

Response to reviewers:

We thanks both referees for the time they spend on this discussion paper and their remarks.

Referee #1:

You use certified reference material SLRS-4 from NRC, Canada. However, I've been perusing in the NRC web and only could find reference material SLRS-5 (River water reference material for trace metals). Was this one the one you used?

Because old CRMs are wiped out of the NRC web site, we added references in which relevant data are reported (Yeghicheyan et al., 2001; Heimburger et al., 2013).

Did you use any reference material for P?

P is not certified in SLRS-4. However, we used measurements from SLRS-5 (Yeghicheyan et al. 2013) and elemental composition ratio between SLRS-4 and SLRS-5 to validate our measurements of P. P is also reported in Yeghicheyan et al 2001 for SLRS-4 but with a higher value which seems false. Only one laboratory (situated at Toulouse) measured P in SLRS-4. Our calibration line for phosphorus was made with pure dry sodium hydrogencarbonate salts dissolved in water and diluted. Sodium content of the solutions was found equal to the stoichiometry and a commercial 10mg/L solution was diluted to 1000 µg/L to check our calibration slope. P concentration determination in SLRS-5 is better than in SLRS-4 because it used more recent technics and as described in Heimburger et al. 2013, SLRS-5/SLRS-4 ratio measurement is completely insensitive to calibration issues. For these reasons, we trust better new SLRS-5 measured values than old SLRS-4 and used well determined SLRS-5/SLRS-4 ratio to validate our P measurements based on SLRS-4 checking. We modified the paragraph to include this discussion.

Page 2627 line 19. Specify how the calcium index of dust is calculated.

We have removed this term which is not commonly used and not necessary here. In the new sentence we only state that dust sourced from Tunisia has high calcium content.

Page 2628 paragraph 5-10. You comment here the pH results from the leachings. The actual data are provided in Supplement Table 1. However, my opinion is that a Table containing the results is needed here. I suggest to include here a Table with the averages of the pH values and the nutrient solubilities in the 3 leachings at each pH step. To emphasize the differences between the 3 results you can also provide the range of values.

The supplementary reading is moved to the text as Table 2. A 3rd column is added to table 1 showing the elemental composition rather than oxide to remove completely supplementary reading. We added a line with detection limit (DL) as requested by Referee #2. To be comparable with DL which is an uncertainty, we changed standard deviation SD in uncertainty (U): $U = 3*SD/2$ where 2 is the square root of 4, the number of replicates we displayed on average. In the discussion section, we also changed SD in U.

Page 2628 paragraph 15-20. The sentence starting with "Gleyzes et al (2002) and ending with Filgueiras et al 2002" is confusing. Please clarify what is stated by which of the authors.

Done. Both write the same behaviour of carbonate. Filgueiras add a consideration to the 5 hours dissolution time which is not useful here and has been removed.

Page 2630 paragraph 0-5. There is an error in the Mn%, since 21% corresponds to pH1 (from data in Fig 3) and here this value is attributed to pH3. At pH3 the solubility of Mn is 18%. Once this is corrected, one can see that the comparison between results from leaching with solution

pH3 and results from processing with synthetic cloud water (as reported in Wuttig et al 2013) are not that similar: for Mn and Al, pH3 solubilities are about half those obtained with cloudwater (if we take 34 as a medium value for the range 27-41 % for Mn in cloudwater). On the other hand, for Fe the solubility at pH3 (from data in Fig 3) is about double that of the cloudwater processed dust. Could you comment on that?

We have modified the text and based our comment on an average behaviour of Mn, Al and Fe, taking into account large uncertainties in the solubility determinations in mesocosms.

Minor corrections

Page 2625 Line 11. Instead of “These leaching tests”, write “The leaching tests reported here”

Done

Page 2630 line 4, instead of “let us assume” use “indicates”

Done

Page 2630 line 26, instead of “without invoking... “ use “with the acidic conditions typical of cloud water”.

We write both "with the acidic conditions typical of cloud water and without invoking extreme acidic conditions"

Page 2630 line 27, instead of “liability” use “lability”

Done

Referee #2

General answer: We wrote a short scientific paper for the DUNE special issue. In this paper, we aim to present new results on chemical properties of a material which is a proxy of Saharan aerosol and to discuss their biogeochemical implications. In this context, we think that this paper must stay short and focused on this objective. We have done our best to include most of the comments of Referee #2 but not all of them to maintain the original goals of this paper and to limit its size.

