Anonymous Referee #3

Recommendation: Major revision

General Comments:

Manuscript entitled “Application of TXRF in monitoring trace metals in particulate matter and cloud water” measured the concentrations of trace metals in the particulate matter and cloud water using a highly sensitive surface technique TXRF. The authors compared the influence of different ˇ factors such as digestion procedure, filter baking, and plasma ashing on the measurement of trace metals. This is a useful fundamental work to improve the application of TXRF. However, I have several major concerns about the manuscript, besides the writing of this manuscript. Therefore, I think this manuscript needs substantial revisions.

We thank the reviewer for the comments that have enable us to improve on the manuscript. In the following, we have addressed these concerns in a point-by-point format.

Specific Comments:

1. If the quartz fiber filters also need digestion procedure to conduct TXRF analysis, what is the advantages of TXRF compared with ICP-MS? We know the digestion procedures waste the most time, if the digestion procedure id required, why don’t I choose the ICP-MS. I think the precision of ICP-MS is much higher than TXRF. If there is a possibility that the TXRF can analyze the quartz fiber filters directly without digestion procedure? I think this may be the advantage of TXRF.

The presently available quartz fiber filters are unfortunately too thick (> 10 µm) to be analyzed directly by TXRF, as the thickness of the filter prevents the total internal reflection of the X-ray on TXRF carrier surface, thereby increasing the attenuation of the signal and can furthermore destroy the detector. If thinner quartz fiber filters are available, they can be measured directly with the TXRF without digestion, as it is the case with the Teflon or polycarbonate filters. As demonstrated in the manuscript, PM collected on polycarbonate foils do not require any digestion procedure as presented for the SRM2783standard reference material and for size-resolved aerosol samples. Using the ICP-MS, these filters would have to be digested, which presents the advantage of the TXRF over the ICPMS, as despite its higher precision to TXRF, ICP-MS always requires digestion of the filters since it is adapted for analyzing mainly liquid samples. Using thin filter material, TXRF provides a digestion free, high precision alternative to ICP-MS, especially for samples with very little PM mass concentrations such as size-resolved PM samples.

A corresponding sentence has been added on L100-102 “*In addition, the thickness of the quartz filters increases the attenuation of the X-ray signals when measured directly* (Klockenkamper and von Bohlen, 2014) *requiring thinner filters as those currently commercially available.”*

2. The figures in the manuscript need to take more time to make them more beautiful.

The figures in the manuscript have been improved. Figures 3 and 4 were modified. The regression lines in figure 3 were replaced with a 1:1 line. Figure 4 was modified to have the same format as the other figures with the correct legends.

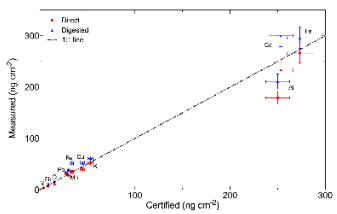


Figure 3

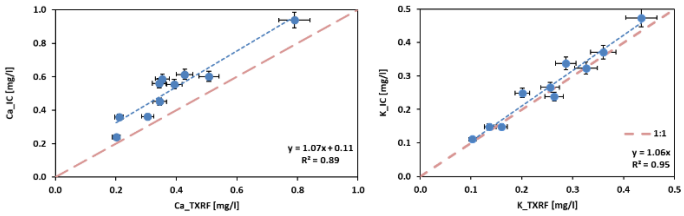


Figure 4

Line13: I think it is better to modify the sentence "Ambient particulate matter and cloud trace metals are considered key elements" to "Trace metals in ambient particulate matter and cloud are considered key elements" to avoid the ambiguity.

The correction has been done and the sentence now reads as suggested. "Trace metals in ambient particulate matter and cloud are considered key elements"."

4. Line31: "Backing" should be "Baking". This mistake occurs at many places in the whole manuscript, please pay attention.

