Reply to referee comment 2 on Kau et al. “Thermal-optical analysis of snow samples – challenges and perspectives introduced via the occurrence of mineral dust”

We thank X. Wang for taking time to review our manuscript. The text of the referee comment is in **bold**, while our reply is in regular type.

Comment on amt-2022-145

X. Wang (Referee)

Referee comment on "Thermal-optical analysis of snow samples – challenges and perspectives introduced via the occurrence of mineral dust" by Daniela Kau et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-145-RC2, 2022

The authors present an approach which utilizes this interference to determine the concentration of hematite via thermal-optical analysis using a Lab OC/EC Aerosol Analyzer (Sunset Laboratory Inc.) and the EUSAAR2 protocol. Generally, the manuscript is well written and easy to follow. The investigation fits the scope of this journal. However, I think the major defect of this study is that only illustrates the Fe effect on EC measurement, but without any discussion about the detection of OC concentration. Therefore, I suggested that the manuscript can be accepted only with major revisions as follows.

We thank the referee for the positive evaluation. We agree that the bias of the split point introduced by MD affects both EC and OC concentrations. Quite often OC concentrations are much higher than EC concentrations. Hence, variations of the OC/EC split have, on a relative base, a great impact on the EC concentrations. This is why we had our focus on EC. As we agree that MD has an impact on the OC concentrations as well, we revised the manuscript to address this problem in more detail. The respective changes are listed below, when addressing the referee’s comments. Thus, we are confident that we could resolve the major point of criticism.

Major issues:

- **The calibration of Fe in snow samples by the TOA method is quite useful. However, I am a little puzzled that why the authors are only interested in the occurrence of mineral dust in snow samples. Does it mean that this investigation is only useful for snow samples? As the author illustrated that the PM_{10} samples can also obtain high amounts of Fe loadings, such as tunnel samples.**

We absolutely agree, aerosol samples are affected as well, and this is why we included PM_{10} samples collected at the background site to show the applicability of the method for PM_{10} samples. The samples collected in a railway tunnel show the limitations of the method, as the TOA method failed to approximate iron loadings. Particles collected in the railway tunnel derive to a large extent from abrasion of tracks and wheels and iron is present in different forms than in mineral dust samples.

The importance of the method for analyzing particulate matter samples is further emphasized by increasing the number of PM_{10} samples collected at the high alpine site with recent measurements (line 292 - 296, Figure 4 and Figure 5a). Furthermore, the Conclusions were revised to address this point further.

- **Reconstructed the abstract, as shown above, why only mineral dust and elemental carbon in snow samples are pained more attention? The mineral dust can also lead large bias of EC and OC concentrations for aerosol samples due to the temperature dependency of the transmittance signal determination.**

The abstract was changed to address both EC and OC and to refer to particulate matter samples more extensively (line 11 and 18 in the revised manuscript).

Other passages in the manuscript, where we originally just referred to EC, were changed as well and both EC and OC are mentioned now.

- **I wonder to know what's the relationship between the attenuation and the hematite loading of less than 10 µgFe cm^{-2}. Because the bulk aerosols or snow samples can be loaded with lower Fe concentrations.**

Figure 3 includes all data points of filters loaded with snow samples, i.e. also filters with loadings below 10 µgFe cm^{-2}. Filters with such low loadings show a small value for $ATN_{700-400}$ or even negative values (line 235 – 238). Thus, the scatter gets quite broad and no correlation is possible any longer. Figure 5(a) includes also high alpine PM_{10} samples with loadings below 10 µgFe cm^{-2} ($ATN_{700-400}$ close to 0).

- **Although the major issue of this study focused on the bias of Fe on TOA techniques, However, there may be a large bias to account for insoluble OC concentration by using a microwave during the snow melt process.**

The snow melt process is a delicate procedure. Concerns are expressed in literature that OC is lost when using a microwave or that, when melting the sample at room temperature, EC is lost on the walls of plastic bags and glassware. Evaluating these two sides, we decided to use the melting process via microwave, which is, according to Wang et al. (2020), a widely performed snow-melting procedure.

Authors applying our method in the future can still either use the microwave for melting or any other appropriate method.

