

Interactive comment on “Application of TXRF in monitoring trace metals in particulate matter and cloud water” by Khanneh Wadinga Fomba et al.

Anonymous Referee #2

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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.

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

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methods.

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.

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.

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 CaCO₃ (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.

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.

P5. L157-159. “În a clean bench, the polycarbonate membranes from the five-stage 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.

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

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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).

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 ?

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.).

L8.L272-273. “The particulate matter mass concentration during the sampling period was up to 145 $\mu\text{g}/\text{m}^3$, 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 ?

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 check and correct.

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

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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.

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. Additionally, is really Ti associated with crustal matter ?

Technical comments

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

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

P1. L24-26. “It involves trace metal analysis of particulate matter collected on polycarbonate 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 about PM. Something is not clear. Please check, because the end of the sentence is not understandable (“as well as analysis of aliquots of acid digested particulate matter filters.”)

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

P2.L65-66. “Understanding 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.” The places of the

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commas are not adequate. I suggest: “Understanding 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 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 the third comma put “and”. Add a space after “Inductively”. I suggest: “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.”

Everywhere: Please choose one sole abbreviation for Liter, L or l, for the sake of uniformity (text, tables and figures).

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...”

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.”

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

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

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using the...”

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.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.”

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. ...”)

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...”

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.

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

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

P15.L521. Table1. In the first line of the table, “Certified” should be aligned with the second “Mean” in order to avoid confusion.

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P17. Table 3. Why do you specify the cut off only for the first stage ? It would be better to delete it.

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