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 #1 Received and published: 9 January 2018

RC - General The manuscript presents a comprehensive lab and field evaluation of the CES Xact 625 XRF spectrometer. Various alternative methods with different time resolutions and particle sizes are compared with the XRF measurements, with generally good agreement to XRF and between methods. Explanations for deviations are given. The manuscript adds to the literature on quality assessment of the Xact online spectrometer, an instrument with great potential for monitoring environmental metals and other elements in airborne particles. The study is more comprehensive than previous studies that compare those methods, although some questions with Xact data quality remain. The structure of the manuscript, the results and the presentation of the material are good. The data has been analyzed and presented with care. The language is impeccable. The topic is relevant and well worth publication in AMT.

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 - Major comments

The study describes intercomparisons of time series of metal concentrations measured with the Xact and with other techniques. The statistical work horse is Deming regression which assigns individual measurement uncertainties to each technique. This approach is straightforward and has been applied in other studies. Comparisons are made between Xact and ICP-MS (with different digestions), ACSM, URG, and XRF (measuring filters with the Xact itself). Data were collected in field studies and in laboratory experiments.

The field studies show good regressions with a slightly positive bias of the Xact vs. ICP-MS, in agreement with previous studies. It is nicely demonstrated that the slope depends on the digestion method used for ICP-MS, and an overestimation of the XRF values compared to the ICP-MS values may turn into an underestimation when using the other digestion method. This makes a generalization of regression results (which technique is best or better?) rather difficult. Comparisons with ACSM and URG suffer from the different size classes sampled (PM2.5, PM1) and the different particle characteristics (non-sea salt, non-refractory). A comparison then requires additional assumptions to bring the values into closer agreement. This is discussed by the authors, but it also makes the comparisons more qualitative than quantitative. Interesting is the comparison between Xact measurements and filters analyzed with the Xact (Table S1). Slopes ranging from 0.8 to 1.85 with R2 values > 0.9 (excluding the extreme cases of As and Se) might indicate more serious issues with the calibration of the Xact or with the spectral deconvolution algorithm, even though the number of samples is only 12, and slopes of 1.31 (Ba) and 1.62 (V) are not significantly different from unity, according to the authors. Here I would like some comment from the authors.

Author’s response: The authors do not believe that the differences in slope indicate an issue with the calibration of the XACT. The reasons for the discrepancies can more likely be found due to the small sample size of this pilot study, the authors feel that the analysis method, including filter substrate and punching technique could be optimized. Nevertheless, every effort was made to make this as robust as possible - blank filters were analysed and used to correct for the filter background and to calculate the limit of detection when the XACT was used with filters on a 15 min analysis cycle. In comparison to the online XACT measurements which were made on an hourly basis, the LOD of the filter method was much higher. This was likely due to the shorter analysis time, the different area of deposit on a filter sample and the filter material (Zeflour has a density of around 16 mg cm^{-2} whereas our filter tape has a density of about 2 mg cm^{-2}; the mass density of the filter material will impact the XRF detection limit by the ratio of the square root of the mass density. Further the fitting routine in the deconvolution software is optimised for the filter tape used and is another potential area of optimisation if this approach were to be pursued.

To make this clearer in the manuscript we have added the following to the “Materials and Methods” section 2.4 (P7L30):
“For quality assurance purposes, field and laboratory filter blanks were analysed and used to correct for the filter background. The blank measurements were also used to calculate the limit of detection for this method.”

We have also expanded the results section 3.3 (P12L18) to include the above discussion:
“Reasons for the discrepancies in the slopes may be caused by the difference between the filter material and analysis time used for the filter samples (Zeflour, 15 min) in comparison to the online method (proprietary PTFE tape, 1 hr). Additionally the fitting routine used in the deconvolution software is optimised for the filter tape used and might also contribute to the observed differences.”

We have further added a comment in the conclusions section 4 (13L18):
“Further, to develop the filter analysis method using the XACT and piloted in this study, different filter materials should be tested and the deconvolution approach optimised if necessary.”

RC - The laboratory experiment regressions in Fig. S2 show very good agreement between Xact and TEOM, except for some outliers for S. The concentration maxima are extremely high compared to typical ambient concentrations. Except Zn, all elements should be prone to self-absorption effects in XRF analysis when the deposited layer becomes too thick, but no such effect can be seen in the regressions. Are self-absorption effects so well compensated by the Xact software? It would be helpful to add information on particle sizes (as measured with the SMPS) and/or deposit thickness to understand why XRF self-absorption effects do not show up in the graphs.

Author’s response: Sample self absorption depends mostly on the thickness of the deposit and its composition and even at these high concentration levels sample absorption effects contribute a relatively small amount to the overall analysis result. Sample self absorption was calculated for S and even at the highest concentration self absorption effects are less than 1%. Please also see response to referee 5.

Nevertheless the authors have changed the sentence in section 3.1:
“All calibrations resulted in a linear relationship between the mass calculated using TEOM mass concentrations and measured by the XACT for the standard range used.”
It now reads (P8L32):
“All calibrations resulted in a linear relationship between the mass calculated using TEOM mass concentrations and measured by the XACT for the standard range used. Sample self absorption effects were calculated to be <1% for the maximum concentration of S (the lightest element used) and therefore insignificant in the use of this instrument.”

Minor comments

RC - P7L1: Middlebrook instead of Middlebook

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 - P7L34-36: Strange sentence.

Author’s response: Changed the sentence “Including values below the LOD had the advantage of being able to include daily XACT mean concentration was calculated from hourly concentrations that might have been lost if data below LOD was excluded and the daily data capture was not met.”
to (P8L3)
“By including values below the LOD it was possible to calculate daily XACT mean concentrations, which might have been lost if data below the LOD had been excluded and the daily data capture had not been met.”

RC - P8L11: remove one ‘.’ after Table 3.

Author’s response: Removed the duplicated “.” On P8L18
“…; these are shown in Table 3. For the ACSM…”

RC - P12L7: remove one ‘.’ after filter measurements.

Author’s response: Removed the duplicated “.” On P12L18
“…resulted in higher results than off-line filter measurements.”

RC - P21 Table 7: Check the arrangement of rows carefully.

Author’s response: Formatted Table 7 on P22 using Font “Times New Roman” and Font Size 8 as used in the other tables; this corrected the formatting problem as follows:

Table 1: Deming regression results and coefficient of determination for XACT comparison with ICP-MS, separated by HF/$HClO_4$ and HNO_3/H_2O_2 digestions

Element	HF/$HClO_4$			HNO_3/H_2O_2		
	Slope	Intercept	R^2	Slope	Intercept	R^2
As	2.0 (1.49-2.6)	-0.33 (-0.65-0)	0.95	3.8 (1.90-5.7)	-0.23 (-0.49-0.020)	0.90
Ba	1.04 (0.73-1.35)	-1.50 (-4.8-1.79)	0.98			
Ca	1.14 (0.84-1.45)	-9.2 (-31-13)	0.70			
Cr				0.99 (0.92-1.06)	-1.70 (-2.6--0.79)	0.95
Cu	1.31 (1.05-1.57)	0.29 (-3.1-3.7)	0.93	0.95 (0.92-0.98)	-0.03 (-0.22-0.17)	0.89
Fe	1.26 (0.65-1.87)	-1.29 (-220-210)	0.89	1.03 (0.99-1.07)	-10 (-18.19--2.0)	0.96
K	1.03 (0.92-1.15)	-1.23 (-14.83-12.37)	0.96			
Mn	1.28 (0.70-1.86)	0.050 (-1.97-2.1)	0.92	1.10 (1.07-1.14)	0.17 (0.020-0.32)	0.99
Ni	0.73 (0.48-0.98)	-0.20 (-0.45-0.05)	0.67	1.07 (1.00-1.14)	-1.21 (-1.64--0.77)	0.99
Pb	1.44 (1.31-1.57)	0.140 (-0.37-0.65)	1.00	1.02 (0.99-1.06)	0.36 (0.10-0.61)	0.99
Se				0.83 (0.73-0.94)	-0.45 (-0.57--0.33)	0.67
Sr	1.25 (1.14-1.36)	-0.0100 (-0.19-0.17)	1.00			
Ti	1.44 (0.68-2.2)	0.91 (-0.42-2.2)	0.72			
V				0.87 (0.74-1.01)	-0.130 (-0.22--0.04)	0.89
Zn	1.62 (1.17-2.1)	-4.4 (-13.15-4.5)	0.50	1.04 (0.98-1.09)	0.37 (-0.58-1.31)	0.94

RC - P17 Fig. 7 and Figs. S3-S5: It might make the graphs more consistent when the coloring of all figures were in agreement. I suggest to color the dots in the Figures S3-S5 in red (HF/HClO4), and blue (HNO3/H2O2), to correspond to the colors in Fig. 7.

Author’s response: To avoid confusion with the different colouring, the authors decided to keep the colouring of Fig. 7 as it is, but change Figs. S3-S5 and S7 to use black dots for all graphs.

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 #2 Received and published: 4 January 2018

RC - The paper refers to a very important issue in the characterization of an aerosol sampling/analyzing device, namely, its analytical accuracy. Therefore, the work is relevant. There is a careful design of the methods used to validate the quantitative results. They are carefully explained and presented. It is remarkable that several analytical techniques are used to carry out the comparisons. I could find no scientific errors or misleading discussions. The conclusions actually point out to the results obtained in the text. Also, proposals to extend (and improve) the results are given. In short, I consider the paper should be accepted for publication.

Nevertheless, I would like to suggest a few (minor) corrections and additions.

Author’s response:
We would like to thank the anonymous referee for the very 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 - 1. In section 2.1, I recommend adding a few lines mentioning the x-ray source and its operating conditions employed, as well as the detector type and characteristics (resolution, in particular). This may help the reader to better understand the results given in this manuscript. Also, the software and atomic databases used to analyze the x-ray spectra.

Author’s response: The authors have added further information on the XRF analysis to section 2.1. to help the reader understand the results. The section has changed from:
“The instrument measures 24 elements between Silicon and Uranium at a time resolution between 15 minutes and four hours using ED-XRF. The size fraction of the PM sample collected onto the Teflon filter tape depends on the size selective inlet chosen. The instrument samples with a volumetric flow rate of 1 $m^3 h^{-1}$ through an inlet tube heated to 45 ˚C when the ambient relative humidity (RH) exceeds 45% to avoid water depositing on the tape. Sampling and analysis is performed continuously and simultaneously, except for the time required to advance the filter tape (~20 s) from the sample to the analysis position. Daily automated quality assurance checks are performed every night at midnight and consist of an energy alignment (an energy calibration using a copper rod, inserted into the analysis area); and upscale measurement to monitor the stability of the instrument response (for Cd, Cr and Pb); and a flow check through an independent mass flow sensor. Additional quality assurance checks employed here included flow calibrations, regular external standard checks, field blanks performed using a HEPA filter as well as tape blanks before and after each tape change.”

It now reads (added text is underlined, P4L30 onwards):
“The instrument measures 24 elements between Silicon and Uranium at a time resolution between 15 minutes and four hours using ED-XRF. The size fraction of the PM sample collected onto the Teflon filter tape depends on the size selective inlet chosen. The instrument samples with a volumetric flow rate of 1 $m^3 h^{-1}$ through an inlet tube heated to 45 ˚C when the ambient relative humidity (RH) exceeds 45% to avoid water depositing on the tape. Sampling and analysis is performed continuously and simultaneously, except for the time required to advance the filter tape (~20 s) from the sample to the analysis position. During the analysis, the sample is excited using an x-ray source (Rhodium anode, 50 kV, 50 Watt) in three successive energy conditions, which target three different suites of elements. The resulting x-ray fluorescence is measured with a silicon drift detector and the spectra are analysed using a proprietary spectral analysis package which takes into account all peaks associated with a given element. Daily automated quality assurance checks are performed every night at midnight and consist of an energy alignment (an energy calibration using a copper rod, inserted into the analysis area); and upscale measurement to monitor the stability of the instrument response (for Cd, Cr and Pb); and a flow check through an independent mass flow sensor. Additional quality assurance checks employed here included flow calibrations, regular external standard checks, field blanks performed using a HEPA filter as well as tape blanks before and after each tape change.”

