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Discussions

# Interactive comment on "Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols" *by* Anja H. Tremper et al.

**Anja H. Tremper et al.**

anja.tremper@kcl.ac.uk

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Please find below the author's response to the interactive discussion comments from the anonymous referee.

Referee comments: RC

Author's response given below individual referee comments

RC - Overall the manuscript presents relevant results in a comprehensive and wellor-

ganized manner. So the publication in AMT is recommended. Still some conclusions need to be revised or softened, or better supported. Please see the comments below.

Author's response: We would like to thank the anonymous referee for the positive feedback and the 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 - Abstract. State which elements are compared with ICP and which with 'other high time resolution measurements', because the differences in slopes (median 1.07 vs 1.41-4.6) may be due to the different elements being assessed rather than to differences between techniques?

Author's response: The authors have added the elements to the relevant sections in the abstract: "The XRF technique agreed well with the ICP-MS measurements of daily filter samples in all cases with a median R2 of 0.93 and a median slope of 1.07. Differences were likely due to recovery rates from the sample digestion as well as filter sampling artefacts and matrix effects in the XRF technique. The XRF technique also agreed well with the other high time resolution measurements but showed a significant positive bias (slopes between 1.41 and 4.6), probably due to differences in the size selection methodology, volatility and water solubility of the PM in aerosol mass spectrometry and ion chromatography, respectively."

It now reads (P2L15 onwards, please note this section changed further due to other comments): "The XRF technique agreed well with the ICP-MS measurements of daily filter samples in all cases with a median R2 of 0.93 and a median slope of 1.07 for the elements As, Ba, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, Se, Sr, Ti, V and Zn. Differences in the results were attributed to a combination of inlet location and sampling temperature, variable blank levels in filter paper and recovery rates from acid digestion. The XRF technique also agreed well with the other high time resolution measurements but showed a clear positive difference (slopes between 1.41 and 4.6), probably due to dif-

ferences in the size selection methodology, volatility and water solubility of the PM in aerosol mass spectrometry (SO4) and ion chromatography (Ca, Cl, K, SO4), respectively."

RC - Page 3. Line 4. The positive and negative sampling artefacts are true for some species but not for others, e.g. metals concentrations determined on filter samples by digestion+ICP do not suffer from sampling artefacts.

Author's response: The authors agree with the above statements and have thus amended the following sentence: "This approach is time consuming, labour intensive and prone to positive and negative sampling artefacts (Chow et al., 2015)."

It now reads (P3L6): "This approach is time consuming, labour intensive and prone to positive and negative sampling artefacts for some components (Chow et al., 2015)."

RC - Page 3. Lines 34-36. Furger et al. (2017) used both ICP-OES and ICP-MS, not only ICP-MS for the list of elements reported in this manuscript.

Author's response: The authors have included ICP-OES and gold amalgamation atomic absorption spectrometry in the following sentence: "Furger et al. (2017) tested the XACT during a summer campaign in Switzerland in 2015 and compared the XACT data with measurements made using ICP-MS on filters sampled for 24 hours (both PM10) as well as ACSM measurements (PM1)."

It now reads (P3L40 onwards): "Furger et al. (2017) tested the XACT during a summer campaign in Switzerland in 2015 and compared the XACT data with measurements made using ICP-OES (inductively coupled plasma optical emission spectrometry) , ICP-MS and gold amalgamation atomic absorption spectrometry on filters sampled for 24 hours (both PM10) as well as ACSM measurements (PM1)."

RC - Page 6. Lines 39-40 and page 7, line 1. Wasn't the RIE for ammonium calculated from the calibration with ammonium nitrate? And hence only the RIE for sulphate calculated from calibration with ammonium sulphate? Please correct if necessary.

Author's response: The authors have amended the following sentences: "The ionisation efficiency was calculated using a mono-disperse supply of ammonium nitrate aerosols that were size selected through a differential mobility analyser and counted using a condensation particle counter (CPC). The relative ionisation efficiencies of sulphate and ammonium were calculated from separate calibrations using a mono-disperse supply of ammonium sulphate aerosols."

It now reads (P6L39 onwards): "The ionisation efficiency of nitrate and the relative ionisation efficiencies of ammonium and sulphate were calculated using a mono-disperse supply of ammonium nitrate and ammonium sulphate aerosols. These were size selected through a differential mobility analyser and counted using a condensation particle counter (CPC) as described by Crenn et al. (2015)."

