

Author's response to the interactive discussion comments

Please find below the author's response to the interactive discussion comments from the anonymous referee. The original comments are written in black and the author's reply and changes to the manuscript are coloured in blue/green, respectively.

Anonymous Referee #3 Received and published: 10 January 2018

The paper "Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols" by Tremper et al. is a comprehensive study aiming at providing laboratory and in-field information on the performance of the X-ACT 625 instrument. The paper is well structured, data presentation is adequate and well commented. X-ACT is an innovative instrument and improving its characterization is important for the scientific community. Thus, in my opinion the paper is of interest for publication in AMT and publication can occur after few revisions are performed.

Author's response:

We would like to thank the anonymous referee for the positive feedback and the detailed suggestions to our manuscript. Please find the answers to the individual comments below. The original comments are written in black and the author's reply and changes to the manuscript are coloured in blue/green, respectively.

RC - Major concerns:

RC - P10L18: why is Cd not mentioned? Cd is the element providing the strongest differences in all cases, but its discussion is completely missed in the text. Please add comments about it, or give explanation why it should be rejected. In this case, please remove it throughout the manuscript.

Author's response: Cd was mostly below the detection limit and thus did not give meaningful results in the Deming regression. To make this clearer the text section 3.2.1 was changed from "For the remaining elements (Ni after HF/HClO₄ digestion and Cu and Se after HNO₃/H₂O₂ digestion) the concentrations measured by the XACT were significantly lower than those measured by the ICP-MS. Cr and V were not reported for HF/HClO₄ due to contamination of the HClO₄ used in the digestion. The remaining elements were mostly below the limit of detection and thus did not produce meaningful regression results." to (P10L28 onwards)

"For the elements Ni (after HF/HClO₄ digestion) Cu and Se (after HNO₃/H₂O₂ digestion) the concentrations measured by the XACT were significantly lower than those measured by the ICP-MS. Cr and V were not reported for HF/HClO₄ due to contamination of the HClO₄ used in the digestion. In case of Cd and Ce a large number of concentrations were below the LOD, and thus the elements were excluded from further comparison." For clarity and completeness in the description of the method these elements have been left in the rest of the manuscript.

RC - P11L30-35: Parallel sampling of PM₁₀ and PM_{2.5} is needed to determine PM_{2.5}/PM₁₀ element ratios. Sampling different aerosol size fractions in different seasons and using ratios to separate fine and coarse contributions by elements is misleading. Please remove.

X-ACT is an on-line device providing elemental composition of atmospheric aerosol. Other instruments (e.g. streaker sampler, rotating drum impactors) can provide high time-resolved measurements by off-line analyses performed at accelerator facilities (e.g. by Particle-Induced X-Ray Fluorescence or Synchrotron Radiation XRF). I think a comparison with such measurements should be mentioned as a perspective.

Author's response: In the study mentioned (Visser et al., 2015), different size fractions were sampled in parallel using a rotating drum impactor. This, however, was not clear in the text and we have changed "Measured chemical composition of different size fractions at Marylebone Rd during winter and summer campaigns during 2012 and the percentage of the element in the PM_{10-2.5} fraction can be used to highlight how these elements are distributed between the fine and coarse particle sizes: S 35 %, K 57 %, Ca 72 %, and Cl 73%..." to (P12L2)

"The chemical composition of different size fractions was sampled using a rotating drum impactor (RDI) and analysed with synchrotron radiation-induced X-ray fluorescence spectrometry (SR-XRF) during a winter campaign at Marylebone Road in 2012 (Visser et al., 2015b) and the percentage of the element in the PM_{10-2.5}

fraction can be used to highlight how these elements are distributed between the fine and coarse particle sizes: S 35 %, K 57 %, Ca 72 %, and Cl 73%.”

RC - Minor concerns:

RC - P2L2: please evidence that modelling approaches (and not only measurements of aerosol chemical composition) are needed to gain information on aerosol sources

Author’s response: To evidence that modelling approaches are needed the authors have changed the introductory sentence “Measuring the chemical composition of airborne particulate matter (PM) can provide valuable information on the concentration of regulated toxic metals and their sources and assist in the identification and validation of abatement techniques.” To (P2L1onwards)
“Measuring the chemical composition of airborne particulate matter (PM) can provide valuable information on the concentration of regulated toxic metals, support modelling approaches for sources detection and assist in the identification and validation of abatement techniques.”