RC - 2. The aforementioned information might be useful to understand several of the apparently incorrect results, like the As overestimation. For instance, the As Kalpha x-ray peak overlaps the Pb Lalpha peak. Therefore, it is very important to carefully integrate and correct both peaks using the corresponding beta lines. This may be the reason of the extremely high overestimation in the measured As concentrations. Although it is not explained in depth, Se is another element with possible problems in quantification (see Fig. S7).

Author's response: The authors added text relating to the spectral peak fitting process, which takes into account all peaks associated with a given element, in the answer to the comment above.
Further the equipment supplier has made us aware of a US-EPA verification report (US-EPA, 2012) which analysed Se and found an excellent agreement (R^2= 0.926) and a brief summary of this has been added to the introduction Thus the paragraph was changed from:
"Despite these limitations, the XACT is unique in measuring elements automatically using energy dispersive XRF (ED-XRF) and has been successfully evaluated in a number of field studies (Furger et al., 2017; Park et al., 2014). Park et al. (2014) found…"
It now reads (P3L33 onwards):
"Despite these limitations, the XACT is unique in measuring elements automatically using energy dispersive XRF (ED-XRF) and has been successfully evaluated in a number of field studies (Furger et al., 2017; Park et al., 2014; US-EPA, 2012). In a verification test carried out by the US-EPA (2012) measurements of Ca, Cu, Mn, Pb, Se and Zn by the XACT were compared to filter based measurements (filters analysed using ICP-MS). This verification test showed that the daily average Xact 625 results were highly correlated and in close quantitative agreement with ICP-MS analysis results for the six metals, except Cu, which was close to the detection limit in many cases. Park et al. (2014) found…"
The reference was added to the reference list:
„US-EPA: Environmental Technology Verification Report. Cooper Environmental Services LLC Xact 625 Particulate Metals Monitor, Report no. EPA/600/R-12/680. Agency, U. S. E. P. A. (Ed.), U.S. Environmental Protection Agency, Cincinnati, OH 45268, 2012."

RC - 3. The plots in Figs. 2 and 6 need a larger lettering to facilitate reading. Moreover, instead of using thousands of nanograms, possibly using micrograms is easier.

Author's response: Increased the overall figure size of Figs. 2 and 6 to facilitate reading as increasing the font size of the equations would have interfered with the lines/graph, especially in Fig.6. For consistency throughout the manuscript it was decided to keep ng m^{-3} for all graphs and tables.

RC - 4. Only as minor but important corrections in writing style, expressions like the one given in page 6, line 13, "75-650 nm" must be written as "75 nm to 650 nm," according to the International System style rules (please, read the official document in the IBPM web site). This must be corrected in all the manuscript. Similar changes must be made when writing quantities (like those in page 6, lines 35 and 38), where a space between the numerical value and unit symbol is missing.

Author's response: Changed the manuscripts according to the International System of Units rules.

RC - 5. Also referring to the official document of the SI, the units "ppb" must be avoided, because of the different meaning of "billion" in diverse countries and languages.

Author's response: Changed "(18.2 MΩ, TOC < 5 ppb, PURELAB® Ultra Analytic, ELGA (Veolia Water Technologies))" to (P5L16):
"(18.2 MΩ, TOC < 5 µg L^{-1}, PURELAB® Ultra Analytic, ELGA (Veolia Water Technologies))."

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/$HClO_4$ digestion and Cu and Se after HNO_3/H_2O_2 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/$HClO_4$ due to contamination of the $HClO_4$ 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/$HClO_4$ digestion) Cu and Se (after HNO_3/H_2O_2 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/$HClO_4$ due to contamination of the $HClO_4$ 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 PM2.5 is needed to determine PM2.5/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 ($(NH_4)_2SO_4$, 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 PM_1 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/√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 PM2.5 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 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 - 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 (SO4) 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 (HNO3). 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."

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 #4 Received and published: 15 January 2018

RC - Overall the manuscript presents relevant results in a comprehensive and wellorganized 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 R^2 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 R^2 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 differences in the size selection methodology, volatility and water solubility of the PM in aerosol mass spectrometry (SO_4) and ion chromatography (Ca, Cl, K, SO_4), 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 PM_{10}) as well as ACSM measurements (PM_1)."
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 PM_{10}) as well as ACSM measurements (PM_1).”

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 PM_{10} 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 PM_{10} 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} SO_4 (non-sea salt) and 58 ng m^{-3} to 8,300 ng m^{-3} for non-refractory SO_4.
The comparison of the XACT with the URG was carried out in PM_{10} during winter 2014/2015. The 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. “

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} SO_4 (non-sea salt) and 58 ng m^{-3} to 8,300 ng m^{-3} for non-refractory SO_4.
The comparison of the XACT with the URG was carried out in PM_{10} 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 SO_4 measurements in $PM_{2.5}$ by XACT (SO_4* calculated as non-sea salt SO_4 using S and Cl measurements) and ACSM (ng m^{-3}); and SO_4, K, Cl, Ca measurements in PM_{10} by XACT (SO_4** calculated as predicted SO_4 using S measurements) and URG (ng m^{-3})”
It now reads (P22L3 onwards)
“Table 3: Overview of Marylebone Road, London hourly SO_4 measurements in $PM_{2.5}$ by XACT (SO_4* calculated as non-sea salt SO_4 using S and Cl measurements) and ACSM (ng m^{-3}); and hourly SO_4, K, Cl, Ca measurements in PM_{10} by XACT (SO_4** calculated as predicted SO_4 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 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 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 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.

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-, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in PM_{10} 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…"

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 #5 Received and published: 10 January 2018

RC - The new version of the article has been greatly improved. Some modification have still to be done before publication:

Author's response:
We would like to thank the anonymous referee for the 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 - 1) In section 3.1 the authors should explicitly cite the fact that in XRF there are neither self-absorption problems for the medium-high Z elements nor matrix effects. There can be self-absorption effects only for low Z elements (the only one, which can be affected in their comparison, is Si) even with samples with high loading unless the deposit on a very small area.
Those effects depend mostly on the absorption within the single particle therefore they are present also in the samples prepared by the authors. The use of self-made standard can be useful, but I do not see any problem in the use of commercial standards as it is done in many laboratories which routinely use XRF for aerosol analysis.

Author's response: The authors agree that self-absorption would not be a significant problem even at the thickness of deposit and composition encountered in this experiment. Please also see response to referee 1. Nevertheless the authors have changed the sentence in section 3.1:
"All calibrations resulted in a linear relationship between the mass calculated using TEOM mass concentrations and measured by the XACT for the standard range used."
It now reads (P8L32 onwards):
"All calibrations resulted in a linear relationship between the mass calculated using TEOM mass concentrations and measured by the XACT for the standard range used. Sample self absorption effects were calculated to be <1% for the maximum concentration of S (the lightest element used) and therefore insignificant in the use of this instrument."

A common criticism of the commercial standards is that they are 1) not at the concentration range expected from ambient air sampling and 2) not on the same filter matrix as those typically used in ambient air sampling. The development of new calibration techniques at a wider range of concentrations and using different compounds provides a method of validating the current quality assurance techniques. This is evidenced by the comparison between the XACT and TEOM that is linear down to concentration levels well below those found on commercial XRF standards.

RC - 2) Again what is reported at the end of section 3.2.1 page 11 lines 12-13 is not correct (same comment as above)

Author's response: In section 3.2.1 the authors address the common criticism of XRF standards and believe it would be an oversight not to do so. See also answer to comment above.

RC - 3) Section 3.2.2: the use of Cl to calculate non sea-salt sulphate can give a strong overestimation of that component due to the possible volatilization of Cl in case of aged sea-salt as reported in many works regarding also the sites analyzed by the authors. Normally Na is used. The authors must make a comment about this

Author's response: The method used for calculating non-sea salt sulphate has been included in section 3.2.2. and reference is made to the possible depletion of Cl. 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 (HNO3). 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 - 4) All the information reported by the authors are interesting and better explained in this new version. However, in my opinion, it cannot be neglected that the best way to assess the performances of the XACT spectrometer would have been to use a standard aerosol sampler (like one of those used by the authors), the proper collection filters (e.g. Teflon or polycarbonate filters) and XRF analysis of the collected filters. The authors should make an explicit comment about this.

Author's response: The authors believe that an instrument field evaluation needs to include commonly used reference methods, such as the European reference method EN14902 and other studies, such as the verification test carried out by the US-EPA (US-EPA, 2012) have taken a similar approach. As reference methods are used for regulatory purposes this provides the context in which element concentrations and their changes are viewed; other commonly used techniques were included in the field analysis, which was not claimed to be exhaustive. The US-EPA study was added to the introduction as explained in comment to Referee 2 and the reference was added to the reference list:
„US-EPA: Environmental Technology Verification Report. Cooper Environmental Services LLC Xact 625 Particulate Metals Monitor, Report no. EPA/600/R-12/680. Agency, U. S. E. P. A. (Ed.), U.S. Environmental Protection Agency, Cincinnati, OH 45268, 2012."

However, the filter analysis technique using the XACT and piloted in this study would allow a direct comparison of the XACT and other XRF systems as mentioned in the conclusions (13L15).

Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols

Anja H. Tremper[1], Anna Font[1], Max Priestman[1], Samera H. Hamad[2], Tsai-Chia Chung[3], Ari Pribadi[1], Richard J. C. Brown[4], Sharon L. Goddard[4], Nathalie Grassineau[3], Krag Petterson[5] Frank J. Kelly[1] and David C. Green[1]

[1] MRC-PHE Centre for Environment and Health, King's College London, London, SE1 9NH, United Kingdom
[2] Department of Behavioural and Community Health, School of Public Health, the University of Maryland, College Park, MD 20742, USA
[3] Earth Sciences Department, Royal Holloway University of London, Egham TW20 0EX, UK
[4] Chemical, Medical and Environmental Science Department, National Physical Laboratory, Teddington, TW11 0LW, UK
[5] Cooper Environmental Services, LLC, 9403 SW Nimbus Ave. Beaverton, OR 97062

Correspondence to: Anja H. Tremper (anja.tremper@kcl.ac.uk)

Abstract. 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 ~~and their sources and~~ assist in the identification and validation of abatement techniques. Undertaking these at a high time resolution (1 hour or less) enables receptor modelling techniques to be more robustly linked to emission processes. This study describes a comprehensive laboratory and field evaluation of a high time resolution x-ray fluorescence (XRF) instrument (CES XACT 625) for a range of elements (As, Ba, Ca, Cd, Ce, Cl, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Pd, Pt, S, Sb, Se, Si, Sr, Ti, V, Zn) against alternative techniques: high time resolution mass measurements, high time resolution ion chromatography, aerosol mass spectrometry, and established filter-based, laboratory analysis using inductively coupled plasma mass spectrometry (ICP-MS). 1) Laboratory evaluation was carried out using a novel mass-based calibration technique to independently assess the accuracy of the XRF against laboratory generated aerosols, which resulted in slopes that were not significantly different from unity. This demonstrated that generated particles can serve as an alternative calibration method for this instrument. 2) The XACT was evaluated in three contrasting field deployments; a heavily trafficked roadside site (PM_{10} and $PM_{2.5}$), an industrial location downwind of a nickel refinery (PM_{10}) and an urban background location influenced by nearby industries and motorways (PM_{10}). The XRF technique agreed well with the ICP-MS measurements of daily filter samples in all cases with a median R^2 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~~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~~clear positive difference (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 ((SO_4)) and ion chromatography ((Ca, Cl, K, SO_4)), respectively. 3) A novel filter analysis technique using the XACT showed promising initial results: filters analysed off-line with the XACT compared well to in-situ XACT measurements with a median R^2 of 0.96 and median slope of 1.07. The resulting range of slopes was comparable to slopes produced in the ICP-MS comparison. This technique provides an opportunity to use the XACT when it is not deployed in the field; thus expanding the potential use of this instrument in future studies.