- **In section 2.3, the author should provide more description of the relationship between the MD and Fe_2O_3, withoutonly cited with previous studies.**

The topic of taking hematite as a reference substance is explained in more detail in the revised version of the manuscript. MD is a complex mixture of various compounds. Fe oxides (hematite, goethite) in MD account for 2 to 5 % of MD mass and approximately 58 % of the mass of elemental Fe (Formenti et al., 2014). The exclusive use of hematite as a reference substance is appropriate as goethite changes to hematite at elevated temperature (250 – 600°C; Liu et al., 2013), which is exceeded during the inert phase of TOA. Thus, hematite will be the main Fe compound on the sample filters loaded with MD when TOA switches to the oxygen phase, i.e. at times when the split point is set, and during the calibration phase. This information is now added in the revised manuscript in the Introduction already (line 57 - 63) and we refer to this again in section 2.3 (lines 94 to 97).

To evaluate our own data, PXRD of filters loaded with snow samples was conducted and showed Fe_2O_3 on the filters. The results of these measurements are presented in lines 148 - 149 (section 4.1.) in the original manuscript.

- **Same as above section 3.1 is too general, the author should provide more details about the procedure of the treatment.**

We added some details about the method (line 106 – 109 in the revised manuscript) and included a table in the Supplement defining the temperature steps of the EUSAAR2 protocol (Table S1 in the revised Supplement) and mention this in line 112 in the revised manuscript.

- **In section 3.2, as least, the detection limit of Fe_2O_3 should be given by ICP-MS or OES.**

We agree that the limit of detection was missing for these methods and added them in line 126 in the revised manuscript. The limit of detection for ICP-MS and ICP-OES was 0.1 and 0.4 µgFe cm^{-2}, respectively.

- **Actually, section 3.4 and Figure S2 are nothing useful and can be deleted directly.**

The Figure (note that S2 changed to S3 in the revised version of the Supplement) presents the differences between the reference materials and the filter loaded with snow sample and explains why the correlations between iron loadings of the filters and $ATN_{700-400}$ (as presented in Figures 2 and 3 in the manuscript) are different. We included additional results of SEM and revised the text to explain the idea of the SEM analyses more clearly.

The new information is given in lines 256 - 262 and 269 - 271 of the revised manuscript.

- **The caption of Figure S2 is unclear. Does Figure S2 is standard samples or observed samples?**

'Fe_2O_3 samples' refer to filters loaded with reference material throughout the manuscript. As more information was added to this Figure (Fig. S2 became Fig. S3 in the revised version), the caption was rewritten.

- **Finally, as Wang et al. (2012) indicated that the mineral dust mainly induces an extra decrease in optical reflectance during the 250 oC heating stage, thereafter, lead potential bias in the EC and OC split. But I didn't find any related illustration or explanation of such an issue in this study. I suggested the author should provide further details on this major issue of the split of EC and OC in snow samples to prove this useful approach.**

Figure 1(b) shows an example thermogram of a filter loaded with a snow sample that contained MD. The transmittance signal of the reruns, which cannot be attributed to carbonaceous compounds, shows a reduction at the 250°C, but even more pronounced reductions at higher temperatures. The aim of this manuscript is to highlight the influence of Fe on the transmittance logged during TOA and to deduce a method to quantify Fe loadings. Further recommendations for a correction of the split point are beyond the scope of this manuscript. This is actually a topic we are currently working on. To illustrate the topic of the OC/EC split in more detail, we included a thermogram containing the FID-signal in the Supplement and added a reference to this new Figure S2 in the main text (line 171 - 172 in the revised manuscript).

- **Finally, the author should note that there is potential mass loss of BC or MD on 1.0 µm quartz fiber filters compared with 0.4 µm Nuclepore filters, as shown in Figure 5 by Wang et al. (2020).**

The possibility of undercatch during filtration was mentioned in line 40 – 41; however, we thank the referee for the suggestion of the current work and added the citation in line 47 in the revised manuscript as well as in the References section in line 486 - 488. For TOA, no suitable alternative filter material to quartz fiber is available, as high temperature resistance and stable optical properties over a wide temperature range are indispensable. Thus, TOA with Nuclepore filters is not possible.

References:

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