

## ***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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1. The problem of this manuscript that begins by the Title and the Abstract is the generalization of ideas. First I suggest that the authors be more specific in the Title, it should focus on the soluble fraction Fe(II)/Fe(III) issue, which is something important but not enough to account a full story about the Amazon rainforest ecology. R: Yes, we agree with the reviewer, and the title was changed to: “Soluble iron nutrients in Saharan dust over the central Amazon rainforest” to match better with the main goal. The text was also restructured to emphasize the iron soluble fraction and the frequent long-range transport of African aerosols.
2. In the introduction, clarify at Line 124 (pag 6) when the authors say “: Considering C1

that iron is absorbed by plants only as soluble Fe(II)/Fe(III)”, previously the authors have stated that Fe(III) was also recovered by the action of rhizosphere. R: The sentence was confusing as indicated by the reviewer. Plants require the micronutrient iron in small amounts and the absorption can vary according to the species. Iron uptake can be as Fe (II) or (III) and the absorption fraction depends on the ability of the plant to reduce it to Fe (II). In this role, the pH is important for solubility and therefore the iron availability. The text has been changed accordingly.

3. In methods, Line 142, pag 6, provide filter porosity. R: The information was added to the text as follows: (L. 111-112)“Atmospheric particles were collected on Nuclepore<sup>®</sup> polycarbonate filters (47 mm diameter, 0.8  $\mu\text{m}$  pore size, Whatman<sup>®</sup> Nuclepore)”

4. In Item 2.5, specify how the samples were storage and if the observations were conducted in the field or in a particular laboratory condition? R: After sampling the filters were stored at 4°C in the field and then carried to a laboratory to perform the ion chromatography analysis. The information was added to the text: (L. 117-118) “After sampling, the filters were immediately stored in sterile flasks under refrigeration until laboratory analysis.”

5. The sentence in Line 229-231 “The mass concentration of particles over the Amazon Basin in the wet season is typically around 10  $\mu\text{g m}^{-3}$  in locations that are influenced by biomass burning emissions”, : : : here there is confusion on the wet season and biomass burning season. Which reference is attributed to the mass concentration mentioned? R: The reviewer is right, the information was confusing. The text was rewritten as follows: (L. 297-303)“ The mass concentration of PM10 particles in Amazonia is close to background in most areas throughout the basin during the wet season. Central Amazonia is characterized by a weak influence of anthropogenic emissions and aerosol mass concentrations are low during the wet season - typically 7  $\mu\text{g m}^{-3}$ ; even the most impacted areas do not exceed 10  $\mu\text{g m}^{-3}$  due to intensive rain and the corresponding inhibition of biomass burning (Artaxo et al., 2002; Artaxo et al. 2013;

Martin et al., 2010). Increased mass concentrations may occur due to African dust events that reach the Amazon forest in this season (Talbot et al., 1990; Martin et al., 2010).”

6. Part of the text in Lines 254 to 268 (pages 11-12) could be placed at Material and Methods. If possible the authors could place BCe time series superimposed to mass concentrations at Figure 1. This could give some idea on the contribution of BC to the bulk atmospheric concentrations, or if they are lagged in time. R: Following the referee’s suggestion, we moved part of the text from the Results to the Material and Methods section. Part of section 2.4 was reformulated as follows: (L. 160-168) “Equivalent black carbon concentrations (BCe) were obtained by a Multi Angle Absorption Photometer (MAAP, Model 5012, Thermo Electron Group, USA;  $\lambda = 670$  nm), based on light absorption measurements at 637 nm. An absorption cross section value of  $6.6 \text{ m}^2 \text{ g}^{-1}$  was used for the conversion of measured absorption coefficients into BCe concentrations (Petzold et al., 2005). 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).” The information was also added in section 3.2: (L. 316-317) “The concentrations of black carbon equivalent (BCe) measured online during this intensive campaign represented on average 1.5% of PM10 mass concentrations, ranging from 0 to  $0.3 \mu\text{g m}^{-3}$ .” (L. 321-323) “Figure 2 and Table 1 show that BCe concentrations significantly increased regionally during 1-8 April, coinciding with the increase in PM10 and particle soluble fraction concentrations”

7. In Table 2, how the elemental analysis was conducted for Cu, Zn, Na, Ca, K and Mg? and about the  $\text{NH}_4$ ? R: The experimental details were included in the Methods section as follows:(L. 140-146) “For the cation analysis, ultrapure water and methanesulfonic acid (MSA) was used as the eluent at a 20 mM constant concentration, with automatic

