

## ***Interactive comment on “Characterising the surface microlayer in the Mediterranean Sea: trace metals concentration and microbial plankton abundance” by Antonio Tovar-Sánchez et al.***

### **Anonymous Referee #1**

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Review for consideration for its publication in Biogeosciences of Characterising the surface microlayer in the Mediterranean Sea: trace metals concentration and microbial plankton abundance by Antonio Tovar-Sánchez, Araceli Rodríguez-Romero, Anja Engel, Birthe Zäncker, Franck Fu, Emilio Marañón, María Pérez-Lorenzo, Matthieu Bressac, Thibaut Wagener, Karine Desboeuf, Sylvain Triquet, Guillaume Siour, Cécile Guieu.

This manuscript contains the measurement of many ancillary and biological parameters and trace metal concentrations in the surface microlayer and immediate underlying water collected during a Mediterranean cruise that covered all the main basins of

C1

the western and middle Mediterranean Sea. The manuscript is a fine effort in shedding light in the description of this microenvironment and the parameters that can affect its special biochemical characteristics. Despite its importance for interface processes, not many efforts are dedicated to the surface microlayer and this work is addressed to partially cover this deficit. Due to the amount of work involved and the relevance of the work for the common readers of Biogeosciences I think that the manuscript is well suited for its publication in this journal. The manuscript is well organized although it is obvious that more than one researchers have taken care of different parts, not all of them showing the same skill to write scientific English. Some parts will require grammar revision before publication. I would also miss that they present more data in the text since as it is the reader has to be continuously going back and forth to the tables and those are not reader friendly due to their size. Overall, I would back a major revision decision; the database presented here is very interesting and many parts of the interpretation are very useful but I think that the manuscript can be substantially improved in many aspects.

Before publication, I have three major concerns that the authors need to address: Photoreactions. In a layer so exposed to solar radiation and with a heavy presence of organics prone to form radicals, the authors should have a better understanding of how these processes can affect species distribution in the SML and fluxes off it. However, these reactions are only invoked when the authors cannot explain, with their limited battery of processes, the distribution of a particular trace element. Just as a last resource. And I want to underline that not all metals are equally prone to those effects. It is well known the strong dependence of Cu and Fe redox seawater chemistries on solar radiation. Under strong solar radiation it is very likely that most of Cu and Fe are present as Cu(I) and Fe(II). Then the regular chemistry in seawater shifts, Cu(I) is a weaker acid and binds preferentially weaker acids (S-2) and Fe(II) is far more soluble (6 orders of magnitude!!!) and forms weaker complexes than Fe(III). I have to accept that not much is known about the speciation (organic and redox) of trace elements in the SML but the authors should try to gather all information available and use it for

C2

interpretation. Surprisingly, solar radiation is claimed to play a role in Ni speciation, a metal that is not likely to experience redox changes in seawater conditions (page 13, 15-18). I suggest a better compilation of bibliography referred to photochemical reactions of trace metals in surface waters, clearly identify those metals that can suffer redox reactions and apply this knowledge to the interpretation of distributions from the introduction and not as a last resource. Residence times of trace metals in the SML. There is a section where the authors argue that most of the material in suspension is of Atlantic or European origin except for a few exceptions. Then in order to calculate the residence times of different metals in the SML the authors assume that all metals are present in particles of a certain size except for iron that is in mineral particles ten times higher; and this assumption is for the whole dataset. It is true that if dust is present, its contribution to the rest of the metals measured in this work would be at least 2 orders of magnitude below iron levels (Guieu, Dulac et al. 2010). This supports that Saharan aerosols are not the main source of trace metals. Then why is it suggested that Fe is in thicker particles of "mineral" origin from a different source? Furthermore, there is no relationship between iron levels (high, > 100 ng m<sup>-3</sup>, in 5 samples) and the proximity to the Sahara or the trajectories shown in the supplementary material or the referred episodes of wet deposition. In my opinion, there is not enough evidence to argue that iron is present in particles of a different nature and those are 10 times bigger. I suggest that the authors repeat calculations assuming all the particles have a common origin and size and then if they want to keep their original assumption, discuss Fe using two scenarios. The use of high regressions as a cause-effect relationship between variables, specifically the whole discussion about Ni toxicity for bacterioplankton. This needs to be toned down several notches. Although possible, high correlations are indicative of a distribution dependent of common causes and not necessarily of a toxic relationship. If that was the case, salinity would be very toxic for bacterioplankton since the regression coefficient is even higher than that of Ni. Ni concentrations in phytoplankton (I am not familiar with bacterioplankton) are quite high (Twining and Baines 2013) despite their limited physiological relevance without causing deleterious effects.

