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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Temporal evolution of main ambient $PM_{2.5}$ sources in Santiago, Chile, from 1998 to 2012" *by* Francisco Barraza et al.

Anonymous Referee #1

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Temporal evolution of main ambient PM2.5 sources in Santiago, Chile, from 1998 to 2012 From: Francisco Barraza, Fabrice Lambert, Héctor Jorquera, Ana María Villalobos, Laura Gallardo.

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. 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. 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. 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.

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.

You discussed the impact of sources to PM2.5. 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.

Specific comments

Page 1 – line 18: the word WERE was missing 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. 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... Page 3 line 5 – upperscript for ug/m^3... 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/m^3 for each element?.

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?

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.

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. 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".

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. 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.

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.

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"

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".

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