

Response to the additional comments from referee 1 – Dr Rachel Shelley

General Response: We thank Dr Shelley for supporting the findings of this manuscript. The comments have been addressed point by point below.

Comment at Line 48: As you give the solubility as a percentage, the equation should be dissolved Fe/ total Fe x 100

Response: The reviewer comment has been implemented in the manuscript

Comment at Line 55. Put a comma between sources and with

Response: This has been revised.

Comment at Lines 179-182. 89% recovery is a bit low. Usually, you would want at least 90% to demonstrate good recovery. Morton et al. (2013) demonstrated that HF was required for full recovery of marine aerosols. Rather than saying around 89% it would be better to give a mean and standard deviation. In addition, to the CRM and the Saharan soil, it is possible that the CFAs wouldn't have fully digested, although I am slightly reassured by your good recovery for the ATD. It would be worth highlighting this. If you contact Peter Morton (pmorton@fsu.edu), he will be able to provide you with the latest consensus value for total Fe in the ATD. For this reason (ATD recovery), and because you have now stated that fractional solubility might be slightly over-estimated and demonstrated that your Fe dissolution scheme has improved the performance of the IMPACT model, this study should be published. However, before publication I'd like to see more detail about the digestions, such as the model and the programme used (times, temp and pressure – could be a table in the supplement) and the masses of the material digested included in the manuscript.

Response: As suggested, a detailed description of the digestion method used in this study was added to the supporting information (Text S1). Dr Peter Morton has provided us with the latest up-to-date average Fe content measured in ATD ($33,039 \pm 3,834$ ug/g). The estimated recovery of Fe from the ATD samples calculated using the reference total Fe in ATD (from Dr Morton) and the total Fe measured in this study using the microwave digestion method (for the calculation we used the total Fe values prior the correction for the Fe recovery based on the NIST results) is $94.0\% \pm 1.5\%$. Although Fe recovery from NIST was slightly lower than 90% ($89.0\% \pm 0.4\%$), the ATD samples showed good recovery. This has been highlighted in the text. We agree that ideally the recovery would be better to be over 90%. We feel that the reliability of the recovery is also more important. 89% recovery is indeed very good in analytical chemistry. We also noted that the uncertainty associated with this recovery is more than an order of magnitude lower than model simulations of fractional Fe solubility. We therefore suggest that such uncertainty does not affect the conclusion of the study.

Lines 179-187 have been updated as follows:

“The total Fe content in the samples was determined by microwave digestion in concentrated nitric acid (HNO₃) followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis. A detailed description of the digestion method is provided in the supporting information (Text S1). The total Fe content obtained for the Arizona Test Dust (ATD, Iso 12103-1, Power Technology, Inc.) was comparable with the latest consensus value for the total Fe in ATD which indicates a good recovery (94.0% ± 1.5%). The recovery of Fe assessed using a standard reference material for urban particulate matter (NIST SRM 1648A) was 89.0% ± 0.4%. It is possible that some of the Fe in aluminosilicate minerals are not fully digested but the uncertainty associated with this analytical method is very small, particularly when we compare this with the large uncertainty in simulated Fe solubility in models”.

Description of the microwave digestion method added to the supporting information as Text S1:

“1-3 mg of dust/ash were weighed on quartz filters (1.5 cm² punch). The filters were placed into vessels with 10 ml of 68% ultrapure nitric acid (HNO₃, Romil). The vessels were loaded into a MARS 6 Microwave Digestion System (CEM Technology). The filter-membrane programme was used to digest the samples. This consists of an increase in temperature to 200°C (15-min ramp time) followed by 15 min at 200°C and pressure 800 psi. The sample solutions were then diluted to 2% HNO₃ and filtered through 0.45 µm membrane filters. The samples were stored in the fridge at 4°C prior the analysis. The Fe concentration in the filtrates was measured by inductively coupled plasma mass spectrometry (ICP-MS) analysis.

After each digestion, the vessels were cleaned to prevent contamination. These were first washed with DI water and dried in the oven at 70°C. Subsequently, 10 ml of concentrated HNO₃ was added to each vessel which were placed into the microwave to undergo the cleaning programme (ramp time of 15 min to 190°C, followed by 10 min at 190°C and pressure 800 psi). Finally, the vessels were rinsed with DI water and air-dried in a fume hood. All glassware was acid washed in 10% HNO₃.

To assess the recovery of Fe, we used a standard reference material for urban particulate matter (1 mg of NIST SRM 1648A on quartz filter). The recovery of Fe from NIST was 89.0% ± 0.4%. We used the Arizona Test Dust (ATD, Iso 12103-1, Power Technology, Inc.) to test the method. The estimated total Fe content in the ATD was 3.501% ± 0.056% which is comparable with the latest consensus value for the total Fe in ATD. Here, the estimated recovery of Fe from the ATD samples calculated using the reference total Fe in ATD and the total Fe in the ATD samples obtained in this study (prior the correction for the Fe recovery based on the NIST results) is 94.0% ± 1.5%”.

Comment at Lines 183-185. Could you add the wt%s of Fe in ATD and the standard deviations that are in table S2 to the text and move the RSDs to the table as the abundances of each fraction are of more interest than the RSDs. You should also include your percent recovery, as ATD is a community-consensus reference material.

Response: The reviewer comment has been implemented in the manuscript.

The Fe recovery from ATD was added to the text and supporting information (Text S1) and Lines 188-191 have been updated as follows:

“The sequential extraction techniques were tested using the ATD. The wt% of Fe obtained for each extract using the ATD was 0.057 ± 0.002 for FeA, 0.394 ± 0.045 for FeD, 0.047 ± 0.006 for FeM (n=7) and 3.501 ± 0.056 for the total Fe (n=3). A summary of the results for the ATD is reported in Table S2.”

Comment at Line 287. ...the western Sahara

Response: The reviewer comment has been implemented in the manuscript.

Comment at Line 335. Photo-induced

Response: The reviewer comment has been implemented in the manuscript.

Comment at Line 370. Although the peak in PM_{2.5} could be an outlier, it could also be real reflecting Fe from a different mixture of sources to the days either side, thus illustrating one of the challenges of modelling such a dynamic parameter. I wonder if you could add a few words to the end of line 370 to reflect this.

Response: We agree with the reviewer. Lines 372-378 have been updated as follows:

On the other hand, the model could not reproduce the peak in total Fe concentration (1.8% of Fe content in PM_{2.5} sample) reported around 29 December 2008. The total Fe observed in PM₁₀ (430 ng m^{-3}) on 29 December 2008 is lower than that measured on the day before (667 ng m^{-3}) and the day after (773 ng m^{-3}), whereas that in PM_{2.5} peaked on 29 December 2008 (Srinivas et al., 2012). Thus, the extreme value recorded only for PM_{2.5} on this date may be an outlier. But we do not have sufficient data to confirm this. One of the possibilities is that the sample collected aerosol particles from a mixture of different aerosols sources (e.g., dust and anthropogenic aerosol). This reflects one of the challenges of modelling such a dynamic parameter.