This spelling errors have been corrected through out the manuscript

5. Line48: Please modify the sentence "Aerosols and cloud water trace metals" to avoid ambiguity.

Line 48 has been modified to read *"Trace metals in aerosols and cloud water play an important role in defining aerosol and cloud physicochemical properties as they control key reactions within these media."*

6. Line 124-125: The symbol Ga and Y should provided in a parentheses following Gallium and Yttrium.

The chemical symbols of Ga and Y have been added beside their names. Lines 126 now reads *"Internal standards consisting of Gallium (Ga) inductively coupled plasma (ICP) standard solution with the concentration of 1000 mg/l (Merck, Germany) and Yttrium (Y)…"*

7. Line 173: if the diameter of the spot is 8 mm, the area should be 0.5 cm2, please to check.

The correct area of 0.5 cm^2 has been included. Thank you

8. Line 206: Please use the right symbol but not the letter x in "2 x 25"

"2 x 25 " has been replaced by *"… and 25 ml of the sample pipetted twice onto polished… "*

9. Line 209: how the authors get the filed blanks of cloud water samples? Should clarify in the method section.

The blank collection procedure has been added on L 159-161 and now reads:

"For the collection of the cloud water blanks, the CASCC2 strands were cleaned with deionized water and ethanol, and deionized water was thereafter sprayed onto the cleaned strands and the resulting droplets were collected and used as blanks".

10. Line 210- 215: the authors add 5 µl of concentrated nitric acid in the size-resolved samples, but why not for the SRM standard?

The same procedure was performed on the SRM. A corresponding sentence has been added on line 218-219

"…subsequent spiking with an internal standard, and 5µl of concentrated nitric acid similar to the procedure used for the size-resolved samples."

11. Line 222-223: "The maximum values of the measurements were then used for further analysis" if I have not left it out, I did not see the further analysis the whole manuscript.

This sentence has been changed as it seems misleading. Line 222-223 now reads,

" The maximum values of the measurements were then used for subsequent analysis"

12. 13. Line 28: what is the "as a total number" meaning? I can understand what the authors want to express, but the expression is not appropriate.

Unfortunately, we could not identify the phrase "as a total number" on line 28 in the manuscript.

14. Line 109: what is the spin-up period meaning?.

Unfortunately, we could not identify the phrase "spin-up period" on line 109 of the manuscript.

15. Line 120-122: According to the example in the parentheses, the word "attributed" should be "convert"? But the authors should indicate why conduct this process? And "In the second simulation, the module marked chemical production regions of SIA", According to what, the authors can judge "the chemical production regions of SIA".

Unfortunately, we could not identify this phrase "In the second simulation, the module marked chemical production regions of SIA" in any section of the manuscript and, simulations were not performed in this study.

16. Line 226: why only 18 elements were analyzed, as you know, the standard has 28 elements.

The standard had 28 elements but the PICOFOX instrument can detect only 23 elements in this standard. The other 5 elements of the standard including Li, B, Be,Na, Mg cannot be determined by TXRF. A corresponding sentence has been added.

Lines 142-143 now reads *"…with a concentration of 100 mg/l for 28 elements (23 detectable with TXRF, excluding lighter elements such as Li, B, Be, Na. Mg) were purchased from Sigma Aldrich, Germany and C.P.A. Ltd, Bulgaria, respectively."*

The 18 elements that were analyzed where those that were identified in the samples. Elements such as Co, Cd, Ag, Bi, As, Se, were not often observed in all the samples, leading to mainly.

L 226 now reads "*Typically about 18 elements or more were analyzed based on their abundance in the PM and cloud water field samples."*

17. Line 229: Please make the equation more beautiful. For Nnet and Nback, I do not understand what is the count rate meaning?

N_{net} and N_{back} are the x-ray signal counts of the sample and the background signals, respectively. These values are used in determining the signal to noise ratio of an element and in assessing its limit of quantification.

A corresponding sentence has been included in Line 238 to read: *"…N_{back}, background count rate of the fluorescent X-ray signal".*

3. σblank, please write the equation correctly.

The equation is now written in Line 239 as: "$3\sigma_{blank}$"

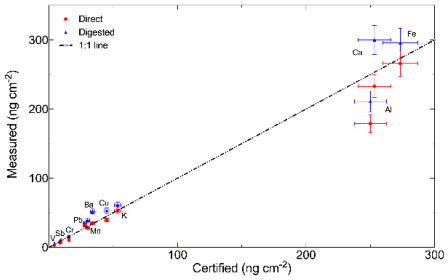
18. Line 251-252: "In the absence of certified metal concentrations on quartz fiber filters" if it is the blank filters used?