C3

Moreover, in the sampled waters, there is a factor of only two between the highest and the lowest Ni concentrations. It is very unlikely that such a small variation can cause strong toxic effects. I simply do not buy the hypothesis, could be mentioned but only as a hypothesis and I advocate from its removal from abstract and conclusions.

I would also like to see a better explanation about the striking accumulation of certain metals in the SML despite their absence in aerosols (Cd, Mo Pb) even if using bibliographic water column values. I would also like to see d and aerosol mass data in the final version of the manuscript. Comments Page 1 "the total fraction of some reactive metals in the SML (i.e. Cu, Fe, Pb and Zn) showed negative trends with salinity, these trends of concentrations seem to be associate to microbial uptake". Here we have again the problem that a positive or negative high correlation cannot directly be interpreted as a cause-effect relationship. For such statement the authors have first to show that the microbial biomass found in their oligotrophic samples can make a dent in metal concentrations in those waters (from known metal:C ratios). I would find very surprising that the trace element microbial budget is significant when compared to the trace metal phytoplankton budget. Second, why for Cu, Fe, Pb and Zn a negative correlation is indicative of uptake and for Ni is indicative of toxicity? Pb is far more toxic and Ni cellular quotas (at least in phytoplankton, Twining papers) are very high in healthy cells. What are the regression coefficients of those trace elements with respect to salinity? Page 2 5-10 Questions for the authors: Is the relevance of dust deposition also related to the lack of major riverine discharge? The enrichment at surface is not related to the combination of minimum mix with adjacent seas and strong evaporation (close basin)? 13 I would write here may play since most of the following text are considerations and hypotheses. 21 I suggest to define the thickness of this SML or at least what the authors consider here (a brief description of the Wurl formula and the parameters it depends upon) since d data are not shown. 25 The 3 orders of magnitude wide range provided is too much non definition. Are there many different ways to calculate this thickness? Page 3 1 "Characterized by the dominated abundance of microorganisms" bad grammar 3 please remove although. One part of the sentence is not modifying

C4

the other 9 influences 10 “concentrations of Cu, Fe or Pb in the SML increase by a factor of up to 800, 200 and 150 times compared with the underlying water”. Interestingly, this is not the case here. This has to be discussed in detail later on. 18 This is likely long enough to be chemically missing word? and biologically missing word? alter the SML and affect the composition and activity of the neuston community Page 4 Section 2.1 is quite confusing and the quality of English drops substantially. It has to be revised (grammar and spelling) and modified 14 Is this sentence correct and/or complete? It does not make much sense to me. This inlet was developed for sampling both fine and coarse particles, with particles of aerodynamic diameter of about 40  $\mu\text{m}$  18 No bibliographic mention to the combination of standard optical and electrical mobility analyzers? 20 a filtration unit 23 all filters / rinsed 23 please rewrite “A sampling strategy was made to avoid the contamination by the cruise smoking” Here add a period and then First 25 the PEGASUS container and the boat’s chimney / opposite side of the deck (opposite ship boards?) 28 bad grammar again Page 5 6 Not all metals measured are presented here. Why Cr and Nd are not included? 7 Why rain data are not commented? 18 the glass plate is not conditioned to the seawater matrix before first collection? I wonder how much metal is adsorbed and extracted from the sample from a plate which surface has been activated after acid cleaning and has only be risen with ultrapure water. Can the authors discard that the first extraction of the day is not lower? 21 what was the result of blank checking? Please describe briefly. Here I also warn that if the blank is run immediately after the ultrapure rinsing, metals could be adsorbed by the plate. 23 Wurl’s formula? /The total. . . . . was directly 24 while the. . . . . Page 6 5 why only samples for totals were UV digested? Metal organic ligands and DOM were certainly present in the dissolved samples. Cu and Co analysis in dissolved samples are especially dependent in this digestion step (Rapp, Schlosser et al. 2017). 23 Microorganisms in the . . . . . were sampled at the same time than. . . . . using a 25 what does it mean “manually sampled”? I hope not what it literally indicates. 29 please split sentence in two. Page 7 Sections 2.3.1 and 2.3.2 are almost free of the bibliographic references where the methodologies have been proved for these specific

