Both reviewers have concluded that your manuscript is of high interest and suitable for publication in Biogeosciences. Based on the recommendations provided by the reviewers, I am happy to accept publication of a revised version of the manuscript that incorporates the reviewers' major comments (see also attached annotated manuscript); These are:

We really thank to this new referee for the effort made in the review process of this manuscript. We are sure that his/her constructive comments have helped to improve our manuscript. We have modified the text following her/his suggestions and incorporated further clarification where requested. The response and actions taken to accommodate the reviewers' comments are described in the following pages.

- "splitting the metal sources in between one type of big particles that bring only iron and ten times smaller particles that bring the rest of the metals is in my opinion unrealistic. The authors have done a better effort in trying to justify this approach but I still remain skeptic."

--> Provide residence-time values for Fe contemplating two scenarios (the new one would be to assume that iron could come from particles of the same origin and size) but this was ignored.

Response 1. In response to the previous reviewer, we believe that the use of big particle for Fe was well justified and unrebutted. However, we agree in the fact that the recalculated residence time of Fe using same particle size than rest of metals was ignored. The residence time calculation of Fe using the same deposition rate than the rest of metals (i.e. 0.1 cm/s instead 1cm/s) results in a residence time 10 times longer (i.e. average 0.6 h instead 0.06h), even so, the residence time of Fe remain being the shortest of all studied metals.

-" Ni toxicity. Here the authors brought again better arguments (Ni could generate toxic ROS and displace Fe from some enzymes) although this has not been tested in the ocean. However, I cannot accept that a simple correlation, where the concentration of metal spans by a factor of only 2, can be indicative of toxicity for bacteria. One thing is a simple suggestion but another matter is a discussion of more than one page that makes its way into the abstract. First, this type of line of reasoning assumes that correlation implies causation, second, toxic effects of trace metals are revealed when the concentration of the toxic element spans for at least an order of magnitude and here this factor is of less than 2 (Figure 2)."

Response 2. During the first round of this review, we agreed that simple correlation is not a valid proof to demonstrate Ni toxicity and for that reason we rewritten this finding as a *"hypothesis", toning down our statements and increasing the discussion to argument the hypothesis. We indicated that: "Although difficult to demonstrate with the existing data, we consider possible the toxicity of Ni by the following reasons: 1) the strongly and negative correlations between dissolved Ni (i.e. bioavailable) and microbial abundance in both, SML and SSW. This kind of correlation was not found with any other metal; 2) previous study demonstrated Ni toxicity in the same region although with concentrations 13 times higher that our measured background; and 3) we have included now the potential effect that intense UV radiation happening in the SML could have on the binding capacity of colloidal-Ni, and consequently on its bioavailability and/or potential toxicity. Even so, we are aware that this hypothesis remains speculative and we don't have enough information to demonstrate it."*
However, these arguments have been ignored by the reviewer. Since this argumentation remain unrebutted we consider this hypothesis valid although needs to be tested, which should result very useful for the oceanographic community.

- -> think a table should be added with more details than only the recovery on the chemical analyses with ICPMS. A table with the CASS values for example related to the defined concentration in the CASS sample.

<u>Response 3.</u> We have included the requested information in the text. The ms now reads: *"The accuracy of the pre-concentration method and analysis for trace metals was established using Seawater Reference Material for Trace Elements (CASS 6, NRC-CNRC) with the next concentrations (in µg/L) regarding the certified values (in brackets): Cd: 0.02 (0.022); Co: 0.07 (0.067); Cu: 0.44 (0.418); Fe: 1.58 (1.56); Mo: 8.1 (9.15); Ni: 0.41 (0.418); Pb:0.01 (0.011); V: 0.45 (0.49); Zn: 1.14 (1.127)."*

--> In the abstract the authors write about particulate metals, these were not determined. Unfiltered water was analysed, so call these values unfiltered concentrations. Particulate metals were not sampled and were as far as I understand also not calculated by subtracting dissolved from total concentrations (which I do not recommend, let that be clear).

<u>Response 4.</u> The reviewer is right, only dissolved fraction and unfiltered fractions were measured in the SML. It has been clarified along the text. However, in the abstract we refer to the calculated residence times of particulate metals derived from aerosols deposition, which was calculated using the Total (unfiltered fraction) of the SML.

