Source apportionment of highly time resolved trace elements during a firework episode from a rural freeway site in Switzerland

Pragati Rai[1], Markus Furger[1], Jay Slowik[1], Francesco Canonaco[1], Roman Fröhlich[1], Christoph Hüglin[2], María Cruz Minguillón[3], Krag Petterson[4], Urs Baltensperger[1] and André S.H. Prévôt[1]

[1] Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen PSI, 5232, Switzerland
[2] Laboratory for Air Pollution / Environmental Technology, Empa, 8600 Dübendorf, Switzerland
[3] Institute of Environmental Assessment and Water Research (IDAEA), CSIC, 08034 Barcelona, Spain
[4] Cooper Environmental Services (CES), 9403 SW Nimbus Avenue, Beaverton, OR 97008, USA

Correspondence to: André S. H. Prévôt (andre.prevot@psi.ch) and Markus Furger (markus.furger@psi.ch)

Response to Reviewer #2

We kindly thank the reviewer#2 for taking our manuscript into consideration and we value the comments raised to improve the manuscript. A point-by-point answer (in regular typeset) to the reviewers' remarks (in italic typeset) follows. Changes to the manuscript are indicated in blue font.

In the following page and lines references refer to the manuscript version reviewed by anonymous Reviewer#2.

This paper examines data previously reported by Furger et al (2017) applying PMF source apportionment techniques to a subset of the reported data to provide insight into the chemical composition of different sources. It focuses on firework / burning sources associated with local celebrations (which are a common influence on air quality for short periods in many countries) and to a lesser extent on suspended dust from road and surface sources. The article is generally well written and the approach is methodologically robust. However, the data used is somewhat limited and the authors have not taken advantage of the aerosol mass spectrometer data which was available. I have many suggested edits and some points which require consideration by the authors.

Major Comments –

Pg 5, line 16 – the authors reduce the data set from 24 to 14 based on manufacturer supplied MDLs to produce 'better' source apportionment results. Firstly, even though the measurements are below the detection limit, they could contain 'valuable' information on variability, especially during firework periods as some of the excluded elements are potential firework components (e.g. Cd). They have been excluded based on %below MDL at a rather arbitrary value e.g. Bi at 93% was included while Cd at 87% was not. It would be worth including this data and downweighting rather that excluding it or at least performing sensitivity test. A further 4 elements are excluded based on data quality but no detail on what constitutes data quality is given.

We agree with reviewer#2 and therefore we had included Bi which shows fireworks peaks while for the rest of time it is below MDL. We inspected all the elements before preparing the PMF input data based on MDL. V, Co, As, Se, Cd and Pt were close to or below their Xact MDL. The inter-comparison of Xact vs ICP data for Co, Ni, As, Se, Cd and Hg was not justified based on the weak correlation (r^2). Pt was below MDL (98%), and it was not measured on the filters, therefore no conclusion about the Pt accuracy can be drawn. We did not find any fireworks

peaks for any of these elements. The detailed discussion on Xact data quality is described in more detail in the previous study (Furger et al., 2017).
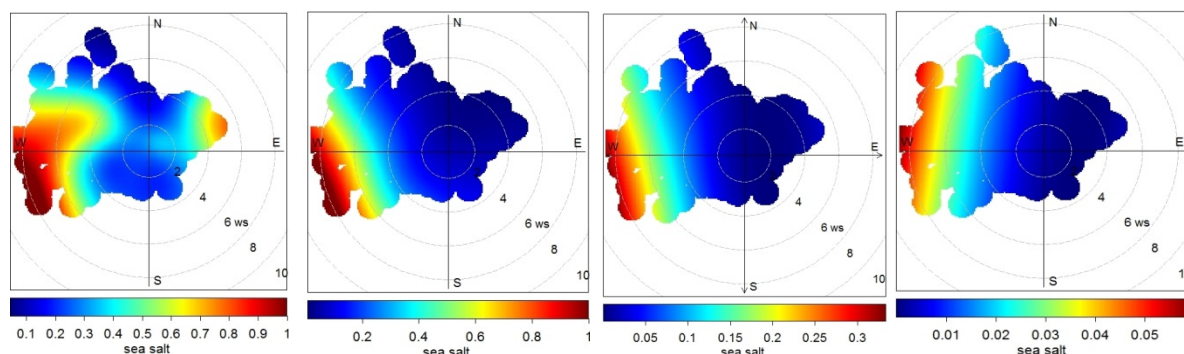
We modified the text on Pg 5 line 20:

Elements (% of data points below MDL, r^2 value) which had more than 50 % of data points below MDL and low r^2 (0.5) between Xact and offline data were not included in the PMF input, such as: V (98 %, 0.57), Co (100 %, 0.05), Ni (32 %, 0.22), As (96 %, 0.5), Se (62 %, 0.3), Cd (87 %, 0.18), Sn (15 %, 0.27), Sb (6%, 0.42), Hg (13 %, 0.12) and Pt (98 %, not measured on the filters). The element Bi (93% data points below MDL) was an exception to include in the PMF input due to an excellent correlation between Xact and offline data ($r^2 = 0.98$) during fireworks peaks. The detailed description of the Xact data quality is given in the previous study (Furger et al., 2017).

Furger, M., Minguillón, M. C., Yadav, V., Slowik, J. G., Hüglin, C., Fröhlich, R., Petterson, K., Baltensperger, U., and Prévôt, A. S. H.: Elemental composition of ambient aerosols measured with high temporal resolution using an online XRF spectrometer, Atmos. Meas.Tech., 10, 2061–2076, https://doi.org/10.5194/amt-10-2061-2017, 2017.

Pg 8 Line 4 and later – The CBPF is an important analysis which is used to justify the identification of sources and the charts should not be shunted to the appendix. Further, the reliance on 90th percentile to identify the sources is flawed when considered on its own, especially when the distribution of measurements is heavily skewed (as it is with Cl). A range of CBPFs should be presented (at least in the supplementary) to support the interpretation. The authors should also consider the use of the min bin statistic to ensure that individual points are not skewing the interpretation. Finally, the conclusion that the two dust sources are from different sources (based on these plots) when their direction is broadly similar is rather weak.

