Review1

General comments

The article presents the study and comparison of some methods for the analysis of metal elements in ambient particulate matter and clouds by total reflection X-ray fluorescence (TXRF). It is well written even if some sections (like Abstract and Materials and Methods) needs some clarifications and precision. All the values given in the text (and tables) need some checking. The results are very interesting and can help for various applications in atmospheric pollution science.

We thank the reviewer for his comments and recommendations, which has enable us to improve on the manuscript. We have responded to the comments and concerns in a point-by-point basis below.

Specific comments

P1. The abstract. It needs to be improved. The introduction of the abstract is too long. The methods used are presented but with some confusion. There is no result of the methods.

The abstract has been significantly improved. The introduction has been shortened to 2 sentences.

P1 L13-16 now reads "Trace metals in ambient particulate matter and cloud are considered key elements of atmospheric processes as they affect air quality, environmental ecosystems and cloud formation. However, they are often available at trace concentrations in these media such that their analysis requires high precision and sensitive techniques. "

The methods have been explained concisely and have been described in L18-24

"These methods considered the measurement of filter samples directly without and with chemical pretreatment. Direct measurements involved the analysis of PM samples collected on polycarbonate filters and cloud water samples after they are brought onto TXRF carrier substrates. The chemical treatment method involved the assessment of different acid digestion procedures on PM sampled on Quartz filters. The solutions applied were reverse aqua regia, nitric acid and a combination of nitric acid and hydrogen peroxide. The effect of cold-plasma treatment of samples on polycarbonate filters prior to TXRF measurements was also investigated."

The results of the methods and the study are now included in lines. L26-30.

"Digestion with the reverse aqua regia solution provided lower blanks and higher recovery in comparison to other tested procedures. The detection limits of the elements ranged from 0.3 to 44 ng/cm². Ca, K, Zn, and Fe showed the highest detection limits of 44, 35, 6 and 1 ng/cm² while As and Se had the lowest of 0.3 and 0.8 ng/cm², respectively. The method showed higher recovery for most trace metals when applied to commercially available reference materials and field samples"

Lines P1 L 31-34

"Cold plasma treatment did not significantly lead to an increase in the detected concentration and the results were element-specific. Baking of the quartz filters prior to sampling showed a reduction of more than 20% of the filter blanks for elements such as V, Sr, Mn, Zn, Sb"

Lines 36-39

"The obtained concentrations were within the range reported using different techniques from similar remote and background regions elsewhere, especially for elements of anthropogenic origins such as V, Pb, and Zn with concentrations of up to 10, 19 and 28 ng/m³, respectively."

P2. L70. The Energy Dispersion X-ray fluorescence is also used for the analysis of PM (e.g. Kchih et al. (2015) Aerosol and Air Quality Research, 15, 454-464). In order to be exhaustive, you can add this method in your list.

The similarities and differences with the Energy dispersion X-ray fluorescence has been highlighted and discussed. Line P2. L72 now reads "*The TXRF is a highly sensitive surface technique, which is a variation of the energy-dispersive X-ray fluorescence (XRF) Kchih et al 2015), designed such that the X-ray beam is incident at a glancing angle on a polished substrate to enable a total internal reflection of the incident beam at its surface*"

P3.L80. You did not present the Ion Chromatography system, only the TXRF spectrometer is presented here. You are comparing the results of both methods p9 so both instruments should be presented here.

The Ion Chromatography system has been introduced amongst the instruments and P3 L81-83 now reads "*As with other established methods for cloud water analysis such as ICP-MS, ICP-OES as well as AAS (Xu et al., 2018) and also ion chromatographic techniques for cations and transition metal ions (Fomba et al. 2015), sample preparation steps are few and fast.*"

P4.L138. Please mention that you freeze the cloud samples. The freezing sometimes have an impact on the results as it is the case for Ca: its freezing induces the formation of insoluble $CaCO_3$ (Cherif et al. Environmental Pollution 103 (1998) 301-308). It is important when you use ionic chromatography (IC) and analyze the soluble phase, the concentrations will therefore be less than expected. As you compared here analysis with IC and TXRF, this point could be important.

We thank the reviewer for this important hint about the effect of freezing. The aspect of freezing has been added to the manuscript. P5 L 159 now reads "*The cloud water volume ranged between 30 and 150 ml and the samples were frozen immediately after sampling.*" *Although freezing may induce the formation of insoluble carbonates e.g. $CaCO_3$ in the sample as indicated by Cherif et al., (1998) the freezing help prevent microbial decomposition of organics and subsequent chemical reactions in the samples*.

