Response to referee comments

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Performance evaluation of an online monitor based on X-ray fluorescence for detecting elemental concentrations in ambient particulate matter
by I. Trebs et al.

Anonymous Referee #1

Reviewer #1: *The authors describe the use of an online XRF instruments to detect metallic constituents of particulate matter. The instrument is evaluated in controlled, laboratory settings as well as at field sites in Luxembourg with varying anthropogenic influences. Online XRF is a relatively new method, and this work helps fill in gaps of evaluation and near-real time observations. There are a few areas that could be improved prior to publication.*

Reply to Reviewer #1: We would like to thank the referee for the positive evaluation of our manuscript. The proposed revisions will substantially improve the quality of the paper. Please find our detailed responses below:

Scientific Questions/Issues

Line 32 – It was surprising for OC and EC to be listed first in the description of PM. First, because they are generally not the dominant components by mass, nor are they chemically defined. The EC and OC parameters are operationally defined depending on the method of analysis. I would recommend moving these after SNA at least.

Reply: Thanks for the hint. We will change the order of words here.

Line 59 – "difficulties in the analysis of trends" should be elaborated, since several large networks have been deducing atmospheric trends using discontinuous collection on filters for decades.

Reply: We agree that this statement might be misleading. This will be corrected.

Lines 83-84 – I recommend including the latest census population estimate with "moderately inhabited rural area", as this can mean very different populations internationally.

Reply: This will be included.

Line 130 and subsequent – The ordering of the elements is not conventional. I am guessing that this was done purposely to highlight elements analyzed at the two different energy levels. You may choose to order your elements by atomic number, which aids interpretation of the results and figures.

Reply: In fact, the elements listed in Table 2, Table 3 and Table 5 are already sorted according to atomic number, but separately for the two energy levels. We will reverse the order in these tables (15kV before 50kV) so that all elements are sorted by atomic number. However, the timeseries plots cannot be changed as only the elements with comparable ambient concentration ranges can be plotted together.

Line 131 – The US EPA does not manufacture or specify a manufacturer for PM10 inlets. I recommend listing the actual manufacturer for clarity.

Reply: The PM10 inlet is manufactured by Met One Instruments, Inc. This will be corrected.

Line 167 – Based on the description, it sounds like σ_b is calculated from three standard deviations (n=3), one from each set of 10 blank analyses. If that is not correct, maybe more clarity is required here.

Reply: Yes, this is correct. We will modify the text to make it clearer.

Section 2.5 – Are there any uncertainty estimates or potential for stretching of the PTFE membrane? If not, this should be stated.

Reply: To our knowledge, there is no uncertainty associated with this. The PTFE could stretch a bit, but its deformation is negligible. We keep the criterion for tear strength (> 8 [N / 25mm].

Table 2 – This table would benefit from an additional column showing LoD estimates from an applicable air monitoring program, such as EMEP or Eurotrac-2.

Reply: LoDs are sensitive to the integration time of each collection method and cannot be directly compared. Additionally, less than half of the compounds detected here are monitored by EMEP or Eurotrac-2. Also, for some compounds wet/dry deposition is estimated, which is not comparable to the air concentrations in our study.

Line 229 – Many readers will find fault with the use of "perfect" in an experimental result. I suggest replacing with a different adjective (e.g., strong) validated with the metric you used to evaluate it (e.g., r2 = 0.99).

Reply: We agree and will change the text accordingly.

Lines 241-243 – XRF sensitivity to light elements decreases only under insufficient atmospheric control. LoD for light elements can be similar to other elements when using vacuum (< 1mTorr) or even with helium purge. The choice of detector also matters; Ge and CdTe detectors have inherently low sensitivity to light elements while Si and Si-vortex can have better sensitivity.

Reply: For modern silicon drift detectors (SDDs) used in XRF, the sensitivity to Al is relatively consistent. For elements such as Na, it depends on the thickness of the window material Be and whether different window materials are used. Indeed, using a vacuum or a helium purge can help in detecting light elements better. These methods reduce the interference from air (or other gases) that can absorb or scatter X-rays. However, the PX-375 does not rely on these methods, which means the detection of light elements like Na might be less effective due to the presence of air. Light elements generally have poor XRF sensitivity compared to transition metals (e.g., Cu). This will be elaborated in more detail in the text.

Figure 4 – While this view of the precision results is sufficient, it may be better represented with mass loading on the x-axis and viewed as a scatterplot. This may help explain the observed differences.

Reply: This is a good idea and provides a more detailed view. We will replace the plot including this information and revise the discussion of the results in the text.

Line 276 – How was the 20 % Type B uncertainty determined?

Reply: This is just a hypothetical value in case the deviation of the particle deposition spot from the analysis area becomes very large. We have observed this deviation in previous campaigns before making instrument adjustments. The value is estimated from the erroneous crescent area using the erroneous distance of both circle centres. We will clarify this in the text.

Table 4 – The Remich and Vianden instrument comparisons are both close to 10 % while Belvaux is ~ 50 %. This should be discussed or noted for further investigation.

Reply: We agree and will make additional remarks in the text.

Lines 381-384 and Table 6 – This is not a valid argument or presentation of the data. Trace elements are so called because they contribute little to total mass under normal circumstances. Chronic exposure to elevated levels of toxic metals can induce health effects, in spite of its percent contribution to total PM10 loading. For example, Ni may be three times the EU limit of 20 ng/m3 and only contribute 0.15 % to an acceptable level of PM10 (< 40 µg/m3).

Reply: We agree and will make corrections in this part of the text.

A better comparison would be to calculate relative differences or enrichment with regard to either local geology or the most rural site.

Reply: We have considered the use of enrichment factors while writing the manuscript but noticed that we do not have all data available (e.g., local soil properties). In the revised manuscript, we will include another Table comparing enrichment regarding the most rural site Vianden and some more discussion on this topic.

Technical Corrections

Line 65 – "… breakdown spectroscopy determine allow for a …"; maybe just "determine"

Reply: This is a typo and will be corrected.

Line 137 – The "X" in "X-ray" should be capitalized.

Reply: This will be corrected.

Line 152 – The citation for GUM should be capitalized.

Reply: This will be corrected.

Lines 161 and 164 – The citations for IUPAC should be capitalized.

Reply: This will be corrected.

Figure 2 – There is an excessive amount of space below -15 % and error bars would be useful.

Reply: The space below -15 % will be removed in Figure 2. Error bars will be added.

Line 274 – "… achieved due to the carful filter tape …"; maybe "… due to careful filter …"

Reply: This is a typo and will be corrected.