We agree that it would be helpful moving the CBPF plots from the Supplement to the main manuscript. We presented a range of CBPF plots in the supplementary for these four factors (as shown in the figure below). We partially agree with reviewer#2 for min bin statistics. The min bin parameter provides the minimum number of points required to provide a result in a wind speed/wind direction bin and is 1 in this analysis. If we set it >1, there is the risk of removing real data. Concerning the two dust factors, comparing the two CBPF ranges, there are indeed differences in terms of source directions. The road dust factor is quite consistent with southerly winds except for a few low concentration data points (at the 50th percentile) while the background dust source direction is quite variable for different ranges of data.
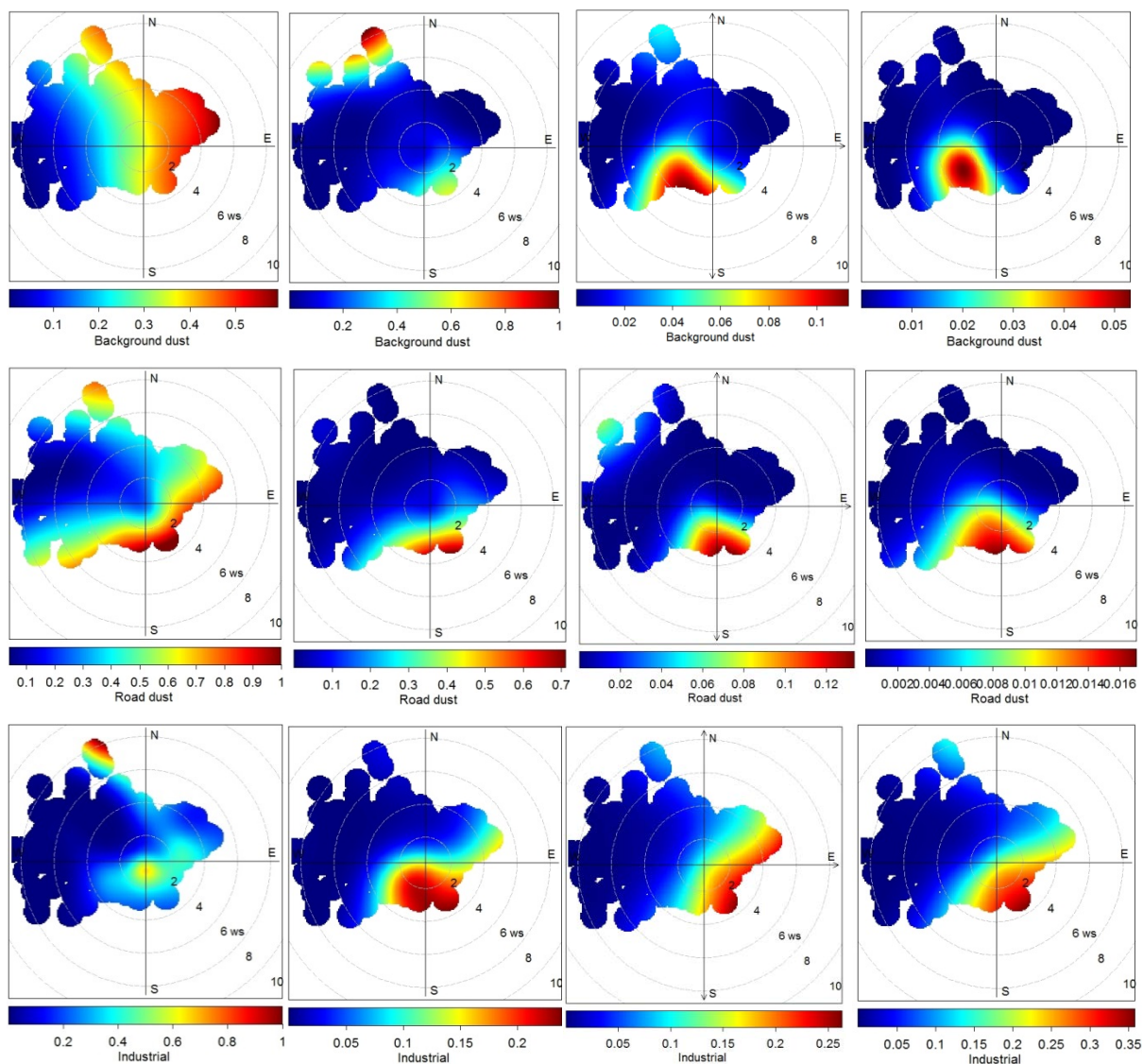
Figure S16: CBPF analysis (from left to right: 50th, 75th, 90th, 95th percentiles) of factors (sea salt, background dust, road dust, industrial) in terms of wind speed (m s^{-1}) and wind direction. The color code represents the probability of the factor contribution.

Pg 8 Line 9 and later – KNO3 is quoted as comprising 74% of fireworks. In which case NO3 could be a useful tracer for unburnt firework material - it was measured but is not reported. A recognition of this point, even to say that there was no correlation would help. The same is true of the other mass concentrations and m/z measured by the ACSM – were these examined or even considered for inclusion in the PMF or data analysis?

We added a figure in the supplement to show the ACSM inorganics concentration along with NO_2 and NO_x during the fireworks episode. From the figure it is very obvious that neither particulate nitrate nor ammonium is generated in the fireworks in significant amounts. The ACSM nitrate showed a quick drop immediately before the main fireworks (1 August 2015 23:00 LT). The sulphate peaks coincide with a strong drop of the nitrate concentration, which indicates that ammonium nitrate may have reacted with sulfuric acid, releasing nitric acid to the gas phase. The absence of fireworks nitrate has been observed previously (Drewnick et al., 2006) and indicates that most of the black powder nitrate is converted to other forms of nitrogen species. We calculated the measured NO_2 / K

mass ratio for enhanced NO_2 concentration during the fireworks based on K concentration. The ratio was 1.66 on the main fireworks hour (1 August 23:00 LT) which is close to the atomic ratio of NO_2 / K (1.17). This measured ratio is in-line with the NO_2 / K^+ (2.03) ratio measured during Chinese Spring Festival in Shanghai (Yao et al., 2019).

