

Interactive comment on “Mineral nutrients in Saharan dust and their potential impact on Amazon rainforest ecology” by Joana A. Rizzolo et al.

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General Comments: Although this is a very important aspect as they correctly present it, the main topic Fe (II)/Fe (III) availability is not well described. In some aspect they are too brief such that their final results cannot be appreciated. However, it is an important topic that meets the requirements of publication at ACP. I would recommend that major revisions are done prior to consideration of a possible publication.

1. There is not enough evidence that the high soluble content they observe is due to Saharan dust. They need to show some correlations which lead to such arguments. R: Yes, we agree with the reviewer's comment. The text was adjusted to show the correlations of the soluble contents with physical and chemical properties of long-range

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transported aerosol plumes. We are confident that the manuscript in its revised version convincingly shows that indeed a pronounced Saharan dust plume has been collected, which is the only plausible explanation for the increased Fe concentrations. Our argumentation is further supported by a broad set of related literature that is consistent with our observations. In general, this experiment was designed to obtain soluble iron measurements in aerosols originating from Saharan dust plumes. To achieve this goal, the following strategies were adopted: Location - the progress of African dust occurrences across the Amazon can be readily followed by satellite images, which typically show that it takes about 1 week for dust outbreaks to cross to the Atlantic (Yu et al., 2015). The sampling site is located in the common transport pathway of Saharan dust and receives dust laden air masses on seasonal cycles. Period of the year - several papers have shown that Saharan dust reaches the Amazon Basin especially during the months of March/April/May: (L.106-108) “The sampling period ranged from 19 March to 25 April 2015, which is within the typical season when dust transport to the Amazon Basin has been reported before (Talbot et al., 1990; Swap et al., 1992; Prospero et al., 2014; Yu et al., 2015)” Iron source - studies have shown that in Central Amazonia, the iron content in aerosols originates from crustal sources or long range transport: (L. 349-351): “Soil dust related elements are typically present at the highest concentrations during the early wet-to-dry season transition (May), as has been shown in previous studies (Pauliquevis et al., 2012; Andreae et al., 2015)” (L. 364-367): “Pauliquevis et al. (2012) also observed increases in the concentration of total Fe with values reaching 60 ng m^{-3} in the fine mode mostly during February to April in the Amazon Basin, with a seasonal average of 36 ng m^{-3} . They attributed this to episodes of Saharan dust transport.”

2. Simply because the air mass originates from Africa does not imply all chemical components in the aerosol are from the Saharan Desert. This aspect has to be clarified and the identification of the sources that could lead to different soluble iron concentrations in this region has to be discussed. R: We agree with the reviewer. The long-range transported aerosol from Africa typically comprises a complex mixture of desert dust,

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biomass burning smoke, maritime aerosols, and biological particles. The revised discussion on the elements measured in the aerosol samples and their potential origin from the aforementioned sources has been extended. We show that the dust fraction is the only plausible explanation for most of the Fe content, whereas Na, Cl, Mg, K, and other elements are associated with sea spray and biomass burning aerosol fractions in the long-range transport plumes. Specifically, we are referring to the Sahara and Sahel region together as “Sahara”. This has been stated in the abstract. In addition to mineral dust aerosol from the Sahara and/or Sahel region, there is also marine aerosol introduced from the Atlantic Ocean, which can contribute sea salt elements and biogenic sulfate. Because the northern hemisphere winter is also the fire season in West Africa, biomass burning smoke often arrives together with African dust. This can be seen in the BCe concentration of up to $0.3 \mu\text{g m}^{-3}$ on 4 April. At a typical fraction of 7% of BC in biomass TPM, this could contribute about $4 \mu\text{g m}^{-3}$ of TPM, or about 20% of the TPM at the peak of the BCe concentration. We have added a comment on this in the text. But regarding our main goal, Longo et al. (2016) indicated that the iron in Saharan dust exhibits different oxidation states across the different sampling sites, suggesting that the longer an aerosol remains in the atmosphere, the more reduced the iron becomes. These complex interactions suggest that the various particle-aging mechanisms, such as acidic reactions and photoreduction, may be working simultaneously. (L. 221-224) Although the Hysplit backward trajectories do not guarantee that pure end members were sampled, they help to demonstrate that most air masses were of North African origin during the sampling time periods. (L. 357-361) The concentration of iron (II) obtained recently at Barbados is in the same order of magnitude as the amounts that we measured (Zhu et al., 1997). Additionally, the increase in particle number measured during the sampling period correlated with the presence of Saharan aerosols at the ATTO site.