1 Introduction

It has long been known that increased air pollution, and specifically particle pollution is associated with adverse health effects (Brunekreef and Holgate, 2002; Kelly et al., 2012). Particulate matter (PM) also affects atmospheric visibility and radiative forcing (Fuzzi et al., 2015). PM is not a homogenous air pollutant but rather a complex mixture; it varies in chemical and physical composition depending on the contributing sources and the atmospheric processes (WHO, 2000). The composition of PM influences its harmfulness and therefore it is important to gain better knowledge about which chemical components might cause particle toxicity (Kelly and Fussell, 2015). Understanding the chemical composition of PM also provides information on the sources and thus helps implement policies on targeting these emission sources (WHO, 2013). Trace metals in particular, even though they do not contribute substantially to the mass of PM, act as markers for specific source categories

(Visser et al., 2015a) and evidence is emerging that some metals in ambient PM are associated with adverse health effects at concentrations near to current ambient levels (Chen and Lippmann, 2009).

Accurate measurements of the PM composition are important and are mostly carried out by collecting PM on filters using high or low volume filter samplers (e.g. Digitel-DAH-80, Partisol 2025) and subsequently digesting and analysing these in a laboratory. 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). This approach is time consuming, labour intensive and prone to positive and negative sampling artefacts for some components (Chow et al., 2015). Also, it only gives compositional information with a considerable time delay and at low temporal resolution which cannot be effectively associated with meteorological variability or short term variations in emissions.

To run the above filter samplers on a higher time resolution means they become even more labour intensive to operate. To address this limitation, sampling devices were developed to collect PM either hourly or sub-hourly without the need for frequent filter changes. These include the Rotating Drum Impactor (Bukowiecki et al., 2005) which collects three size ranges: $PM_{10-2.5}$ (coarse), $PM_{2.5-1.0}$ (intermediate) and $PM_{1.0-0.3}$ (fine), by passing sequentially through three rectangular nozzles of decreasing size; and the Streaker (PIXE International Corporation) which consists of two collecting substrates rotating at constant speed producing a circular continuous deposition of both $PM_{10-2.5}$ and $PM_{2.5}$ (Formenti et al., 1996). Nevertheless the analysis is still performed in the laboratory and thus does not improve the time delay of the analysis.

Several online high time resolution instruments have also been developed in recent years which address some of the sampling artefact, resource and time resolution limitations of laboratory approaches. These include aerosol mass spectrometers such as the ACSM (Aerodyne Research Inc.) (Ng et al., 2011); ion chromatography approaches such as the MARGA (Metrohm) (Rumsey et al., 2014), PILS (Brechtel) (Weber et al., 2001) and URG’s 9000 ambient ion monitor (Beccaceci et al., 2015); and x-ray fluorescence (XRF) such as the XACT instrument (Cooper Environmental Services) (Park et al., 2014). However, these high time resolution instruments only measure a subset of chemical components each, depending on their collection, extraction and analysis methodology. Therefore multiple collocated instruments are needed to measure the full PM composition. Furthermore, the high time resolution instruments tend to ~~sample~~ 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. For example, the synchrotron radiation-induced XRF (SR-XRF) used by Visser et al. (2015b) measured elements with atomic numbers greater than 11 while the XACT measures elements with atomic numbers greater than 14 thereby missing important contributors to PM mass such as Na, Mg and Al; the LODs reported for the SR-XRF analysis (Visser et al., 2015b) are generally lower than those for the XACT (Furger et al., 2017; Park et al., 2014).

Despite these limitations, the XACT is unique in measuring elements automatically using energy dispersive XRF (ED-XRF) and has been successfully evaluated in a number of field studies (Furger et al., 2017; Park et al., 2014; US-EPA, 2012). In a verification test carried out by the US-EPA (2012) measurements of Ca, Cu, Mn, Pb, Se and Zn by the XACT were compared to filter based measurements (filters analysed using ICP-MS). This verification test showed that the daily average Xact 625 results were highly correlated and in close quantitative agreement with ICP-MS analysis results for the six metals, except Cu, which was close to the detection limit in many cases. Park et al. (2014) found a good agreement between the XACT and 24 hour filter based measurement collected in South Korea (filters analysed using ED-XRF). 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~~ICP-MS~~ on filters sampled for 24 hours (both PM_{10}) as well as ACSM measurements (PM_1). They found an excellent correlation, with R^2 values ≥ 0.95, between the XACT and ICP-MS data for ten elements (S, K, Ca, Ti, Mn, Fe, Cu, Zn, Ba, Pb). However, they found that the XACT was systematically higher than the filter based technique. In Jeong et al. (2017) hourly trace elements measured by the XACT were included in positive matrix factorisation (PMF), which allowed a more robust apportionment of PM sources (Jeong et al., 2017).

For all analytical techniques, in the field and laboratory, the confidence in measurements largely depends on high quality, traceable calibration of the instruments (Indresand et al., 2013). In the case of the XACT, the calibration is carried out using thin film standards, which are thin element films deposited on Nuclepore substrates and are available for elements between atomic number 11 and 82 (EPA Compendium Method IO-3.3 for the Determination of Inorganic Compounds in Ambient Air, EPA/625/R-96/010a, Table 2, page 3.3-16). This is an established method but has been reported to have various limitations (Indresand et al., 2013): the standards are much higher in concentration than most ambient samples; the element mix of the standard might not be representative of ambient particle mix; and the collection properties on a filter may also differ. Alternative calibration methods have therefore been tested to address these issues. For example Indresand et al., (2013) produced sulphur reference materials that replicated PM samples to successfully calibrate XRF systems.

In this study a novel mass-based calibration technique for the XACT 625 has been developed to independently assess the accuracy of the XRF method for a range of elements at more atmospherically relevant concentrations. This study also reports the field evaluation of the XACT at both traffic and industrial sites in the UK where it was compared to independent measurements of $PM_{2.5}$ and PM_{10} on daily filters, analysed by ICP-MS; and also to alternative high time resolution chemical speciation instruments (ion chromatography and aerosol mass spectrometry). Additionally, the ability of the XACT to analyse PM_{10} filter samples in the laboratory was piloted and the results compared to collocated in-situ XACT measurements. Using the instrument in this way potentially diversifies experimental sampling programmes with this single resource by deploying additional sampling devices.

2 Materials and Methods

2.1 XACT 625

The instrument measures 24 elements between Silicon and Uranium at a time resolution between 15 minutes and four hours using ED-XRF. The size fraction of the PM sample collected onto the Teflon filter tape depends on the size selective inlet chosen. The instrument samples with a volumetric flow rate of 1 m^3 h^{-1} through an inlet tube heated to 45 ˚C when the ambient relative humidity (RH) exceeds 45 % to avoid water depositing on the tape. Sampling and analysis is performed continuously and simultaneously, except for the time required to advance the filter tape (~20 s) from the sample to the analysis position. During the analysis, the sample is excited using an x-ray source (Rhodium anode, 50 kV, 50 Watt) in three successive energy conditions, which target three different suites of elements. The resulting x-ray fluorescence is measured with a silicon drift detector and the spectra are analysed using a proprietary spectral analysis package which takes into account all peaks associated with a given element. Daily automated quality assurance checks are performed every night at midnight and consist of an energy alignment (an energy calibration using a copper rod, inserted into the analysis area); and upscale measurement to monitor the stability of the instrument response (for Cd, Cr and Pb); and a flow check through an independent mass flow sensor. Additional quality assurance checks employed here included flow calibrations, regular external standard checks, field blanks performed using a HEPA filter as well as tape blanks before and after each tape change.

For the field studies the instrument sampled PM_{10} or $PM_{2.5}$ as detailed below (see Sect. 2.3.1). The elements reported are As, Ba, Ca, Cd, Ce, Cl, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Pt, S, Sb, Se, Si, Sr, Ti, V, Zn and were chosen to represent a range of source categories (i.e. regulatory, traffic, industry), plus the internal Palladium (Pd) standard. The internal standard measurement is the reported response from a Pd rod inserted in a fixed position under the filter tape.

2.2 Laboratory Experiments

An independent mass-based calibration technique was developed for the XACT. This used laboratory generated aerosols and a schematic of the instrument set-up is shown in Figure 1~~Figure 1~~. Ammonium sulphate ($(NH_4)_2SO_4$~~NH_3SO_4~~, ACS reagent grade, Sigma-Aldrich), potassium chloride (KCl, analytical grade, VWR Chemicals) and zinc acetate ($Zn(O_2CCH_3)_2$, analytical grade, VWR Chemicals) were dissolved in high purity water (18.2 MΩ, TOC < 5 $\mu g\ L^{-1}$~~ppb~~, PURELAB® Ultra Analytic, ELGA (Veolia Water Technologies)) to obtain a range of standard solutions spanning the ambient concentration range.

Aerosols were generated using an ATM 226 - Clean Room Aerosol Generator (Topas) and were driven through two Permapure driers set in reflux method to reduce the relative humidity to approximately 40%. The flow was then split isokinetically using a TSI 3708 flow splitter and passed to three instruments: a tapered element oscillating microbalance (1400ab TEOM, Thermo), with which continuous direct mass measurements of particulates were taken; a scanning mobility particle sizer (TSI SMPS 3080); and the XACT. HEPA filtered make-up air was provided where necessary. The mass concentration of the deposited $(NH_4)_2SO_4$, KCl and $Zn(O_2CCH_3)_2$ as measured by the TEOM were used to calculate the S, Cl, K and Zn mass concentrations and compared to the element concentration measured with the XACT. The SMPS was used to give qualitative diagnostic information on the size distribution of the aerosol.

2.3 Field Experiments

2.3.1 Monitoring Locations

Three field evaluation campaigns were carried out in the UK (Table 1~~Table 1~~): a traffic site in central London (Marylebone Road: lat 51˚31'21"N, long 0˚09'17"W) and two industrial sites (Pontardawe in Wales: lat 51˚43'12"N, long 3˚50'49"W; and Tinsley in Sheffield: lat 53˚24'38"N, long 1˚23'46"W) (map in Supplement S1). Marylebone Road is a kerbside monitoring station in a central London street canyon adjacent to a six lane highway (60-80,000 vehicles per day). During this deployment the XACT sampled PM_{10} except for a period from October to December 2014 that sampled $PM_{2.5}$. Pontardawe is an urban industrial site in South Wales, surrounded by metallurgical industries. Tinsley, located north-east of Sheffield, is approximately 200 m east of the M1 motorway, with a residential area to the east and light industry to the west. In Pontardawe and Tinsley, the XACT was collocated with the monitoring site belonging to the UK Ambient Air Quality Metals Monitoring Network from which daily filters measured by ICP-MS were available.

2.3.2 Comparison Instruments

A number of comparison instruments were used to evaluate the XACT in the field. The main comparison was carried out using filter samples collected with a Partisol 2025 and subsequent ICP-MS analysis. Further, an Aerosol Chemical Speciation Monitor (ACSM) and Ambient Ion Monitor-URG-900B (URG) were used for the evaluation of XACT at a high time resolution. 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~~they provide useful information for studies where source contributions may be assumed based on one of these measurement techniques~~.

Partisol 2025

A Thermo Scientific Partisol 2025, with a flow rate of 1 m^3 h^{-1}, was used to collect filter samples (mixed cellulose ester filters, VWR 514-0464) for subsequent analysis using ICP-MS. At Marylebone Road, where samples were taken specifically for this study, a 23 hour sampling period was used (01:00-00:00) to ensure comparability with the XACT once the equivalent hour lost to quality assurance was removed. The filters were acid-digested on a hotplate using a 1:2 mixture of $HClO_4$ and HF in open 10 ml Teflon crucibles. After complete evaporation, HNO_3 has been added to each sample, and the remaining solution was made up to the required volume. Filters were fully dissolved with this method (adapted from ISO-14869-1:2001). For quality assurance, blank filters (field and laboratory blanks), internal (rhyolite) and international (NIST SRM 1648a) certified reference materials were also prepared following the same procedure. The samples were analysed for a range of elements using ICP-MS (Table 3).