We have added the following text in the revised manuscript on pg8 line 10:

The ACSM inorganics concentrations during the fireworks episodes indicate that neither particulate nitrate nor ammonium is generated in the fireworks in significant amounts (Fig. S7). Consistent with previous measurements of submicron fireworks aerosol (Drewnick et al., 2006; Vecchi et al., 2008; Jiang et al., 2015), nitrate was not enhanced during the fireworks period, suggesting conversion of KNO_3 to other forms of nitrogen. The NO_2 / K mass ratio (1.66) on the main fireworks hour (1 August 23:00 LT) is close to the atomic ratio of NO_2 / K (1.17). This measured ratio is also in agreement with the NO_2 / K^+ (2.03) ratio observed during Chinese Spring Festival in Shanghai (Yao et al., 2019). However, the NO_2 and/or NO_x variation was not significant during the fireworks peaks in the present study (Fig. S7), which is in agreement with the former studies (Vecchi et al., 2008; Retama et al., 2019; Yao et al., 2019).

Drewnick, F., Hings, S. S., Curtius, J., Eerdekens, G., and Williams, J.: Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany, Atmos. Environ., 40, 4316–4327, https://doi.org/10.1016/j.atmosenv.2006.03.040, 2006.

Vecchi, R., Bernardoni, V., Cricchio, D., D'Alessandro, A., Fermo, P., Lucarelli, F., Nava, S., Piazzalunga, A., and Valli, G.: The impact of fireworks on airborne particles, Atmos. Environ., 42, 1121–1132, https://doi.org/10.1016/j.atmosenv.2007.10.047, 2008.

Jiang, Q., Sun, Y. L., Wang, Z., and Yin, Y.: Aerosol composition and sources during the Chinese Spring Festival: fireworks, secondary aerosol, and holiday effects, Atmos. Chem. Phys., 15, 6023–6034, https://doi.org/10.5194/acp-15-6023-2015, 2015.

Yao, L., Wang, D., Fu, Q., Qiao, L., Wang, H., Li, L., Sun, W., Li, Q., Wang, L., Yang, X., Zhao, Z., Kan, H., Xian, A., Wang, G., Xiao, H., and Chen, J.: The effects of firework regulation on air quality and public health during the Chinese Spring Festival from 2013 to 2017 in a Chinese megacity, Environ. Int., 126, 96–106, https://doi.org/10.1016/j.envint.2019.01.037, 2019.

Retama, A., Neria-Hernández, A., Jaimes-Palomera, M., Rivera-Hernández, O., Sánchez-Rodríguez, M., López-Medina, A., and Velasco, E.: Fireworks: a major source of inorganic and organic aerosols during Christmas and New Year in Mexico city, Atmos. Environ., 2, 100013, https://doi.org/10.1016/j.aeaoa.2019.100013, 2019.
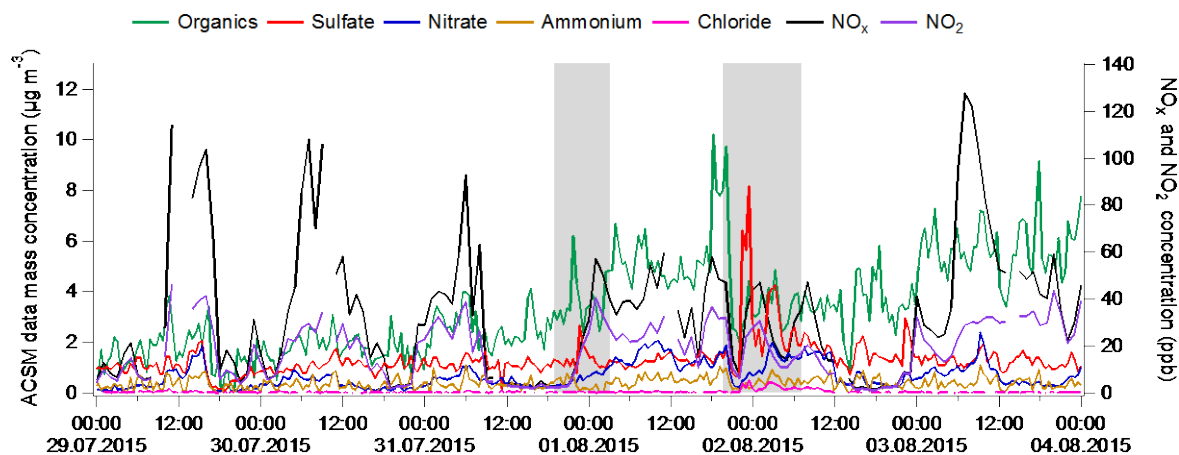
Figure S7: Time series of the non-refractory aerosol components (measured with the ACSM), NO_2 and NO_x concentration. The fireworks episodes are underlain in grey color.