3. There should be more clarity on the experimental approach on how they measured the soluble metals. R: We agree with the reviewer. The experimental details in section 2.2 have been specified in more detail (L.128-146) “All the analyses were performed

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on the TPM soluble fraction. Each sampled filter immersed in nitric acid solution was extracted by an ultrasonic bath for 10 mins. The extract of each sample was filtered with a polyvinylidene difluoride (PVDF) sterile membrane ($0.22 \mu\text{m}$ pore size, diameter 25 mm, Millipore, Merck) and analysed by ion chromatography (ICS 5000, Dionex-Thermo Scientific, USA). For the transition metal quantification and iron speciation, pyridine-2,6-dicarboxylic acid (PDCA) was used as eluent and 4-2-2-pyridyl resorcinol (PAR) was used as a post-column reagent, stabilized by a PC-10 nitrogen pump. The system flow was 0.3 mL min^{-1} through an IonPac CG5A (2 x 50 mm) guard column, CS5A capillary column (2 x 250 mm) and UV-Vis spectrophotometry with detection at 530 nm (Cardellicchio et al., 1997). For soluble Fe (II), Fe (III), Cu and Zn the detection limits (USEPA, 1997) were 1.7, 0.4, 1.3, $4.1 \mu\text{g L}^{-1}$, respectively and the expanded uncertainties at the 95% level of confidence (BIPM, 2008) were of 3, 42, 46, 56 %, respectively. For the cation analysis, ultrapure water and methanesulfonic acid (MSA) was used as the eluent at a 20 mM constant concentration, with automatic suppression (CSRS suppressor - 2 mm), and with a 0.33 mL min^{-1} system flow through an IonPac CG-12 guard column (2 x 50 mm) and CS-12 (2 x 250 mm) capillary column. This resulted in a 14 min running time for each injection. For soluble Na, NH_4^+ , K, Mg and Ca the detection limits (USEPA, 1997) were 2.0, 1.3, 0.9, 0.7, $1.8 \mu\text{g L}^{-1}$, respectively, and the expanded uncertainties at the 95% level of confidence (BIPM, 2008) were of 9, 7, 21, 11, 23 %, respectively.”

Specific Comments:

4. How long did the samples stay in the nitric acid flask and were they any measurements done to ensure that the transition from Fe (II) to Fe (III) or vice versa did not occur during the time frame of storage? R: The samples stayed in the nitric acid flask during the sampling period of March 19th to April 25th and no test was performed during the storage period. Based on Cwiertny et al (2008), the dissolved Fe(II) / Total dissolved Fe ratio of Saharan Dust, is practically constant over time: “Nitric acid suppresses the formation of iron(II) at low pH; therefore, pH can also act as a control of oxidation state

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of aerosol iron.”

5. Where the extracts filtered? The experimental part is too brief to follow the obtained results. R: The method section was rewritten with more details and the required information was added to the text as follows: (L. 128-132) “Each sampled filter immersed in nitric acid solution was extracted by an ultrasonic bath for 10 mins. The extract of each sample was filtered through a polyvinylidene difluoride (PVDF) sterile membrane, 0.22 μm pore size, diameter 25 mm (Millipore, Merck) and analysed by ion chromatography (ICS 5000, Dionex-Thermo Scientific, USA).”

6. What were the concentrations of the total fractions of each of the elements? R: The focus of the sampling efforts was to quantify the soluble fraction. In order to keep the oxidation state of iron stable, we immersed the filters in the acidic solution. The chemical analysis performed was Ion Chromatography and to assess the total fraction we used TPM elemental composition results sampled simultaneously at another site, as detailed in Table 1: (L.269-272). Previous studies have shown that the aerosol composition and burden is almost identical at the two sites when long-range transport is dominant, as it was during our study.