Detailed comments:

P2624, line 2: "sieved at 20um", this is the only place where it mentioned 20um sieving. The methodology has been briefed in the Methodology section. Is it a wet sieving or dry sieving? What are the implications of wet sieving for more soluble elements such as P? This needs to be discussed in the main text.

We add "dry sieved" in the experimental protocol and abstract. Our paper is included in a special issue and all the protocol is well detailed in Guieu et al. 2010 which is an introduction paper for all the other papers.

P2624, line 6-7: This is the only place where the authors have chosen different pHs to simulate the atmospheric processing of dust. A substantial reference to literature is needed in the text to justify the chosen conditions. The statement that "the lowest of which could be reached during cloud conditions" is most likely wrong. Low pH is not commonly seen in cloud conditions and may only occur when there is serious pollution in the fog droplets. Such conditions have nothing to do with dust though. There are some French papers that you may refer to:

Deguillaume, L., Charbouillot, T., Joly, M., Vaitilingom, M., Parazols, M., Marinoni, A., Amato, P., Delort, A.M., Winatier, V., Flossmann, A., Chaumerliac, N., Pichon, J.M., Houdier, S., Laj, P., Sellegrí, K., Colomb, A., Brigante, M., Mailhot, G., , 2014. Classification of clouds sampled at the puy de Dome (France) based on 10 yr of monitoring of their physicochemical properties. *Atmos. Chem., Phys.*, 14, 1485–1506, 2014. Deguillaume, L., Leriche, M., Desboeufs, K., Mailhot, G., George, C., Chaumerliac, N., 2005. Transition metals in atmospheric liquid phases: sources, reactivity, and sensitive parameters. *Chem. Rev.* 105(9), 3388–3431.

We removed the end of the sentence in the abstract because our purpose is not to discuss on the physicochemical properties of clouds.

P2624, line 9: "strength", it is not clear what is the meaning of this word and the sentence here?

We added "chemical" strength to be clearer.

P2624, line 11-12: "...with a maximum solubility at pH 3". This statement is inaccurate and misleading. Because the authors have used a sequential extraction, it is wrong to say that the maximum solubility is at pH 3. What if the sample is left at pH 1 or 2 without the pH 3 step? It is most likely that the maximum solubility is at pH 1 or 2 rather than 3 for all of these elements if not using a sequential leaching, which most previous studies did not use. It is clear that it is appropriate to group the elements into two categories but the statement has to be precise to avoid misunderstanding. Similar comment applies to that related to Fe and Al.

We changed here "solubility" in "sequential solubility"

P2624, line 15: "unexpected high liability"; why this is "unexpected"? This needs to be justified in the discussions in context of literature.

We have removed "unexpected".

P2624, line 18: "finest"; There are much finer and lots of nanoparticles in the soil dust.
<20um cannot be defined as finest?

It is the finest fraction relative to the various fraction we obtained using dry sieving. All the details of sieving is related in Guieu et al. 2010. We change the beginning of the second paragraph of section 2: "Approximately 10 mg of the **20 μm dry sieved** fine fraction of the soil described in Guieu et al. (2010)"

P2624, line 20: "true" should be "natural"

Done

P2624, line 22: Only three types of minerals in this sample? There must be some other minerals. If this statement is to stay here, it needs to be re-worded, taking account that these three mineral types are the dominant ones.

We changed to: This soil fraction was **mainly** a mixture....

P2625, line 1: "soluble"; this needs to be defined. The following methodology suggests that this fraction is <0.2um so not really "soluble". It is more appropriate to say "dissolved" here.

The difference in meaning between the two words "soluble" and "dissolved" is not consensual. We believe it is clearly explain what we have done so that the reader will not be confused.

P2625, line 3: "Basically. . ."; the reviewer is completely confused with the statement here? What does basically mean here? Does it mean a common "practice" in the community?

The common significance of this adverb is: "in essence; in summary; put simply". This means here that for the community, "solubility experiments" are those explained in this sentence.

P2625, line 10: Processed (P, R1, R2); these notations are confusing so need to be fully detailed.

Details are fully explained in Desboeufs et al, in the same special issue. We changed this group of sentences: "**Cloud** processed (P, R1 R2) and non-processed (Q) dust samples were used to seed the large **DUNE** mesocosms (Desboeufs et al., this issue, 2014). **The cloud-processed dust samples have been put in contact in the laboratory with synthetic cloud water (Guieu et al., 2010).**" The leaching tests reported here were performed on Q sample, which has not been modified."