At Pontardawe and Tinsley, where an established measurement programme was adapted for comparison, a 24 hour period was sampled. Thus the frequency of PM_{10} filter sampling at the adjacent UK Heavy Metals Network sites was increased from weekly to daily for these field evaluations. The filters were digested using HNO_3/H_2O_2 digestion following the European reference method EN14902 and analysed for a range of elements (Table 4 and Table 5) using ICP-MS (Goddard et al., 2016).

The certified reference material was used for quality control in both filter digestion protocols. As standard reference materials are usually not an exact match for the matrix of the sample, the resulting recovery rates serve as a quality control parameter rather than a calibrant. Samples were thus not corrected for the recovery rate but checked for compliance with the requirements described in EN14902; recovery rates for both digestions methods are given in S5.

Aerosol Chemical Speciation Monitor (ACSM)

The ACSM measured the chemical composition of non-refractory PM_1 (NO_3, SO_4, NH_4 and organic mass) and is fully described in Ng et al. (2011). Briefly, air was drawn through an URG $PM_{2.5}$ size selective inlet (URG-2000-30EQ) at 0.18 m^3~~-~~h^{-1} and subsequently dried using a Permapure^{TM} drier (Perma Pure PD Dryer, PD-07018T-12MSS). Particles were focused using an aerodynamic lens with a 50 % transmission range of 75 nm to~~–~~ 650 nm (Liu et al., 2007) and subsequently flash vaporised, ionised and analysed using mass spectrometry at

0 amu to~~-~~100 amu. The signal was resolved into NO_3, SO_4, NH_4 and organic mass using a library of known fragmentation characteristics. The aerosol was sampled and analysed alternately with background air, allowing a continuous air subtraction, and averaged to an hourly time resolution. 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)~~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~~. The collection efficiency was calculated using the Middlebrook parameterisation (Middlebrook et al., 2012), which calculates an optimum collection based on aerosol acidity, inlet humidity and particle composition. The ACSM measurements were combined with Aethalometer measurements and compared to $PM_{2.5}$ mass measured using the TEOM FDMS or PM_1 mass estimated using SMPS measurements as described by Crenn et al. (2015)~~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)~~.

Ambient Ion Monitor- URG-900B (URG)

The URG-900B Ambient Ion Monitor continuously measured water-soluble anion and cation concentrations (Cl^-, SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in PM_{10} and is described in ~~(~~Beccaceci et al. (~~,~~ 2015). Briefly, the sample was drawn at a flow rate of 1 $m^3\,h^{-1}$ through a size selective inlet (PM10); the sample was then split isokinetically through a flow splitter to allow a 0.18 $m^3\,h^{-1}$ flow into a liquid diffusion denuder containing H_2O_2 to remove interfering acidic and basic gases. The remaining particles in this air stream were then enlarged in a super saturation chamber and finally collected in an aerosol sample collector and injected into the (anion and cation) ion chromatographs every hour.

2.4 Laboratory based filter analysis using the XACT

To trial a filter analysis technique using the XACT, PM_{10} was sampled onto polytetrafluoroethylene (PTFE) filters (Zefluor, 0.5 µm, 47 mm disc, Pall Life Sciences 516-8908) for 24 hours using a Partisol 2025 during the field campaign in Sheffield in February/March 2017. These PTFE filters were a similar material to the XACT filter tape but the stronger structure enables easier handling during punching and analysis. After exposure a 25mm punch was taken out of the exposed filters for analysis with the XACT on its return to the laboratory. The punching tool was always aligned with the edge of the exposed area. The punch was transferred into a filter holder, identical to the one used for instrument calibration with thin film standards, and transferred into the holder slot in the analysis block of the XACT. The analysis was performed on a 15 minute sample time using the XRF control program in a manual analysis mode. The energy condition set up remained the same as during the field sampling in the automation mode. Each filter was analysed four times, and the filter punch was rotated 90 ° in the filter holder in between replicates in order to account for non-uniformity of the particle deposit on the filter punch. The XACT results were used to calculate daily ambient element concentrations, which were compared to the daily mean concentration measured by the XACT in-situ. A total of 12 filters were analysed.

For quality assurance field and laboratory filter blanks were analysed and used to correct for the filter background. The blank measurements were also used to calculate the limit of detection for this method

2.5 Regression Analysis Approach

All comparisons were carried out using the Deming regression which minimises the sum of distances between the regression line and the X and Y variables taking into account the uncertainties in both variables (Deming, 1943).

2.6 Treatment of Measurements below Limit of Detection

In all comparisons data under the detection limit was used as measured unless the value was zero or below, in which case 0.5*LOD was used to replace the value. By including values below the LOD it was possible to calculate daily XACT mean concentrations, which might have been lost if data below the LOD had been excluded and the daily data capture had not been met.

~~Including values below the LOD had the advantage of being able to include daily XACT mean concentration was calculated from hourly concentrations that might have been lost if data below LOD was excluded and the daily data capture was not met.~~

2.7 Uncertainty Evaluation

The expanded uncertainty, representing a 95 % level of confidence, was calculated by taking the root of sum square of the separate sources of uncertainty as shown below:

$$U = \sqrt{LOD_i^{\,2} + (b.c_i)^2}$$

Where LOD_i is the limit of detection of element i (here calculated as the 3 times the experimental standard deviation of field or laboratory blanks), c_i is the measured concentration of the element (in ng m^{-3}), and b is an element dependent factor which was derived from experimental and literature values (US-EPA, 1999). For the XACT measurements, the combined uncertainty included contributions of $\frac{3}{\sqrt{3}}$~~3/√3~~ % from flow (CEN, 2014), 5 % from calibration standard uncertainty (US EPA, 1999), 2.9 % from long term stability (calculated from the standard deviation of hourly internal Pd reference) and an element-specific uncertainty associated with the spectral deconvolution calculated by the instrument software for each spectra. The XACT LOD was determined using HEPA field blank measurements during each campaign; these are shown in Table 3. ~~.~~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).

3 Results and Discussion

3.1 Laboratory Experiment

For the calibration test a range of solution concentrations were produced to assess the instrument response (see supplement S2). A subset of concentrations, which span the concentrations encountered during the field campaign, was used for the final comparison (see Table 2~~Table 2~~). Thus, the highest element concentrations in the standards used for comparison were between 9 (S) and 25 (Zn) times lower than the commercial thin film standards.

All calibrations resulted in a linear relationship between the mass calculated using TEOM mass concentrations and measured by the XACT for the standard range used. Sample self absorption effects were calculated to be <1% for the maximum concentration of S (the lightest element used) and therefore insignificant in the use of this instrument~~All calibrations resulted in a linear relationship between the mass calculated using TEOM mass concentrations and measured by the XACT for the standard range used~~. TEOM and XACT results agreed well in all cases with slopes between 0.94 and 0.99. Slopes are not significantly different from the 1:1 line for all comparisons (95% confidence interval). The coefficient of determination (R^2) ranged between 0.98 (S) and 0.99 (Cl, K, Zn). The XACT response to the generated particles was thus comparable to the response of the commercial standards used for calibration. A similar result was found by Indresand et al. (2013) using prepared sulphur reference materials for XRF calibration.

3.2 Field Evaluation: overview

An overview of the data recorded in each comparison is given in Table 3-6 and includes the limit of detection for all elements. Sb was not included in the analysis as spectral interference resulted in a high LOD.

The sampling at Marylebone Road was carried out using a $PM_{2.5}$ inlet during a period ~~that was~~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^{-} ~~to~~^{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.

Sampling at Pontardawe, Wales was carried out in an area dominated by metallurgical industry, which is reflected by the high Nickel concentrations measured (i.e. the mean Nickel concentration at Pontardawe was 27 times higher than that measured at Marylebone Road). Overall, t~~T~~he mean elemental concentrations measured in this campaign ranged from 0.24 ng m^{-}~~ to~~^{3} to 5,200 ng m^{-3}. 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 PM$_{10}$ head. The order of elements in terms of mean concentration in Wales was:

Cl > S > Si > Fe > Ca > K > Ni > Ti > Zn > Cu > Pb > Mn > Cd > Sr > Cr > Ba > Mo > V > Ce > As > Pt > Se.

In Wales, the availability of high time resolution data, in conjunction with meteorological data and source emission activity allowed us to pinpoint pollution sources more accurately. Cr concentrations from local sources were studied to identify contributions from different industries. As can be seen in Figure 4~~Figure 4~~ the 24 hour filter data leads to very different source directions than the higher time resolution data by the XACT (Font et al., 2017). This could be used to address policy breaches with more targeted abatement measures.

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~~ with~~ mean elemental concentrations overall ranged from 0.186 ng m^{-}~~ to~~^{3} to 1,370 ng m^{-3}. The order of elements in terms of mean concentration in Tinsley was:

Cl > S > Fe > Ca > Si > K > Zn > Cr > Mn > Ni > Ti > Pb > Cu > Mo > Cd > As > Ba > V > Sr > Se > Ce > Pt.

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} SO$_4$ (non-sea salt) and 58 ng m^{-3} to 8,300 ng m^{-3} for non-refractory SO$_4$.

The comparison of the XACT with the URG was carried out in PM$_{10}$ 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.

3.2.1 Comparison with ICP-MS

The filter comparison results were split by the two ~~ICP-MS~~ digestion methods: HF/HClO$_4$ and HNO$_3$/H$_2$O$_2$. This had the additional advantage of grouping the two industrial campaigns that were carried out in PM$_{10}$ and separating the campaign at Marylebone Road in PM$_{2.5}$. LODs were not consistently higher for either the ICP-MS or the XACT measurements (Table 3 -5). All elements were compared using Deming regression and a summary of all calculated slopes and intercepts are given in Table 7 (including R^2 values); the corresponding figures are available in the supplementary information section. The XACT agreed well with the ICP-MS measurements and R^2 ranged from 0.50 ~~-~~to 1.00 and 0.67 ~~-~~to 0.99, with a median of 0.91 and 0.95, following HF/HClO$_4$ and HNO$_3$/H$_2$O$_2$ digestion, respectively. Deming regression for Fe resulted in slopes that were not significantly different from unity for either subset. Slopes were also not significantly different from unity for Ba, Ca, K, Mn and Ti following digestion with HF/HClO$_4$ and for Cr, Ni, Pb, V and Zn following digestion with

HNO_3/H_2O_2. For the element As the XACT recorded significantly higher concentrations than those measured by ICP-MS, irrespective of digestion method. This was also the case for elements Cu, Pb, Sr and Zn after $HF/HClO_4$ digestion and for Mn after HNO_3/H_2O_2 digestion. For the ~~remaining~~ elements ~~(~~Ni (after $HF/HClO_4$ digestion),~~ and~~ Cu and Se (after HNO_3/H_2O_2 digestion) the concentrations measured by the XACT were significantly lower than those measured by the ICP-MS. Cr and V were not reported for $HF/HClO_4$ due to contamination of the $HClO_4$ 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.~~The remaining elements were mostly below the limit of detection and thus did not produce meaningful regression results.~~

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;~~ positive and negative filter artefacts could also influence the concentrations when sampling onto filters;~~ many concentrations were close to the detection limit for the elements As in ~~both~~ all campaigns and Ni during the Marylebone Road campaign. These stated reasons might influence the two digestions methods to different extent~~d~~s. 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).

3.2.2 Comparison with ACSM at Marylebone Rd

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 values of S and Cl measured with the XACT were used to calculate hourly non-sea salt sulphate (SO_4), which~~ 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 mean (median) concentrations were 2,600 (1,880) ng m^{-3} and 2,000 (1,460) ng m^{-3}, respectively. The time series of these measurements is shown in Figure 5 and demonstrates the excellent temporal agreement, which is reflected by an R^2 of 0.93. The correlation resulted in a slope of 1.41 (95% CI 1.35-1.46) and an intercept of 53 (95% CI 13.4-93) ng m^{-3}. The larger non-sea salt SO_4 means/medians and slope >1 likely resulted from measuring different size fractions; $PM_{2.5}$ for the XACT vs PM_1 for the ACSM.