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suppression (CSRS suppressor - 2 mm), and with a  $0.33 \text{ mL min}^{-1}$  system flow through an IonPac CG-12 guard column ( $2 \times 50$  mm) and CS-12 ( $2 \times 250$  mm) capillary column. This resulted in a 14 min running time for each injection. For soluble Na,  $\text{NH}_4$ , K, Mg and Ca the detection limits (USEPA, 1997) were 2.0, 1.3, 0.9, 0.7, and  $1.8 \mu\text{g L}^{-1}$ , respectively, and the expanded uncertainties at the 95% level of confidence (BIPM, 2008) were of 9, 7, 21, 11, and 23 %, respectively.”

8. In the title of Table 2, it is not “aerosol characterization” it is aerosol composition; it does not correspond to “during the Saharan dust event”, it is before, along and after the event. R: The reviewer is correct. Table 2 was removed from the text, and essential information was added to Figure 2 and in the text.

9. In Lines 279-282 the authors say that K, Zn and Cu are of biogenic sources, probably mostly emitted during biomass burning. If the detected pulse of dust in this work is coincident with an African biomass burning event as pointed by the authors, what is the level of certainty to say that their main source is the mineral fraction? R: Biomass burning in Africa could have contributed some 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 an Fe content of 0.016% in savanna smoke TPM, which with a peak biomass smoke concentration of  $4 \mu\text{g m}^{-3}$  would only give  $0.6 \text{ ng Fe m}^{-3}$ . Using the BC/Fe ratio of ca. 40 from Maenhaut et al. (1996) and the peak BCe concentration of  $0.3 \mu\text{g m}^{-3}$ , we can estimate ca.  $8 \text{ ng Fe m}^{-3}$ . Finally, using the Fe emission factor of 0.026 g/kg for African savanna fires from Andreae et al. (1998) and the BC emission factor of 0.6 g/kg from Andreae and Merlet (2001 and updates), we can estimate a peak pyrogenic Fe contribution of  $13 \text{ ng m}^{-3}$ . This compares to  $64 \text{ ng m}^{-3}$  of soluble iron 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. Discussion on this issue has been added in Section 3.1.

10. In Line 322, the comparison of the present work with Andreae et al. (2015): does

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both work have same methods and associated errors? Results of Andreae et al. (2015) correspond to what period of the year. Specify please. R: The results of Andreae et al. (2015) correspond to the period from 7 March to 21 April 2012, and the chromatography analyses have the same method and associated errors. The information was added to the text as follows: (L. 373-375)“ The soluble Fe(III) concentrations were significantly higher than those reported by Andreae et al. (2015) from earlier measurements at the same site, which had also been made during the wet season and using the same quantification method.”

11. Text in lines 333-338 is unnecessary. R: We agree with the reviewer, the text was removed.

12. Dates in Figure 2 is unreadable. R: We agree with the reviewer, the Figure 2 was replaced by another with readable information.

13. Figure 3 should be completely edited. It is not possible to use the Hysplit output directly. For Figure 3, use ensembles, not a single trajectory; a family of trajectories gives a better idea of all geographical contributions. R: We agree with the reviewer and the figure was edited as requested, showing the backward trajectories to illustrate the intercontinental transport.

15. Lines 369-374; Figure 1 shows before, along and after the “dust storm”, I suggest that the authors run the Hysplit model in these 3 circumstances and then make their conclusions. R: We agree with the reviewer. Figure 1 was replaced and comments changed with new conclusions added according to the suggestion.

16. In Line 387 provide complete localization of the three AERONET sites: Dakar and Ilorin in Africa, and Embrapa/ Manaus in Amazon. R: The geographical coordinates of these AERONET sites have been included for the AERONET sites (L. 228): Dakar (14° 23' 38"N; 16° 57' 32"W) and Ilorin (08° 19' 12"N; 04° 20' 24"E) in Africa, and Embrapa/Manaus (02° 53' 12"S; 59° 58' 12"W) in Amazonia (L. 804).