Line 29 and later – The use of SoFi to separate highly correlated sources such as the two firework sources is the reason for this paper. The consideration of Cl displacement is interesting and has evidence to support it, why does it therefore come after 2 purely speculative thoughts about possible alternative sources. Promote this point and consider the speculations as alternatives. One of these - the separation of bonfires from fireworks may have been helped by considering the ACSM data.

We have rearranged the text from line 26 onwards as follows:

Chemical reactions of KCl with H_2SO_4 will result in a release of gaseous HCl and may explain the absence of particulate Cl in the fireworks-II factor profile. The time series variations in both fireworks suggest that fireworks-I might be related to the main fireworks celebration while fireworks-II might result from burning of leftover crackers after the main fireworks day, as well as the influence of other sources such as bonfires, which are a common activity during Swiss National Day celebrations. Another possibility could be the advection of fireworks clouds from nearby cities where grand firework displays and bonfires are carried out at large scale to celebrate the Swiss National Day.

General Comment-
The authors use the term 'trace' elements. I would not consider S or Fe trace elements in ambient PM. I suggest the authors just refer to them as elements.

We removed "trace" from the manuscript.

Pg 1 Line 13 - Source Finder software, please quote version number, supplier and country
Done.

Line 19 - The abstract is partly written in the present tense – 'experiences' should read 'experienced', 'concentrations are similar' should read 'concentrations were similar'

We corrected the grammatical error in abstract.

Further, there were minor contributions (on the order of a few percent) of sea salt and industrial sources. The regionally influenced secondary sulfate factor showed negligible resuspension, and concentrations were similar throughout the day. The significant loads of the traffic-related and road dust factors with strong diurnal variations highlight the continuing importance of vehicle-related air pollutants at this site.

Pg 2 Line 29 – clarify that you are talking about off line sampling systems

We added the word "offline" in the text.

Line 33 – the sampler don't specifically need those analysis techniques, they require techniques with high precision and low detection limits – such as these methods

We modified this line as follows:

These offline analyses require high precision and low detection limit techniques such as synchrotron radiation induced X-ray fluorescence spectrometry (SR-XRF) of aerosol samples collected with a RDI, particle induced X-ray emission (PIXE) with the streaker sampler and graphite furnace atomic absorption spectrometry (GFAAS) with the SEAS.

Pg 3 Line 28 – delete XACT manufacturer already provided line 4
Done.

Line 30 – with should read at Line 31 onwards – be consistent with how you name equipment – model, make, supplier, country
Done.

Line 31 – quote filter manufacturer
Done.

Pg 4 Line 2 – TEOM and FDMS in full then in brackets or just the abbreviation, not a mixture
Done.

Line 20 – can values be applied to individual data points; this implies that individual points can be used for a-value constraining. Is this true? Certain sections in a time series can but individual points cannot be separated out in this way.

Yes, it is possible to apply an *a*-value on individual data points because PMF renormalizes the factors at the end.

Line 28 – this is not the first use of sofi in the manuscript - the reference, version number and supplier should go there.

Done, except reference. The first use of SoFi is in the abstract section. One should not use references in the abstract.

Pg 5 Line 1 – 'PMF' rather than 'model'
Done.
Line 4 – 'identify' rather than 'find'
Done.
Line 4 – this only helps to identify the high concentration peaks and whether then influence the mean will depend on the distribution of data (see Cl results in fig 4)

We partially agree with the reviewer#2. CBPF gives directional information of sources contributing to pollutant concentrations at the sampling site.

Line 22 – Bi a major component of fireworks –a reference, some evidence would be good here and even justify the exclusion of other elements.

We deleted Bi a major tracer of fireworks from line 22 and added the reference for Bi on Pg8 line 12. Concerning exclusion of elements, please see the response in the major comments section.
We added a sentence on Pg 8 line 12 as follows:
Bi is used in crackling stars (Dragon's eggs) in the form of bismuth trioxide or subcarbonate as a non-toxic substitute for toxic lead compounds (Perrino et al., 2011).
Perrino, C., Tiwari, S., Catrambone, M., Torre, S. D., Rantica, E., and Canepari, S.: Chemical characterization of atmospheric PM in Delhi, India, during different periods of the year including Diwali festival, Atmos. Pollut. Res., 2, 418–427, https://doi.org/10.5094/apr.2011.048, 2011.