C5

purposes. Example: “value of 26,000  $\mu\text{gC L}^{-1}$  was used for the concentration of dissolved inorganic carbon”, where is this value coming from? 14 I guess fumes were used before filter use. Not clear with the current sequence. 26 linear least squares regression? Page 8 4-5 I find that here the bibliographic revision is too short. There are many more works on the presence of metals in dry aerosols. I would be interested in a very simple study about temporal trends adding studies from the 90s (Roy Chester and several others). In any case the bibliographic search has not been good enough Lines 7-10 Here the discussion is very difficult to follow. Figure 1 does not include sampling dates and figure S1 is confusing with so much overlapping of curves of similar colours. Then it is difficult to follow this discussion. For me it is like all the trajectories do not show Saharan sources but on those two dates the African input was so high that in those cases particle trajectories were “not convenient” and sided for interpretation. Could the authors be clearer about the use of the different information sources? Total mass collected is not provided in the manuscript. 9 loaded with? Lines 15 to 20 In my opinion this section has to be revised by an English native speaker. Furthermore there are comments about data that are not shown in tables or graphs. 27 trace metals conc of. . . . ., with the exception of Pb, were lower than those measured. . . . . in previous MS studies. “In previous studies” but only one manuscript is cited. I stress that the bibliographic search on trace metals in dry deposition in the Mediterranean area has to be extended and results put in that context before publication Page 9 This discussion is very hard to follow unless ranges supporting arguments are provided in the text. It forces the reader to go back and forth to Table 1 that is actually quite hard to read. 7 My question here is how rain affects SML composition and thickness. 8-17 this is a very interesting paragraph. Please discuss the low SML/SSW ratios in the context of the huge ratios referred in the introduction for Cu, Fe and Pb (p 3, 10-11). For Ni, V and Fe the authors should say explicitly that there were no differences between SML and SSW (average close to 1 and standard deviation bigger than the difference). What are the removal processes the authors suggest? Differential dissolution of different metals from the same material? Radiation driven processes? Is taken into account the high ef-

C6

efficient mixing in the turbulent 1st meter of the ocean? 18-20. An efficient mixing should be given by close values (as both watermasses mix efficiently they have the same concentrations) and not simply by high regression. If the slope is close to 1, there is good mixing (line constitutes by identical values, if the slope (not  $r^2!!!$ ) is different from 1 that means poor mixing since one of the concentrations is consistently higher than the other and that would mean gradients. Page 10 Cu and Fe experience redox changes as a function of the solar radiation and Pb has a limited solubility of inorganic forms at pH 8. I do not know whether this explains their distribution but I think it is worth mention it. 15-16 this statement disentangling metals from particles sizes is very concerning to me. The statement assumes that 1 Fe is included in some particles and the rest of metals in other particles 2 particles including Fe are so much bigger that sink at 10 times faster speed. I think this requires more discussion, if all metals were part of the same particles and no other process was accounted, this would underestimate Fe residence time by a factor of 10 and its residence time would be perfectly aligned with those of Cu, Zn, V and Pb. First, previous discussion in this manuscript concluded that most of the aerosols had a European or NA origin. Now the authors consider that Fe has a mineral behaviour far from fine anthropogenic particles. Second, I am not familiar with studies showing that fine particles are low in iron with respect to the rest of the metals in this study, especially those found at the same order of magnitude. If the rest of the metals come from a different thinner material, and some are at concentrations close to the Fe conc in aerosols, then this thinner material is iron free. Third, this sedimentation velocity through the mixed layer is going to be strongly dependent on the energy of the system and a single value for the whole cruise at any location seems a huge source of error to me. Often we have to make simplistic assumptions but I would like that the authors at least make the effort to discuss the consequences of their decisions in terms of uncertainty. How variable was the mixed layer depth during the cruise? 19 I think the shortest residence time in table 3 is 1.2 minutes and not 12. 24-25 I could not find  $d$  values in tables. In Wurl's equation  $d$  is a function of the sample volume, number of dips and the screen area with the assumption that the presence of surfactants would