P5.L154-155. "For these measurements, quartz sample carriers were used due to the high abundance of silicon on the filters." I cannot understand what do you mean with this sentence, as you already mentioned that the filters where siliconized (p3 L105-107: "Sample carriers were, thereafter, siliconized by 5 µl of a silicon solution in isopropanol (Merck, Germany) to avoid the spreading of the samples on the surface of the carriers."). Please add more information if you meant something additional regarding this sentence.

This was to indicate that the TXRF carrier used for the sample preparation and measurement was of quartz, which is the same material as the filters. However, we realized the sentence was not clear. The sentence has now been restructured to highlight this point.

P5 L195-196 now reads "* For these measurements, quartz TXRF sample carriers were used and their surfaces siliconized as previously described*".

P5. L157-159. " In a clean bench, the polycarbonate membranes from the five-stage ˇ cascade impactor were cut according to the number of impaction spots on the filters. For St. 1 to St. 5, filter pieces with

six, three, two, one, and one, spots were cut-out, respectively. " Please rewrite this sentence, it is not understandable.

The sentence has been rewritten. P6 L 197-199 now reads
"In a clean bench, a defined area of the polycarbonate filters collected with the five-stage cascade impactor were cut out. The cut-out filter area contained six, three, two, one, and one, impaction spots corresponding to the filters of St. 1 to St. 5, respectively."

P7. L250-251. " Figure 4 shows a TXRF spectrum of a bulk PM10 aerosol sample indicating some elements that were identified in the sample with the PICOFOX C2 instrument." Please specify the origin of the sample that is described in this figure. A suggestion: "Particulate matter PM10 samples collected at the AM5 station and measured with TXRF with the Mo-excitation anode are analyzed for their metal elements (Figure 4).

The origin of the sample has been specified. The sentence P10 L350-351 now reads "*Particulate matter PM10 samples collected at the AM5 station and measured with TXRF with the Mo-excitation anode are analyzed for their metal elements (Figure 5)*

P7. L253. Did you adjust the values obtained for the real samples with the percentage of recovery from the standards? Would it be justified and more accurate?

The real sample data were not adjusted with the recovery values since the samples were collected under different conditions as the spiked sample. However, this could be done to show the highest possible concentration that could be obtained without recovery lost. Nevertheless, this will not change the abundance or trends as already described.

An additional note has been made on L275-278: "*For the field samples, the values of Al was not adjusted with the percentage of recovery as the sample composition and adhesion of the particles on the filters are different, which could lead to an over estimation of the values. "*

L8. L265-271. & P9. L310-311. Why don't you also compare to closer and similar regions? There is a study in Northern Africa on the composition of PM10 and PM2.5 for elements, ions and source apportionment that points out the influence of Sahara dust on PM composition (Kchih et al. 2015: Investigation of desert dust contribution to source apportionment of PM10 and PM2.5 from a southern Mediterranean coast. Aerosol and Air Quality Research, 15, 454-464.).

Comparison with a study close to the sample region such as that of Kchih et al., has been done.

Lines 382-385 now reads: "*In comparison to concentrations reported for different locations in Tunis, Tunisia (Kchih et al., 2015), the values in this study were similar for elements such as K, Cr, Cu, Mn, Ni, V and Zn. Lower values for Ca (<10µg/m³), and Pb (< 2µg/m³) as well as higher values for Fe (<0.7 µg/m3), Al (<0.6 µg/m³), and Ti (0.08µg/m³) were observed."*

L8.L272-273. "The particulate matter mass concentration during the sampling period was up to 145 µg/m3, indicating a strong influence of Saharan dust." Could you explain how do you conclude to a strong influence of Sahara dust according only to the mass concentration value?

The influence of Sahara dust was deduced from the color of the filter samples, which were reddish-brown, compared to the other days, Southwest winds and the air mass trajectories that indicated that the air mass that arrived at the site during this period crossed over the Saharan desert.

Lines P10 L 399-400 now read: "*Based on the reddish-brown color of the filters, the predominant southwest winds and back trajectory information, this high concentrations were indicative of a strong influence of Saharan dust*"

P8. L279-282. "For Cu and Sb, the 12.08.2017 and 26.08.2017 were the days with the highest and lowest concentrations, respectively. Air mass trajectory investigations indicated that during these days, air mass from the Saharan desert passing through urban cities arrived at the AM5 site, while on the 26.08.2017 and 21.08.2017 the air masses mainly originated from the cities with little influence of Saharan dust." There is a confusion here. First, you talk about 26.08.2017, and mention that the air mass arrived from Sahara desert, and the next sentence, for the same date, the air mass originates from cities with no Sahara influence. Please chack and correct.

