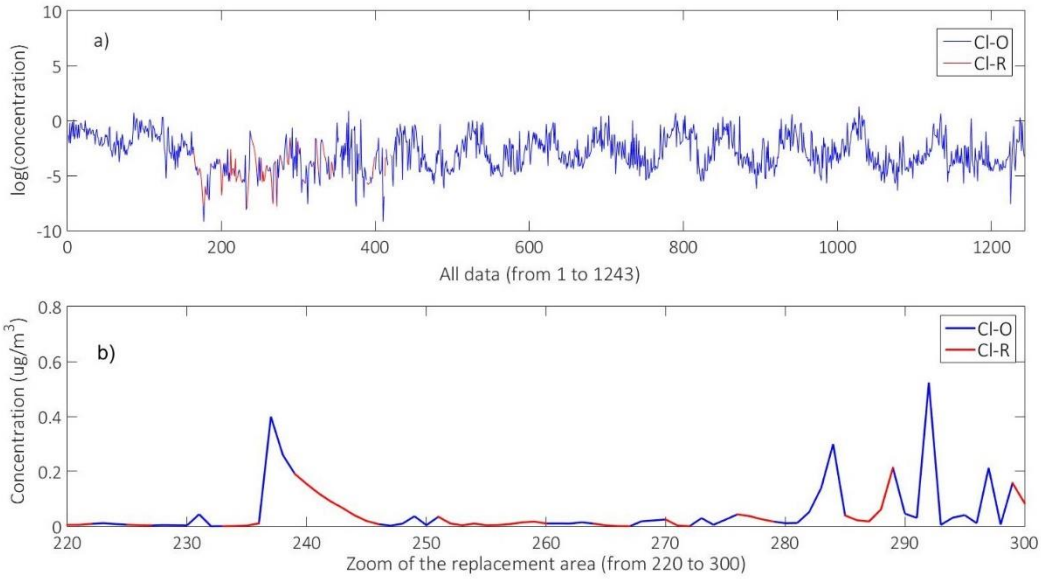
Page 5 – Treatment of missing values: Again: This is described under the section sampling, and this is not appropriate. The treatment of missing values (up to 30% of the samples) is important and needs better description. Substitute the missing values by the median is certainly not appropriated, and I am surprised to see that the results using this wrong procedure and interpolation using better algorithms provide similar results. I really do not believe that this is the case. As up to 30% of data for some variables was artificially introduced in the analysis, a much better discussion on the effects must be provided in the manuscript.

Answer: We actually discarded all species that featured large data gaps from our analysis. We only used 12 species that were relatively compete and feature only small data gaps. This is why the results were not very different between the two methods. We have included a more thorough description in the revised manuscript, as follows:

The missing data in those twenty-two species were dealt with as follows. First, we let the receptor models' (PMF5, UNMIX6) internal algorithms deal with them, which 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 $\cos^2$ 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 F. Lambert. We ensured that only relatively small missing data gaps were filled by using this method, so no large data sections were artificially created. The original and interpolated data are shown in Supplementary figure S1. 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 Supplementary figure S1).

In the supplementary file we have included the following figure:

Figure S1 Example of replacement of missing data. Original data for Cl (in blue) with missing data filled using a custom-written algorithm (in red). Shown are a) Cl concentration on a logarithmic scale, b) zoom of a data range with small and large filled data gaps



Page 5 Line 17: You need to define very precisely what you mean by BEST Model in the phrase: "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".

Answer: The "best model" means the model that has the best regression parameters and at the same time the highest number of resolved sources (statistically significant regression coefficients). We have added the next sentence:

"*This model had the most robust regression parameter and the highest number of statistically significant source factors"*

Page 5 lines 25-27. The factor 0.3 relating K to Fe as in the methodology of Lewis et al., can change a lot from site to site. You mentioned that you have done a regression, but you certainly needs much better explanation.

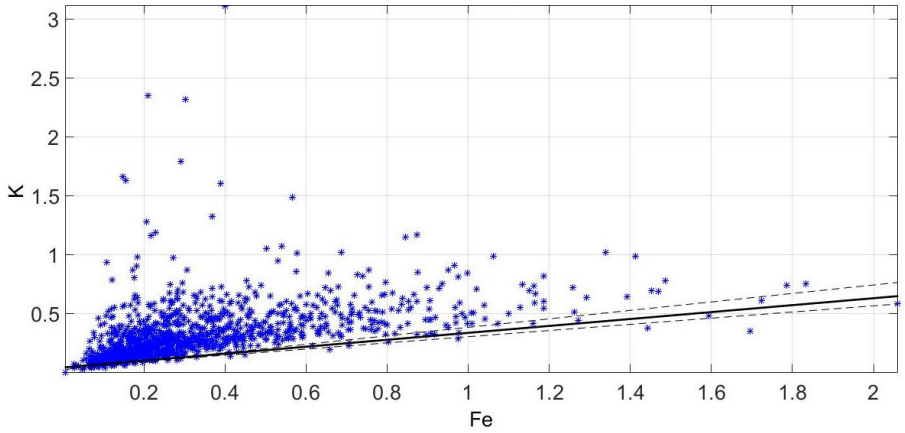
Answer: Indeed, the factor 0.3 is specific for the sampling site and was calculated with the data collected therein. We have added a supplementary figure with the K-Fe scatter plot showing a lower edge with a 0.3 slope (see figure in our next answer below).

You added a new variable that is not statistically independent from the others. This can bring problems in multivariate models. This needs to be much better discussed and explained.

Answer: We knew about this problem, so we have added Kns in and removed K from the model. We have added the following sentence to the manuscript:

To provide a tracer associated with wood burning, we have added the non-soil potassium parameter Kns calculated as Kns=(K-0.3•Fe) and removed K from the model. The 0.3 coefficient was obtained from a K-Fe edge plot (supplementary figure 2)"

Figure S2 K-Fe edge plot. To provide a tracer associated with wood burning we added the non-soil potassium parameter Kns calculated as Kns=K-0.3•Fe, from the K-Fe edge plot



Page 6 line 3: Even with a very high number of samples, you have NOT explained the origin of 25% of the variance of the PM2.5. Why you only explained 75% of the variance? This is a low value for multivariate analysis from urban areas. This is mentioned as " PMF 5.0 produces a six factors solution that explained 74% of the variance in ambient PM2.5 " You have not discussed this important point. It is strange that the unexplained PM2.5 is only 5-7% in Figure 2, and you explained only 75% of the variability.

Answer: The average source contributions must add up to the average $PM_{2.5}$ concentration by design (except by an intercept value). On the other hand, model variability stands for the scatter of individual (daily) model estimates compared with the actual observed (daily) $PM_{2.5}$. These are different parameters. It is difficult to find receptor models that explain more than 90% of the variance. In our case, the unexplained 25% may be ascribed to the following causes:

i) Actual source profiles do not stay constant over the whole modeling period, adding uncertainty to the model results.
ii) We could not include organic/elemental carbon into the model. The lack of these two components may increase uncertainty in the resolved source profiles. For instance, the ratio OC/EC is helpful in discriminating motor vehicles from wood burning.
iii) We only had inorganic tracer species in the dataset, which put a limitation on our analysis. We knew that secondary organic aerosols (SOA) may be relevant in the warm season (October – April), as shown by Villalobos et al (2015) for Santiago in 2013 (application of CMB with organic molecular markers); these authors estimated that nearly 30% of total $PM_{2.5}$ was identified as SOA.

We have added these new comments in the discussion section.

Page 7 – Line 13: There is a very important lack overall in the whole manuscript of standard deviation for the reported values. Even mean concentrations for PM2.5 do not report their standard deviation. This is unacceptable in science: All reported average values needs to have their standard deviation reported together with the mean value. For instance in the phrase: "Over the whole study period, the daily mean (24 h)
concentration of PM2.5 was 35.60 µg/m3 and the median 24.19 µg/m3"

Answer: We agree with this comment. Since data have a non-normal distribution, we have used the median absolute deviation (MAD) as a measure of dispersion for each reported median and mean value.

Page 8 line 20: Very strange that the reduction in industrial sources was attributed to decrease in sulfur in the DIESEL, used in the transportation. This needs to be correctly explained. This is on the phrase: "In Figure 5 we show temporal evolution of the source identify by PMF as industrial sources. This source reduced its 20 contributions from 1998 to 2012 by 2.63 µg/m3 (39.23%, p=0.11x10-8). This improvement can be explained by the reduction policies for sulfur in diesel fuel".

Answer: The quality of industrial diesel fuel was also improved. We put in the page 8 (3.3.2 section) the following new sentence: "[…], that can be explained by a reduction of sulfur in industrial diesel, which was reduced from 1000 to 300 ppm in 2001 […]"

Response to comments by Reviewer 2

Interactive comment on "Temporal evolution of main ambient PM2.5 sources in Santiago, Chile, from 1998 to 2012" by Francisco Barraza et al.

Anonymous Referee #2

General: The project seems to be carefully thought out. The analytical methodology (PMF 5.0 and Unmix 6.0) seems appropriate; however, a separate detailed sampling and QA/QC section is needed. Language and spellings need to be improved. Concentrations should be expressed in 3 significant figures throughout the text and in the figures and tables. The author should compare the data with other studies in urban areas. As such I recommend that it be published with major revision:

1) Page 3: "µg/m3" should be "µg/m3" - be consistent throughout the text, figures, and tables.

Answer: This was corrected in the revised manuscript

2) Page 3: "24-hour" or "24-hours" or 24 h" – be consistent with one of them.

Answer: This was corrected in the revised manuscript

3) Page 3: No mention for the sampling and analysis for PM2.5? How PM2.5 samples were obtained? Which type of filter was used? Were the filters weighed in the clean room? Which analytical balance was used? Any QA/QC?

Answer: the follow section was added with this information.

2.2 Laboratory and QA/QC analysis

Filters were inspected before being used, and the particles' concentration were 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 a least 24-hours 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, 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, 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, which 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 $\cos^2$ 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 F. 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 Supplementary figure

S1. 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 Supplementary figure S1).

4) Page 3: A detailed QA/QC section for XRF analysis should be included. How often were the "QC" samples run? (What % age?). No estimates of recovery. What is the limit of quantitation? What is the uncertainty? Any blank correction? Precision and accuracy?

Answer: A new section on Laboratory and QA/QC analysis was added with the most of this information.

5) Page 4: Did the authors find selenium?