RC - Page 9, lines 22-23. Please modify the sentence. As written now it seems you are still taking about the Ni, and according to Table 4, Ni concentration is reported to be 20 and min and max 0.24 and 320. Hence, from Table 4, one can see that 0.24-5200 is the range of mean concentrations for all the species analysed, but from the text is not clear at all.

Author's response: Thanks to this comment and a further comment by anonymous referee 3, 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 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 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 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 ng m-3."

RC - Page 9, line 25. The reason for high Cl concentration is not only the PM10 head, as at Tinsley the head was also PM10 but Cl is not so high. I guess the proximity to ocean played a role here.

Author's response: The proximity of the ocean will certainly have played a role, and thus we included the site characteristic in our example in the following sentence: "The concentrations and dominant elements will be influenced by the site characteristics as well as the size range sampled; e.g. Cl from sea salt is predominantly found in the coarse fraction and thus much higher at Pontardawe as sampling was carried out using a PM10 head."

It now reads (P9L31 onwards): "The concentrations and dominant elements will be influenced by the site characteristics as well as the size range sampled; e.g. Cl from sea salt is predominantly found in the coarse fraction and thus much higher at Pontardawe as the sample site is closer to the sea and sampling was carried out using a PM10 head."

RC - Page 10, line 2. With hourly concentration ranging. . .? Is it hourly? Or?

Author's response: The concentrations used in the comparison with the ACSM and URG are indeed hourly, which was not clear in the text and has been changed: "The mean concentration of non-sea salt sulphate (XACT) and non-refractory sulphate (ACSM) during the fireworks campaign at Marylebone Road was 2,600 ng m-3 and 2,000 ng m-3, respectively, with concentration ranging from 240 ng m-3 to 10,500 ng m-3 SO4 (non-sea salt) and 58 ng m-3 to 8,300 ng m-3 for non-refractory SO4. The comparison of the XACT with the URG was carried out in PM10 during winter 2014/2015. The concentration of water soluble anions and cation ranged from 154 ng

C5

m-3 (K) to 1,790 ng m-3 (Cl) compared to 145 ng m-3 (K) to 2,700 ng m-3 (Cl) in total element concentrations. "

It now reads (P10L8 onwards) "The mean hourly concentration of non-sea salt sulphate (XACT) and non-refractory sulphate (ACSM) during the fireworks campaign at Marylebone Road was 2,600 ng m-3 and 2,000 ng m-3, respectively, with hourly concentration ranging from 240 ng m-3 to 10,500 ng m-3 SO4 (non-sea salt) and 58 ng m-3 to 8,300 ng m-3 for non-refractory SO4. The comparison of the XACT with the URG was carried out in PM10 during winter 2014/2015. The hourly concentration of water soluble anions and cation ranged from 154 ng m-3 (K) to 1,790 ng m-3 (Cl) compared to 145 ng m-3 (K) to 2,700 ng m-3 (Cl) in total element concentrations. "

To further clarify this point, we have changed the caption of Table 6 : "Table 2: Overview of Marylebone Road, London SO4 measurements in PM2.5 by XACT (SO4* calculated as non-sea salt SO4 using S and Cl measurements) and ACSM (ng m-3); and SO4, K, Cl, Ca measurements in PM10 by XACT (SO4** calculated as predicted SO4 using S measurements) and URG (ng m-3)"

It now reads (P22L3 onwards) "Table 3: Overview of Marylebone Road, London hourly SO4 measurements in PM2.5 by XACT (SO4* calculated as non-sea salt SO4 using S and Cl measurements) and ACSM (ng m-3); and hourly SO4, K, Cl, Ca measurements in PM10 by XACT (SO4** calculated as predicted SO4 using S measurements) and URG (ng m-3)"

RC - Page 10, line 8. They are not ICP-MS digestion methods, they are digestion methods. The ICP-MS is used afterwards. Please re-write.

Author's response: The text has been changed from "The filter comparison results were split by the two ICP-MS digestion methods. . ." to (10L16) "The filter comparison results were split by the two digestion methods. . ."

