Response to comments of Referee #2

We would like to thank Referee #2 for his valuable and thoughtful comments, which helped us to improve the content and quality of our manuscript. In the following we have addressed all the comments of the Referee #2 and incorporated changes in the manuscript as follows:

Blue: Comments of the Referee

Black: Answers of Authors

Black, italic, "": "Changes in the manuscript"

General:

This work by Crazzolara and Held developed a new cascade impactor that improves the detection limits of heavy metals in aerosol particles. What's more, the newly equipment was in small size with low detection limits for metal elements, which is beneficial to monitoring work in field observation. This article is well organized, informative and in line with the scope of AMT. I suggested that the manuscript can be accepted and published after addressing the following concerns.

Thank you very much for this assessment.

2.1. The author stated that the detection limit of TXRF is superior to XRF (Yoneda and Horiuchi, 1971), and can reach down to a few picograms of absolute mass on the sample carrier substrate (Streli 2006). Can the author give the detailed detection limits of TXRF of some elements for comparison? And more latest references should be provided here.

The detection limits achievable by TXRF analysis depend on several factors, in particular the type of fluorescence excitation, the respective sample characteristics, and the TXRF spectrometer used. For the configuration used in the present study (X-ray excitation, SiO_2 sample carrier, aerosol particles deposited on the sample carrier by an impactor, portable Bruker S4 T-Star spectrometer), the lower detection limits are, for example, 0.005 ng for Fe and Cr and 0.002 ng for Ni. Recent publications report that even detection limits in the range of fg (10^{-15} g) can be achieved with TXRF analysis, for example by using synchrotron excitation of the sample.

The manuscript has been revised in section 1, line 52 to 55 of the revised manuscript by adding the corresponding references:

„… and can reach down to a few picograms of absolute mass on the sample carrier substrate (Streli 2006). Even detection limits in the range of fg (10^{-15} g) can be achieved with TXRF analysis (Eichert 2020), and also light elements (with low Z-number) can be excited effectively by using synchrotron excitation of the sample (Beckhoff et al. 2007, Streli et al. 2008). Recently…"

The following references have been added to the preprint manuscript:

Eichert, D. (2020). The Fundamentals of Total Reflection X-ray Fluorescence. Spectroscopy, 35(8), 20-24.

Beckhoff, B., Fliegauf, R., Kolbe, M., Müller, M., Weser, J., & Ulm, G. (2007). Reference-free total reflection X-ray fluorescence analysis of semiconductor surfaces with synchrotron radiation. Analytical chemistry, 79(20), 7873-7882.

Streli, C., Wobrauschek, P., Meirer, F., & Pepponi, G. (2008). Synchrotron radiation induced TXRF. Journal of Analytical Atomic Spectrometry, 23(6), 792-798.

2.2. Line 84-85: "…… without exceeding a critical Reynolds number of 3000" and Table 1. It puzzles me that why the criterion set as 3000 in a circular area with a diameter of less than 5 mm on stages 3, 4 and 5?

A laminar flow (which is generally desirable in the impactor nozzles) can turn into a turbulent flow if the Reynolds number *Re* to be calculated according to equation 3 in the manuscript exceeds a critical value. For this reason, a critical Reynolds number was set as an upper limit when designing the new impactor.

The VDI 2066 guideline on PM_{10} and $PM_{2,5}$ particulate matter measurement by impaction method specifies in Part 10, point 4.2.c) that the Reynolds number for the nozzle flow in the impactor should be within a range of laminar flow between 100 and 3000. Accordingly, when designing the new impactor, the number and diameter of the impactor nozzles in stages 3 to 5 were selected so that the Reynolds number does not exceed 3000.

And why small nominal nozzle diameters corresponded to the high Reynolds number?

The Reynolds number *Re* is calculated for the air flow in the impactor nozzles according to equation 3 in the manuscript. Accordingly, the Reynolds number *Re* is proportional to both the flow velocity v_o and the nozzle diameter d_n. The following rough calculation shows that smaller nozzle diameters result in higher Reynolds numbers: If, for example, the nozzle diameter d_n is reduced by 50 %, this leads to a reduction of the nozzle cross-sectional area to 25 %; therefore, assuming a constant gas volume flow, the flow velocity v_o increases to 400 %. As a result, the Reynolds number doubles when the nozzle diameter is halved.