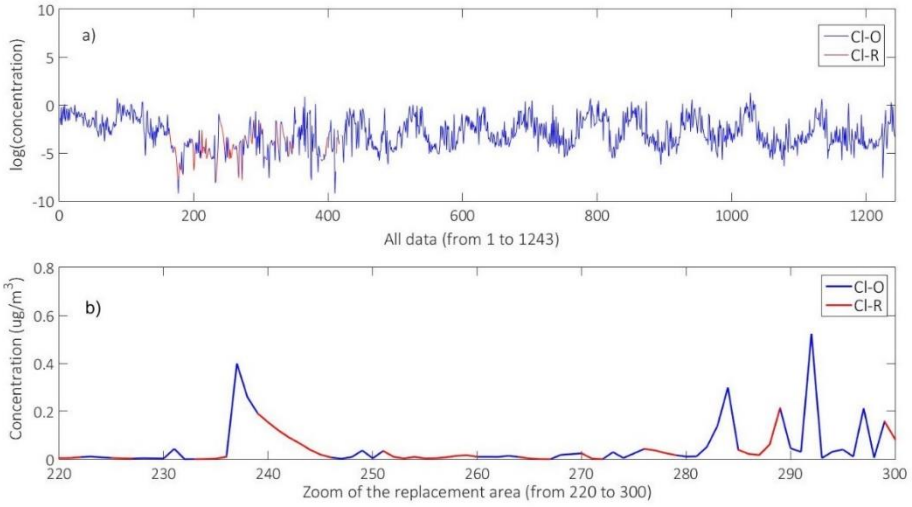
Answer: Selenium was initially considered, but finally removed, because we couldn't get a source apportionment model using Se. Near 27% of Se data were either below LOD or missing; this might explain why we couldn't get a statistically significantly model that included Se.

6) Page 4: Did the authors do the PMF analysis for the missing data? How was this handled?

Answer: We only selected 12 species for our analysis that only feature small data gaps. Any species with large data gaps was discarded from the analysis. The missing data were treated in two separate ways. The first one consisted in leaving them blank and letting the models use their internal algorithm to deal with them, which consists of replacing them with the median values of the complete time-series, for each element. Since replacing missing data with the median can lead to 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 considered to fill in the missing data, to avoid creating artificial variability in the data. The original and interpolated data are shown in Supplementary figure S1. 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 Supplementary figure S1).

In the supplementary file we have included the following figure

Figure S3 Example of replacement of missing data. Original data for Cl (in blue) with missing data filled using a custom-written algorithm (in red). Shown are a) Cl concentration on a logarithmic scale, b) zoom of a data range with small and large filled data gaps



7) Page 5: The contribution of Pb from industrial emissions cannot be ruled out. Motor vehicle is not the only source of Pb.

Answer: We agree with the reviewer. More discussion about the Pb from industrial emissions is added.

8) Page 7: “artefact” should be “artifact”

Answer: This was corrected in the revised manuscript

9) Page 8: “Gramsch et al. (2013)”. Missing in the reference section.

Answer: This was corrected in the revised manuscript

10) Page 8 Lines 10 – 12: Did the private cars use diesel as a fuel? Primary source of BC are emissions from diesel engines, cook stoves, wood burning and forest fires.

Answer: The sentence from lines 9-12 is a summary of the conclusions in (Gramsch et al, 2013). After reviewing that paper again, we have decided to drop this reference from that paragraph. The reason is that those authors compared ambient concentrations of BC in June 2005 and June 2007 in several streets (roadside sites). However, monthly precipitations were 173 and 80 mm, respectively, so the ambient BC changes reported by those authors are explained by changes in traffic emissions *and* meteorological conditions as well.

11) Page 12: “Boisier, J.P., ...Mu?????oz, F.,” should be corrected.

Answer: This has been corrected in the revised manuscript

Revised manuscript with Trach Changes

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 ~~M.~~María Villalobos[2], Laura Gallardo[3,4]

[1] Geography Institute, Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile
[2] Department of ~~chemical engineering~~Chemical Engineering and ~~bioprocesses~~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~~CEDEUS), 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~~steady economic growth, and stable atmospheric conditions~~, averse~~ adverse to mixing and ventilation ~~and favorable for~~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. ~~Knowledge about~~Estimating the ~~temporal~~ evolution of ~~the contribution of each~~ source contributions to ambient pollution levels is also paramount to ~~evaluate~~evaluating the effectiveness of pollution reduction measures that have been implemented ~~in~~over the past decades. Here, we quantify the main sources that have contributed to fine particulate matter ($PM_{2.5}$) between April 1998 and August 2012 in ~~Santiago's center~~ downtown Santiago by using two different source-receptor models (PMF 5.0 and ~~Unmix~~UNMIX 6.0), that ~~re~~were applied to elemental measurements ~~on~~of 1243 24-hour filter samples of ambient $PM_{2.5}$ ~~collected between April 1998 to August 2012. Both models resolve~~. PMF resolved six sources that ~~contribute~~contributed to ambient $PM_{2.5}$, with UNMIX producing similar results: motor vehicles (37.3±1.1%), industrial sources (~~19~~18.5±1.3%), copper smelters (14.4±0.8%), wood burning (12.3±1.0%), coastal sources (~~10~~9.5±0.7%), and urban dust (3.0±1.2%). Our results show that over the 15 years analyzed here, four of the ~~emissions from~~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 ~~declined by about 21, 39, 81, 59, and 59% respectively,~~58.9% [38.5, 72.5], while wood burning didn't significantly change, and urban dust ~~increase~~increased by 72~~%.~~% [48.9, 99.9]. These changes are consistent with emission reduction measures, such as improved vehicle ~~and~~emission standards, cleaner smelting technology, introduction of low sulfur ~~fuel~~diesel 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~~the above regulations has been ~~largely nullified~~partially offset by the ~~ever-rising number~~increasing amount of private vehicle ~~journeys~~use in the ~~past decade. As a consequence~~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-~~hours~~hour 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 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~~.) (Figure 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 south-westerly winds in the afternoon and down-slope north-easterly winds in the night and morning hours, especially during summer (Muñoz and Undurraga, 2010; Rutllant and Garreaud, 2004; Schmitz, 2005). 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;). ~~, 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 inter-annual variability connected to 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 cielometer readings (Muñoz and Undurraga, 2010; Muñoz and Alcafuz, 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; 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 ~~). 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 the 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~~gathered a ~~continuous~~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 (Supplementary table 1). 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~~High concentration levels ~~are~~of $PM_{2.5}$ have been 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).~~(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~~abatement polices that have significantly decreased $PM_{2.5}$ ~~– Figure 3~~ (Mena-Carrasco et al., 2014; MMA, 2015). These measures included ~~removing~~phasing lead ~~from~~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~~) and~~, EURO IV since 2012), modernization of the ~~new~~ public transport fleet, selective ~~ban~~bans on private car usage during ~~emergencies~~high pollution days, a mandatory car inspection and maintenance program, ~~and~~ street sweeping and cleaning programs ~~(Sax et al., 2007; Moreno et al., 2010; Jhun et al., 2013;Villalobos et al., 2015).~~, 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 (World Health Organization-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 ~~24 hours Chilean standard of 50 µg/m3 and the~~ WHO 24-hour guideline of 25 µg/m^3 (WHO, 2005~~).~~) and the 24-hour Chilean standard of 50 µg/m^3. These episodes are recurrent and typically last several days~~.~~ (Saide et al, 2011).

~~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~~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. 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 below

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 ~~created~~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),~~(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 in Santiago has changed with time. However, no study to date has investigated the ~~temporal~~ 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), ~~analyse~~analyze how each source varied through time, ~~and~~ 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 37 mm diameter Teflon filter (Pall Flex) since 1998 using the same sampling and analysis methodology. Filters were collected using a Low-Vol dichotomous samplers (Anderson Instruments, Inc., Smyrna, GA) operating at 15 L/min for 24 hours ~~(Andersen Instrument, Inc.).~~, with the sampler inlet located 3 meters above ground. The monitoring ~~stations~~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,)~~(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)~~(Koutrakis et al., 2005; Sax et al., 2007; Moreno et al., 2010; Valdes et al., 2012).

A total of 1243 daily samples (24 ~~h~~-hour filters) were collected about every four days (mean and median) 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 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 Laboratory and QA/QC analysis

Filters were inspected before being used, and the particles' concentration were 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 a least 24-hours 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, 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, 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, which 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 $\cos^2$ 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 F. 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 Supplementary figure S1. 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 Supplementary figure 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, ~~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 *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~~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~~above described ~~above~~equation. The first method is Positive Matrix Factorization (PMF) based on a multivariate factor analysis (Norris et al., 2014). The second method (~~Unmix~~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~~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 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~~(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 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 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 ~~from~~due to specific ~~government initiatives in~~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 ~~younger~~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 therefore a significant change in concentration between ~~the~~those two periods.

3 Results and Discussion

3.1 Receptor Modeling Results

We have run the two receptor models — PMF 5.0 and ~~Unmix~~UNMIX 6.0 — for different numbers of factors in equation (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 ~~13~~12 species that ~~yield~~produced the best model: Al, Si, S, Cl, non-soil K (Kns), Ti, Cr, ~~Mn,~~ Fe, Ni, Cu, Zn and As. This model had the most robust regression parameter and the highest number of statistically

significant source factors. We ~~note that 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 ~~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 have added the non-soil potassium parameter Kns calculated as Kns=(K-0.~~3xFe).~~3•Fe) and removed K from the model. The 0.3 coefficient was obtained from a K-Fe edge plot~~.~~ (supplementary figure 2). This methodology has been used before by Lewis *et. al.* (Lewis et al., 2003) ~~to remove soil contribution to the~~and Cohen *et. al.* (Cohen et al., 2010) to remove soil contribution from total potassium.

Both models found species regressions with coefficient (R^2) greater than 0.7. These species ~~constitute significant identifier~~are tracers for the interpretation of each ~~chemical~~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 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.~~

Both models produced a similar six-factor solution that explained 74% of the variance in ambient $PM_{2.5}$ (Figure 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 is no available data for either organic/elemental carbon or secondary organic aerosols (SOA). The addition of these two components would have reduced the uncertainty in the resolved source profiles. For instance, the ratio OC/EC is helpful in discriminating motor vehicles from wood burning. 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 (figure 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; Artaxo et al., 1999). 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 (0.32) in Santiago (Jorquera and Barraza, 2012) for motor vehicle sources. This source has a characteristic weekly ~~behaviour~~behavior, with weekend ~~contribution~~contributions around half the working ~~days contribution~~days' contributions.

