Response to comments of Referee #3

We would like to thank Referee #3 for his valuable 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 #3 and incorporated changes in the manuscript as follows:

Blue: Comments of the Referee

Black: Answers of Authors

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

General:

In this study, a new impactor optimised for TXRF analysis was developed, demonstrating that a large number of different heavy metals can be detected and quantified in the PM10, PM2.5 and PM1 size fractions after collection periods of 30 minutes. Overall, the new impactor bears potential to improve the quantification of particulate trace metals and other elements in PM10, PM2.5 and PM1 with high time resolution. Major comments are as follows:

Thank you very much for this assessment.

3.1 In the introduction, it is said that "Despite promising results, commercial impactors are not fully optimised for TXRF analysis: The area on the sample carrier in which the classifying nozzles deposit the particles is usually significantly larger than the area analysed by TXRF." The inappropriate area was the only limitation? More advances should be showed.

The overall design of the newly developed impactor has multiple benefits:
By arranging the impactor nozzles of the newly developed impactor in such a way that all particles impacted on the respective sample carrier can contribute to the TXRF analysis (and not losing a significant proportion of the impacted particles for the TXRF analysis right from the outset), shorter sampling times are possible, as explained in lines 61 and 62 (introduction) of the preprint manuscript. This opens up new possibilities for identifying pollutant sources, as outlined in line 380 of the preprint manuscript.

The reduction of the lateral dimensions of the deposition patterns or the corresponding arrangement of the impactor nozzles could not be achieved simply by compressing a previous deposition pattern, but rather the number and lateral arrangement of the impactor nozzles had to be recalculated as well as the diameters of the impactor nozzles, as described in detail in section 2.2 of the preprint manuscript.

As a result of these considerations, the newly developed impactor was designed for a significantly reduced gas mass flow compared to commercially available impactors, which facilitates the use of smaller pumps, and thus, portable and mobile battery-powered operation of the impactor in the field, as outlined in lines 381 to 384 of the preprint manuscript.

Another aspect in the development of the new impactor was to provide low blank values and minimum cross-contamination between subsequent sampling periods, as explained in lines 64 and 65 (introduction) of the preprint manuscript. Several constructive measures were taken for this purpose, which are explained in lines 86 to 104 of the preprint manuscript. The effectiveness of these measures was verified by the experiments described in sections 3.1 and 3.2 and the results presented in sections 4.1 and 4.2 demonstrate very low blank values and cross-contamination for the new impactor.

Last not least, a new method for coating the sample carriers with an adhesive layer was developed and described in detail in section 2.3 of the preprint manuscript.

3.2 Why did the new impactor select PM10, PM2.5 and PM1, but not PM1, PM1-2.5 and PM2.5-10? PM0.11-1, PM1-2.5 and PM2.5-10 were showed in Figure 5, so what the impactor actually sampled?

Indeed, specific particle size fractions are separated at the individual stages of the impactor, which means that there is no single impactor stage at which the entire PM2.5 or the entire PM10 fraction is collected. Rather, the PM1, PM2.5 and PM10 fractions are calculated by summing up the mass contents of the particles impacted at the relevant individual stages.

For each stage of the impactor, particles with an aerodynamic equivalent diameter given as the separation diameter are sampled with a nominal collection efficiency of 50 %, larger particles are sampled with higher collection efficiency, and smaller particles are sampled with lower collection efficiency. For example, on stage 1, which has a separation diameter of 10 µm (Table 1), particles that are equal to or larger than 10 µm are sampled with a collection efficiency of 50 % or larger, while the majority of particles smaller than 10 µm pass through stage 1 and enter stage 2 of the impactor. At stage 2, the separation diameter is 2.5 µm (Table 1), thus collecting particles equal to or larger than 2.5 µm on the sample carrier of stage 2, and so on. Accordingly, particles larger than 2.5 µm and smaller than 10 µm are impacted on the sample carrier in stage 2, or in other words, the PM10 - PM2.5 fraction.