Yes, it was a blank filter that was used. A corresponding line has been added to the manuscript.

Line 260 now reads *"In the absence of certified metal concentrations on quartz fiber filters, an 8 mm diameter area of a bank filter …"*

19. In my opinion, Figure 3 is not the proper type to present the data. It is not proper to do the linear regression analysis for different elements. It is suitable for different concentrations with the same element.

The dotted line is not a regression line. It was plotted to indicate the 1:1 line between the measured and certified values. The lines have been removed and only one plotted to indicate this as shown in the new figure 3 below.



20. Line 355: the authors mentioned the results of nighttime and daytime samples, I think the related figures or tables should be provided.

The nighttime and daytime concentrations have been added as a new table 6. And a corresponding line has been included in the text. Line 375-381 now reads: *"Indeed, the variation of the elemental concentrations between daytime and nighttime samples was often less than 5% as illustrated in Table 6. Elements such as Pb, V, Ni, and Cu, showed an increase during the nighttime measurements in comparison to the daytime measurements. This indicates that these elements could have had a small nighttime source from the nearby cities and the changing air mass inflow to the mountains at nighttime. Ca, Al, Ti, K, and Fe were higher during the daytime which was coincidental as most dust events were stronger during daytime than nighttime."*

21. Line 358 and 371: "long-range transport from nearby cities" I think it is contradictory. When the authors discussing the source of the pollutant, I think it is better to air mass backward trajectories.

This statement has been improved. The expression of Long-range transport has been removed as it is misleading.

Line 378 now reads: "This indicates that these elements could have had a small nighttime source from the nearby cities due to the changing air mass inflow to the mountains at nighttime.

Line 395-396 now reads; *"This could be partly due to interference of Sb signal with the high Ca signal in the samples as well as the different sources in the respective regions."*

22. I am very confusing about Table 2. The content in the manuscript and in the Table were not consistent. Besides, for element Co, Cd, and Al, though their concentration below the LLD, their LLD must be exist.

The inconsistency between the table values and those in the manuscript has been resolved. The correct values are now included in the text.
The reviewer is correct that the LLD of Co, Cd and Al were missing. These elements were not detected in the blank filters and, therefore, their LLD were not determined and provided by the instrument. The bdl was in this case misleading and has been removed from the table.
It id funny that the authors compared their data with Upadhyay et al. 2009, how can the authors know it is because of the application of HF lead to the increase of the blank for elements such as Ca, Ti, Fe, but not the different blank filters?

Our comparison with Upadhyay et al, is because they also analyzed blanks of different quartz filter batches for their trace metal concentrations. Since similar quartz filters were used, we assume that the differences in our values are related to the different digestion procedures used as it is known that different digestion procedures may lead to different elemental concentrations (Cullen et al.1999, Buck et al. 2012). We have added a line to indicate that the differences may also arise from the different filter batches used in the studies.
Line 300-301 now reads "*The differences between these studies may also be due to the use of the different filter material used the various studies. However, the use of HF has often been associated with high blank values for quartz filters (Buck and Paytan, 2012;Cullen and Sherrell, 1999).*"

23. Line 455: the authors only compared their results with some European regions, I think more comparison should be made with the heavily polluted region, such as China and India.

Reference:

Li, W.; Wang, Y.; Collett, J. L.; Chen, J.; Zhang, X.; Wang, Z.; Wang, W. Microscopic evaluation of trace metals in cloud droplets in an acid precipitation region. Environ. Sci. Technol. 2013, 47, (9), 4172-4180.
Liu, X.; Wai, K.; Wang, Y.; Zhou, J.; Li, P.; Guo, J.; Xu, P.; Wang, W. Evaluation of trace elements contamination in cloud/fog water at an elevated mountain site in Northern China. Chemosphere. 2012, 88, (5), 531-541.

Liu, L.; Zhang, J.; Xu, L.; Yuan, Q.; Huang, D.; Chen, J.; Shi, Z.; Sun, Y.; Fu, P.; Wang, Z.; Zhang, D.; Li, W. Cloud scavenging of anthropogenic refractory particles at a mountain site in North China. Atmos. Chem. Phys. 2018, 18, (19), 14681-14693.