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~~SO_2 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~~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 ~~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~~28×10^{-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 ~~marine~~sea salt component~~.~~, present ~~during~~ all ~~seasons~~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 ~~emissions~~contribution (Malm et al., 1994)~~;~~. For example, its Si/Al ratio of 2.26 ~~compares well with~~is close to source apportionment results from other Chilean cities (Temuco, 2.17; ~~Rancagua, 2.95;~~ Valparaíso, 2.58) (Kavouras et al., 2001). Also, this source did not present any contribution of the pseudo species Kns as expected; this validates that using Kns was a proper 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 ~~from the ground.~~ (ratio working day/weekend = 1.18; p=3.~~53x10~~53×10^{-4}).

~~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).~~

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 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.

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~~artifact. For the ~~Unmix~~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 Figurefigure 2.

3.2 Mass concentration and seasonal behavior

Over the whole study period, the daily mean (24 h-hour) concentration of $PM_{2.5}$ was 35.60 (standard deviation 27.89) µg/m^3 and the median 24.19 µg/m^3 (Figuremedian absolute deviation of 11.81) —figure 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 seasons and warm season concentrations (Table 2).(Table 3). During the spring and summer seasons, boundary layer height increases (Muñoz and Undurraga, 2010; Muñoz and Alcafuz, 2012) along with wind speeds, and ambient. 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 decrease and so do the contributions of most sources. Almostincreases during the cold season, with almost all episodes with $PM_{2.5}$ levels over the Chilean and WHO standards occuroccurring during autumn and winter.

The six identified sources have distinct seasonal contributions to $PM_{2.5}$. During winter, when $PM_{2.5}$ shows thereaches its largest number of harmful episodesconcentrations and ambient temperatures are lowest, we foundfind a distinctmaximum contribution from residential wood smoke with a 30.6% of the to total amount of $PM_{2.5}$. The because of the widespread use of fire wood for heating purposes. On the other hand, the other five sources have their highest contributions during autumn. ThisUnlike wood burning, the emissions from these sources are more constant through the seasons and their contribution to $PM_{2.5}$ concentrations 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, while there is more rainfall to remove $PM_{2.5}$ by wet deposition produces the maximum contributions in winterthese sources.

3.3 Time series of each source contribution

3.3.1 Motor Vehicles

In Figure 4 we show the temporal evolution of the source identifyidentified by PMF as motor vehicles. Over the 15 years of coveredanalyzed in this study, the motor vehicles contribution to $PM_{2.5}$ diminisheddecreased significantly by 2.17 (±1.91) µg/m^3 (21.30%, p=0.0250). (21.3%, 95% CI [2.6%, 36.5%]) 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), improvementreduction of fuel qualitysulfur in 2001,gasoline and a complete overhauldiesel, 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 the contribution of this source contributionmotor vehicles' contributions has not been linear. Between 2000 and constant. In 2002, there was a reduction of 2.891.53 µg/m^3 (27.6515.6%), 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). These gains were partially reversed between 2003 and 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.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 µg/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. Brudgge

et.. al., concluded over several studies in several cities that proximity to highways increase the exposition to air particles (Brudgge et al., 2007).

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~~increased by ~~5.68~~1.34 μg/m^3 (~~56.64%) in~~13.4%) during 2007-2008. Unfortunately, the ~~early days~~beginning of Transantiago ~~were plagued by~~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 (

Figure S4 ~~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.~~ and S4).

~~The improvement of~~Subsequent improvements in the Transantiago public transport system ~~in subsequent years~~after 2007 led to a reduced contribution of motor vehicles. The measures included i) ~~an~~a renewed increase of the bus fleet ~~by~~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 μg/m^3 (27.7%) that can be ascribed to Transantiago's full implementation.

3.3.2 Industrial sources

In Figure 5 we show the temporal evolution of the source ~~identify by PMF~~identified as industrial sources. This source reduced its contributions from 1998 to 2012 by 2.63 (±0.71) μg/m^3, p=1.1×10^{-9} (39.~~23%, p=0.11x10^{-8}).~~3%, 95% CI [28.6, 48.4%]). This improvement can be explained by ~~the reduction~~abatement policies for sulfur in industrial 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). We found a significant reduction of 2.52 μg/m^3 (34.3%) in 2002 compared with 2001, that can be explained by a reduction of sulfur in industrial diesel, which was reduced from 1000 to 300 ppm in 2001 (CMM, 2014; MMA, 2015).

Between 2005 and 2007 we find a significant increase of ~~Industrial~~industrial sources contributions, which was triggered by the ~~gradual reduction~~phasing out of natural gas imports from Argentina. During ~~these~~those years, a large number of industries were forced to switch back to diesel fuel~~, which has a greater amount of sulfur than natural gas.~~ or fuel oil. Since 2008, the Chilean ~~state~~government imports liquefied natural gas from other countries, which ~~is apparent in~~explains the ~~subsequent~~ reduction ~~in~~between 2009 and 2010 caused by industries ~~changing again from diesel~~switching back to natural gas (Figueroa et al., 2013; GNL-Quitero, 2016). The period 2010-2012 shows a reduction of 1.76 μg/m (31.~~17~~2%) compared with the period ~~when the~~without natural gas imports ~~stopped~~ (2004-2008).

3.3.3 Copper Smelters

In Figure 6 we show the temporal evolution of the source ~~identify by PMF~~identified as copper smelters. ~~The~~This contribution ~~from copper smelters~~ features the largest reduction of 5.24 (±1.38), μg/m^3 ~~(81.46%,~~ p ~~=~~ =0.~~82x10~~82×10^{-33}~~)~~ (81.5%, 95% CI [75.8%, 85.9%]) between 1998 and 2012. ~~These improvements~~This decrease can be attributed to technological improvements at the Caletones and Ventanas smelters near Santiago (see ~~Figure~~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~~between 2002 and 2010 shows ~~values lower by~~ a reduction of 4.13 μg/m^3 (69.~~04%) than those during~~0%) compared to the period 1998-2001. We find another significant reduction of 1.41 μg/m^3 (64.~~66~~7 %) 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).

3.3.4 Wood Burning

In Figure 7 we show the temporal evolution of the source ~~identify by PMF~~ identified as wood burning. It is the only ~~identified~~resolved source with no net significant change in the period 1998-2012 ~~(~~: 0.43 (±0.60) μg/m^3, p=0.~~1390).~~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 μg/m^3 (43.~~39~~4%), compared with 2004-2006, and ii) a reduction in 2010-2012 of 1.16 μg/m^3 (30.~~13~~1%) compared with 2007-2009.

To curb down wood burning emissions, Chilean authorities have ~~prohibited~~forbidden open chimneys since 1997~~, only~~. Only allow the use of certified woodstoves ~~can be used, and~~. 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) to reduce wood burning contribution to $PM_{2.5}$. 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 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 Figure 8 we show the temporal evolution of the source ~~identify~~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 (±0.51) μg/m^3 ~~(58.66%,~~ p=0.~~88x10~~88×10^{-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 μg/m^3 (77.~~46~~5%) from 2000 to 2002 compared with the period 1998-1999 that can be explained ~~in same the availability of~~by cleaner industrial fuel, as 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~~industrial source contribution case. Likewise, those coastal industries were also affected by the ~~stopping~~shortage of natural gas imports from Argentina, increasing their contributions from 2004 – 2008 due to a temporary switch to diesel, and then reducing ~~again~~contributions after 2009 ~~after the second conversion to~~following LNG imports. Since 2010, coastal sources have reduced their contribution by 1.05 μg/m^3 (76.~~17~~2%) compared with the period 2007-2008.

3.3.6 Urban Dust

In Figure 9 we show the temporal evolution of the source ~~identify by PMF~~ identified as urban dust. It is the only ~~identified~~resolved source that has increased its contributions significantly by 0.49 (±0.18) μg/m^3 ~~(72.19%,~~ p = 0.~~26x10~~26×10^{-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 μg/m^3 (48.~~84~~8%) 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 there for a long time.

A second change was an increase of 0.67 μg/m^3 (171.~~788~~%) 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)~~(Boisier et al., 2016; CR2, 2015), which leads to drier conditions and promotes aeolian aerosol resuspension.

In Table 6 we summarize ~~of~~ the main ~~shifts~~changes in ~~concentration levels for~~ each source contribution and the corresponding air quality ~~measure~~regulation or other events that ~~provoked~~caused these changes.

3.3.7 ~~Source percentage change~~Relative changes in source contributions

From 1998 to 2012 total $PM_{2.5}$ concentrations have been reduced as a consequence of the ~~measures~~air quality regulations described above. However, individual sources did not vary in the same proportion, and their relative ~~contribution~~ contributions changed over the 15 years (Figure 7). The main reduction was ~~obtained from~~ effected for copper smelter ~~emissions~~contributions that ~~lowered~~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 ~~motorized~~motor vehicles increased significantly~~, with~~ in relative terms, to the point that this source ~~becoming~~has become the largest $PM_{2.5}$ contributor ~~in~~ since 2003-2005. In connection with the rise in motor vehicle numbers after 2005, the 73% increase in urban dust ~~also increased~~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 (Supplementary figure 5), 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 contributions 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~~UNMIX 6.0) to a multiyear database of ambient $PM_{2.5}$ concentrations measured ~~on~~in air ~~filter~~filters (1243 samples) collected in a central site in Santiago, Chile. Both models ~~identify~~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 ~~show a pronounced~~feature significant seasonal ~~trend~~variability, increasing their ~~contribution significantly~~contributions during autumn and winter, ~~which together with inadequate ventilation triggers~~and triggering a high number of episodes with harmful concentrations of $PM_{2.5}$.

During the 15 years ~~investigated~~analyzed in this study (1998-2012~~),~~) several ~~government~~air quality regulations ~~have been~~were implemented by regional authorities, with the aim ~~to reduce~~of reducing ambient ~~PM$_{2.5}$~~particle levels in Santiago. The most successful measures were ~~on~~those that targeted industrial ~~emissions~~sources, particularly the regulation of copper smelter emissions and the ~~shift to~~introduction of cleaner fuels. ~~The copper~~Copper smelters, coastal sources and industrial sources ~~reduces~~reduced their contribution by 5.24~~,~~ (±1.38), 1.48 (±0.51), and 2.63 (±0.71) μg/m^3, respectively ~~(~~, or 81.~~46,~~5%, 39.~~23~~3% and 58.~~66%).~~ 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 (Supplementary figure 5).