In the conclusion it reads:
"While some metals entering the SML (e.g. Cd, Co, Ni and V) show efficient diffusive mixing from the SML to the SSW, more reactive metals such as Cu, Fe, Pb and Zn seem to exhibit a slower diffusion."

--> Diffusion and diffusive mixing was not discussed, residence times were. And these residence times show that the residence time of Cu is one of the largest whereas the one of Fe is the shortest, as is also stated in the abstract. Still Fe and Cu both seem to exhibit a slower diffusion. This has to be explained better or if not supported by the results changed into another conclusion

<u>Response 5.</u> The reviewer is right. Since we don't have enough data to confirm this conclusion we have changed/replaced it and now reads: *"Residence times of particulate metals derived from aerosols deposition were highly variable, with the largest residence times for Cu (5.8 ± 6.2 h) and the lowest for Fe (3.6 ± 6.0 min)"*

Quote
" 3.2.1. Trace metals in the SML
Dissolved concentrations of Co, Zn, Pb, Cu and Ni showed a decreasing trend from the SML to the SSW, with average concentrations (± SD) 10.4 ± 0.7, 9.3 ± 5.5, 4.2 ± 1.8, 3.1 ± 1.5, and 1.2 ± 0.1 times higher in the SML than in the SSW, respectively. The SML to SSW concentration ratio for V (1.2 ± 0.42) and Fe (1.3 ± 1.5) indicated only slight enrichment in the SML over the underlying water, while the ratio for Mo (1.0 ± 0.1) indicated no difference between layers (Table 1). Only Cd concentrations were consistently lower in the SML compared to the underlying water (0.8 ± 0.2 times lower). Such depletion of dissolved metals in the SML compared to the underlying water has been previously observed in areas without significant aerosol inputs (Ebling and Landing, 2015, 2017). Although not fully understood, some mechanisms such as the dominance of removal mechanisms versus diffusion, or the higher influence of underlying metal sources have been suggested previously to explain this metal depletion (Ebling and Landing, 2017; Hunter, 1980)."

--> Ni enrichment is lower (significantly?) than Fe but equal (significantly?) to V

<u>Response 6.</u> We are not sure if we understood the reviewer criticism. We did not aim to make a comparison between elements but between compartments for each element. In this sense we can confirm that the differences of one metal between compartments are or not significantly different.

Second: Such depletion: Only Cd has a lower ratio. So is it Cd the authors write about or is the enrichment factor so low compared to ??? that the word depletion is used. This needs explanation or a different reasoning.

<u>Response 7.</u> The reviewer is right. We referred to Cd and it has been clarified in the ms that now reads: "Such low ratio of dissolved metals (as it is the case of Cd) in the SML compared to the underlying water has been....."

Third : Apart from my confusion about this, the actual word depletion in my book has a relation to not enough for biology, blooms stop. Perhaps the word depleted must be changed by low ratio, low concentration. (but the above first and second comments, remain)

--> see annotated manuscript

Response 8. To avoid confusion, we have changed two sentences where the word "depletion" was used. Now, the ms reads:
- "Such low ratio of dissolved metals (as it is the case of Cd) in the SML compared to….…"
- "….the dominance of removal processes over diffusion, or the higher influence of metal sources from underlaying water have been suggested previously to explain this difference of metal concentrations between compartments …"

Pae 11 lines 11 onwards
Quote: "During the cruise, Al and Fe atmospheric concentrations were correlated at all the stations and the ratio Fe/Al is typical of a crustal source (Fu et al., in prep.). It is known that the atmospheric iron deposition fluxes are associated to mineral dust particles even during the period when the Saharan dust inputs are very low (Desboeufs et al., 2018; Guieu et al., 2010). On the contrary, no correlation with Al is observed for the other metals, except during FAST1-3. Thus, we used a velocity of mineral dust deposition for Fe 1 cm.s- 1 and an average velocity of fine anthropogenic particles for the other metals, i.e. 0.1 cm.s-1 (Baker et al.,2010; Duce et al., 1991)."
It is all very well that Fe correlates with Al, but there is hardly transport from the south. And this Fe/Al ratio, is that not related to the mineral lattice? So not really Fe that will dissolve so easily in such a short residence time. Moreover, this factor 10 difference in velocity decreases the residence time with a factor 10. If the authors had used the same deposition for Fe, the residence time ± the error would overlap the residence time of Co and Zn. And then only Ni would have a residence time that is extremely short, which would fit the lack of reactivity of this element in contrast to an element as Fe. This might interfere with the role of Ni in the discussion though.