3.2.3 Comparison with URG

Hourly concentrations of water-soluble Cl, K and Ca measured by URG were compared to the hourly measured total Cl, K and Ca measured by the XACT. Furthermore, hourly measured water-soluble SO_4 (URG) was compared to hourly SO_4 calculated from the S measurement by the XACT instrument (Table 6, Figure 6). The XACT measured higher concentrations for all these components. The slopes were similar for the SO_4 (1.65) and Cl (1.68) and slightly higher for Ca (1.89). Deming regression for K resulted in a very high slope (4.55) but this was likely the result of concentrations being close to the LOD for the URG, result was consistent with the findings presented by Beccaceci et al. (2015). The R^2 for Ca, Cl, K and SO_4 was 0.86, 0.93, 0.36 and 0.95, respectively.

The higher concentrations measured by the XACT relative to the URG was likely caused by the low water-solubility of Cl, K, Ca and S containing minerals as well as the penetration efficiency of larger aerosols through the URG annular denuder (Beccaceci et al. 2015). The range of sources of these ions/elements resulted in variations in particle size and solubility and hence the relative response of the two instruments. When considering solubility, the larger slopes are associated with the least soluble compounds. In order of decreasing solubility (and increasing slope) SO_4 exists predominately as $(NH_4)_2SO_4$ (solubility of 754 g L^{-1}~~g/L~~ in water), Cl is principally from marine sources as NaCl (solubility of 359 g L^{-1}~~g/L~~ in water at 20 ºC); Ca in the urban environment is typically from mineral or construction sources and is comprised of $CaCO_3$ and $CaSO_4 \cdot 2H_20$ (solubilities of 0.013 g ~~/~~L^{-1} and 2.55 g L^{-1} ~~g/L~~ respectively) as well as calcium silicates (which are insoluble) (Dean and Lange, 1999). When considering particle size, the sources of aerosols containing Cl, K, Ca and S are often larger than $PM_{2.5}$ and may therefore be influenced by the reduced penetration efficiency of the URG annular denuder (Dick et al., 1995; Visser et al., 2015b). 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) ~~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 $PM_{10\text{-}2.5}$ 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%. This illustrates that a sampling bias, due to the penetration efficiency of the annular denuder may play a role in the difference between the URG and the XACT, however due to the additional variation in solubility this is difficult to quantify.

3.3 Laboratory based filter analysis using the XACT

With a mean R^2 of 0.95 daily concentrations measured on the filter by the XACT compared well with the measurements made by the XACT when deployed in the field. The resulting regression slopes are compared with those from the ICP-MS comparison (Figure 7). The small sample number (N = 12) resulted in a higher uncertainty in the slopes but in general the slopes were comparable to those from the ICP-MS filter analyses. The intercepts for most elements were not significantly different from 0. The slopes for the elements Ba, Cl, Cr, Cu, Mn, Ni, Sr, V and Zn were not significantly different from the 1:1 line. For the elements As, Ca, Fe and Ti the XACT measurements were lower when deployed in the field than when measuring the 24hr filter samples. Whereas for the elements K, Mo, Pb, S and Se online field measurements resulted in higher results than off-line filter measurements~~.~~. Reasons for the discrepancies in the slopes may be caused by the difference between the filter material and analysis time used for the filter samples (Zeflour, 15 min) in comparison to the online method (proprietary PTFE tape, 1 hr). Additionally the fitting routine used in the deconvolution software is optimised for the filter tape used and might also contribute to the observed differences. ~~-~~Full results can be found in the supplementary information.

Punching and subsequent filter analysis was found to be practically achievable, although time consuming, when compared to automated laboratory techniques.

4 Conclusions

This study was performed to evaluate the XACT 625 in the field and under laboratory conditions. In the field, the XACT was evaluated in three contrasting environments and compared to laboratory-based ICP-MS analysis as well as alternative high time resolution instrumentation. The XACT was found to be a highly reliable measurement instrument which showed an excellent correlation with standardised laboratory analysis (ICP-MS) albeit with a slight overall positive bias (median 1.07). Differences in the individual results we~~a~~re element specific but ~~were~~ generally attributable~~ed~~ to a combination of variable filter blank levels ~~in filter paper~~, ~~This was attributed to~~ recovery rates from acid digestion, instrument calibration, sampling temperature and small differences in ~~and~~ inlet location ~~and temperature of the instruments~~ ~~and filter sampling~~. 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~~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, ~~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.

The laboratory experiment, which compared the XACT measurements of the elemental constituents of generated aerosols with the mass measured using a TEOM, proved to be a successful method for verifying the response of the XACT over environmentally relevant elemental concentrations. The slopes were close to, and not significantly different from, unity (0.94 – 0.99). 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~~was more likely due to filter artefacts and recovery rates following acid digestion~~. It further shows that generated aerosols can be used to calibrate the XACT to provide ongoing quality assurance checks.

An ambient filter sampling analysis technique, using the XACT as a laboratory based instrument, was also evaluated. The concentrations measured on the sampled filter compared well with the in-situ XACT with median slopes of 1.07 and was therefore comparable with the ICP-MS filter-based technique. This technique diversifies further the use of the XACT, especially if the instrument has downtime between campaigns. This technique also allows a direct comparison of the XACT and other XRF systems using a filter sample.

Future work should include a repetition of the laboratory calibration using an overall lower range of standards and combining solutions in order to have a more complex particle composition. A standard reference material, either in solution or on filter should also be included in future calibration tests. Further, to develop the filter analysis method using the XACT and piloted in this study, different filter materials should be tested and the deconvolution approach optimised if necessary.

5 Acknowledgments

This study has been partly funded by the Welsh Government under contract C224/2015/2016 and by the UK Department for Environment Food & Rural Affairs under contract AQ0740. It used equipment funded by the Natural Environment Research Council Traffic Grant (NE/1007806/1) and by the UK Department for the Environment and Rural Affairs Black Smoke and Heavy Metals Monitoring Networks.

6 References

Beccaceci, S., McGhee, E. A., Brown, R. J. C., and Green, D. C.: A comparison between a semi-continuous analyzer and filter-based method for measuring anion and cation concentrations in PM10 at an urban background site in London, Aerosol Sci. Tech., 49, 793-801, 2015.

Brown, R. J. C., Yardley, R. E., Muhunthan, D., Butterfield, D. M., Williams, M., Woods, P. T., Brown, A. S., and Goddard, S. L.: Twenty-five years of nationwide ambient metals measurement in the United Kingdom: concentration levels and trends, Environ. Monit. Assess., 142, 127-140, 2008.

Brunekreef, B. and Holgate, S. T.: Air pollution and health, Lancet, 360, 1233-1242, 2002.

Bukowiecki, N., Hill, M., Gehrig, R., Zwicky, C. N., Lienemann, P., Hegedus, F., Falkenberg, G., Weingartner, E., and Baltensperger, U.: Trace metals in ambient air: Hourly size-segregated mass concentrations determined by Synchrotron-XRF, Environ. Sci. Technol., 39, 5754-5762, 2005.

Chang, R. Y. W., Leck, C., Graus, M., Müller, M., Paatero, J., Burkhart, J. F., Stohl, A., Orr, L. H., Hayden, K., Li, S. M., Hansel, A., Tjernström, M., Leaitch, W. R., and Abbatt, J. P. D.: Aerosol composition and sources in the central Arctic Ocean during ASCOS, Atmos. Chem. Phys., 11, 10619-10636, 2011.

Chen, L. C. and Lippmann, M.: Effects of metals within ambient air particulate matter (PM) on human health, Inhal. Toxicol. , 21, 1-31, 2009.

Chow, J. C., Lowenthal, D. H., Chen, L. W. A., Wang, X. L., and Watson, J. G.: Mass reconstruction methods for PM2.5: a review, Air Qual. Atmos. Hlth., 8, 243-263, 2015.

Chu, S. H.: PM2.5 episodes as observed in the speciation trends network, Atmos. Environ., 38, 5237-5246, 2004.

Crenn, V., Sciare, J., Croteau, P. L., Verlhac, S., Fröhlich, R., Belis, C. A., Aas, W., Äijälä, M., Alastuey, A., Artiñano, B., Baisnée, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillón, M. C., Močnik, G., O'Dowd, C. D., Ovadnevaite, J., Petit, J. E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Estève, R., Slowik, J. G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prévôt, A. S. H., Jayne, J. T., and Favez, O.: ACTRIS ACSM intercomparison – Part 1: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments, Atmos. Meas. Tech., 8, 5063-5087, 2015.

Dean, J. A. and Lange, N. A.: Lange's Handbook of Chemistry, McGraw-Hill, 15th Ed., 1999.

Deming, W. E.: Statistical adjustment of data, John Wiley & Sons; Chapman & Hall, New York: London, 1943.

Dick, W., Huang, P. F., and McMurry, P. H.: Characterization of 0.02 to 1.0 µm particle losses in Perma Pure dryers: dependency on size, charge and relative humidity, PTL Publication No. 936: Particle Technology Laboratory, Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, 1995.

Font, A., Prietsman, M., Tremper, A., Carslaw, D., and Green, D. C.: Identifying Key Sources of Emissions of Problem Pollutants in Wales A Research Collaboration to Utilise Novel Monitoring and Data Analysis Assessment Techniques to Drive Innovation - Pontardawe Report, Environmental Research Group, King's College London, London, 2017.

Formenti, P., Prati, P., Zucchiatti, A., Lucarelli, F., and Mando, P. A.: Aerosol study in the town of Genova with a PIXE analysis, Nucl. Instrum. Meth. B, 113, 359-362, 1996.

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. Discuss., 2017, 1-26, 2017.

Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., van Der Gon, H. D., Facchini, M. C., Fowler, D., Koren, I., Langford, B., Lohmann, U., Nemitz, E., Pandis, S., Riipinen, I., Rudich, Y., Schaap, M., Slowik, J. G., Spracklen, D. V., Vignati, E., Wild, M., Williams, M., and Gilardoni, S.: Particulate matter, air quality and climate: lessons learned and future needs, Atmos. Chem. Phys., 15, 8217-8299, 2015.

Goddard, S. L., Brown, R. J. C., Butterfield, D. M., McGhee, E. A., Robins, C., Beccaceci, S., Lilley, A., Bradshaw, C., and Haynes, E.: Annual Report for 2015 on the UK Heavy Metals Monitoring Network National Physical Laboratory, 2016.

Godri, K. J., Green, D. C., Fuller, G. W., Dall'Osto, M., Beddows, D. C., Kelly, F. J., Harrison, R. M., and Mudway, I. S.: Particulate Oxidative Burden Associated with Firework Activity, Environ. Sci. Technol., 44, 8295-8301, 2010.

Hamad, S., Green, D., and Heo, J.: Evaluation of health risk associated with fireworks activity at Central London, Air Qual. Atmos. Hlth., 9, 735-741, 2016.

Indresand, H., White, W. H., Trzepla, K., and Dillner, A. M.: Preparation of sulfur reference materials that reproduce atmospheric particulate matter sample characteristics for XRF calibration, X-Ray Spectrom, 42, 359-367, 2013.

Jeong, J. H., Shon, Z. H., Kang, M., Song, S. K., Kim, Y. K., Park, J., and Kim, H.: Comparison of source apportionment of PM2.5 using receptor models in the main hub port city of East Asia: Busan, Atmos. Environ., 148, 115-127, 2017.

Kelly, F. J. and Fussell, J. C.: Air pollution and public health: emerging hazards and improved understanding of risk, Environ. Geochem. Hlth., 37, 631-649, 2015.

Kelly, F. J., Fuller, G. W., Walton, H. A., and Fussell, J. C.: Monitoring air pollution: Use of early warning systems for public health, Respirology, 17, 7-19, 2012.