~~The motor~~Motor vehicles ~~source also reduced its~~ contribution was reduced by 2.17 (±1.91) μg/m^3 (21.~~30~~3%) over the whole period~~.~~ ~~However~~, 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 ~~cancelled out a significant~~offset part of the gains achieved from ~~more stringent~~tighter vehicle emission standards ~~implemented so far. The main~~. Thus, a big challenge for the future ~~therefore seems to be the implementation~~is the promotion of behavioral changes in ~~the population~~commuters to ~~prefer~~choose public transportation or non-motorized travel over private cars.

Urban dust (a mixture of crustal and road dust) is the only identified source that has significantly increased its contribution ~~significantly by~~to total $PM_{2.5}$. Our estimated 0.49 (±0.18), μg/m^3 (72.~~49%). This~~6%) increase since 1998 is likely an upper bound in dust emissions changes. It might be due to the ~~increase~~rise in private vehicle trips over the years, leading to road dust suspension ~~or perhaps to~~, combined with drier conditions in central Chile as experienced since 2010~~.~~ (Supplementary figure 5). Its overall contribution to $PM_{2.5}$ was nevertheless minor (< 1.41 μg/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 ~~explains~~account for roughly 30.6 % of $PM_{2.5}$. Measures to reduce this source's contribution are urgently needed ~~and may greatly~~to improve winter air quality in Santiago ~~at relatively little cost.~~. 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 ~~partially~~ successful at improving air quality over the past 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. ~~Based on this study it~~It is apparent that ~~industry emissions~~industrial sources have ~~already~~ been capped significantly. ~~Without calling for a halt to~~ Besides further industrial emission reductions ~~we suggest to shift the focus on~~, our study suggests that policies ~~to reduce~~ aimed at reducing traffic and residential ~~and motor vehicles emission~~emissions should be emphasized, as there is still a large reduction potential ~~in~~for these ~~sources.~~ two sources. Table 2 shows that in developed countries with similar climate it is feasible to achieve source contributions that are substantially lower than the current estimates for Santiago.

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. The data filling algorithm is a MATLAB code that is available upon request to F. Lambert.

References

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

Andrade, M. de F., de Miranda, R.M., Fornaro, A., Kerr, A., Oyama, B., de Andre, P.A., Saldiva, P., 2012. Vehicle emissions and PM 2.5 mass concentrations in six Brazilian cities. Air Qual. Atmos. Heal. 5, 79–88. doi:10.1007/s11869-010-0104-5

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, Santiago, Chile.

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

Commission of the Environment. Santiago, Chile.
Artaxo, P., 1996. Aerosol source apportionment at Santiago Chile Winter 1996: technical report for the National Commission of the Environment, Santiago, Chile.
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~~Muñoz, 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~~CMM, 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, Santiago, Chile.
CMM-MMA, 2011. Análisis de Tendencia Para Material Particulado en la Región Metropolitana (2008-2010). Santiago, Chile.
CODELCO, 2015. Memoria anual 2014, Corporación Nacional del Cobre Chileno, Chile.
Cohen, D.D., Crawford, J., Stelcer, E., Bac, V.T., 2010. Characterisation and source apportionment of fine particulate sources at Hanoi from 2001 to 2008. Atmos. Environ. 44, 320–328. doi:10.1016/j.atmosenv.2009.10.037
CR2, 2015. Informe a la Nación La megasequía 2010-2015: Una lección para el futuro (in Spanish). Rep. 28 pp. Center for Climate and Resilience Research (CR2). Santiago, Chile.
Doug Brugge,D. Durant, J.L., Rioux C., 2007. Near-highway pollutants in motor vehicle exhaust: A review of epidemiologic evidence of cardiac and pulmonary health risks. Environmental Health 2007, 6:23. doi:10.1186/1476-069X-6-23.
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.
Garreaud, R.D., Vuille, M., Compagnucci, R., Marengo, J., 2009. Present-day South American climate. Palaeogeogr. Palaeoclimatol. Palaeoecol. 281, 180–195. doi:10.1016/j.palaeo.2007.10.032
GNL-Quitero, 2016. ~~No Title [WWW Document].~~ URL http://www.gnlquintero.com/ (accessed: January 2017)
Godoy, M.L.D.P., Godoy, J.M., Roldão, L.A., Soluri, D.S., Donagemma, R.A., 2009. Coarse and fine aerosol source apportionment in Rio de Janeiro, Brazil. Atmos. Environ. 43, 2366–2374. doi:10.1016/j.atmosenv.2008.12.046
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. (accessed: January 2017)
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~~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. Chile.
MMA, 2015. Ministerio del Medio Ambiente - Anteproyecto del plan de prevención y descontaminación atmosférica para la región metropolitana de Santaigo. Santiago, Chile.
MMA, 2012. Norma primaria de calidad ambiental para el material particulado fino respirable. Chile.
Montezuma, A.I., 2016. Inversiones y exigencias ambientales en las fundiciones estatales de cobre chilenas: 1990-2014 - Master thesis. Pontificia Universidad Católica de Chile~~.~~, Santaigo, 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
Mugica, V., Watson, J., Vega, E., Reyes, E., Ruiz, M.E., Chow, J., 2002. Receptor model source apportionment of nonmethane hydrocarbons in Mexico City. ScientificWorldJournal. 2, 844–60. doi:10.1100/tsw.2002.147
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. U.S. Environmental Protection Agency, Washington, DC.

Norris, G., Vendantham, R., Duvall, R., Henry, R.C., 2007. EPA Unmix 6 . 0 Fundamentals & User Guide. U.S. Environmental Protection Agency, Washington, DC.

~~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.

Schmitz, R., 2005. Modelling of air pollution dispersion in Santiago de Chile. Atmos. Environ. 39, 2035–2047. doi:10.1016/j.atmosenv.2004.12.033

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

WHO, 2017. Database on source apportionment studies for particulate matter in the air (PM10 and PM2.5) [WWW Document]. URL http://www.who.int/quantifying_ehimpacts/global/source_apport/en/ (accessed: January 2017)

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.

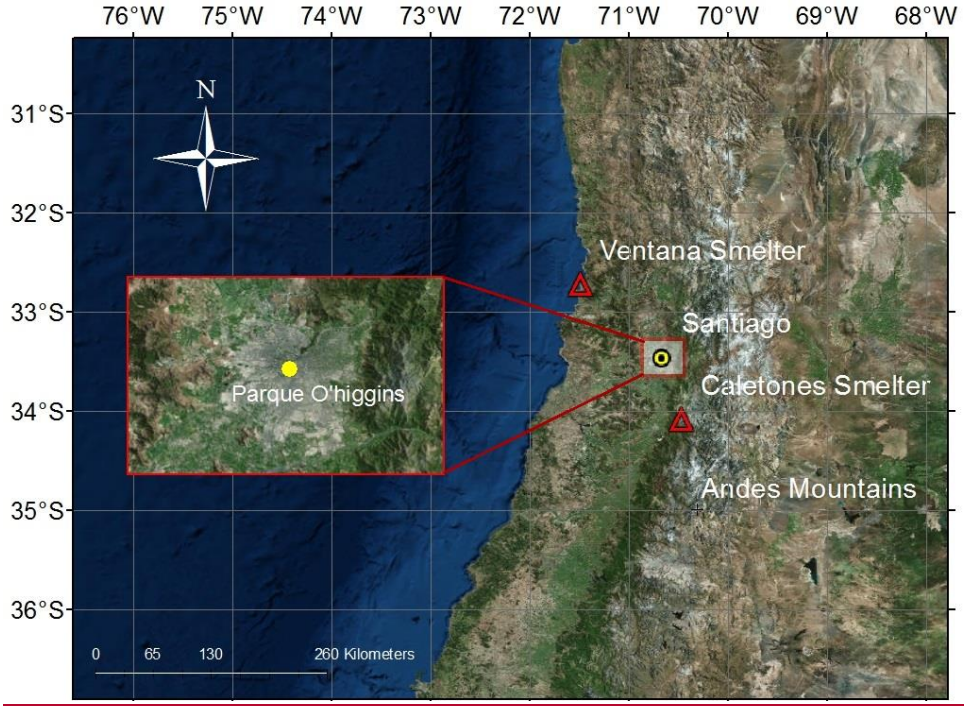


Figure 3 Map of Santiago region, Chile, with the metropolitan area indicated by the red rectangle, and the yellow circle showing the location of the monitoring site in Parque O'Higgins. The red triangles show the location of the major copper smelters close to Santiago.

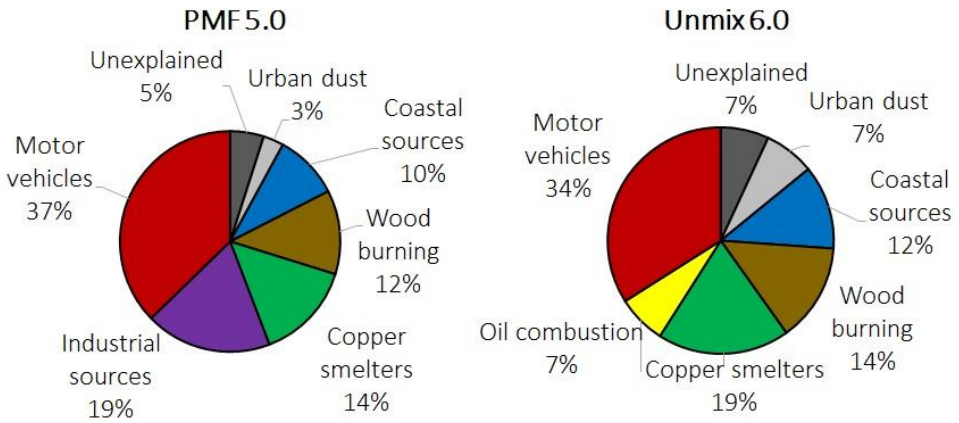
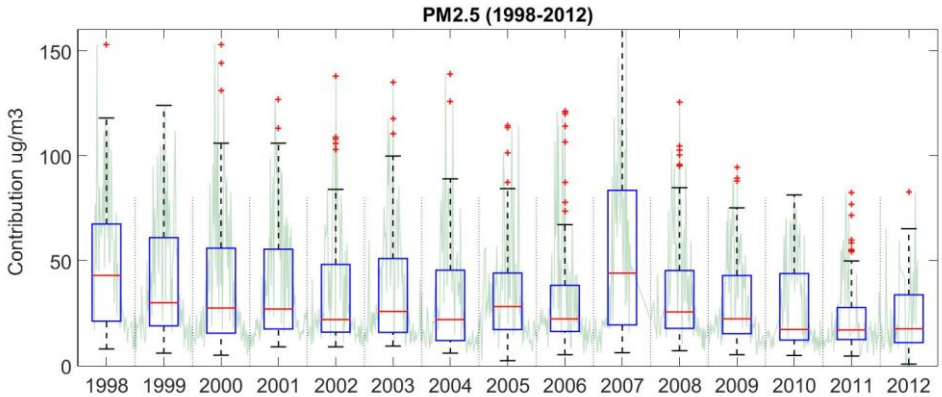


Figure 4 ~~Global percentage of source~~Source apportionment ~~to~~of fine particulate matter in Santiago, Chile, over the whole period 1998-2012~~. using two different models.~~ The PM2.5 median over 15 years was 24.19 µg/m3.