RC - It is not so clear that the differences XACT vs ICP can be attributed to the recovery

C6

rates in the digestion processes prior to ICP analysis. Please amend through the manuscript this explanation (especially conclusions, page 12 lines 15 and following, line 28). One needs to asses this statement based on the individual elements. If that statement was true, the elements with the lowest recovery rates would have highest slopes, but this is not the case e.g. recovery for Ni (HF/HClO4) is 87

Author's response: Please see combined response with next point as the comments overlapped.

RC - In the conclusions, again, please make sure you don not attribute the difference between XACT and ICP to filter artefacts when you discuss elements that do not suffer from filter artefacts (page 12, line 28, among others).

Author's response: The authors accept that it was not clear from the manuscript that the differences of the XACT and filter based method followed by analysis with ICP-MS are caused by a multitude of reasons. Some of the potential reasons had been omitted and are now included in the current revision Also the authors agree that the elements compared do not suffer from what were loosely described as filter artefacts and thus this was amended accordingly. Please see the changes below.

In the abstract the following sentence was changed: "Differences were likely due to recovery rates from the sample digestion as well as filter sampling artefacts and matrix effects in the XRF technique."

It now reads (P2L17 onwards): "Differences in the results were attributed to a combination of inlet location and sampling temperature, variable blank levels in filter paper and recovery rates from acid digestion."

In section 3.2.1 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 section now reads (P10L33onwards): "There are a variety of possible reasons

C7

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)."

In the conclusions the following sentences were changed: - "This was attributed to recovery rates from acid digestion and filter sampling."

It now reads (P12L30 onwards): "Differences in the individual results were element specific but generally attributable to a combination of variable filter blank levels, recovery rates from acid digestion, instrument calibration, sampling temperature and small differences in inlet location."

- "This suggests that the XACT accurately measures elemental ambient aerosol composition and that the positive bias, when compared to the ICP-MS measurements identified in the field experiments, was more likely due to filter artefacts and recovery rates

C8

following acid digestion."

It now reads (P13L6 onwards): "This suggests that the XACT accurately measures elemental ambient aerosol composition and that the positive bias, when compared to the ICP-MS measurements identified in the field experiments, was not due to the XACT calibration but more likely due to the remaining reasons listed above."

RC - Conclusions, page 12, lines 17-18. If the sampling size was different and it is true that the size range 1-2-5 um has so much sulphate, then the 1.68 is not a bias. The 1.68 is not a bias but would have actual meaning. Please re-phrase.

Author's response: The authors agree with the referee that the difference in slope has actual meaning. To make this clearer they have changes the wording in the following section: "When compared to the alternative aerosol mass spectrometry and ion chromatography based high time resolution techniques, the XACT showed good temporal agreement but with a significant positive bias (median 1.68) compared to the ICP-MS; this was likely due to the differences in the size selection methodology employed by the different techniques as well as particle volatility and water solubility. However, these differences in solubility and volatility could be utilised to provide information about different sources and their contributions; such as the difference between refractory sodium chloride and non-refractory ammonium chloride."

It now reads (P12L32 onwards): "When compared to the alternative aerosol mass spectrometry and ion chromatography based high time resolution techniques, the XACT showed good temporal agreement but with a clear positive difference (median 1.68) compared to the ICP-MS; this was likely due to the differences in the size selection methodology employed by the different techniques as well as particle volatility and water solubility. However, these differences (size, solubility and volatility) could be utilised to provide information about different sources and their contributions; such as the difference between refractory sodium chloride and non-refractory ammonium chloride." The introduction was amended accordingly.

C9

RC - Technical corrections:

RC - Page 7, line 8. Shouldn't it say ". . .described in Beccaceci et al. (2015)"?

Author's response: Changed the referencing on P7L10 from "...described by (Beccaceci et al., 2015) to: "The URG-900B Ambient Ion Monitor continuously measured water-soluble anion and cation concentrations (Cl-, SO42-, NO3-, Na+, NH4+, K+, Mg2+, and Ca2+) in PM10 and is described in Beccaceci et al. (2015)."

RC - Page 8, line 11. Remove 1 point after "Table 3".

Author's response: Removed the duplicated "." "...; these are shown in Table 3. For the ACSM..."

RC - Page 8, line 13. A space is missing before "For".

Author's response: Included a space before "For" on P8L20: "...and the LOD was determined using HEPA field blank measurements as 34.9 ng m-3. For the URG..."

Please also note the supplement to this comment:
https://www.atmos-meas-tech-discuss.net/amt-2017-363/amt-2017-363-AC5-supplement.pdf