RC - P3L2: please add ion chromatography for inorganic ions (as it is cited in the following and applied in the paper)

Author’s response: The authors have included inorganic ions in the following sentence: “These filters are collected over a period of time, usually 24 hours to a week, and then analysed for different components such as metals (Brown et al., 2008), polyaromatic hydrocarbons (Pandey et al., 2011), elemental and organic carbon (Chu, 2004).” It now reads (P3L3-5):
“These filters are collected over a period of time, usually 24 hours to a week, and then analysed for different components such as metals (Brown et al., 2008), polyaromatic hydrocarbons (Pandey et al., 2011), elemental and organic carbon (Chu, 2004) and inorganic ions (Beccaceci et al., 2015).”

RC - P3L23: “sample a narrower range of components”. Please change “sample” with “measure” (instruments sample what is in air but are not always able to quantify)

Author’s response: Changed “sample” to “measure” in the following sentence (P3L26):
“Furthermore, the high time resolution instruments tend to measure a narrower range of components with a higher Limit of Detection (LOD) than equivalent laboratory based methods, generally because less material is collected on each sample.”

RC - P5L3: wrong formula for Ammonium sulphate (cfr. P5L13 where it is correct)

Author’s response: Corrected the formula for Ammonium sulphate (P5L14):
“Ammonium sulphate ((NH₄)₂SO₄, ACS reagent grade, Sigma-Aldrich) ...”

RC - P6L6: “where source contributions may be assumed based on one of these measurement techniques”. I guess the authors refer to receptor modelling approaches for source apportionment. Please change into “where source contributions may be estimated by receptor modelling using measurements of chemical components as input” (the measurement techniques do not provide source contributions, but quantify chemical components)

Author’s response: The authors amended the sentence incorporating the referee’s suggestion. The sentence “Although the measurands are not directly comparable, they provide useful information for studies where source contributions may be assumed based on one of these measurement techniques.” now reads (P6L7onwards):
“Although the measurands are not directly comparable, they provide useful information for studies where source contributions may be estimated by receptor modelling using measurements of chemical components based on one of these measurement techniques.”

RC - P7L3-5: obscure. Please add some explanation

Author’s response: For clarification the authors have changed the following sentence:
“The measurements were quality assured against measurements of SMPS (for volume to ensure the collection efficiency is suitable) and PM_{2.5} mass when combined with Aethalometer measurements as described by Crenn et al. (2015).”
It now reads (P7L5)

“The ACSM measurements were combined with Aethalometer measurements and compared to PM_{2.5} mass measured using the TEOM FDMS or PM₁ mass estimated using SMPS measurements as described by Crenn et al. (2015).”

RC - P8L7: 3 or sqrt(3)?

Author's response: To clarify, the format of the formula was changed from on from” For the XACT measurements, the combined uncertainty included contributions of $3/\sqrt{3}\%$ from flow (CEN, 2014) ...” to (P8L14):

“For the XACT measurements, the combined uncertainty included contributions of $\frac{3}{\sqrt{3}}\%$ from flow (CEN, 2014) ...”

RC - P8L12&15: what is k?

Author's response: The following text has been changed: “ For the ACSM, the sulphate measurement uncertainty was estimated as 14 % (k = 2) for sulphate at a 30-min resolution by Crenn et al. (2015) and the LOD was determined using HEPA field blank measurements as 34.9 ng m⁻³. For the URG, the chloride and sulphate LODs were reported by the manufacturer as 100 ng m⁻³ and verified by Beccaceci et al. (2015). The uncertainty of the species measured by ion chromatography was estimated at 4.5 % (k = 2) by Yardley et al. (2007) and combined with the additional 97 % extraction efficiency of a particle-to-liquid sampler system estimated by Orsini et al. (2003).” to explain k (coverage factor). It now reads (P8L18 onwards):

“For the ACSM, the sulphate measurement uncertainty was estimated as 14 % (coverage factor k = 2) for sulphate at a 30-min resolution by Crenn et al. (2015) and the LOD was determined using HEPA field blank measurements as 34.9 ng m⁻³. For the URG, the chloride and sulphate LODs were reported by the manufacturer as 100 ng m⁻³ and verified by Beccaceci et al. (2015). The uncertainty of the species measured by ion chromatography was estimated at 4.5 % (coverage factor k = 2) by Yardley et al. (2007) and combined with the additional 97 % extraction efficiency of a particle-to-liquid sampler system estimated by Orsini et al. (2003).”