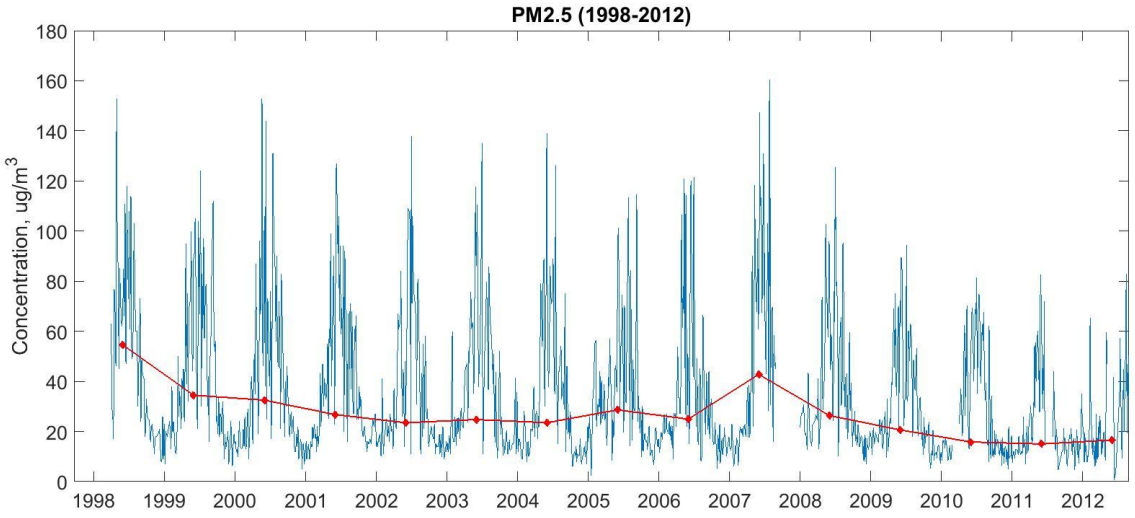
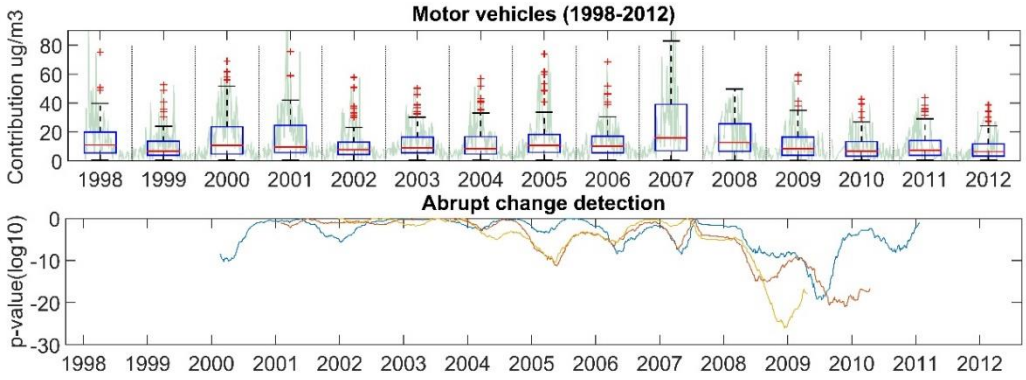


Figure 5 Temporal evolution of PM2.5 concentrations in Parque O'Higgins monitoring station in central Santiago. The red line shows the annual median.



5

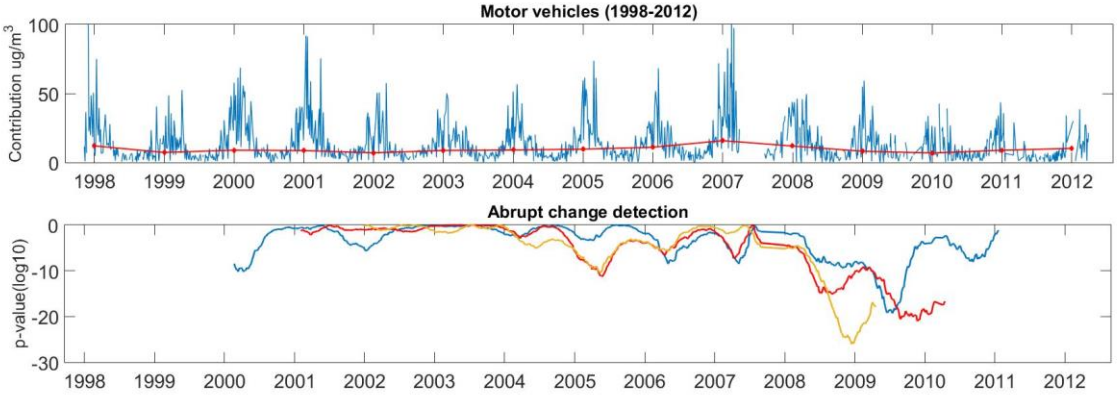


Figure 6 Top panel: Time series ~~(green) and boxplot of the~~ of motor vehicles contribution to PM2.5~~.~~ and the annual median in red. Bottom panel: p-value from a Mann-Whitney hypothesis test comparing the ~~median~~medians of both halves of a sliding window, repeated for 3 different windows lengths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

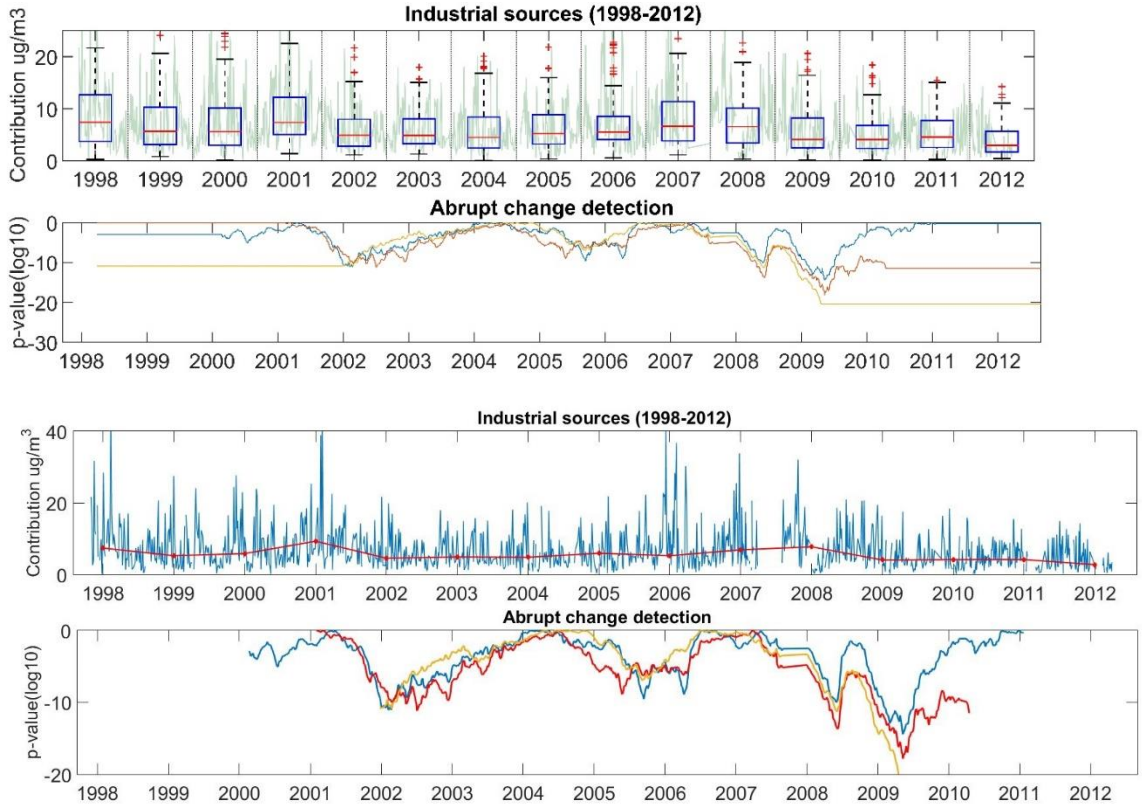
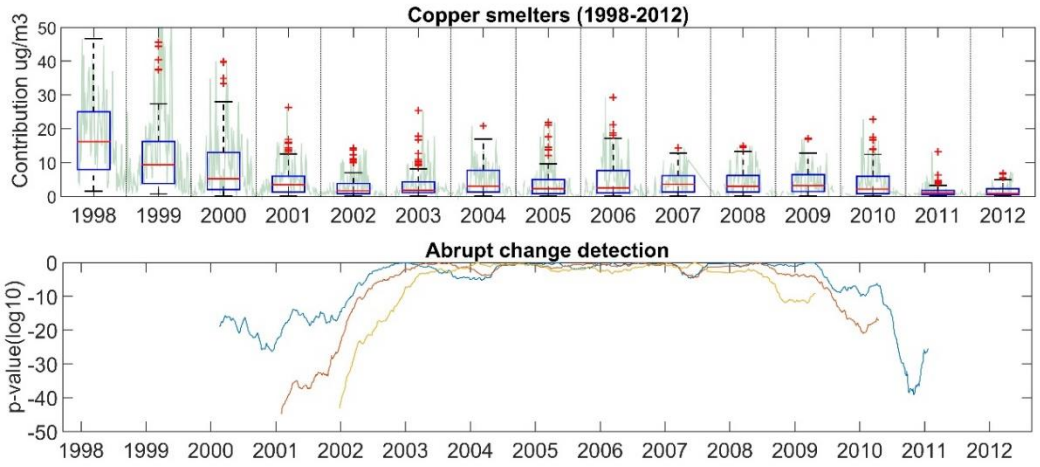