P2625, line 25: "fine fraction": as commented above, the method of sieving and where exactly the sample was from need to be briefed here.

We do not wish to repeat here what is perfectly detailed in Guieu et al. 2010. This head paper was specially written and published to avoid such repetitions in the papers of the same special issue.

P2625, line 26: How the samples were deposited to the filter? Re-suspended in the air and filtered? Or just pour the soil into the filtration device?

Just put on the filter from a stock flask.

P2626, line 5: It is crucial here to justify why the different pHs are used with support from literature.

We don't think so because we did not discuss on general methodology and this particular aspect is of poor interest for a reader. We deduced these pH steps following the leaching literature, referring in particular to both Filgueiras et al. (2002) and Gleyzes et al. (2002) nice papers, which review most of the methods, and taking into account the analytical constraints at ultra-trace levels by ICP-AES.

P2626, line 8: pH 6.5; Is it the measured pH in filtered solution? Does the pH change among different leaching? It reads like that the pure water has a pH of 6.5, which is wrong. Later sections also mentioned pH of 6.7 with pH 5 leaching? Why pure water would make a lower pH than pH 5 (you mean 7?)?

pH evolution is explained later p 2627 line 23. pH of pure water is supposed to be 7 at ambient temperature. When you take pure water in air from your system, you cannot avoid dissolution of CO₂ and therefore a slight decrease of pH 6.5 is an average pH we measured for pure water in our lab. We changed in (pH~6.5, **lower than 7 due to ambient CO₂ dissolution; hereafter referred as "pH 7"**)

P2626, line 9: What acid was used? Why this particular pH is chosen? 10-5 M acid does not necessarily mean 10-5 M H⁺ (pH 5).

It is explained p2626 line 5 to 11: we used nitric acid. For a strong monoacid in pure water at concentration c greater than μ M, pH is equal to -log (c).

P2626, line 21-25: Define the detection limit here? From what was described below (page 2627, line 3-5), this DL appears to be the instrument DL rather than the protocol DL. In any case, this needs to be clarified. It is suggested that a table is added here to detail the DL in terms of both ppb and the percentage to that in dust used here.

Yes, it is. We move the paragraph "To test the cleanliness.... limit" up just after. This paragraph tells that protocol DL is the same than instrumental DL. We put the detection limit values in new table 2 (see referee #1 comments). Dissolved elements are ever expressed as percentage of its total quantities, so DL must be expressed in the same unit and compared to the dissolution values and associated uncertainties.

P2627, line 18: A review paper by Formenti et al. (2011), Recent progress in understanding physical and chemical properties of African and Asian mineral dust. Atmos Phys Chem should be a good reference here as well.

The proposed additional reference is a large review, we already have 3 well focused references to support our statement.

P2627, line 20 and Table 1: the Ca in the dust is extremely high? Is this soil from the lake deposit? How representative are these type of dust to the western Mediterranean? For example, what are the frequencies of such dust reaching the western Mediterranean? A review paper by Formenti et al. (2011) may also provide some useful data.

We aim in this paper to stay focused on the solubility, not on general properties of the aerosol. This aspect is already discussed in Guieu et al. (2010), in this special issue.

P2628, line 5: It appears that the high Ca has resulted in significant buffering. This raises a question over the methodology used in this paper. Such a high buffering capacity would make the dust from this source very unlikely to be acidified to low pH such as 1 during its transport from the source to the western Mediterranean. How realistic is the leaching conditions?

Another issue here is that if the pH has been buffered to 6.7 for the so-called pH 5 solution, the applicability of the results to other dust is compromised because other dust might have such a high buffer capacity so dissolution behaviour of elements might be different.

Yes, the highest pH were modified by the dust, but it is not an issue. We do not claim that we made experiments at pH 7 or 5. The names "pH7", "pH5" are only labels of experiments that refer to the pH of the original leaching solution. We have measured the pH in the leaching solution and summarize in table 2 the description given in plain text

P2628, line 10: pH of 1.1; this is not surprising due to design of the pH meter
Indeed, it is not.

P2628, line 25: Phosphate may be taken by calcium carbonate in seawater and fresh water but here it is dust. A major problem in this manuscript is the interpretation of the P data. The close correlation of P with Ca solubility is more likely caused by the Ca present as apatite rather than P being absorbed onto calcite. Apatite is a major species of P in the Saharan dust (Nenes et al., 2011). Also, Fe oxides also have a strong tendency to absorb phosphate.