RC - P8L27: Are the authors referring to statistical significance?

Author's response: Yes, the authors are referring to statistical significance as the results of the Deming regression are given at a 95% confidence interval. To clarify this in the text, the CI was added to the sentence “Slopes are not significantly different from the 1:1 line for all comparisons.” and it now reads (P8L36): “Slopes are not significantly different from the 1:1 line for all comparisons (95% confidence interval).”

RC - P9L1: “dominated by fireworks activity (Oct-Dec 2014)”. Do the authors mean that fireworks were the main source impacting the area in those 3 months? If not, please rephrase.

Author's response: During this sampling period there were a number of events and thus peak concentrations were dominated by fireworks rather than fireworks being the main source overall. To clarify this, the sentence was changed from “The sampling at Marylebone Road was carried out using a PM_{2.5} inlet during a period that was dominated by fireworks activity...” to (P9L7)

“The sampling at Marylebone Road was carried out using a PM_{2.5} inlet during a period when peak concentrations were dominated by fireworks activity...”

RC - P9L7-19: First of all, suitable references to fireworks tracers in aerosol are missing. Secondly, high time resolved measurements of elemental composition during fireworks has already been presented in the literature. In one case, they were also exploited for source apportionment by receptor models (Vecchi et al., 2008. DOI: 10.1016/j.atmosenv.2007.10.047)

Author's response: The authors have now included suitable references and have also highlighted the fact that high time resolved measurements of elemental composition during fireworks has been use in source apportionment before. The section has been changed as follows (with the added references and text changes underlined) and the reference list has been updated (P9L7 onwards):

“The sampling at Marylebone Road was carried out using a PM_{2.5} inlet during a period when peak concentrations were dominated by fireworks activity (Oct-Dec 2014). The mean concentrations across all elements measured during this campaign ranged from 0.177 ng m⁻³ to 600 ng m⁻³ and elements typically used in fireworks such as Ba, Sr, K and Ti (Godri et al., 2010; Moreno et al., 2007; Vecchi et al., 2008) had high

maximum concentrations. Traffic emissions further influenced the metal concentrations at Marylebone Road. Overall the order of the elements in terms of mean concentration was: $S > Fe > Cl > K > Si > Ca > Zn > Cu > Ba > Pb > Mn > Ti > Cd > Sr > As > Cr > Ce > V > Ni > Mo > Pt > Se$. This dataset helps highlight that high time resolution data has the advantage of giving much more detailed information on high pollution events, which can be used e.g. in source apportionment (Vecchi et al., 2008) and for health studies (Godri et al., 2010; Hamad et al., 2016). Figure 3 shows the daily filter and hourly XACT measurements of K and Ba during a period of increased bonfire and fireworks activity due to Diwali (Hindu festival of light) and Guy Fawkes celebrations. The daily filter measurements show that the highest concentrations of K, which is used as an oxidiser in fireworks (Moreno et al., 2007) but also a tracer for biomass burning, were measured on the 5th and 6th November 2014, followed by slightly lower concentrations on the 7th and 8th of November. On the other hand Ba, which is used in green fireworks (Moreno et al., 2007), displays similarly high concentrations on all four days. Looking at the K concentration in a higher time resolution as measured by the XACT, it is evident that peak concentrations were comparable on the nights of the 5th, 7th and 8th of November (data is missing for the 6th of November due to instrument failure) but the high concentrations did not last as long on the 7th and 8th of November. The highest Ba concentration on the other hand was measured on the 8th of November with lower concentrations on the 5th and 7th. This difference in contribution might point to different fireworks being used.”

RC - P9L22&34: “mean concentrations”. Please change into “mean elemental concentrations”

Author’s response: Thanks to this comment and a further comment by anonymous referee 4, the authors realised that it was not clear which concentration/elements they were referring to. Thus the following sentences were changed:

- “The mean concentrations measured in this campaign ranged from 0.24 ng m^{-3} to $5,200 \text{ ng m}^{-3}$.”

Now reads (P9L30): “Overall, the mean elemental concentrations measured in this campaign ranged from 0.24 ng m^{-3} to $5,200 \text{ ng m}^{-3}$.”