Figure 5 Top panel: Time series ~~(green) and boxplot of the~~ of industrial sources contribution to PM2.5~~.~~ and the annual median in red. Bottom panel: p-value from a Mann-Whitney hypothesis test comparing the ~~median~~medians of both halves of a sliding window, repeated for 3 different windows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



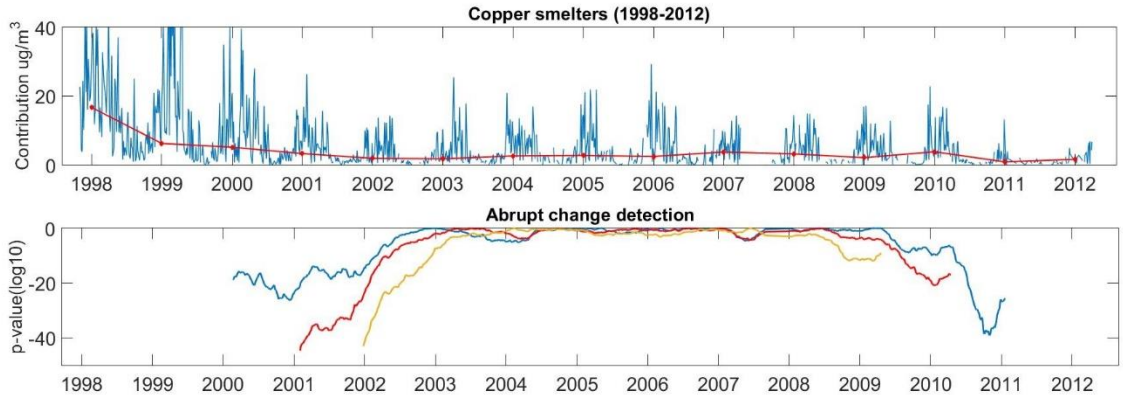


Figure 6 Top panel: Time series ~~(green) and boxplot of the~~ of copper smelters contribution to PM2.5~~.~~ and the annual median in red. Bottom panel: p-value from a Mann-Whitney hypothesis test comparing the ~~median~~medians of both halves of a sliding window, repeated for 3 different windows lengths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

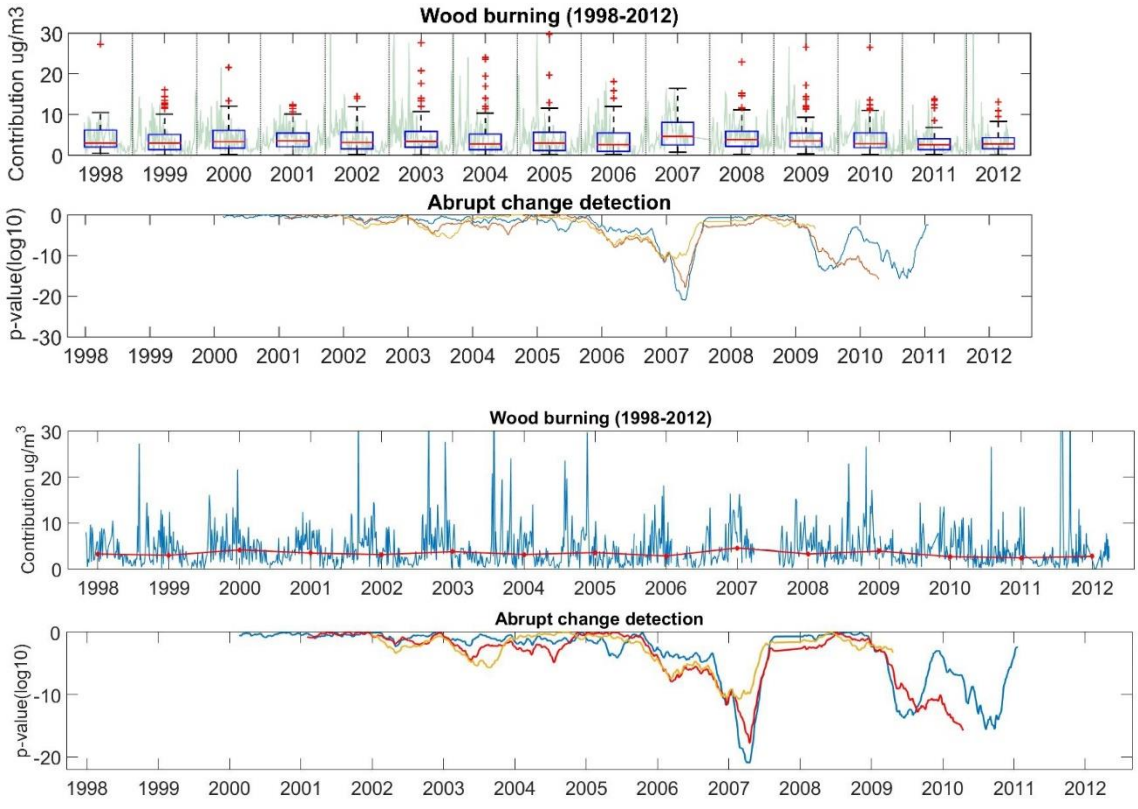


Figure 7 Top panel: Time series ~~(green) and boxplot of the~~ of wood burning contribution to PM2.5~~.~~ and the annual median in red. Bottom panel: p-value from a Mann-Whitney hypothesis test comparing the ~~median~~medians of both halves of a sliding window, repeated for 3 different windows lengths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

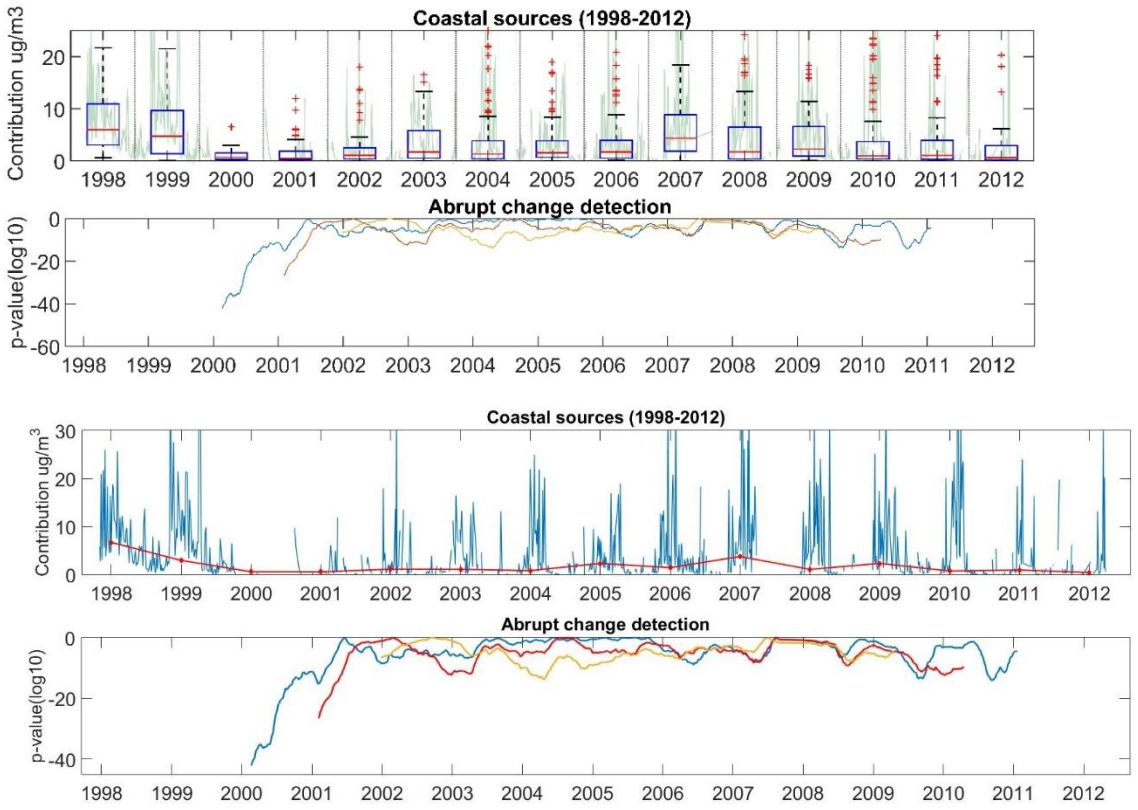


Figure 8 Top panel: Time series ~~(green) and boxplot of the~~ of coastal sources contribution to PM2.5~~.~~ and the annual median in red. Bottom panel: p-value from a Mann-Whitney hypothesis test comparing the ~~median~~medians of both halves of a sliding window, repeated for 3 different windows lengths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