Table 7 (Now Table 8) has been extended to contain the concentrations of other mountain regions in China and the United States to provide a broader comparison of the observed concentrations of this study as recommended. A corresponding description has been included in the text.

Lines 488-497 now reads "*Similarly the concentrations were lower than those observed at Mt. Elden in Arizona (Hutchings et al., 2009). Despite the differences in the mean concentrations, the reported concentrations of this study are within the range of concentrations observed in other regions in Europe and the USA. The differences in the absolute values are related to the different sample collection locations. In comparison to measurements performed in regions in China, the trace metal concentrations in this study was significantly lower. Liu et al., (2012), reported concentrations of Zn (249.1 µg/l), Mn (42.84 µg/l), Fe (108.8 µg/l), Pb (46.2 µg/l) at Mt. Tai which are*

more than an order of magnitude higher than those at the Atlas mountain. Similar high concentrations were also reported at Mt. Heng in china (Li et al., 2017), Zn (224.6 µg/l), Pb (100.5 µl), As (19.9 µg/l) indicating a strong contrast in the trace metal levels in cloud water in Northern Africa mountain regions as compared to more polluted regions in China."

24. Line 474: why the author choose Ti as a reference element to calculate the EF? More explanation should be provided here.

Ti is amongst the abundant elements in the earth's crust and does not have many anthropogenic sources as iron or Aluminum making it a good proxy for crustal matter (Lawson et al. 1967). Hence, Ti has been used as a reference element for crustal matter in other studies (Shelley et al. 2015, Buck et al. 2019), indicating its acceptance in the community as a proxy. A corresponding sentence has been included in the text line 474 now reads

"Ti was used as the reference element for crustal matter as it had a higher recovery to Al and has been used in many studies as its anthropogenic sources are few (Shelley et al. 2015, Buck et al. 2019)".

References:

Buck, C. S., and Paytan, A.: Evaluation of commonly used filter substrates for the measurement of aerosol trace element solubility, Limnol Oceanogr-Meth, 10, 790-806, 10.4319/lom.2012.10.790, 2012.

Buck, C. S., Aguilar-Islas, A., Marsay, C., Kadko, D., and Landing, W. M.: Trace element concentrations, elemental ratios, and enrichment factors observed in aerosol samples collected during the US GEOTRACES eastern Pacific Ocean transect (GP16), Chem Geol, 511, 212-224, 10.1016/j.chemgeo.2019.01.002, 2019.

Cullen, J. T., and Sherrell, R. M.: Techniques for determination of trace metals in small samples of size-fractionated particulate matter: phytoplankton metals off central California, Mar Chem, 67, 233-247, Doi 10.1016/S0304-4203(99)00060-2, 1999.

Hutchings, J. W., Robinson, M. S., McIlwraith, H., Triplett Kingston, J., and Herckes, P.: The Chemistry of Intercepted Clouds in Northern Arizona during the North American Monsoon Season, Water, Air, and Soil Pollution, 199, 191-202, 10.1007/s11270-008-9871-0, 2009.

Shelley, R. U., Morton, P. L., and Landing, W. M.: Elemental ratios and enrichment factors in aerosols from the US-GEOTRMES North Atlantic transects, Deep-Sea Res Pt Ii, 116, 262-272, 10.1016/j.dsr2.2014.12.005, 2015.

Li, T., Wang, Y., Zhou, J., Wang, T., Ding, A. J., Nie, W., Xue, L. K., Wang, X. F., and Wang, W. X.: Evolution of trace elements in the planetary boundary layer in southern China: Effects of dust storms and aerosol-cloud interactions, J Geophys Res-Atmos, 122, 3492-3506, 10.1002/2016jd025541, 2017.

Liu, X. H., Wai, K. M., Wang, Y., Zhou, J., Li, P. H., Guo, J., Xu, P. J., and Wang, W. X.: Evaluation of trace elements contamination in cloud/fog water at an elevated mountain site in Northern China, Chemosphere, 88, 531-541, 10.1016/j.chemosphere.2012.02.015, 2012.