

# ***Interactive comment on “Mineralogy and physicochemical features of Saharan dust wet deposited in the Iberian Peninsula during an extreme red rain event” by Carlos Rodriguez-Navarro et al.***

## **Anonymous Referee #2**

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General comments: This manuscript reports the mineralogical, chemical, morphological characterisation, as well as number size-distribution and optical properties of Saharan dust collected in intense wet deposition events occurred in February 2017 in Granada. Finally, this characterisation is used to discuss the potential biogeochemical implication of dust deposition for supplying soluble iron, the direct radiative forcing of dust and the health impact of dust. The physico-chemical data about transported dust are rare and hence always precious information. However, some shortcuts on the experimental description may question the findings and conclusions of this paper.

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The manuscript is generally well-written, logically organized, and adequately illustrated. Abstract is succinct and accurate.

The analytical work is widespread and careful. However, the discussion about data is often supported by rough approach (see specific comments) and some critical information about protocol are missing, making sometimes the conclusions of this paper unpersuasive:

For deposition sampling (p4 and 5), the used protocol is not clear since the authors talk about both wet and dry dust? : “Wet deposited dust was collected at 3 different locations in the urban area of Granada .. In all cases, dry dust was collected (scrapped) directly from clean horizontal surfaces and/or clean ceramic rain/dust collection dishes (21 cm in diameter) with the aid of a spatula and/or a brush. Do you mean that the dry insoluble residue deposited on dishes after wet deposition is collected for analysis? In this case, the dust is collected after evaporation of rain water and it is possible that the precipitation process of salts or amorphous phases happened during this evaporation step. For example, the presence of fibrous calcite could support a potential precipitation. It's critical to detail this step of sampling since a possible precipitation modify all your discussion about the presence of nano-sized ferrihydrite in the collected dust, which is one of finding of this paper. Indeed, the authors argue on a key finding: “a significant fraction of Fe in Saharan dust is already present in the source region as potentially bioavailable nanosized amorphous and/or poorly crystalline iron oxihydroxides which is Fe is present in dust region as very soluble ferrihydrite”(p33, L34).. If ferrihydrite is very soluble, why do the authors detect it in the particulate insoluble phase of wet dust deposition?

In the same way, if the sampling corresponds to insoluble dry residue of dust, it is important to specify that during the discussion on the chemical composition. Indeed, this implies a potential underestimation of soluble species as Ca, Mg (see Fu et al., 2017) but could also support such of your data for few soluble trace metals (e.g. Fe/Al ratio).

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Moreover, this step of evaporation could also enable the formation of aggregates between deposited dust (formation of crust) and hence modify the distribution between clay, silt, and sand ... The collection with a spatula or a brush of dust present also a risk to loss of the finest particles (not collected or re-suspended by brush movement). It's probably not very important for the methods of mass characterisation, but it's more problematic for individual analysis as microscopic observations. For example, that could explain the presence of large particles ( $>10\mu\text{m}$ ) during SEM observations. The authors cannot exclude the impact of this potential aggregation on their results even for mass analyses. For example, the question appears since the clay fraction found here is smaller than observed in the literature, even during intense local erosion event (56% in Formenti et al., 2014a) and has to be discussed.

Without a detailed discussion about these experimental points, the conclusions of this paper could be wrong.

Specific comments:

P2, L 30 to P3L5: the authors argue an increase of Saharan dust input and dust plume intrusions in Mediterranean on the basis of various phenomena (drought, changes land uses...). However, recent works seem to emphasize a decrease of Saharan dust deposition in western Mediterranean since the beginning of 2000's due to probably changes of atmospheric circulation (Pey et al., 2013; Vincent et al., 2016..). As the dust deposition is in the heart of this paper, I think that it's important to mention these recent results.

In general, I found that the bibliography about dust characterisation is a little bit poor. I suggest to include in your comparison with the literature the works on the dust characterisation carried out over Atlantic as e.g. Lazaro et al., 2008; Patey et al., 2015.

P5, L15: How the organic matter is affected by the different standard treatments? What is the impact on mass budget of minerals?

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P5, L20: For the analysis, it's not clear if the dust collected on the different locations are mixed or separately analysed. Please precise.

Figure 4: Could you provide forward trajectories from PSA1?

P18, L2: The chemical composition is for the bulk samples? Please precise.

P18 from L4: The ratio  $\text{Si}/\text{Al} = 3.6$  and  $\text{Ca}/\text{Fe} = 0.55$  in your sample are consistent with dust from Bodélé depression (PSA5) on the basis of Formenti et al., 2014a. This assumption seems to be confirmed by the observations of septa in your TEM analysis. The dust could be originated from a larger zone than only PSA1 and PSA3 (see also Figure 2 for the 22 Feb). Please add a comment about these observations.

P24, L7: "These results have important implications regarding the possible atmospheric acid processing of the iron-containing phases, as we will discuss below." The calcium nitrate and sulphate formed during atmospheric processing are highly soluble, so it is not surprising the authors did not observe these species onto dust issued from wet deposition sampling. So this result has no important implication. This is not also a good evidence of the "negligible mixing with air masses including anthropogenic-derived pollutants".

P27, L25: Finally, a budget of composition of bulk dust should be provided including carbonate, organic matter and various minerals to give a global view of mass composition.

P31, L16: Several recent works emphasized that the range of solubility of Fe-bearing dust is less than 1% to 80%. Even atmospheric processes increase the iron dust solubility, the highest observed values of solubility are related to the presence of anthropogenic iron (e.g. Sholkowitz et al., 2012). Please modify this part by including the most recent literature.

P32, L2: "The amorphous and/or poorly crystalline ferrihydrite would thus amount to 28 wt% of the free iron.  $\hat{A}$ . This conclusion is based on very rough estimation! so

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please detail the calculation (2.04% issued from calculation from Table 4?) and add the uncertainties on the values since on the basis of free iron =  $1.7\% \pm 0.5\%$  of goethite (containing 63% of Fe) +  $0.5\% \pm 0.4\%$  of hematite (containing 57% of Fe, see Journet et al., 2008) =  $1.3\% \pm 0.7\%$ , so a total of iron content =  $3.34\% \pm 0.7\%$ , that is in the range of total iron content =  $3.43\% - 3.69\%$  found by chemical analysis, meaning that no iron is associated to ferrihydrite..

For part 3.8, 3.9 and 3.10: All the discussions need to be re-written by including the reservations in link with sampling protocol about the presence of nano-sized ferrihydrite and size-distribution (See general comments)

Minors corrections:

P2, L4: “large” instead of “enormous”

P4, L 20: 48h instead of 42h

P8, L15:  $\mu\text{g m}^{-3}$  instead of  $\mu\text{m m}^{-3}$

Figure 4: forward trajectory for the 21 Feb should be presented for 50 m instead 500 m.

Table 1: Please precise that the wt% is for “treated dust samples” without carbonate fraction

P18,L14: Formenti et al., 2014a instead 2014b

Table 3: please precise the uncertainties on measurements for ICP and XRF analysis.

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