The sentence structure was misleading and the has now been restructured and complemented.
L 384 now reads "*… For other elements such as Cu, Zn, and Sb, the 12.08.2017 and 13.08.2017 were the day with the highest concentrations while the 21.06.2017 and 26.08.2017 were the day with the lowest concentrations. Air mass trajectory investigations indicated that on the 12.08.2017 and 13.08.2017, air mass from the Saharan desert passing through urban cities arrived at the AM5 site, while on the 21.08.2017 and 26.08.2017 the air masses mainly crossed over the cities without passing over the Sahara.*"

P8. L283-284. "Elements such as Ca, Al, Ti, Fe showed similar temporal variation of their concentrations similar to Cu, Sb, and Zn." This sentence is not clear. In any case, Fig6 does not show any similar temporal variation of Ca, Al, Ti and Fe. Cu, Sb and Zn C3 are not on the figure at all. Please check the conclusion for the elements shown in Fig 6. And add the other elements if necessary.

The misrepresentation of the figure has been identified and clarified. Indeed, the figure does not show the time series of Cu, Sb, Zn or Pb for the sake of simplicity, since these concentrations are far lower than those of Ca, Al, or Ti. Hence, the sentence relating to their similar temporal variation has been edited the conclusion rephrased.

L413-415 now read: "*Elements such as Al, Ti, Fe, K showed a similar temporal variation of their concentrations especially during the periods of intense dust influence while Ca variation was different after the dust event indicating other source influence on its concentration. These similarities amongst the other elements are indicative of their similar origins either relating to their emission sources or their air mass inflow characteristics.*"

P8. L287. "Typically, Ca, Al, Ti, and Fe are elements with high crustal abundance". How can an element be with crustal abundance ? Are you talking about correlation ? Or crustal composition ? Perhaps you mean "Typically, Ca, Al, Ti, and Fe are elements associated with high crustal abundance" ? Please specify.

The sentence has been changed and now reads "*Typically, Ca, Al, Ti, and Fe are elements associated with high crustal abundance*"

Additionnaly, is really Ti associated with crustal matter?

Ti is also associated with crustal matter and it is often used as a maker for crustal matter in particulate matter just as Al (Buck et al, 2019). An additional sentence has been included on line 508-510

"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)."

Technical comments

General : in the text, sometimes, when you cite a figure, you write Figure and some- ˇ times Fig. Please homogenize.

According to AMT template, "The abbreviation "Fig." should be used when it appears in running text and should be followed by a number unless it comes at the beginning of a sentence, e.g.: "The results are depicted in Fig. 5. Figure 9 reveals that...".

The manuscript is now homogenized following this procedure.

 P1. L23. L24. " This method takes into account... ˇ a. It involves" You talk about all ˇ the methods you present in the article so we suggest to write : " ˇ aThese methods ˇ take... . They involve...". L27 you already come back with the plural.

This line has been edited and L18 now reads"

"These methods considered the measurement of filter samples directly without and with chemical pretreatment.

 P1. L24-26. " It involves trace metal analysis of particulate matter collected on poly- ˇ carbonate and quartz fiber filters, as well as cloud water, analyzed through direct pipetting on TXRF carrier substrates as well as analysis of aliquots of acid digested particulate matter filters" Here, you talk first about PM than about cloud water than again ˇ ab out PM. Something is not clear. Please check, because the end of the sentence in not understandable ("as well as analysis of aliquots of acid digested particulate ˇ matter filters.) ˇ

This line has been edited and L19-20 now reads"

"Direct measurements involved analysis of as collected polycarbonate and cloud water samples after they are brought onto TXRF carrier substrates.""

 P2. L59-60. as well as As, V, Ni for coal and fuel combustion, respectively". ˇ Here, you itemize three metals but too origins, respectively. It is not possible with this sentence to attribute the metals to their origin in this way. Please check this sentence.

This line has been removed.

P2.L65-66. Understanding trace metal composition and their effects in these media, ˇ require sensitive techniques that can quantify the typically low concentration levels of metals, in these media over a wide range of particle sizes. The places of the ˇ C4 commas are not adequate. I suggest: "

Understanding trace metal composition and ˇ their effects in these media require sensitive techniques that can quantify the typically low concentration levels of metals in these media, over a wide range of particle sizes. ˇ

Correction has been done. Thanks. L63-64 now reads as suggested.
"Evaluating the trace metal composition and their effects in these media require sensitive techniques that can quantify the typically low concentration levels of metals in these media, over a wide range of particle sizes."
P2.L65-70. " Studies have shown that although ICP-MS (Inductively Coupled Plasma ˇ Mass Spectrometry), ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy), AAS (Atomic Absorption Spectroscopy), are sensitive techniques, most often, a larger amount of sample substance is necessary for adequate sample preparation and handling. ". The places of the commas are not adequate, in place of ˇ of the third comma put " and ˇ a". Add a space after " Inductively ˇ a". I suggest:
ˇ "Studies have shown that although ICP-MS (Inductively Coupled Plasma Mass Spectrometry), ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) and AAS (Atomic Absorption Spectroscopy) are sensitive techniques, most often a larger amount of sample substance is necessary for adequate sample preparation and handling. ˇ Everywhere: Please choose one sole abbreviation for Liter, L or l, for the sake of uniformity (text, tables and figures).