These proportions are visualised by the different colours of the bars in Figure 5:
the red bar represents the particle mass impacted on stage 2 (PM10 – PM2.5),
the green bar represents the particle mass impacted on stage 3 (PM2.5 – PM1),
and the blue bar represents the sum of particle masses impacted on stages 4 and 5 (adopted as PM1 with additional notes in lines 359 to 363 of the preprint manuscript). In view of referee's comment, the authors amended section 4.2, line 366 to 369 of the

revised manuscript for clarification as follows:

> "…periods in three size fractions, i.e. PM_1 (top of blue bar, i.e. sum of masses of impactor stages 4 and 5), $PM_{2.5}$ (top of green bar, i.e. sum of masses of impactor stages 3, 4, and 5; the green bar represents the particle mass impacted on stage 3 corresponding to $PM_{2.5} - PM_1$) and PM_{10} (top of red bar, i.e. sum of masses of impactor stages 2, 3, 4 and 5; the red bar represents the particle mass impacted on stage 2 corresponding to $PM_{10} - PM_{2.5}$). In addition, the…"

3.3   What elements can be detected by the TXRF? Why the Fe, Cr, and Ni mean blank values were showed in section 4.1, but the concentrations of Zn, Cu, Mn, Pb and Ni were showed in section 4.3? How about other metals, such as Co, V, As? Blank values and detection limits of all the measured elements should be summarized.

Generally speaking, elements can be detected by TXRF if fluorescence can be induced by the excitation radiation and if the induced fluorescence can "be seen" by the detector. Light elements with a low atomic number, such as carbon, are particularly difficult to measure because both efficient excitation with standard X-ray tubes and sufficient detection of the fluorescence are problematic. For particularly heavy elements such as cadmium, on the other hand, excitation with X-rays of higher energy is required. The method works optimally for elements with an order number of 14 or higher. The spectrometer used for the present study offers the possibility of using different excitation energies (see lines 260 to 263 of the preprint manuscript), with which the heavy metals of interest for the present study could be detected very well.

In section 4.1, the blank values of Fe, Cr and Ni were determined because the new impactor was manufactured from stainless steel, i.e. from a material that essentially consists of Fe, Cr and Ni, and because very high blank values of the impactor material were previously reported in the literature (Klockenkämper et al.). Numerous measures to prevent particle abrasion and adhesion were implemented in the design of the new impactor (lines 98 to 104 of the preprint manuscript), and their effectiveness was investigated in the present study. Therefore, the blank values of the elements Fe, Cr and Ni of the impactor material stainless steel were analysed and shown in section 4.1.

In Section 4.3, on the other hand, the results of particles collected in outdoor air were presented using the elements Zn, Cu, Mn, Pb and Ni as examples in order to demonstrate the possibilities and current limits of the analysis options with the new impactor under real conditions in the field. The corresponding blank values measured as part of the analyses for section 3.1 are 0.001 ng for Zn and Cu, 0.003 ng for Pb, and 0.002 ng for Ni, thus well below the values measured in outdoor air.

For the atmospheric conditions at the time (29 August 2022) at the sampling location (Potsdamer Platz, Berlin), the concentration was sufficiently high for some elements (Zn, Cu, Mn) to be detected by taking a 30-minute sample at 5 slm, while other elements (e.g. As) could not be detected (see line 355 of the preprint manuscript). For elements present at very low concentrations, the sampled air volume would have to be increased, for example by using a sampling period longer than 30 minutes.

3.4   The concentrations can largely changed in the environment. How to set the sampling time to ensure that the sample meets the needs of the analysis and is not 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.

3.5   Measurement results using this impactor and those using commercial impactors should be compared, to show the improvement of this new impactor.

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.

Regarding improvement of the impactor, the authors are not aware of a commercial impactor that allows the determination of the concentration of metals in atmospheric aerosol particles using a battery-operated, 30-minute sampling process that does not require an external energy supply and is portable and mobile.