Response to Reviewers for paper "Iron speciation in different Saharan dust advections and effect of the procedural blank on the results from X-ray Absorption Spectroscopy and selective leaching experiments"

To the associated Editor and the Reviewers:

On behalf of all authors I would like to thank the reviewers for taking the time to review our manuscript and for their constructive response to our work. We understand that most of the concerns raised by Referee 1 were on the introduction section of the paper, which indeed set the expectations of the reader and therefore must be improved. On the other side, we are pleased that reviewers 2 and 3 found our work interesting, innovative and worth consideration. We worked to address all the comments, in particular to improve the introduction section, and we hope the suggested corrections really helped improving the manuscript quality. A detailed answer to each of the reviewers' comments is reported below.
We would also like to thank the Editor for facilitating the review process, which was very quick and effective.

Reviewer 2.

The manuscript "Iron speciation in different Saharan dust advections and effect of the procedural blank on the results from X-ray Absorption Spectroscopy and selective leaching experiments" by C. Petroselli and coauthors deals with a characterization of airborne dust particulate carried out by XAS spectroscopy and selective leaching experiments, aimed at assessing the Fe speciation in relation to Sahara dust advections. The manuscript is innovative and well-conceived and it merits consideration. Nevertheless, I found some remarks that merits consideration before publication.

Line 52 – there's an unnecessary repetition of the term "level"
Thank you for noticing this. We have now amended the manuscript.

Table 1 and text – The two terms HVS and SWAM should be defined the first time they are cited. Presently, only HVS is defined in the 4.1 section
SWAM is the name of the instrument according to the manufacturer and it is not an acronym. We have now specified it in the abbreviations list as well.

Table 1 – why the number in the last columns are expressed in brackets? I'm not used to such convention
Following the suggestion, we have now amended the table and added a clarification sentence in the caption.

[New Table 1 caption] Samples description: sampling date, filter code, aerosol mass concentration (PM_{10} and $PM_{2.5}$ in μg m^{-3}) and iron concentrations determined by ICP-OES for HVS (high volume sampler) PM_{10} and SWAM $PM_{2.5}$ samples expressed in μg m^{-3} and converted to atoms cm^{-2}. Errors on the last digit are indicated in parentheses.

Figure 1 – concerning the spectra of the blank samples, the spectrum of SWAM sample is shown, whereas that of HVS no. There's a reason? It could be added?
Unfortunately, the XAS spectrum of HVS blank filters are not available. Synchrotron measurements sessions only allow for a limited amount of scan time, it is therefore not always possible to analyse all the samples. However, since both filters are made of quartz fiber and produced by the same company, we expect the iron local structure to be similar in both cases.

We clarified this aspect in section 2.3.1 as follows:

[Lines 157-159] In order to get an insight on blank filter contribution to the XAS spectrum, a SWAM quartz fiber filter was analysed. Despite the spectrum of a blank HVS filter is not available, we assume the iron local structure to be similar in both cases because the filter material and manufacturer are the same.

Line 122 – ferrihydrite is a poorly crystalline material, while goethite is an hydrated mineral but usually well crystalline

Thank you for this feedback. We have now amended the manuscript.

Line 124 – concerning pre-edge fitting, the number of peaks used in the fit and the criteria followed to this choice should be specified (here, or in the methods)

The number of components depends on the details of the d-states splitting and this can be different for Fe^{3+} or Fe^{2+}, in tetrahedral or octahedral configurations. Following the case this could need from 1 to 4 contributions, a detailed treatment is given in (Galoisy et al. Chemical Geology 174 2001. 307–319). In general, one to two components are sufficient to reproduce the data and we kept the number of components at a minimum in all cases. It is worth noticing that in any case, the relevant parameters are the integrated intensity and the centroid and these are not critically dependent on the number of components used in the fit.

Materials and Methods section 4.4 was changed as follows:

[Lines 331-334] The pre-edge features of the XANES part of the spectrum were fitted keeping the number of components at a minimum in all cases in order to determine the centroid position and the intensity of the peaks using Origin(Pro)8 (OriginLab Corporation, Northampton, MA, USA).

Line 136 - how the model chosen to fit EXAFS compares with the fact that XANES seems to reveal features marking some similarities with "more ordinate Fe3+ compounds"?

The model used for EXAFS is taken from ferrihydrite. However, when analysing EXAFS data the relevant aspect is that the model have an electron density and interatomic distances well comparable with the unknown sample. This in order to generate the correct theoretical XAS signals. A detailed structural similarity with the sample is not required and structural fine details (as the more pronounced order of some shells as in this case) are not relevant for the generation of these signals. The fitting routine successively adapts the theoretical signals to the actual spectrum so permitting to extract the correct interatomic distance or the correct Debye-Waller (disorder) parameter.