Correction has been done. L64-66 now reads as suggested. *"Studies have shown that although ICP-MS (Inductively Coupled Plasma Mass Spectrometry), ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) and AAS (Atomic Absorption Spectroscopy), are sensitive techniques, most often a larger amount of sample substance is necessary for adequate sample preparation and handling"*

P4. L147. "The main objective of digestion was to be wash-off the particles at the surface..." would better be "The main objective of the digestion was to wash-off the particles from the surface..."

Correction has been done. L 198 now reads as suggested. Thank you. *"The main objective of the digestion was to wash-off the particles from the surface"*

P5. L170. "Similar methods were applied to the standard reference material as was used on field samples." would better be "Similar methods to those used on field samples were applied to the standard reference material."

Correction done. P5 L 223 . now reads as suggested. *"Similar methods to those used on field samples were applied to the standard reference material."* Thank you.

P6. L199. "...obtained with the LPA multi-element standard solution..." Do you mean "obtained with the CPA multi-element standard solution" ?

Yes, this was a typo error. LPA has been replaced with CPA on P7 L251 on the revised manuscript.

P6.L193. "The reference materials were measured using the.." In order to avoid confusion, it would be better to specify "The reference materials NIST(SRM) were measured C5 using the..."

The correction has been done and P7 L248 now reads *"The reference materials NIST (SRM) were measured using the S2-PICOFOX and the values obtained were compared with the certified values provided by NIST."*

P6.L216-217. "the lower recoveries were observed for As, Ti, Sb, and Se". There lower recoveries also for Al and Ag. Please add them to the list.

P7 L258 now reads "lower recoveries were observed for As, Ti, Sb, Ag, and Se"

P7.L244-245. "Likewise, the method MDL with the digestion method was higher than that observed for the polycarbonate membranes." You probably mean: "Likewise, the limit MDL with the digestion method was higher than that observed for the polycarbonate membranes."

This sentence has been corrected. L459 now reads *"… the limit MDL with the digestion method is low for most elements in the blank filters except for Ca and Zn in the polycarbonate membrane, and Ca, Zn, and K for the quartz fiber filters."*

P7.L248 to 326. This section is presented as a description of the figures. As the figure is first cited at the beginning of each paragraph than described. The references to the figures would better be in a text (as Figure X) describing the results. (e.g. "3.2.1. Bulk aerosol samples Figure 4 shows a TXRF spectrum of a bulk PM10 aerosol sample indicating some elements that were identified in the sample with the PICOFOX instrument. Figure 5 shows box plots of the identified particulate matter trace metal concentrations at the AM5 station during August and early September 2017. . ..")

P10 L 367 now reads "*Particulate matter PM10 samples collected at the AM5 station and measured with TXRF with the Mo-excitation anode were analyzed for their metal elements (Figure 5).*"

P10 L 369now reads "*Figure 6 shows box plots of the identified particulate matter trace metal concentrations at the AM5 station during August and early September 2017*"

P8. L296. "The difference between the least and the abundant elements..." I think there is a 'most' missing. So the sentence would be : "The difference between the least and the most abundant elements..."

The word most has been added to the sentence as suggested on L 396 "*The difference between the least and the most abundant elements...*"

P8. L293-296. & P10. L341-343. Please check the values that you give. They do not correspond to the values in Table 3 and Table 4, respectively.

The values in the text have been corrected to match with the values in the table.

P10. L375. *"...with very negligible particulate matter rest on the filter"* would better be: "with very negligible particulate matter remaining on the filter".

The word "rest" has been replaced by "remaining" as suggested on P12 L 454

P11.L379. "...elements to improve on their quantification in the given..." would better be: "...elements to improve their quantification in the given..."

The word "on" has been deleted as suggested on P12 L 458 now reads "*…typical recoveries of the required elements to improve their quantification in the given matrix*"

P15.L521. Table1. In the first line of the table, "Certified" should be aligned with the second "Mean" in order to avoid confusion. C6 P17.
The word "Certified " is now aligned with the word "Mean"
Table 3. Why do you specify the cut off only for the first stage ? It would be better to delete it.

The cut off on stage 1 has been deleted

References:

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.

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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.

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