

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 (SO₄), 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 - 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).