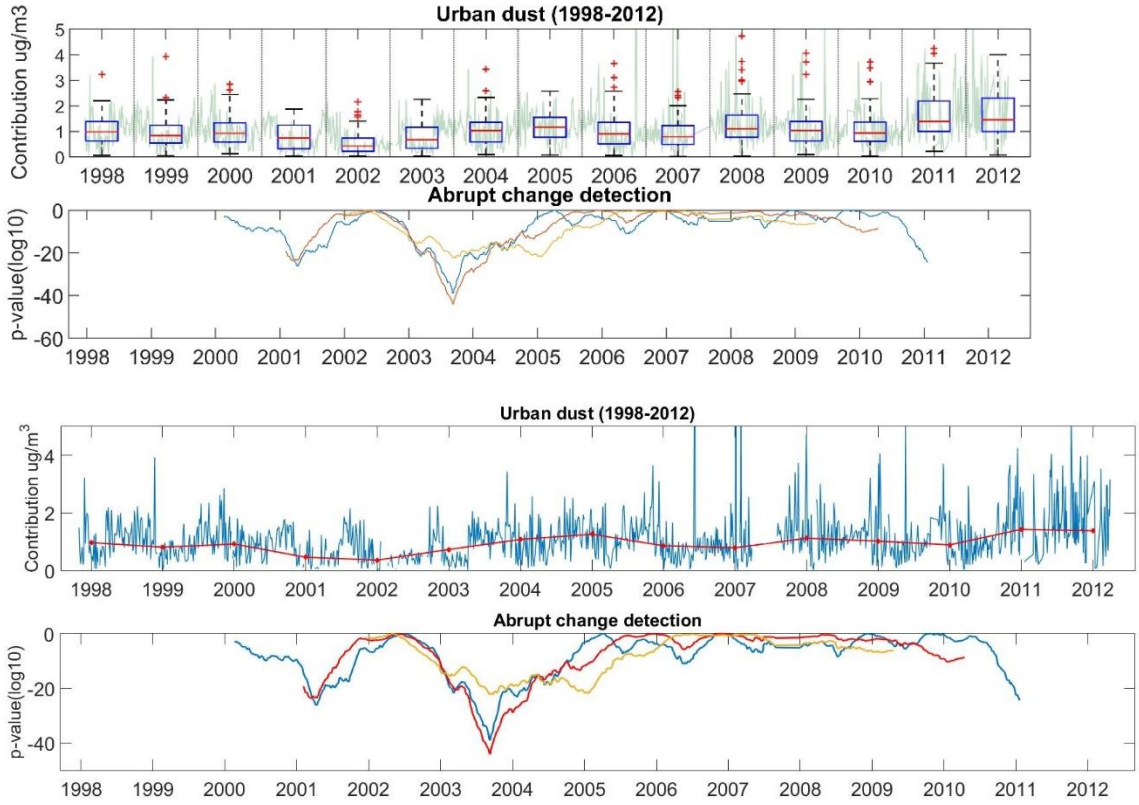


Figure 9 Top panel: Time series ~~(green) and boxplot of the~~ of urban dust contribution to PM2.5~~.~~ and the annual median in red. Bottom panel: p-value from a Mann-Whitney hypothesis test comparing the ~~median~~medians of both halves of a sliding window, repeated for 3 different windows lengths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

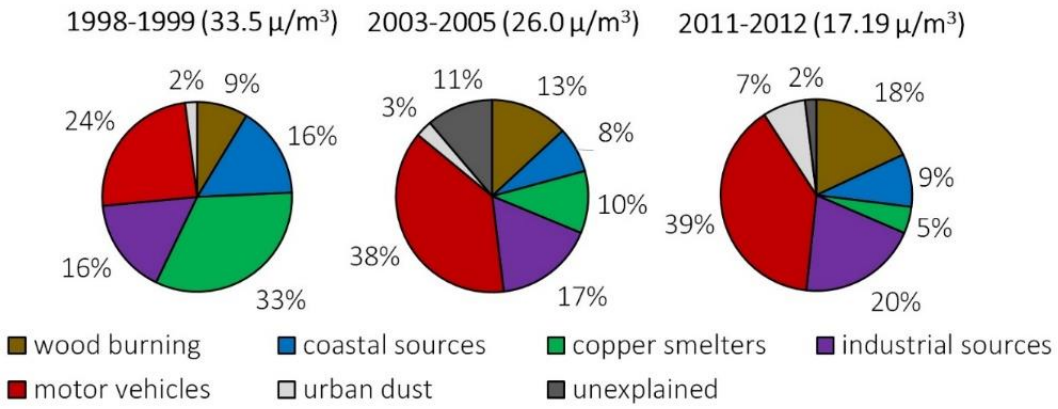


Figure 7 Relative contribution ~~change~~ of each source ~~in~~at the beginning, middle, and end of the period investigated in this study. Median levels of total PM2.5 are given in brackets next to the corresponding time period.

Table 3 Comparison of source apportionment studies in Latin American cities[a]. Total $PM_{2.5}$ and its sources are expressed in µg/m^3.

Site Location	Country	Population	Model used	Reference	Study year	$PM_{2.5}$	Sea salt	Dust	Traffic	Industry	Biomass burning	Other
Cordoba	Argentina	1,272,000	PMF	Lopez[66]	2009/2010	71		39.1	22.7	9.2		0.0
Curitiba	Brazil	2,751,907	APCA	Andrade[1]	2007/2008	12	0.0	0.0	6.6	1.9	0.0	3.5
Porto Alegre	Brazil	1,409,351	APCA	Andrade[1]	2007/2008	16	0.0	0.0	5.6	0.5	0.0	9.9
Belo Horizonte	Brazil	2,375,151	APCA	Andrade[1]	2007/2008	17	0.0	7.5	3.1	2.0	0.0	4.4
Recife	Brazil	1,537,704	APCA	Andrade[1]	2007/2008	18	4.3	1.4	6.7			5.6
Rio de Jainero	Brazil	6,320,000	APCA	Andrade[1]	2007/2008	20		2.8	10.2	3.6		3.4
Sao Paulo	Brazil	11,235,503	APCA	Andrade[1]	2007/2008	28		3.6	11.2	3.6		9.5
Rio de Janeiro	Brazil	6,320,000	APFA	Godoy[5]	2003/2005	10		3.5	2.8	3.4		0.0
Santiago	Chile	5,278,000	PMF	Jorquera[63–65]	2004	32	3.2	1.3	10.0	3.1	9.3	5.3
Santiago	Chile	6,000,000	CMB	Villalobos	2013	33	1.0	2.5	11.0	4.6	5.2	8.9
Moravia	Costa Rica	56,919	PMF	Murillo[67]	2010/2011	18	2.0	3.9	5.2			6.9
San Jose	Costa Rica	288,054	PMF	Murillo[67]	2010/2011	26	2.0	3.5	4.8	6.9		8.9
Heredia	Costa Rica	20,191	PMF	Murillo[67]	2010/2011	37	2.4	5.1	5.8	10.3		13.4
Tijuana	Mexico	1,301,000	PMF	Minguillon[50]	2010	19	2.9		2.6	0.4	7.1	5.6
Mexico City	Mexico	8,851,000	CMB	Mugica[51]	2006	50		13.3	21.0	5.0		10.7
Salamanca	Mexico	152,048	PMF	Murillo[52]	2006/2007	45		7.3	5.8	8.2		23.7

(b) Adapted from WHO, http://www.who.int/quantifying_ehimpacts/global/source_apport/en/.

5 **Table 4 Comparison of long-term source apportionment studies carried out in urban areas.**

Location, period	PM2.5 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
Sidney, 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

(d) Only ammonium sulfate is reported.

(e) Sulfate was expressed as ammonium sulfate.
(f) Whenever more than one type of industrial source has been resolved, they have been lumped together in a single industrial category.

Table 5 Seasonal PM2.5 and source contribution identified by a stratified regression of the contributions obtained by PMF 5.0. The concentration values are given in µg/m3 for each season and source, with corresponding standard errors at 95% confidence level within the brackets. The 24-hour Chilean standard for PM2.5 is 50 µg/m3 and the WHO guidelines is 25 µg/m3.

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 daily Samples	343	315	292	294

Table 6 Significant changes in $PM_{2.5}$ sources in context with Santiago air quality improvement measures taken at that time.

Source	Date Change event	Impact over source contributions	Explanation and comments
Motor vehicles	2002	Reduction of 1.53 µg/m^3 (15.59%)	Fuel quality improvement. Lead removed from gasoline
Motor vehicles	2005 and 2006	Increase of 1.60 µg/m^3 (18.92%).	Operation of urban highways.
Motor vehicles	2007	Increase of 1.34 µg/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 µg/m^3 (43.97%)	Improvement to Transantiago
Industrial sources	2002	Reduction of 2.52 µg/m^3 (34.33%)	Diesel fuel sulfur content reduction in 2001.
Industrial sources	2005-2007	Increase of 1.86 µg/m^3 (45.04%).	Argentinean natural gas import reduction

Industrial sources	2009-2010	Reduction of 1.76 $\mu g/m^3$ (31.17%)	Opening of Quintero terminal for LNG import through marine port
Cooper smelter	1998-2002	Reduction of 4.13 $\mu g/m^3$ (69.04%)	Implementation of emission abatement technology in Caletones smelter
Cooper smelter	2010-2011	Reduction of 1.41 $\mu g/m^3$ (64.66%)	Reduction of SO_2 and PM emissions in Caletones and Ventana smelters
Wood burning	2007-2008	Increase of 1.16 $\mu g/m^3$ (43.39%).	Unknow
Wood burning	2009-2010	Reduction of 0.55 $\mu g/m^3$ (16.98%)	Unknow
coastal sources	2002-2005	Reduction of 1.62 $\mu g/m^3$ (77.46%)	Diesel sulfur content reduction
coastal sources	Since 2010	Reduction of 1.05 $\mu g/m^3$ (76.17%)	Opening of Quintero terminal for LNG import through marine port
Urban dust	2001-2002	Reduction of 0.42 $\mu g/m^3$ (48.84%)	Lead-free gasoline introduction
Urban dust	Since 2004	Increase of 0.67 $\mu g/m^3$ (171.78%).	Increase in the number of motorized car (annual growth rate of 4%)
Urban dust	Since 2011	Increase of 0.48 $\mu g/m^3$ (51.61%).	Increase in the number of motorized car (annual growth rate of 7%), extended drought since 2010

Supplementary material

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

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 burning	26								
Solid dust		15.5	31.3	17	7	24.6	4	4	
Solid dust + industry 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).**~~