--> see previous comments and annotated manuscript

Response 9. We have clarified this point in previous comments and we hope have provided enough arguments to convince the reviewer that about our decision on this issue.

Page 12
Lines 17-21
Quote: " Since, such a quick transfer of these metal particles to the underlying water (in the order minutes) is unlikely (mainly due to their affinities to organic ligands), and the dissolution is not immediately reflected in an increase in the concentration in the dissolved fraction (i.e. D-SML), other variables (linked to physical processes, photochemistry or biological activity) probably affected the residence time of this and the other metals in the SML."
Gerringa et al, 2017 ((mar. chem. 194, 100-113) concluded that ligands are saturated in the surface Mediterranean so that might form one explanation that a quick transfer as particles to the underlying water is possible.One of the co-authors of this manuscript, Wagener (in Wagener et al. 2010), might have some opinions here, that could explain this quick transfer also very well!

Response 10. The argument of the reviewer could be feasible. Nevertheless, this argument would add more speculation to the work since our dataset is not comparable with that obtained by Gerringa et al, where surface data were obtained at 9 m depth and our values are from the SML and 1 m depth.

Quote: "On average, while the highest residence times obtained for Cu and Pb are in agreement with their strong affinity to particles and therefore with a high probability of retention in the SML, other reactive elements such as Fe presented the shortest residence times. Since, such a quick transfer of these metal particles to the underlying water (in the order minutes) is unlikely (mainly due to their affinities to organic ligands), and the dissolution is not immediately reflected in an increase in the concentration in the dissolved fraction (i.e. D-SML), other variables (linked to physical processes,

photochemistry or biological activity) probably affected the residence time of this and the other metals in the SML" .

I cannot follow the reasoning: the long residence times of Cu and Pb are explained by a strong affinity to particles. However, one of the possible explanations for a short residence time is also binding by particles (a quick transfer to particles). Although according to the authorsthis is not the case for Fe, it still served as a possible explanation for a short residence.

Response 11. We agree with the reviewer, and we have rewritten the sentence that now reads: "*Since such a quick transfer of these metal particles to the underlying water (in the order minutes) is unlikely (mainly due to the high content of organic matter in the SML), and the dissolution is not immediately reflected in an increase in the concentration in the dissolved fraction*".

Page 14:
Quote: "Since surface salinity showed the same eastward increase and was closely correlated with those metals (rs ranged from 0.51 p<0.05 for Mo to 0.97 p<0.01 for Ni; Table 3), the exchange with the surface Atlantic Ocean waters seems to be the main cause of this gradient of concentrations in our study, although higher aerosol inputs in the western MS could also contribute to this gradient."

How can more aerosol in the west decrease dissolved concentrations? I think dissolution would increase the conc, if you mean ballasting and adsorption processes are connected with the decrease in dissolved concentrations than this must be better explained.

Response 12. The reviewer is right. We meant eastern instead western which was in agreement with the statement made before (i.e. "*This trend is consistent with previous studies where the increasing eastward trend in concentration along the southern coast of the MS has been suggested to result from several factors such as: more intense Saharan deposition on the eastern MS (Guieu et al., 2002)*"). To avoid to be repetitive we have deleted "..,although higher aerosol inputs in the eastern MS could also contribute to this gradient"

Minor comments:
Abstract, Line 33: Ni concentration: do you mean total or dissolved ? Since both are discussed in the lines just above.

Response 13. We meant both Dissolved and total (unfiltered). It has been specified in the abstract that now reads: "*Our results show a strong negative correlation between the dissolved and total Ni concentration and heterotrophic bacterial abundance in the SML and SSW,…*".

Page 2: lines 17-19
Copied from the Conclusion in Sarthou and Jeandel 2001: "The very low surface concentrations may limit primary production or, at least control phytoplankton species composition. Such an iron depletion was not expected in the Mediterranean Sea, characterised by important continental inputs."

For me "may limit" is not equal to saying that " Fe has been considered an important factor controlling phytoplankton growth (Sarthou and Jeandel, 2001)."

So tone down here please.

Response 14. We have rewritten the sentence, now reads: "Although present in a higher concentration than in other oceans, Fe may control phytoplankton growth and composition (Sarthou and Jeandel, 2001)."