2.3. Line 243-245: The operating temperature of the sensor is ranged from -20 to +80 °C. The question is whether the sensor have an applicable relative humidity RH range? For example, in the coastal regions, high humidity and salinity environment may cause damage to the instrument, such as corrosion.

Due to its measuring principle, the sensor element is heated during operation so that condensation is not to be expected under normal atmospheric conditions.
For long-term exposure, the mass flow sensor is specified for a maximum humidity at a dew point of 40 °C (100 % relative humidity at 40 °C), which corresponds to an absolute humidity of more than 50 g/m^3. Furthermore, the mass flow sensor is arranged downstream of the impactor, and in addition, a filter element is arranged upstream of the sensor element of the mass flow sensor so that no contamination of the sensor element with salt particles can occur. In addition, the sensitive element of the sensor is passivated with silicon nitride.
The authors would also like to thank the referee for this comment, as it drew their attention to an error in the manuscript. The temperature range presented in line 244 of the preprint manuscript is for a different mass flow sensor of the same manufacturer; the correct operation temperature range for the mass flow sensor SFM4300-20-P is only +5 to +50 °C. Although this does not affect the measurement results presented in the manuscript, the manuscript was corrected in section 3.2, line 252/253 of the revised manuscript accordingly:

> "*The sensor is factory-calibrated, has an operating temperature range of ~~-20 to +80 °C~~ +5 to +50 °C and provides a temperature-compensated output signal.*"

2.4. Line 251-254: How to set the duration of the sample time to ensure that the sample meets the needs of the analysis? For example, if the collection time is too short in a very clean environment, the sample volume may be not sufficient for the test, but if the collection time is too long, the sample may be overloaded.

This comment by the referee applies to impactor sampling in general. In practice, expected concentrations of the chemical elements of interest can often be estimated from previous studies. This information can be used to calculate the expected optimum sampling time.

2.5. Line 295: The detection limits of Fe, Cr and Ni by TXRF analysis should be given here.

The detection limits are 0.005 ng for Fe and Cr, as well as 0.002 ng for Ni, as indicated in section 4.1, line 309/310 of the revised manuscript. The wording of this sentence has been amended to enhance clarity and avoid misunderstanding:

> *"…absolute lower detection limits of 0.005 ng for Fe and Cr, as well as 0.002 ng for Ni ~~can be~~ were achieved in realistic conditions utilizing the sample carriers from the blank value experiment.*

2.6. In the section "4.3 Collection of particles in outdoor air", does the lower mass concentrations of Pb in PM10 (ranging from 1.1 to 1.7 ng m-3) and Ni in PM10 (ranging from 0.4 to 0.6 ng m-3) imply that a sampling period of 30 min is not sufficient for analysis.

No, the reported lower mass concentrations of Pb and Ni are well above the detection

limits. The detection limit for Pb was 0.001 ng or 1 pg absolute mass. As the volume of the sampled air was 150 litres at standard condition (30 minutes at 5 slm), the lowest measured concentration of 1.1 ng/m^3 Pb corresponds to an absolute particle mass of 0,165 ng or 165 pg Pb and is therefore well above the detection limit.

The detection limit for Ni was 0.005 ng or 5 pg absolute mass. Accordingly, the lowest measured concentration of 0.4 ng/m^3 Ni corresponds to an absolute particle mass of 60 ng Pb and is also well above the detection limit.

2.7. Have the authors compared the capture efficiency of the new cascade impactor with other commercially cascade impactors such as MOUDI Impactor Series (TSI Incorporated, USA) or Andersen Cascade Impactor (Tisch Environmental, Inc. USA)?

No, a direct comparison with other commercially available impactors has not been performed. A quantitative comparison of chemical composition using TXRF would be difficult because the deposition patterns of these impactors have lateral dimensions in some stages that lie outside the excitation range and/or the detection range of the TXRF spectrometer used in the present study. However, the mass concentrations determined with the new impactor and shown in section 4.3 are consistent with the annual mean concentrations of Pb in PM10 (4.4 ng/m^3 in 2021) and Ni in PM10 (0.6 ng/m^3 in 2021) measured at the Berlin air quality network BLUME station Berlin-Neukölln.

Minor concerns:

1. PM10, PM5 and PM1 should be subscripted. Many similar issues in the manuscript.

The authors would like to thank the referee for pointing this out and adapted this throughout the manuscript:

“PM10”	->	“PM_{10}”
“PM2.5”	->	“$PM_{2.5}$”
“PM1”	->	“PM_{1}”