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

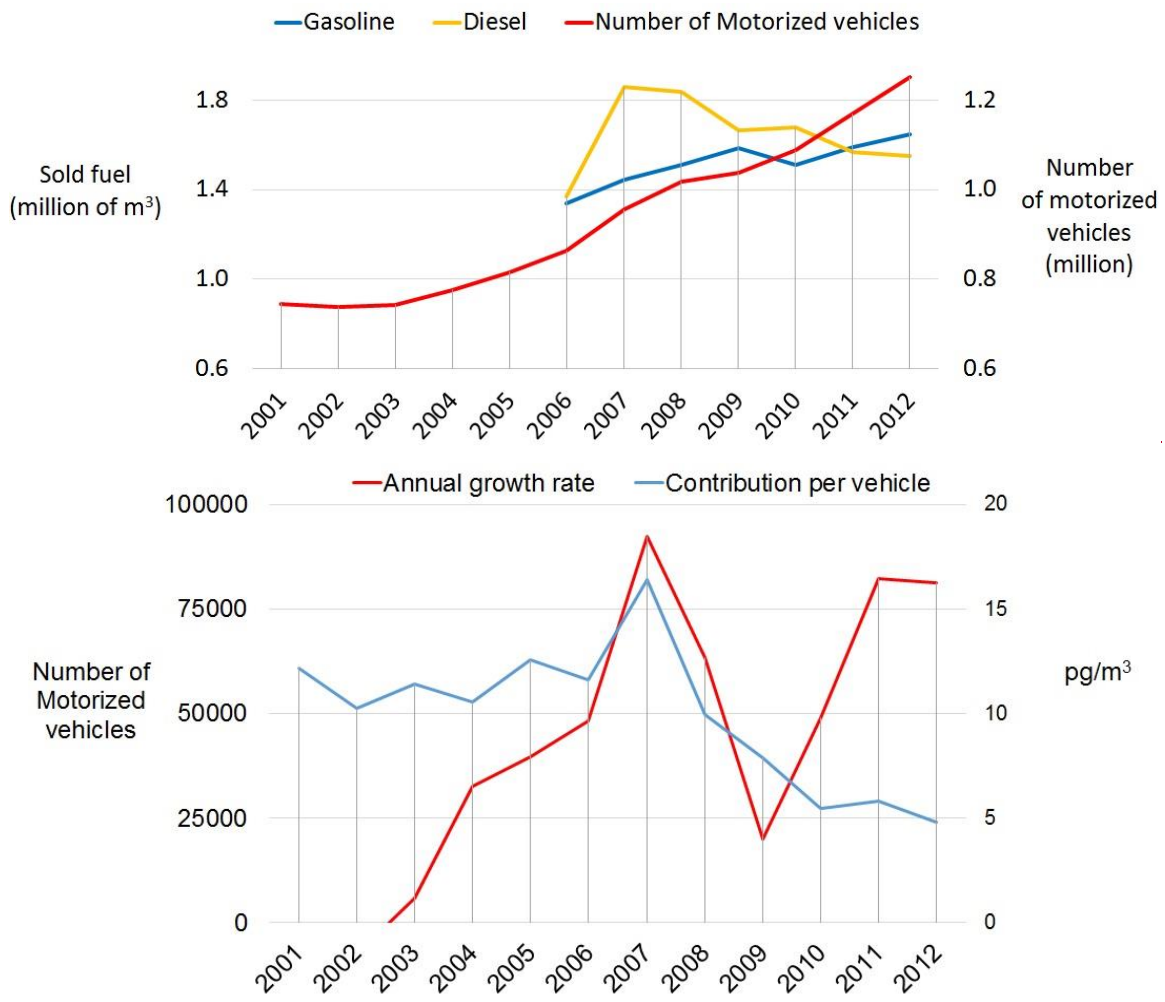


Figure S4 ~~trend of number of motorized vehicles in Santiago city and the vehicles sold fuel. The~~Example of replacement of missing **data** ~~for number of motorized vehicles were provided by INE (www.ine.cl) and for the sold fuel by SEC (www.sec.cl).~~

~~Figure S2 Trend of vehicles annual growth rate and contribution per vehicles for Santiago city. The~~. Original **data for** Cl (in blue) with missing data filled using a custom-written algorithm (in red). Shown are a) Cl concentration on a logarithmic scale, b) zoom of a data range with small and large filled data gaps

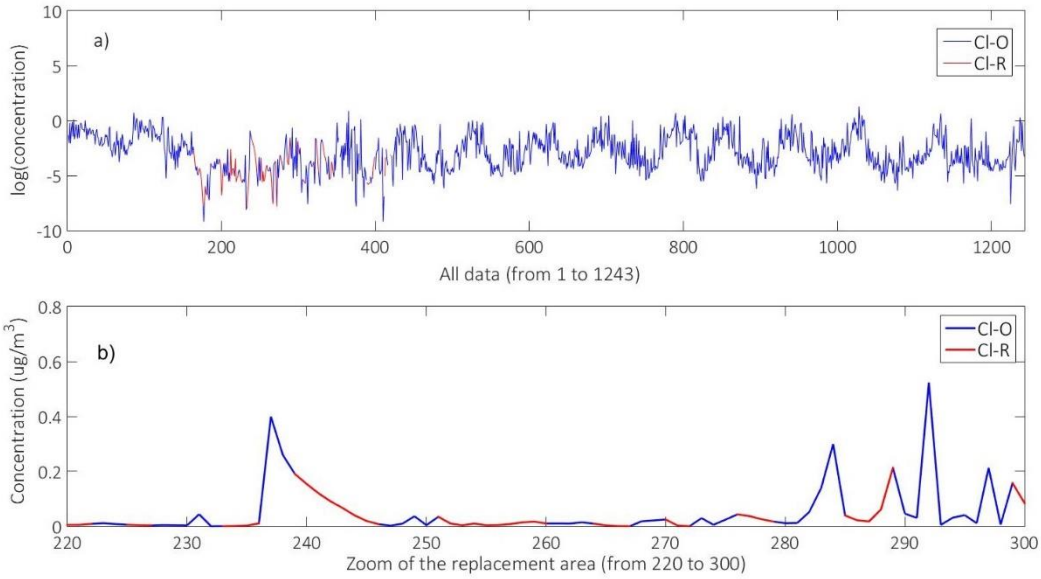


Figure S5 K-Fe edge plot. To provide a tracer associated with wood burning we added the non-soil potassium parameter Kns calculated as Kns=K-0.3•Fe, from the K-Fe edge plot

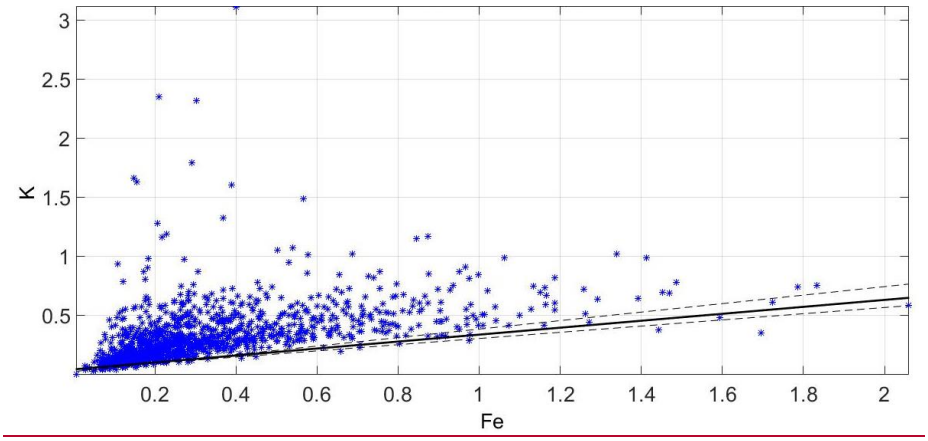


Figure S6 Trend in Santiago motorized vehicles numbers (data provided by National institute of statistics, www.ine.cl) as well as sold vehicle fuel (data provided by Superintendence of electricity and fuels, www.sec.cl).

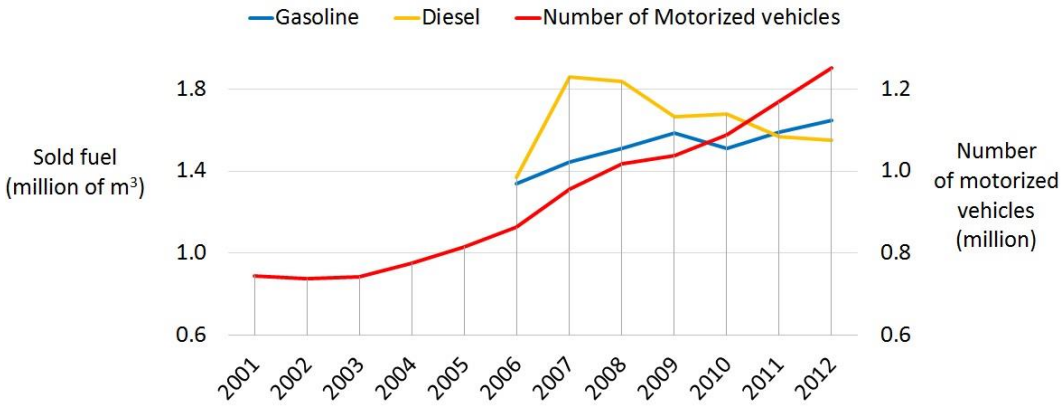


Figure ~~number of motorized vehicles were provided by INE (www.ine.cl)~~S7 Trend in Santiago vehicles annual growth rate (data provided by National institute of statistics, www.ine.cl) and contribution per vehicle to PM2.5 Santiago's levels. The

contribution per vehicle was calculated by the dividing annual median motor vehicles contribution (from PMF) by the number of motorized vehicles in each year.

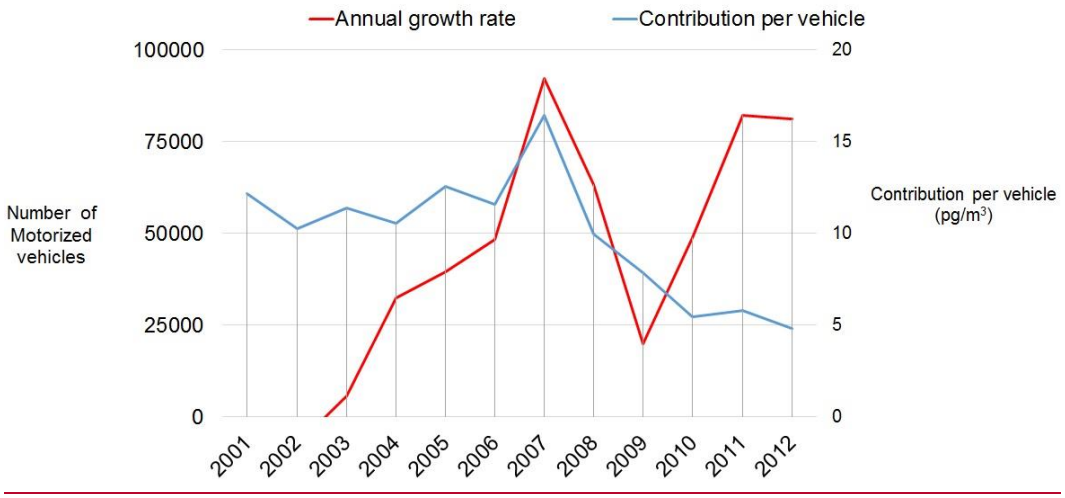


Figure S5 Monthly precipitation anomalies from the mean in downtown Santiago, 1960-2015. Source: http://explorador.cr2.cl/