Lines 153 and following – XANES and EXAFS data on the SWAM filter seem partial contradictory.

The XANES and EXAFS data appear to be good agreement, considering that XANES in not a fully quantitative method. In Fig.2 it is indicated that SWAM falls in the region of Fe3+ with 5 coordination. BVM analysis of the EXAFS data (the first shell radius at 1.84 Å), would point to a 4 coordinated iron. The conclusion can be that in this case Fe is low coordinated and this is expected as the Fe seen in the SWAM filter is the impurity ion contained in the quartz matrix.

We clarified this aspect in section 2.3.1 as follows:

[Lines 160-165] The XANES spectrum of the blank filter is shown in Figure 1b and shows an edge energy of 7121.5 eV, compatible with Fe(II). The EXAFS fit of the blank filter (Figure 3b, Table 3) shows a Fe-O bond distance of 1.84Å, compatible with 4-coordinated Fe(III) (1.87Å, [30], Table S1), and a 4.4 coordination. Considering that XANES data are not quantitative, they are in good agreement with EXAFS data. In fact, in the blank filter iron results low coordinated as expected for being an impurity ion in the quartz matrix.

Line 209 – The authors should give a possible explanation of the changes occurred in the samples here described: how the change from SH to non-SH sources affects Fe valence state and speciation?

While Saharan dust is a well defined and well characterized type of aerosol, which signature is still easily recognizable after long-range transport, the generic term "non-Saharan" is used in this study to mark samples which do not come from the Sahara desert, grouping different provenances and compositions. Moreover, the few non-Saharan samples presented in this study do not allow for a thorough characterization of this type of aerosols at the Monte Martano site, due to their different provenance and the different extent of processing the samples undergo during transport. We therefore evidenced the differences between the samples and pointed out that the trend is not due to the aerosol loading of the filter but rather to the decreasing extent of the well defined Saharan dust contribution.

We added a sentence in the manuscript (section 3.1) to clarify this aspect:

[Lines 214-218] Regarding non-Saharan advections, lower edge energies (7124-7122 eV) are compatible with the results of McDaniel et al. [23] for samples with North American and marine provenances. However, unlike Saharan dust which is a well defined and well studied type of aerosol, the few non-Saharan samples presented in this study do not permit a thorough characterization of aerosol transported from different sources to the Monte Martano site.

Line 288 – sequential extractions were carried out on the same filters used for XAS? Otherwise there were two sets of filters? In which way was accounted the sample heterogeneity in this second case? Please specify this in the 4 section.

The XAS and sequential extraction analyses were carried out on different portions of the same filters. It is now clarified in the text (section 4.1).

[Lines 288-289] Filters were then defrost and cut into pieces of suitable size for the different analyses described in the following paragraphs.

Line 320 – Presently, the 5 section is useless and it should be removed.

Thank you for noticing this. We have now amended the manuscript.

I would also add a more general concern. From Table 1, the differences in sampling events are clearly marked. For the SH event a complete set of samplings were operated; for the mix-SH events only PM10 was sampled, for the non-SH events only PM2.5 was sampled. Although in the text some statements accounting on the different speciation expected linked to the size of the sampled dusts are given, I would appreciate a more comprehensive consideration on the comparison operated between samples that are mainly different in nature. It is well known that mineral dusts mainly contribute to the coarse samples, and thus on can expect that also sample solubilities and Fe speciation could be affected.

We recognize that the database available for this study is quite heterogeneous, with different size fractions, different sampling instruments and filter substrates. As acknowledged in your comment, we tried to be as clear as possible in describing the samples to avoid over-interpretation of the presented results. The strength of the database resides in the SH_Dec event, which was thoroughly characterized in all the different sampling conditions and therefore provides a strong base for the comparison with the other samples. In fact, a comparison between the different size fractions was performed for the SH_Dec event, as reported in section 3.1 (lines 234-239). $PM_{2.5}$ and PM_{10} fractions can be quite different, especially in urban environments where multiple sources are present, and in case of specific advections like Saharan dust. Monte Martano is a rural background site located at mid-altitude and far from significant aerosol sources, mostly observing long-range transports. The PM_{10} and $PM_{2.5}$ concentrations recorded at Monte Martano since 2013 show a very good overlap between the two fractions in absence of remarkable events like Saharan dust or wildfires advections. This is attributable to the atmospheric deposition (size-selective dry deposition) and processing that occurs during transport which might smooth some of the differences between the size fractions. Moreover, as stated in a previous comment, we do not aim to exhaustively characterise non-Saharan transports in this work, because of their possible heterogeneity in terms of sources and processing.