Page 9:
Line 25, were the metals in the FAST station comparable then with Tovar-Sanchez et al., 2014?

Response 15. Yes, for most of them (i.e. Co, Cu, Fe, Mo, V).

Page 10

Response 16. We agree, we have changed the "well known" by "have been studied".

Response 17. The text refers to Fast 1-4 (Fast1, Fast1, Fast 3 and Fast4) and St3 and St4. We have clarified this in the ms, and now reads: "*However, the reasons for the increase at stations St 3 and St 4 are not evident*".

Regarding **annotated comments in the manuscript**, we have corrected all grammatical suggestions and clarified the next specific comments:

Review´s comments – Pag 2 -Line 11. "What do the authors mean by consistent?"
Response to reviewer´s comment: By consistent we meant that are usually present.

Review´s comments – Pag 2 -Line 21. "proxies for atmospheric deposition in Posidonia?"
Response to reviewer´s comment: aerosols in Posidonia tissue.

Review´s comments – Pag 2 -Line 23. "Meaning of this sentence is vague. Is it really necessary?"
Response to reviewer´s comment: We agree. It has been deleted.

Review´s comments – Pag 2 -Line 28. "not necessary?"
Response to reviewer´s comment: We agree. It has been deleted.

Review´s comments – Pag 3 -Lines 14-16. "Is this for the whole MS? Seems little. How relevant is that compared to the amount of Fe in the surface mixed layer?"
Response to reviewer´s comment:Yes, it was calculated for the whole Mediterranean Sea. 2 tons of total (unfiltered) Fe represents only 0.2 of the TSSW pools over the top meter of the surface sea. This amount would be much lower if we compare it with the surface mixed layer.

Review´s comments – Pag 3 -Line 18. "impact on the biogeochemistry of
Response to reviewer´s comment: it has been changed

Review´s comments – Pag 3 -Line 23. "range"
Response to reviewer´s comment: it has been changed

Review´s comments – Pag 5.
Response to reviewer´s comment: All suggested changes have been corrected in page 5.

Review´s comments – Pag 6 -Lines 7-8. "at what depth where the samples collected? Same as for PP? (see p. 7, line 21)"
Response to reviewer´s comment: SSW were collected at 1 m depth (as indicated at the beginning of the first paragraph of the section 2.1.), however, to avoid confusion we included the depth in this sentence ("SSW (~1 m depth) were collected using acid-washed Teflon tubing connected to a peristaltic pump and directly filtered on the same cartridge to collect the dissolved fraction (D-SSW)").

Samples for Primary Production (and Chl-a) were collected at 5m depth, which is indicated in section 2.3.2 and discussed in the last paragraph of section 3.2.4.

Review´s comments – Pag 8 -Line 5. "references?"
Response to reviewer´s comment: This data was obtained from the cruise and are pending of publication.

Review´s comments – Pag 9 -Line 5. "I could not find any analysis including aerosol data in Table 3."
Response to reviewer´s comment: The correlation was not showed but can be done and checked with data from Table 1.

V vs Zn (ng/m3)

$y = 0.3266x + 1.0498$
$R^2 = 0.7967$
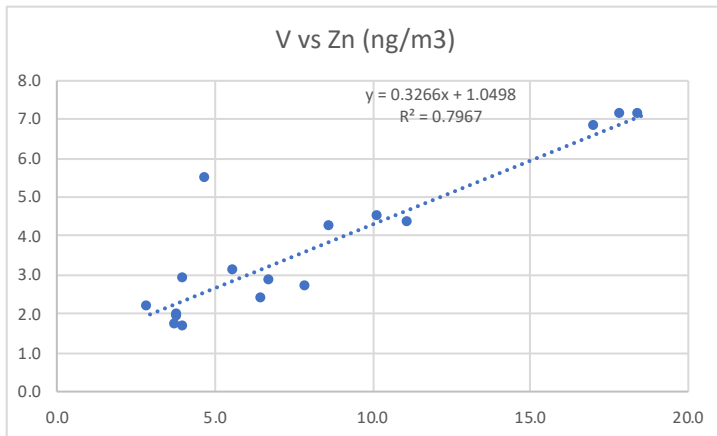
Review´s comments – Pag 9. Line 9: "What is the unit for the color scale in Fig. S4?"
Response to reviewer´s comment: The units are mm/period, it has been included in the legend of the figure.