Liu, P. S. K., Deng, R., Smith, K. A., Williams, L. R., Jayne, J. T., Canagaratna, M. R., Moore, K., Onasch, T. B., Worsnop, D. R., and Deshler, T.: Transmission efficiency of an aerodynamic focusing lens system: Comparison of model calculations and laboratory measurements for the Aerodyne Aerosol Mass Spectrometer, Aerosol Sci. Tech., 41, 721-733, 2007.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci. Tech., 46, 258-271, 2012.

Millero, F. J., R. Feistel, D. G. Wright and McDougall, T.J.: 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, 2008.

Moreno, T., Querol, X., Alastuey, A., Minguillon, M. C., Pey, J., Rodriguez, S., Miro, J. V., Felis, C., and Gibbons, W.: Recreational atmospheric pollution episodes: Inhalable metalliferous particles from firework displays, Atmos. Environ., 41, 913-922, 2007.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, Aerosol Sci. Tech., 45, 780-794, 2011.

Orsini, D. A., Ma, Y., Sullivan, A., Sierau, B., Baumann, K., and Weber, R. J.: Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol composition, Atmos. Environ., 37, 1243-1259, 2003.

Pandey, S. K., Kim, K. H., and Brown, R. J. C.: A review of techniques for the determination of polycyclic aromatic hydrocarbons in air, TrAC-Trend Anal. Chem., 30, 1716-1739, 2011.

Park, S. S., Cho, S. Y., Jo, M. R., Gong, B. J., Park, J. S., and Lee, S. J.: Field evaluation of a near-real time elemental monitor and identification of element sources observed at an air monitoring supersite in Korea, Atmos. Pollut. Res., 5, 119-128, 2014.

Rumsey, I. C., Cowen, K. A., Walker, J. T., Kelly, T. J., Hanft, E. A., Mishoe, K., Rogers, C., Proost, R., Beachley, G. M., Lear, G., Frelink, T., and Otjes, R. P.: An assessment of the performance of the Monitor for AeRosols and GAses in ambient air (MARGA): a semi-continuous method for soluble compounds, Atmos. Chem. Phys., 14, 5639-5658, 2014.

US-EPA: Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy . Agency, U. S. E. P. A. (Ed.), U.S. Environmental Protection Agency, Cincinnati, OH 45268, 1999.

US-EPA: Environmental Technology Verification Report. Cooper Environmental Services LLC Xact 625 Particulate Metals Monitor, Report no. EPA/600/R-12/680. Agency, U. S. E. P. A. (Ed.), U.S. Environmental Protection Agency, Cincinnati, OH 45268, 2012.

Vecchi, R., Bernardoni, V., Cricchio, D., D'Alessandro, A., Fermo, P., Lucarelli, F., Nava, S., Plazzalunga, A., and Valli, G.: The impact of fireworks on airborne particles, Atmos. Environ., 42, 1121-1132, 2008.

Visser, S., Slowik, J. G., Furger, M., Zotter, P., Bukowiecki, N., Canonaco, F., Flechsig, U., Appel, K., Green, D. C., Tremper, A. H., Young, D. E., Williams, P. I., Allan, J. D., Coe, H., Williams, L. R., Mohr, C., Xu, L., Ng, N. L., Nemitz, E., Barlow, J. F., Halios, C. H., Fleming, Z. L., Baltensperger, U., and Prevot, A. S. H.: Advanced source apportionment of size-resolved trace elements at multiple sites in London during winter, Atmos. Chem. Phys., 15, 11291-11309, 2015a.

Visser, S., Slowik, J. G., Furger, M., Zotter, P., Bukowiecki, N., Dressler, R., Flechsig, U., Appel, K., Green, D. C., Tremper, A. H., Young, D. E., Williams, P. I., Allan, J. D., Herndon, S. C., Williams, L. R., Mohr, C., Xu, L., Ng, N. L., Detournay, A., Barlow, J. F., Halios, C. H., Fleming, Z. L., Baltensperger, U., and Prevot, A. S. H.: Kerb and urban increment of highly time-resolved trace elements in PM10, PM2.5 and PM1.0 winter aerosol in London during ClearfLo 2012, Atmos. Chem. Phys., 15, 2367-2386, 2015b.

Weber, R. J., Orsini, D., Daun, Y., Lee, Y. N., Klotz, P. J., and Brechtel, F.: A particle-into-liquid collector for rapid measurement of aerosol bulk chemical composition, Aerosol Sci. Tech., 35, 718-727, 2001.

WHO: Air quality guidelines for Europe (Second edition). World Health Organization., Copenhagen, 2000.

WHO: Review of evidence on health aspects of air pollution – REVIHAAP Project, WHO, Copenhagen, technical report, 2013.

Yardley, R. E., Sweeney, B. P., Butterfield, D., Quincey, P., and Fuller, G. W.: Estimation of Measurement Uncertainty in Network Data, National Pysical Laboratory, 2007.

7 Figures

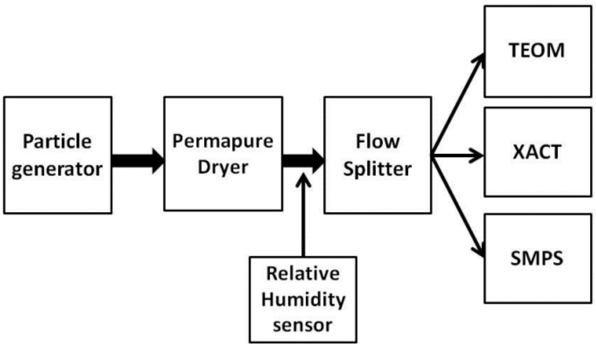

Figure 1: Schematic of instrument set up during laboratory calibration

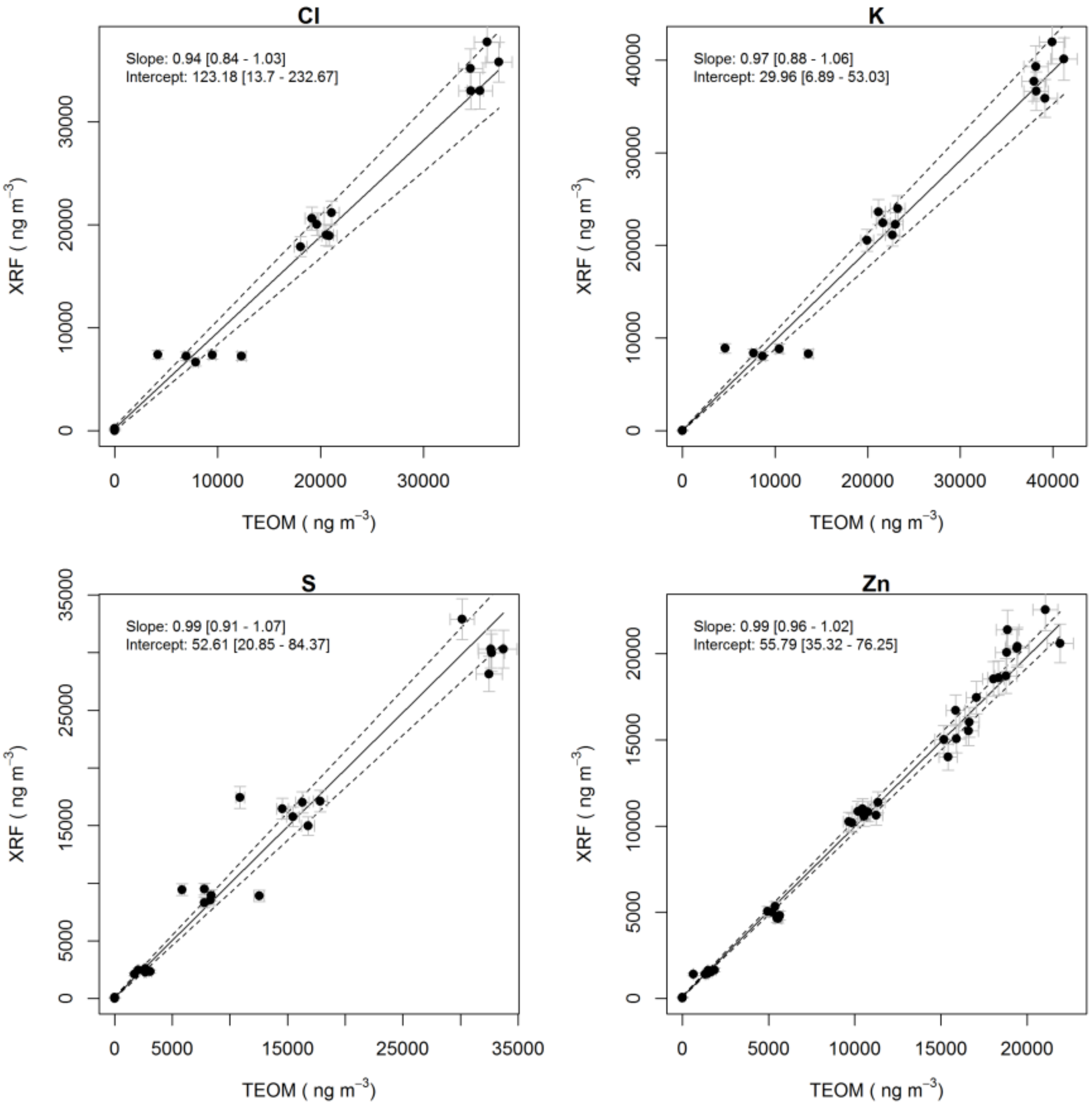

Figure 2: Deming regression of Cl (top left), K (top right), S (bottom left) and Zn (bottom right) mass concentrations measured with the XACT and calculated from TEOM mass measurements

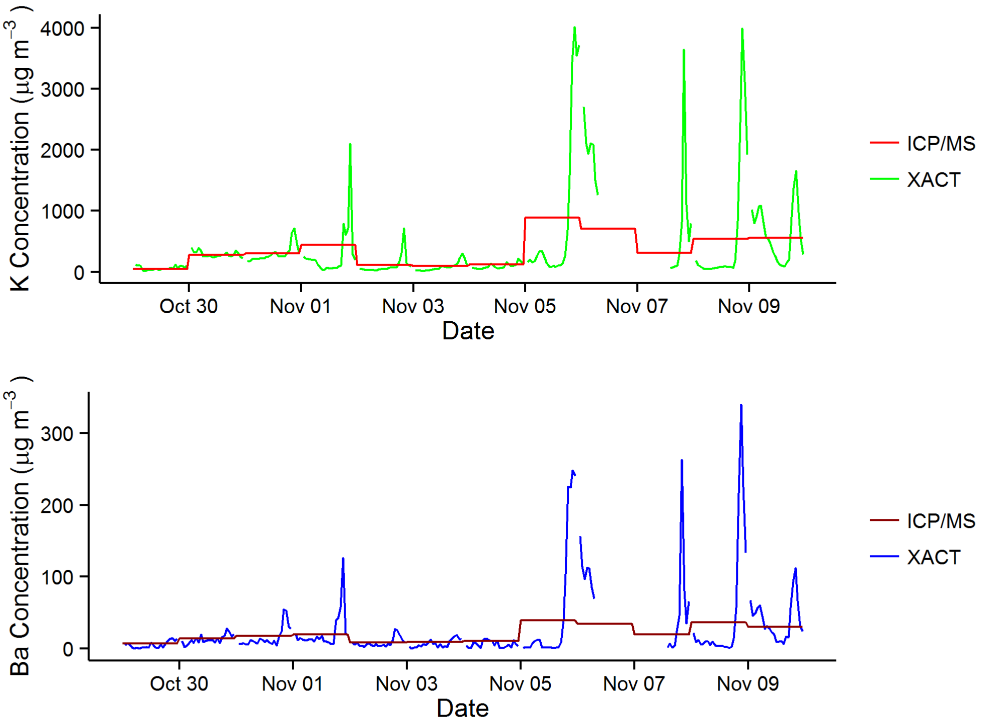

Figure 3: Timeseries of K (top) and Ba (bottom) concentration (µg m^{-3}) using hourly XACT and daily ICP-MS measurements