7. How could the fungi be optimally identified using a light microscope? Was there an algorithm that matched the shapes of the fungi to given types of fungi in a library or was it simply done by intuition? R: The fungi types were identified using consolidated data bases and a certified spore counter with the US National Allergy Bureau: (L. 214-215).

8. How good could the mineral dust adsorption in the black carbon signal be isolated since it's mentioned that mineral dust could also produce similar adsorption signals? R: The absorption Angstrom exponent (AAE) can be used to investigate the relative contribution of different particle sources to the BCe signal. Particle samples impacted by mineral dust typically show AAE greater than 2.0, while soot from fossil fuel combustion shows AAE close to 1.0 (e.g., Bergstrom et al., 2007). There are methods proposed in the literature to distinguish between fossil fuel soot and other light absorb-

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ing particles (e.g., Lack and Langridge, 2013), but we consider that this is not in the scope of the present article. However, to clarify this point, we reformulated part of sections 2.4 and 3.1 as follows: (L. 164-174): “Soot, mineral dust, and biogenic particles are light absorbers (Moosmüller et al., 2009; 2011; Guyon et al., 2004; Andreae and Gelencsér 2006) and may contribute to the observed BCe signal. The relative contributions of particle sources to BCe can be investigated by considering the absorption spectral variability, by means of the so called Absorption Ångström Exponent (AAE). Soot from fossil fuel combustion typically shows AAE close to 1.0, while particles impacted by dust emissions show AAE greater than 2 (Bergstrom et al., 2007). Studies indicate that samples impacted by biomass burning aerosols show AAE in the range of 1.5-2.0 (Bergstrom et al., 2007; Rizzo et al., 2011). The spectral dependency of particle absorption coefficients was monitored using a 7-wavelength Aethalometer (Model AE33, Magee Scientific Company, USA, $\lambda = 370, 470, 520, 590, 660, 880, \text{ and } 950 \text{ nm}$), compensated for filter loading and multiple scattering effects (Rizzo et al., 2011).” (L. 237-253): “Particulate Fe(III) and Fe(II) concentrations increased between 3 and 9 April, simultaneously with an increase in particle absorption and scattering coefficients (Figure 4.a). A decrease was observed in the intrinsic property, single scattering albedo (SSA, Figure 4.b), suggesting the presence of particles that are efficient light absorbers, such as soot from fossil fuel combustion and biomass burning, mineral dust, and biogenic particles. For comparison, Rizzo et al. (2013) reported that a 7% decrease in SSA at another forest site in the central Amazon during the wet season periods proved to be related to advection of African aerosols. The spectral dependency of absorption, AAE, can be used to distinguish between the different sources of light absorbing particles. The elevated AAE values observed between 6 and 10 April (Figure 4.b) contradict the influence of soot from fossil fuel combustion. During the clean periods (25 March to 2 April and 16 to 24 April), dominated by biogenic particles, AAE values were around 1.8, so that this source of particles, ever present at Amazonian forest sites, may not have contributed to the AAE increase between 6 and 10 April. Therefore, two light absorbing particle sources are left to explain the increase in ab-

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sorption and AAE values: biomass burning and mineral dust particles. Fire activity is typically low in the central Amazon between November and April, with less than 2 fire spots per 1000 km² and day on average (Castro-Videla et al., 2013), which is corroborated by the map of fire spots distribution during the campaign period (Figure 5).” (L. 286-289): “Our conclusion that African dust dominates the aerosol budget during the dust event is in agreement with Castro Videla et al. (2013), who, based on a five-year study, concluded that peaks in AOD in the central Amazon during the wet season had a significant contribution from coarse mode particles, pointing to a major role of African advection.”