Review´s comments – Pag 9. Lines 9-12: "I am not sure I follow the logic. How is the composition related to the duration of rain events?"
Response to reviewer´s comment: The reviewer is right, the sentence was not clear. This sentence is to justify, not the duration but the type of wet deposition, as the sampled rain is a dusty rain, we suppose that all the rains occurred during the fast action are dusty rains. Moreover, we used the argument of high metals concentration in rain to justify the high concentration in the surface water of Fast stations. The text now reads: "As the rain composition collected was typical of wet dust deposition with high particulate concentrations of Al, Fe and Ca (Fu et al., in preparation), we suppose the rain-out of dust in the atmospheric column around this station occurred between the 3rd to the 5th of June and hence dusty rain events impacted the concentration of surface waters during Fast stations."

Review´s comments – Pag 9 Line 20: "Why is there no analysis of trend between T-SLM and D-SLM and T-SLM and D-SSW (Table 3)?"
Response to reviewer´s comment: T-SML vs DSSW analysis is included in Table3, however comparison between T-SML and D-SLM was not included since maximum correlation were only found for D-SML Cd and T-SML Cd (i.e. 0.789 p<0.01), however the correlations of D-SML and T-SML versus biology parameters in SML and SSW were done and presented in Table 5.

Review´s comments – Pag 10 Line 12: "Meaning unclear. Do you mean metal sources in the underlying water layer?".
Response to reviewer´s comment: We meant metal sources from underlaying water. It has been rewritten, and the text now reads: "or the higher influence of metal sources from underlaying water have been suggested previously…"

Review´s comments – Pag 10 Lines 2-4: "See reviewers comments. Since there is no evidence here that Al and Fe fluxes come from other sources; reviewer 1 has a fair point in asking for the presentation and discussion of residence times using similar sinking velocities as for other metals."

Response to reviewer´s comment: This have been responded above (Response 1).

Review´s comments – Pag 12 Line 14: "From Fig. S1 and S2 it seems that the source regions for st.3 and 4 are the same as for the FAST location?"
Response to reviewer´s comment: Perhaps the source regions could be similar or close however only FAST stations were affected by run event which help to explain the high metal concentration measured in the SML.

Review´s comments – Pag 13 Lines 4-7: "From Table 2, I do not see evidence of increased bacterial abundances due to the dust input: st. 3 and 4 also have higher bacterial abundance."
Response to reviewer´s comment: The reviewer is right, we have removed the sentence. Also, we have include more references in this section to support our findings.

Review´s comments – Pag 13 Lines 13-16: "Contradicts argument proposed p. 14 lines 5-11."
Response to reviewer´s comment: We don't find contradictory this argument. Here we found that metals in the T-SML (i.e. unfiltered samples, and therefore including bacterioneuston) decreased eastward and was positive correlated with bacterioneuston abundance. In page 14 lines 5-11, we refer to metals concentrations in a different compartment and fraction (i.e. dissolved metals in the subsurface water) and therefore affected by different processes.

Review´s comments – Pag 13-14 Lines 26-27, 1-2 "See reviewers comments. Bacteria and Ni are correlated with salinity, hence, this could be an effect of macronutrients (see p. 13, line 10)."
Response to reviewer´s comment: We already explained this point to the previous reviewer.
The difference found with Ni regarding other metals is that the negative correlation with microbial abundance occurs in both compartments, SML and SSW, and in both fractions, dissolved and total. In the case of total fraction, that includes bacterioplankton metal composition, an uptake of Ni as nutrient should be reflected in an increase of abundance and also in an increase of Ni concentration in the total fraction. Also, the concentration of Ni in the SML is too high to act as nutrient for bacterioplankton.

Review´s comments – Pag 15: "See reviewers comments. This discussion is long as it is based on speculation (Both Ni and bacteria are correlated with salinity and could be the result of other environmental gradients (see previous comments on this and p. 13)."
Response to reviewer´s comment: We have clarified this point above (please, see Response 2).

Review´s comments – Pag 25: "these units do not correspond to those in the Table."
Response to reviewer´s comment: The reviewer is right. It has been corrected and the Table legend norw reads: "Arcillary parameters and metals in water and aerosols measured at all stations. Metals in ng.m^{-3} for aerosols and nM or pM for water compartments"