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17. In Figure 5, AOD do not distinguish dust from biomass burning products. From the location of higher AODs in the diagrams it seems that your source could have some contribution from biomass burning than mineral dust. Also the results presented in the Hysplit are not totally in accordance to wind flows at the charts at Figure 5. Maybe the source is a net combination of both; I strongly suggest that the authors add a map with fire spots for the period of sampling, so to make better differentiate. R: Yes, there is clearly a contribution from biomass burning. To clarify the possible contribution of smoke, we added in Figure 6 fire spots observed during the sampling period in both continents, South America and Africa. Over South America, major fire spots areas (Brazilian cerrado ecosystem and the north portion of the continent) are not upwind of the ATTO site, which reduces the site exposure to smoke plumes from these principal regional spots. In Africa, the main fire spots areas are downwind of the Sahara desert, along the west coast of Africa, therefore on the way of the dust flux toward the Tropical Atlantic and South America, which could promote transport of a mixture of smoke and dust. The referee is right, the AOD does not distinguish dust from biomass burning. Thus, observing exclusively the AOD map it is hard to say which is one dominant, dust or smoke. However, from the analysis of the Angstrom Exponent (AE) against AOD measured using data from AERONET sites located in the Sub-Saharan areas with high AOD (Ilorin, Dakar and Cape Verde) it is possible to assess the dominant aerosol type across west Africa. The AE is close to zero when aerosol plumes are dominated by large particles (e.g., sea salt, soil dust, biogenic) and higher than 1.0 when fine particles (e.g., from biomass burning and fossil fuel combustion) are dominant (Eck et al., 1999). It is well established that an increase in AOD associated with a decrease in AE in the sub-Saharan region is associated with the presence of dust plumes, and the opposite, increase in AE associated with an AOD increase is related to biomass burning plumes (Ogunjobi et al., 2008, Eck et al.1999). Although a contribution from biomass burning smoke is very likely in these areas, the plots of AE against AOD for Dakar, Cape Verde, and particularly Ilorin, during the four periods analyzed in Figure 6 shows that dust plumes clearly dominated during the higher AOD scenarios. The plot

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for the Ilorin case was included as an example in the manuscript to corroborate that the plume that left Africa towards the Tropical Atlantic and South America was dominated by dust aerosols. The same analysis performed for the AERONET station located in central Amazonia (northwest of Manaus) also suggested that regional AOD increases during the sampling period were dominantly connected with decreases in AE, and thus increased coarse mode particles. This is consistent with Castro Videla et al. (2013), who showed that peaks on AOD in Central Amazonia during the wet season had a significant contribution from coarse mode particles. As discussed in the response to Comment 2 of Reviewer 1, a TPM contribution of about 20% from biomass burning can be estimated.

18. In Figure 6, what is MC? Please, correct the legend of time. R: MC stands for Mass Concentration. The legend was corrected as indicated.

19. The discussion on fungi is very poor. There is none description of the species nor anything on their biogeography. The lesson of this result is the fact that a more detail aerobiological research should be conducted to be published. R: The fungi identification underscores long distance transport, but doesn't allude to a specific site. We included our observations of coarse particles during the dust event to see if there were likely to be readily identifiable inputs from the canopy that might add to the iron analysis. Bioaerosol identification would also help confirm if any coarse particles that were mixed with the dust were of other than local origin. The spores identified in the samples do not add soluble iron to the analyzed extracts.

20. In Line 463-465, the authors say "Smoke plumes are known to entrain fungi over long distances (Mims and Mims, 2004). Dust from Lake Chad is rich in bacteria and fungi." Here becomes explicitly that the authors are not able to stablish a source of the particulate matter entering Amazon in the considered event: Saharan mineral dust or sub-Saharan biomass burning? R: The particles found have influence from the plumes originated from the African continent as confirmed by trajectories. The long distance transport is evidence from our findings but we cannot be more precise about the source

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of the fungi without further analysis.

21. The Amazon itself is a fantastic source of bacteria and fungi, and only an endemic specie of Africa, detected in Amazon, at high level (ex. The top of the ATTO) could make a clear distinction. R: The reviewer is correct. We cannot fully compare the bioaerosol results because previous studies cultured air samples of viable spores only, and analysed with high throughput sequencing. Only a few types of fungi were detected at the species level.

22. In item 3.5 the authors says that "a small amount of atmospheric iron could affect the microbiota in the canopy, rather than have a significant effect on soil and root uptake for plants." This is an speculation and from this work it is not possible to conclude anything. R: Yes, we agree with the reviewer. The sentence was removed and the section restructured to emphasize our finding.

23. In my opinion, most of item 3.5 is Introduction to the study since most of the text is compilation from the literature associated to this work. R: Yes, we agree with the reviewer. Some parts of section 3.5 were placed in the Introduction and most of the section was rewritten (L. 439-458).

24. The conclusion unrealistic, should be reduced to the basic findings. R: The conclusion was rewritten to focus on our findings (L. 460-467).

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2016-557/acp-2016-557-AC3-supplement.pdf>

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