9. The soluble Fe concentration seems to be high for pure Saharan dust. It is known that in lower pH the solubility can be as high as 10% or more. However, it would be helpful to explain in detail how the samples were prepared. R: Yes, we agree with the reviewer and the methods section was modified: (L. 128-146). Regarding the required information, each sampled filter immersed in nitric acid solution was extracted by ultrasonic bath. The extract of each sample was filtered through a PVDF sterile membrane, 0.22 μm pore size, diameter of 25 mm and analyzed by ion chromatography for Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Fe³⁺, Cu²⁺, Zn²⁺ and Fe²⁺.

10. How did you differentiate the sources of the soluble Fe? As mention in the literature comparisons, Fe has other sources, such as combustion, industrial emissions. Iron from these sources in some cases has been found to be more soluble than in Saharan dust. It is unclear from your arguments, why you allocate the soluble iron to be originating from Saharan dust. Long range transport is a mixture of different air masses and these air masses may have different chemical compositions. Thus a more detailed tracer analysis or correlation of an intrinsic dust element such as Al or Ti would be helpful to identify how significant the Saharan dust contributed to the obtained soluble iron concentrations. R: The reviewer is correct. It is very hard to determine sources based on trajectories/long transport alone. The ATTO site, especially its location, was chosen to provide the most reliable sampling of natural tropical aerosols in the world.

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It is in one of most remote areas on the planet, and this is the primary reason why we assert that our aerosol samples were mostly from natural contributions. As explained in the answer to the first question, air masses reaching the site have crossed more than 1500 km of primary rainforests in the Amazon Basin. The bulk of the background aerosol at ATTO is biogenic. There are no industries in the path of these air masses. (L. 273-283): “Biomass burning in Africa could also have contributed some of the observed Fe, but unfortunately, little is known about Fe emissions from savanna fires, and the available data span a wide range. From the work of Gaudichet et al. (1995), one can derive a Fe content of 0.016% in savanna smoke TPM, which, at a peak biomass smoke concentration of 4 $\mu\text{g m}^{-3}$, would only give 0.6 ng Fe m^{-3} . Using the BC/Fe ratio of ca. 40 from Maenhaut et al. (1996) and the peak BCo concentration of 0.3 $\mu\text{g m}^{-3}$, we can estimate ca. 8 ng Fe m^{-3} . Finally, using the Fe emission factor of 0.026 g kg⁻¹ d.m. for African savanna fires from Andreae et al. (1998) and the BC emission factor of 0.6 g kg⁻¹ from Andreae and Merlet (2001 and updates), we can estimate a peak pyrogenic Fe contribution of 13 ng m^{-3} . This compares to 64 ng m^{-3} of soluble iron (details follow in section 3.3) at the same time, and, given that only a small fraction of the Fe in biomass smoke is likely to be soluble, it is clear that the dominant fraction of soluble Fe comes from the African mineral dust.” We are quite confident of our results because when we compare with dust obtained at Barbados, we observed that the soluble ferrous iron (Fe(II)) and Total soluble iron (Fe) are in the same order of magnitude (Zhu et al., 1997).

11. What could be the likely reason for the high wind and high Fe (III) correlation observed above the canopy? R: These vertical transport correlations could be analyzed by micrometeorological methods (e.g., eddy covariance). However, this analysis is beyond the scope of this work. The idea of presenting the vertical speed was only to show that regardless of the cloudy conditions, the W values are close to zero, indicating that the vertical transport is very weak. Thus, the text was rewritten to make this clear. The vertical wind data have been removed.

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12. How good did the soluble content correlate with the BC content and total mass concentration? R: We thank the reviewer for this opportune suggestion, and added the time series of B_{Ce} and particle soluble fraction concentration to Figure 2. This clearly shows that the latter are well correlated with total mass concentration, especially during the event from April 1 to 8. We also added the following sentence to the section 3.2: (L. 321-324) "Figure 2 and Table 1 show that B_{Ce} concentrations significantly increased regionally during 1-8 April, coinciding with the increase in PM₁₀ and particle soluble fraction concentrations and indicating that some biomass smoke (probably from fires in West Africa) arrived together with the dust".

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2016-557/acp-2016-557-AC1-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-557, 2016.