- “The influence of the local industry in Tinsley, Sheffield was reflected by high concentrations of metals like Ni and Cr, with mean concentrations more than 30 times that found in the Marylebone Road campaign with mean concentrations ranged from 0.186 ng m^{-3} to $1,370 \text{ ng m}^{-3}$.”

Now reads (P10L3): “The influence of the local industry in Tinsley, Sheffield was reflected by high concentrations of metals like Ni and Cr, with mean concentrations more than 30 times that found in the Marylebone Road campaign. The mean elemental concentrations overall ranged from 0.186 ng m^{-3} to $1,370 \text{ ng m}^{-3}$.”

RC - P10L1&P11L2: how was non-sea sulphate calculated? Please describe or add suitable references. Furthermore, provide references for this choice in the comparison.

Author’s response: The method for calculating non-sea salt sulphate has been included in section 3.2.2. The following sentence was expanded:

“The hourly values of S and Cl measured with the XACT were used to calculate hourly non-sea salt sulphate (SO_4), which was compared to the hourly sulphate (predominantly ammonium sulphate) which is non-refractory measured by the ACSM (Chang et al., 2011).”

It now reads (P11L10 onwards):

“The hourly values of S and Cl measured with the XACT were used to calculate hourly non-sea salt sulphate (SO_4) based on their relative abundance in sea water (Millero et al. 2008). It should be noted that Cl is used in the absence of the preferred Na and Cl concentration measured could be partially depleted by reaction between NaCl and nitric acid (HNO_3). The hourly non-sea salt sulphate was compared to the hourly sulphate (predominantly ammonium sulphate) which is non-refractory measured by the ACSM (Chang et al., 2011).”

The reference Millero et al. 2008 was added to the reference list:

Millero, F. J., R. Feistel, D. G. Wright and T. J. McDougall (2008). “The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale.” Deep Sea Research Part I: Oceanographic Research Papers 55(1): 50-72.

RC - P10L28: “filter artefacts”? What do the authors refer to? Sampling artefacts or something else? Please, clarify.

Author’s response: Following comments by referee 4 the authors have removed the following “...positive and negative filter artefacts could also influence the concentrations when sampling onto filters...” and revised the

section in question. The authors agree that the elements compared between XACT and filter based measurements (analysis with ICP-MS) are not influenced by sampling artefacts per se but there are differences between the sampling methodologies which could result in differences in concentration and these are now reflected in this section.

The section now reads (P10L33onwards):

“There are a variety of possible reasons for the differences observed between the methods. In the case of the filter analysis, the blank filters were found to be variable and thus subtracted values may result in an under- or overestimation of the true concentration; the digestion recovery rates were not taken into account; many concentrations were close to the detection limit for the elements As in all campaigns and Ni during the Marylebone Road campaign. These stated reasons might influence the two digestions methods to different extents. Unfortunately, there was no opportunity to undertake both digestions on the same samples. To provide some insight into how the two digestion methods compared, the XACT measurements were grouped into concentration appropriate bins and the associated ICP-MS measurements from each digestion method were averaged and compared. These are shown in S6 (Deming regression of ICP-MS using different digestion methods). For the XACT, the standards used in calibrations were much higher than ambient concentrations and the calibration matrix differed from sample matrix (Indresand et al., 2013). Despite every effort being made to co-locate the sample inlets in all field trials, slight differences in inlet location, especially when close to the road, could not be avoided. This and different temperatures of the sample inlets may also contribute to differences observed in concentrations. Nevertheless, the results of the XACT comparison with ICP-MS in this study are comparable to those reported in other studies (Furger et al., 2017).”

RC - Typos

RC - P2L31: “implementing” instead of “implement”

Author’s response: The authors believe that “... helps implement policies...” is the correct expression.

P7L1 vs P7L2: Middlebook or Middlebrook?

Author’s response: The spelling of “Middlebrook” has been corrected on P7L4:

“The collection efficiency was calculated using the Middlebrook parameterisation (Middlebrook et al., 2012)...”

RC - P10L30: change “extends” into “extents”

Author’s response: The sentence on P10L38 was corrected from “These stated reasons might influence the two digestions methods to different extends.” to

“These stated reasons might influence the two digestions methods to different extents.”

RC - P11L7: “..” Change into “.”

Author’s response: Removed the duplicated “.”

“...resulted in higher results than off-line filter measurements.”