C7

increase the volume retained per dip and therefore  $d$ . It is necessary to have  $d$  values if we want to evaluate its impact and variability on residence time calculations. Page 11 I would not claim that different behaviours are caused by different reactivities to natural ligands. Of the metals targeted in this study, only Zn has a weak affinity for natural organics (not much is known about V affinity for natural organics). Cu is the clear example of strong affinity to ligands and even is known that this affinity is higher than that for biological membranes (González-Dávila, Santana-Casiano et al. 2000). Here the elephant in the room is photochemical processes. 5 can be known how is  $d$  related to wind force?. No consideration of photoreactions? 16 again it is said of other regions but only one example is provided. Rewrite for this specific case or bring more examples. 21 "In general, and with the exception of phytoplankton middle and CBL-small, microbial abundance was higher in the SML than in the SSW with abundances ranging from 1 to 6 times higher for bacteria and CBL-middle-large, respectively (Table 1)". In Table I the groups with a higher concentration in the SML are autotrophs (phyto and cyanobacteria). However, the extremely low Chl-a concentrations in the SSW (low even for oligotrophic waters, consistently below 0.1  $\mu\text{g l}^{-1}$ , actually they should revise their numbers, I only saw numbers that low in the eastern mediterranean) point to a lack of viable autotrophs in the SSW. And here it is difficult to point to UV effects since the SML should receive even more radiation. It is a real pain that there are no Chl-a measurements in the SML to infer whether the higher cellular content was constituted by viable cells. It is also shocking the lack of correlation of Chl-a with any of the biological variables. 23 rewrite in English please. Page 12 1-2 It makes sense but I would use could instead of would, it is all speculative. I really doubt that assimilation and storage from such a low biomass could explain trace element trends 5 Revise English. It is very surprising that TEP concentrations (of biological origin) could increase after a dust deposition, they should remain or decrease by scavenging. I would tone down this sentence. First it is based on a single value and second it is not higher than Station 9. 6 "we therefore....." Because there are no correlations between metals and TEP the consequence is metal assimilation by microbes explain longer residence

C8

times? I do not follow the cause-effect relation here. Please include here known Cu, Zn and Fe cellular quotas to justify or discard assimilation (Twining papers). 10 and here appears the elephant in the room. It must be taken into account the complexity of photochemical reactions (reducing Fe and Cu) but also the bleaching effect on DOM and ligands. 11 That Ni is strongly anticorrelated to bacterioplankton is indicative of a relation but not necessarily direct. It could be (as for other metals) that is taken up and it is not toxic; as a possible result the higher the bacterial density, the lower the Ni concentration. Figure 3. Are those least square linear regressions? 17-19 please give data ( $r^2$ ) 23 "close correlated" closely Page 13. There is a lot of discussion about possible mix Atlantic and MS waters but no actual bibliographic search on average values in both waters that could justify that some metals could be enhanced by mixing and others not. Please, look for such data. 16" Indeed, UV radiations in this surface layer are highly intense and can acts as a biochemical microreactor where many transformations and photochemical reaction occurs" rewrite after grammar checking. I find that claiming that photoreactions could explain this bioaccumulation is really far fetched. Specially for a metal that has no different redox states in oxygenated seawater Page 14 "It appears that Nickel-dependent toxicity involving ROS may be likely mechanism of oxidative stress in marine microbial organism of the surface ocean" check grammar but better discard here Conclusions Is Co not affected by chemical and biological processes? That is very surprising due to its important requirement

Figure 1. This is a good figure but I do not understand why has been sent vertical. I guess for the publication will be required a reduction in size, shift to horizontal and increase of the font size. Figure 2. I guess DNi refers to DNi in the SSW. Please reduce size. I am not sure this relationship deserves a whole figure. 1 the regression coefficients are in the tables. Second, the supposed bacterioplankton control by Ni toxicity is a nice hypothesis but data do not prove such dependence. Tables are quite difficult to read and I wonder if these will be legible in the final version of the manuscript. In any case all provide useful information and I would not simply remove data from them. Table 3. Station not saturation

C9

Figure S3. Wrong caption.

González-Dávila, M., J. M. Santana-Casiano and L. M. Laglera (2000). "Copper adsorption in diatom cultures." *Marine Chemistry* 70(1-3): 161-170. Guieu, C., F. Dulac, K. Desboeufs, T. Wagener, E. Pulido-Villena, J.-M. Grisoni, F. Louis, C. Ridame, S. Blain and C. Brunet (2010). "Large clean mesocosms and simulated dust deposition: a new methodology to investigate responses of marine oligotrophic ecosystems to atmospheric inputs." Rapp, I., C. Schlosser, D. Rusiecka, M. Gledhill and E. P. Achterberg (2017). "Automated preconcentration of Fe, Zn, Cu, Ni, Cd, Pb, Co, and Mn in seawater with analysis using high-resolution sector field inductively-coupled plasma mass spectrometry." *Analytica Chimica Acta* 976: 1-13. Twining, B. S. and S. B. Baines (2013). "The trace metal composition of marine phytoplankton." *Annual Review of Marine Science* 5: 191-215.

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