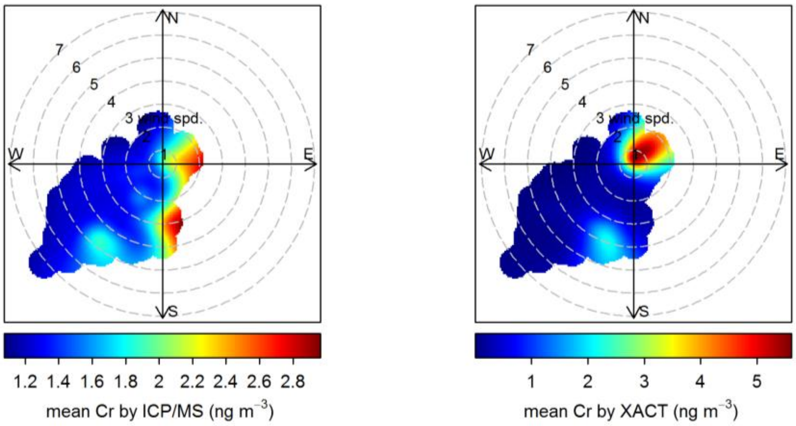

Figure 4: Polar plot of the Cr concentrations (ng m^{-3}) in Pontardawe, Wales using daily ICP-MS measurements (left) and hourly XACT measurements (right)

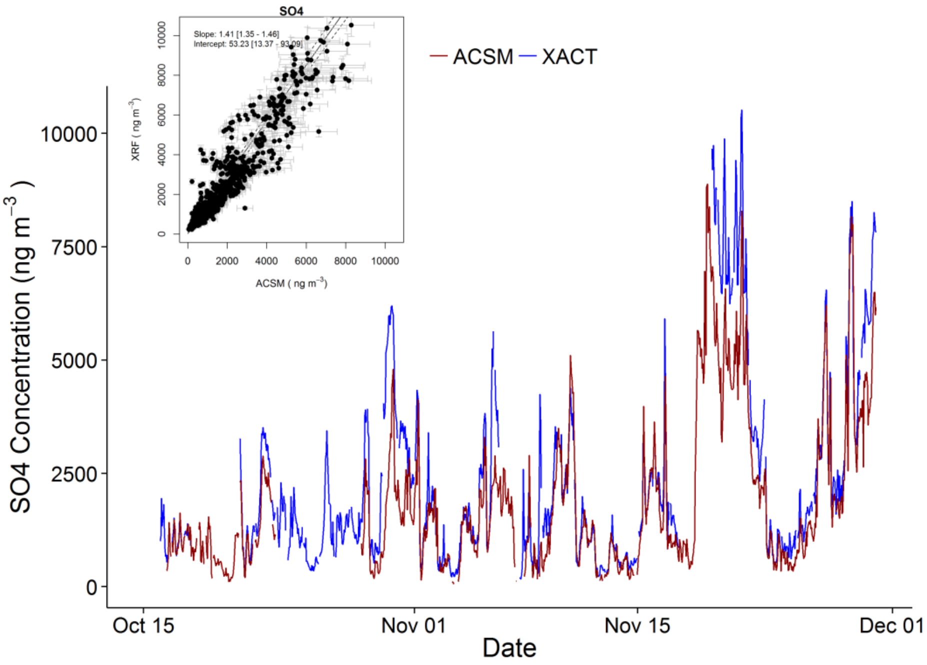

Figure 5: Timeseries of non-sea salt SO_4 concentration (XACT, calculated) and non-refractory SO_4 (ACSM, measured) in ng m^{-3}

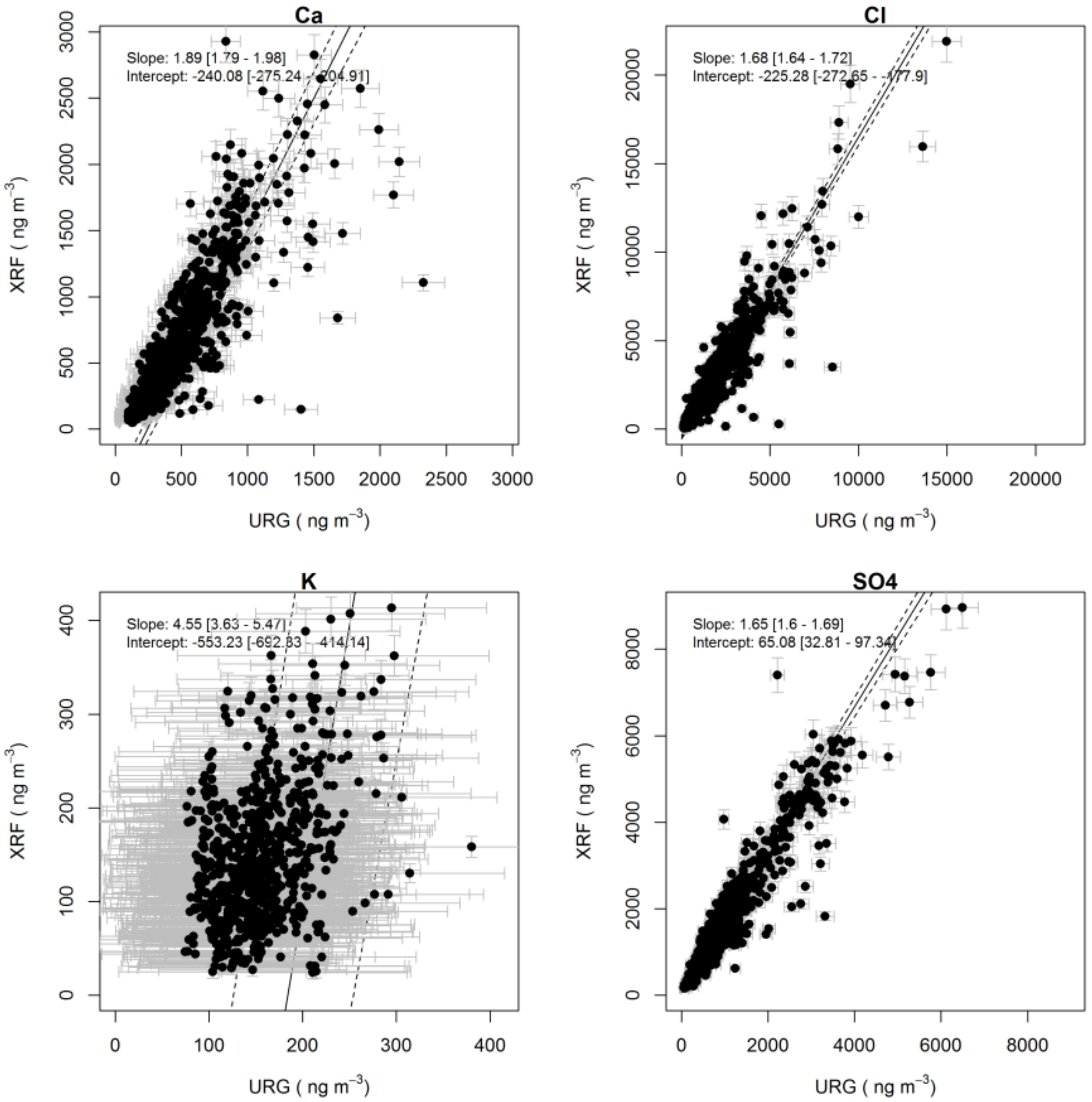

Figure 6: Deming regression of water soluble Ca (top left), Cl (top right), K (bottom left) and SO_4 (bottom right) as measured by URG and Ca, Cl, K and calculated SO_4 (from elemental S) measured by XACT (ng m^{-3})

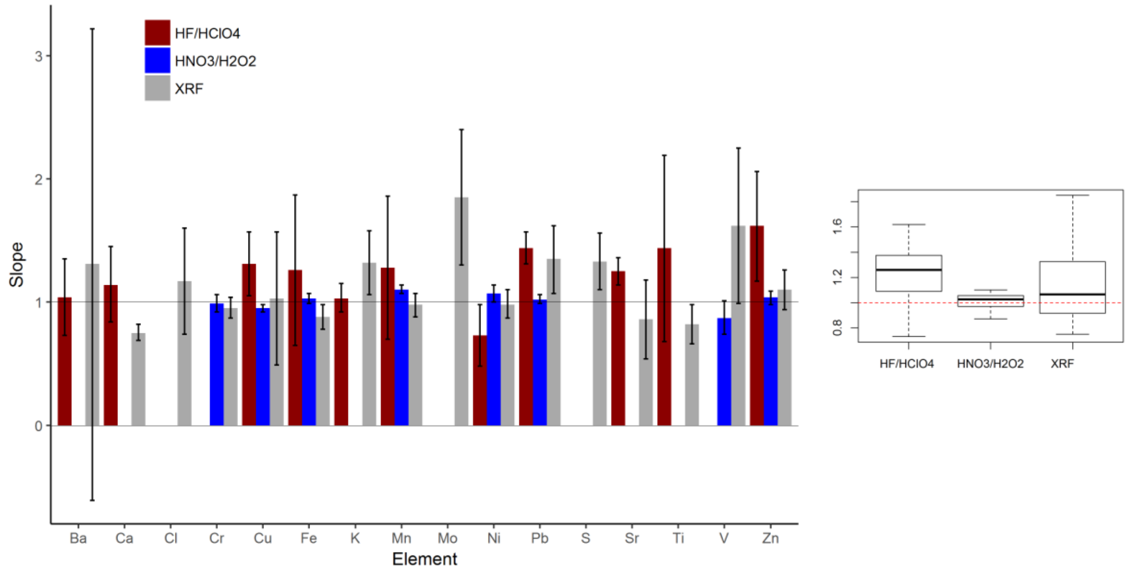

Figure 7: Slope values (+95% confidence interval) of Deming regressions (XACT vs. ICP-MS (split in HF/HCLO$_4$ and HNO$_3$/H$_2$O$_2$ digestion) and XACT vs. XACT (filter)), split by element (left) and corresponding box-and-whisker plots split by method (right).

8 Tables

Table 1: Overview of sites and instrumentation used

	Marylebone Road, London		Tawe Terrace, Pontardawe	Tinsley, Sheffield
	PM$_{10}$	**PM$_{2.5}$**	**PM$_{10}$**	**PM$_{10}$**
XACT	01-Jul-14 to 11-Mar-15	15-Oct-14 to 01-Dec-14	25-Nov-15 to 24-Dec-15	19-Jan-17 to 27-Mar- 17
ACSM (PM$_1$)	n/a	15-Oct-14 to 01-Dec-14	n/a	n/a
URG	07-Jan-15 to11-Mar-15	n/a	n/a	n/a
Partisol	n/a	15-Oct-14 to 01-Dec-14*	25-Nov-15 to 24-Dec-15**	19-Jan-17 to 27-Mar- 17**
				17-Feb-17 to 10-Mar-17$^+$

Filters were digested using * HF/HClO$_4$ and ** HNO$_3$/H$_2$O$_2$

$^+$ Filters were analysed using the XACT in off-line mode

Table 2: Maximum concentration in field campaigns (ng m^{-3}) and highest and lowest concentration used in calibration test

Field campaign	**Concentration (ng m^{-3})**			
	S	**Cl**	**K**	**Zn**
London Kerbsite (PM$_{10}$)	3700	22000	470	310
London Kerbsite* (PM$_{2.5}$)	3500	4600	4000	370
Wales Industrial (PM$_{10}$)	8900	21000	1500	5500
Sheffield Industrial (PM$_{10}$)	4900	10000	1020	4900
lowest standard	2400	7200	8500	4900
highest standard	30000	35000	39000	20000

Table 3: Overview of Marylebone Road, London measurements by XACT and ICP-MS (ng m^{-3}); (* only 18 samples for XACT As)