Pg 6 Line 1 - need a description on xij
Done.

Line 16 – listed s1-s4 but only s2 and s3 relate to this point

We removed S1, S2 and S4 according to text change in the revised manuscript.

Pg 7 Line 18 – how do you know it is coarse Cl, you have two measures of Cl one is non-refractory Cl- in PM1 and one is Cl in PM10?

We replaced "coarse" with PM_{10} in line 18.

Pg 8 Line 6 –are these elements really the main components of fireworks by mass, surely you need a reference here to justify this.

The fireworks factors are mostly dominated by K, S, and Cl, among the elements analysed here. Moreover, Ti, Cu, Ba and Bi are key tracers of these factors.

We have added references in line 6:

(Moreno et al., 2007; Wang et al., 2007; Vecchi et al., 2008; Perrino et al., 2011; Tian et al., 2014; Kong et al., 2015; Lin, 2016; Pongpiachan et al., 2018).

Moreno, T., Querol, X., Alastuey, A., Minguillón, M. C., Pey, J., Rodriguez, S., Miró, J. V., Felis, C., and Gibbons, W.: Recreational atmospheric pollution episodes: Inhalable metalliferous particles from firework displays, Atmos. Environ., 41, 913–922, https://doi.org/10.1016/j.atmosenv.2006.09.019, 2007.

Perrino, C., Tiwari, S., Catrambone, M., Torre, S. D., Rantica, E., and Canepari, S.: Chemical characterization of atmospheric PM in Delhi, India, during different periods of the year including Diwali festival, Atmos. Pollut. Res., 2, 418–427, https://doi.org/10.5094/apr.2011.048, 2011.

Wang, Y., Zhuang, G., Xu, C., and An, Z.: The air pollution caused by the burning of fireworks during the lantern festival in Beijing, Atmos. Environ., 41, 417–431, https://doi.org/10.1016/j.atmosenv.2006.07.043, 2007.

Vecchi, R., Bernardoni, V., Cricchio, D., D'Alessandro, A., Fermo, P., Lucarelli, F., Nava, S., Piazzalunga, A., and Valli, G.: The impact of fireworks on airborne particles, Atmos. Environ., 42, 1121–1132, https://doi.org/10.1016/j.atmosenv.2007.10.047, 2008.

Kong, S. F., Li, L., Li, X. X., Yin, Y., Chen, K., Liu, D. T., Yuan, L., Zhang, Y. J., Shan, Y. P., and Ji, Y. Q.: The impacts of firework burning at the Chinese Spring Festival on air quality: insights of tracers, source evolution and aging processes, Atmos. Chem. Phys., 15, 2167–2184, https://doi.org/10.5194/acp-15-2167-2015, 2015.

Lin, C.-C.: A review of the impact of fireworks on particulate matter in ambient air, J. Air Waste Manage. Assoc., 66, 12, 1171–1182, https://doi.org/10.1080/10962247.2016.1219280, 2016.

Pongpiachan, S., Iijima, A., and Cao, J.: Hazard quotients, hazard indexes, and cancer risks of toxic metals in PM_{10} during firework displays, Atmosphere, 9, 144, https://doi.org/10.3390/atmos9040144, 2018.

Tian, Y. Z., Wang, J., Peng, X., Shi, G. L., and Feng, Y. C.: Estimation of the direct and indirect impacts of fireworks on the physicochemical characteristics of atmospheric PM_{10} and $PM_{2.5}$, Atmos. Chem. Phys., 14, 9469–9479, https://doi.org/10.5194/acp-14-9469-2014, 2014.

Line 7 – chlorate and perchlorate (line 11) will also be detected as Cl in XRF

Indeed, the Xact measures total chlorine including all particulate Cl compounds such that we cannot distinguish them with the Xact measurements.

Line 16 – the sentence starting 'A pronounced: : :) should really come at te start of the para
Done.

Line 29 – this consideration of Cl displacement is interesting and at has evidence to support it, why does it therefore come after 2 purely speculative thoughts. Promote this point and consider the speculations as alternatives.

Please see the response above in the major comment.

Pg 11 – line 6 – there is no fig S12

We corrected it as Fig. S9.