Nenes, A., Krom, M., Mihalopoulos, N., Van Cappellen, P., Shi, Z., Bougiatioti, A., Zarmpas, P., Herut, B., 2011. Atmospheric acidification of mineral aerosols: A source of bioavailable phosphorus for the oceans Atmospheric Chemistry and Physics, 11, 6265–6272, doi:10.5194/acp-11-6265-2011.

The origin of present calcium carbonate on the Earth surface is precipitation in water. This process occurred during the formation of the mineral which is now dust. We added some words to explain: "Kitano et al. (1978) found phosphorus uptake by calcium carbonate in sea water and fresh water, which can explain the presence of this element in the carbonate fraction of the soil; **phosphorous was included in the mineral during its formation in water.**"

We did not measure Ca associated to P, we measured Ca which is quite entirely present as calcium carbonate, mainly calcite. This is not the case for silicated rocks, as indicated in Nezat et al (2007), where Ca is often in apatite with P. Our correlation shows that Ca and P are released together for each of the leaching step. Because most of Ca is part of calcite and the solubility of Ca is high, Ca dissolution is a good proxy of calcite dissolution. Because P dissolution follows exactly calcite dissolution, we have written that soluble P is associated to calcite. If you state that P is associated to another mineral, you cannot explain such a behaviour. This does not exclude the presence of apatite, probably as insoluble P which represents about half of P. We changed the sentence as: "This suggests a linked dissolution of calcium and phosphorus for all of the batches and therefore, provides strong evidence for the association of **soluble** phosphorus with calcium carbonate in the same solid phases."

We have used the proposed paper in another section to compare P solubilities.

P2629, line 15: The discussion on Si was irrelevant because Si was not measured here.

We do not discuss on silica but on silicates ions. Silicates are anions associated to cations and form a network that contains many other elements. SiO₂ is a major component of this soil fraction (Table 1). This sentence tell us the second possible source of dissolved metals and metalloids.

P2629, line 13: Low solubility of Fe in dust at pH >3 has been reported previously such

as Mackie et al. (2005) and Desboeufs et al. (2001). These references need to be taken into account for discussions.

Mackie, D. S., Boyd, P. W., Hunter, K. A., and McTainsh, G.H., 2005. Simulating the cloud processing of iron in Australian dust: pH and dust concentration. *Geophys. Res. Lett.* 32, L06809, doi:10.1029/2004GL022122.

Desboeufs, K.V., Losno, R., Colin, J.L., 2001. Factors influencing aerosol solubility during cloud processes. *Atmos. Environ.* 35, 3529-3537.

Yes, as many other. The purpose of this sentence is not to state as a new result that iron and aluminium are poorly soluble, but to show the relative differences between Al and Fe on one side and the other elements on the other.

P2629, line 18: The statement that “part of Al and Fe could be released by carbonate at pH 3” needs to be justified. No evidence or literature has been provided to judge the credibility of the statement.

We changed this sentence into: Soluble iron is released by clays at pH 1 (Journet et al., 2001). For the carbonated dust studied in this paper, part of soluble aluminium and iron might also be released by carbonates at pH 3.

P2629, line 10: “but excluding oxides. . .”; what are the mineralogy of Fe oxides in this particular sample? What size of these Fe oxides? What crystallinity of these Fe oxides? All these parameters could affect whether Fe oxides will dissolve at low pH (Cornel and Schwertmann, 2003). Unless such parameters are understood, it may not be appropriate to be conclusive that “no Fe will be dissolved from oxides”.

Cornell, R. M., Schwertmann, U., 2003. *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*, Wiley-VCH Publishers, New York.

We removed these words

P2630, line 8: How the total P was measured? The P solubility was calculated but Table 1 did not show P so it has not been measured by XRF.

By XRF, showed in Table 1 just before Sr

P2630, line 18: This sentence is difficult to understand. Re-word.

Line 18 is 4. Conclusion. We have rewritten a part of conclusion.

P2630, line 19-21: This sentence cannot be part of a conclusion. It is a citation of previous results.

This sentence is put here to introduce the next sentences.

P2631, line 8-9: “carbonate as a source of bioavailable nutrients”; What type of nutrients in this case? Is it P?

Nutrients found here to be associated with carbonate are Mn and P and may be Fe