		XACT (ng m^{-3})						ICP/MS (ng m^{-3})					
	species	**mean**	**sd**	**med**	**min**	**max**	**LOD**	**mean**	**sd**	**med**	**min**	**max**	**LOD**
Marylebone Road, London (n=19)	As*	1.51	2.4	0.40	0.001	8.8	0.00020	0.97	1.02	0.53	0.049	4.0	0.099
	Ba	15.8	14.3	10.0	1.74	50	0.31	15.1	9.9	11.0	3.1	39	0.0166
	Ca	67	35	61	19.5	157	1.11	71	32	65	23	142	0.0166
	Cd	4.0	0.37	4.0	3.4	4.7	2.4	0.114	0.106	0.079	0.023	0.39	0.0046
	Ce	1.07	0.198	1.09	0.61	1.42	0.135	0.38	0.128	0.36	0.182	0.62	0.00030
	Cl	400	400	250	4.4	1180	2.1						
	Cr	1.33	0.52	1.35	0.46	2.4	0.025						
	Cu	21	7.3	21	6.5	35	0.29	16.5	6.6	14	3.7	29	0.187
	Fe	470	124	450	240	710	5.4	380	90	360	230	600	1.52
	K	230	230	103	59	870	7.9	230	230	110	48	890	8.1
	Mn	4.9	1.32	4.6	3.0	8.1	0.076	3.9	1.33	3.8	1.91	7.3	0.045
	Mo	0.64	0.109	0.62	0.46	0.97	0.40						
	Ni	0.73	0.60	0.54	0.25	2.2	0.099	1.33	0.74	1.14	0.50	2.8	0.0044
	Pb	11.1	8.7	7.7	1.66	31	0.116	8.1	7.2	5.1	1.10	25	0.093
	Pt	0.177	0.010	0.175	0.161	0.20	0.078						
	S	600	330	460	180	1600	3.3						
	Se	0.177	0.169	0.112	0.070	0.77	0.031						
	Si	110	70	85	72	340	65						
	Sr	3.8	5.8	0.95	0.47	19	0.25	2.9	4.3	0.93	0.106	14.6	0.026
	Ti	4.4	2.7	3.4	1.80	12	0.158	2.9	2.5	1.97	0.28	9.1	0.067
	V	0.84	0.81	0.67	0.138	2.7	0.085						
	Zn	27	16	21	5.2	57	0.195	22	10.9	17.7	7.5	39	1.43

Table 4: Overview of Pontardawe, Wales measurements by XACT and ICP-MS (ng m^{-3})

		XACT (ng m^{-3})						ICP/MS (ng m^{-3})					
	species	**mean**	**sd**	**med**	**min**	**max**	**LOD**	**mean**	**sd**	**med**	**min**	**max**	**LOD**
Pontardawe, Wales (n=25)	As	0.43	0.47	0.22	0.037	2.2	0.00020	0.23	0.31	0.081	0.030	1.12	0.037
	Ba	1.41	0.63	1.10	0.97	3.1	0.31						
	Ca	191	109	155	50	510	1.11						
	Cd	3.0	0.35	2.9	2.5	3.8	2.4	0.085	0.080	0.068	0.004	0.31	0.0110
	Ce	0.85	0.30	0.76	0.46	1.95	0.135						
	Cl	5200	3000	5000	330	12700	2.1						
	Cr	1.62	2.4	0.41	0.065	9.8	0.025	1.52	0.81	1.26	1.26	4.8	1.43
	Cu	3.8	2.2	3.9	0.67	8.9	0.29	4.0	2.2	3.7	0.63	9.1	0.099
	Fe	230	196	154	28	780	5.4	210	168	183	41	700	6.0
	K	154	60	138	83	340	7.9						
	Mn	3.1	2.7	2.3	0.55	11.0	0.076	2.7	2.5	2.1	0.180	9.9	0.071
	Mo	1.15	2.1	0.58	0.45	10.2	0.40						
	Ni	20	64	2.5	0.24	320	0.099	21	58	3.0	0.192	290	0.54
	Pb	3.7	4.3	2.6	0.29	21	0.12	2.9	3.5	1.99	0.140	16.6	0.22
	Pt	0.30	0.47	0.189	0.162	2.5	0.078						
	S	530	240	450	196	1130	3.3						
	Se	0.24	0.164	0.197	0.096	0.88	0.031	1.34	0.37	1.32	0.73	1.92	0.190
	Si	280	420	102	92	1820	65						
	Sr	2.5	1.43	2.2	0.49	6.3	0.25						
	Ti	8.7	15.4	2.8	0.61	65	0.158						
	V	1.11	1.29	0.45	0.159	4.3	0.085	1.10	1.18	0.62	0.094	3.9	0.0160
	Zn	7.3	6.9	5.3	0.69	34	0.195	6.8	7.1	5.8	0.32	34	0.81

Table 5: Overview of Tinsley, Sheffield measurements by XACT and ICP-MS (ng m^{-3})

		XACT (ng m^{-3})						ICP/MS (ng m^{-3})					
	species	mean	sd	med	min	max	LOD	mean	sd	med	min	max	LOD
Tinsley, Sheffield (n=60)	As	2.9	4.8	1.35	0.035	33	0.00020	1.50	3.4	0.78	0.019	26	0.037
	Ba	2.6	3.6	1.75	0.98	28	0.31						
	Ca	400	260	370	37	1100	1.11						
	Cd	3.4	0.57	3.3	2.7	6.6	2.4	0.80	1.64	0.32	0.035	11.7	0.0110
	Ce	0.76	0.22	0.73	0.41	1.52	0.135						
	Cl	1370	1100	1140	36	5100	2.1						
	Cr	53	65	30	0.42	350	0.025	55	51	38	3.9	250	1.43
	Cu	17.5	11.0	14.6	2.3	47	0.29	19.3	12.5	16.0	2.6	56	0.099
	Fe	670	440	570	83	1950	5.4	680	420	580	92	1600	6.0
	K	138	92	108	17.0	420	7.9						
	Mn	47	53	32	1.58	290	0.076	41	44	29	1.82	240	0.071
	Mo	15.1	24	7.0	0.65	130	0.40						
	Ni	25	29	14.0	0.22	113	0.099	24	26	13.8	0.99	113	0.54
	Pb	22	23	13.1	1.33	125	0.116	22	22	11.8	1.21	111	0.22
	Pt	0.186	0.017	0.185	0.166	0.28	0.078						
	S	780	670	550	126	3400	3.3						
	Se	0.93	1.30	0.31	0.075	5.5	0.031	1.83	1.62	0.94	0.26	6.2	0.190
	Si	210	150	164	71	780	65						
	Sr	1.15	0.68	1.10	0.41	3.6	0.25						
	Ti	23	36	14.3	1.42	220	0.158						
	V	1.16	2.0	0.60	0.179	12.9	0.085	1.45	1.47	1.02	0.171	9.6	0.0160
	Zn	100	120	58	4.5	620	0.195	101	117	56	3.8	610	0.81

Table 6: Overview of Marylebone Road, London hourly SO_4 measurements in $PM_{2.5}$ by XACT (SO_4* calculated as non-sea salt SO_4 using S and Cl measurements) and ACSM (ng m^{-3}); and hourly SO_4, K, Cl, Ca measurements in PM_{10} by XACT (SO_4 calculated as predicted SO_4 using S measurements) and URG (ng m^{-3})**

		XACT (ng m^{-3})						ACSM (ng m^{-3})					
species	n	mean	sd	med	min	max	LOD	mean	sd	med	min	max	LOD
SO_4*	737	2600	2200	1880	240	10500	n/a	2000	1700	1460	58	8300	35

		XACT (ng m^{-3})						URG (ng m^{-3})					
species	n	mean	sd	med	min	max	LOD	mean	sd	med	min	max	LOD
SO_4**	1045	1750	1210	1450	164	9000	n/a	1040	810	810	54	6500	100
K	776	145	69	133	24	410	6.2	154	42	150	75	380	100
Cl	1045	2700	2400	2100	42	22000	9	1790	1530	1370	132	15000	100
Ca	996	590	490	430	49	2900	3.3	440	300	360	97	2300	100

Table 7: Deming regression results and coefficient of determination for XACT comparison with ICP-MS, separated by HF/HClO$_4$ and HNO$_3$/H$_2$O$_2$ digestions

Element	HF/HClO$_4$			HNO$_3$/H$_2$O$_2$		
	Slope	**Intercept**	**R^2**	**Slope**	**Intercept**	**R^2**
As	2.0 (1.49-2.6)	-0.33 (-0.65-0)	0.95	3.8 (1.90-5.7)	-0.23 (-0.49-0.020)	0.90
Ba	1.04 (0.73-1.35)	-1.50 (-4.8-1.79)	0.98			
Ca	1.14 (0.84-1.45)	-9.2 (-31-13)	0.70			
Cr				0.99 (0.92-1.06)	-1.70 (-2.6--0.79)	0.95
Cu	1.31 (1.05-1.57)	0.29 (-3.1-3.7)	0.93	0.95 (0.92-0.98)	-0.03 (-0.22-0.17)	0.89
Fe	1.26 (0.65-1.87)	-1.29 (-220-210)	0.89	1.03 (0.99-1.07)	-10 (-18.19--2.0)	0.96
K	1.03 (0.92-1.15)	-1.23 (-14.83-12.37)	0.96			
Mn	1.28 (0.70-1.86)	0.050 (-1.97-2.1)	0.92	1.10 (1.07-1.14)	0.17 (0.020-0.32)	0.99
Ni	0.73 (0.48-0.98)	-0.20 (-0.45-0.05)	0.67	1.07 (1.00-1.14)	-1.21 (-1.64--0.77)	0.99
Pb	1.44 (1.31-1.57)	0.140 (-0.37-0.65)	1.00	1.02 (0.99-1.06)	0.36 (0.10-0.61)	0.99
Se				0.83 (0.73-0.94)	-0.45 (-0.57--0.33)	0.67
Sr	1.25 (1.14-1.36)	-0.0100 (-0.19-0.17)	1.00			
Ti	1.44 (0.68-2.2)	0.91 (-0.42-2.2)	0.72			
V				0.87 (0.74-1.01)	-0.130 (-0.22--0.04)	0.89
Zn	1.62 (1.17-2.1)	-4.4 (-13.15-4.5)	0.50	1.04 (0.98-1.09)	0.37 (-0.58-1.31)	0.94

9 Copyright statement

Authors retain the copyright of the article.

All authors grant Copernicus Publications an irrevocable non-exclusive licence to publish the article electronically and in print format and to identify itself as the original publisher. Further, the authors grant Copernicus Publications commercial rights to produce hardcopy volumes of the journal for sale to libraries and individuals. The authors also grant any third party the right to use the article freely as long as its original authors and citation details are identified.

10 Data Availability

ICP-MS measurements on filters made at Pontardawe and Sheffield are available from https://uk-air.defra.gov.uk/data/metals-data. Additional datasets are available upon request to the corresponding author.

11 Supplement link

The Supplement related to this article is available online at <enter link when available>

12 Author Contribution

Anja H. Tremper - experiment design (XACT filter analysis), field and laboratory experiments, data ratification and analysis, manuscript preparation with contributions from all co-authors

Anna Font - field experiments and data analysis

Max Priestman - field experiments and ACSM data ratification

Samera H Hamad - field experiments (Marylebone Road)

Tsai-Chia Chung - laboratory experiments (calibration test of Cl, K and S)

Ari Pribadi - laboratory experiments (filter analysis)

Richard J. C. Brown - uncertainty calculations

Sharon L. Goddard - filter analysis (Wales/Sheffield)

Nathalie Grassineau - filter digestion (Marylebone Road)

Krag Petterson - technical input for XACT

Frank J. Kelly – manuscript review

David C. Green - experiment design (laboratory calibration test), field and laboratory experiments, uncertainty calculations, manuscript overview

13 Competing interests

Krag Petterson is employed by Cooper Environmental Services, the manufacturer of the instrument, and had input into the manuscript preparation from a technical perspective.

14 Disclaimer

This manuscript has not been published and is not under consideration for publication elsewhere.