

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

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We really thank the reviewers for their constructive comments. We believe that this new version of the manuscript has been improved significantly by the reviewers' suggestions as we have addressed all the points they raised. Generally, the text has been modified and we believe it has significantly improved. Specifically, grammatical and syntactic mistakes have been corrected and in general the text has been grammatically reviewed by an English native speaker. We have incorporated further clarification in all section of the manuscript; we have modified tables and figures, incorporated new references and elaborated new figures and tables. The response and actions taken to accommodate

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the reviewers' comments are described in the following pages.

Reviewers' Comment: This manuscript describes trace metal concentrations, along with biological parameters, in aerosols, sea-surface microlayer (SML), and surface waters (SSW) at a number of stations in the Mediterranean Sea. The data appear to be carefully collected and analyzed and of high quality. However, the manuscript is marred by numerous grammatical and other errors, and it needs to be thoroughly edited before it would be acceptable for publication. **Authors' Response:** We are very grateful by the review and comments made by this referee, we believe that his/her comments and suggestion have helped to improve significantly the manuscript. The manuscript has been revised grammatically by a native English speaker.

Reviewers' Comment: However, more substantively, the manuscript doesn't tell much of a story about most of the data, and a few of the relationships that it does present are not supported. In general, it focusses on correlations between parameters, and these can always be tricky. If a chemical and biological parameter are negatively correlated, is it because the chemical is exerting a toxic influence? Or because biology is drawing down the chemical? Or because both are being differentially affected by something else entirely. We just don't know, but this ms makes some unsupported conclusions nonetheless.

Authors' Response: The reviewer is right. This criticism has been made for both reviewers and we agree with them. We agree that a high regression between two parameters means a relationship but not necessarily a cause-effect. For that reason, we have toned down many of our conclusions and extended our discussion to support them and, at the same time, avoiding being too speculative. During the preparation of the manuscript we deeply discussed the interpretations of these correlations, because, as pointed out by the reviewer, a same linearity could be interpreted either, as toxicity or biological uptake. 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,

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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 than 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. Therefore, we have toned down the conclusion along the manuscript.

Reviewers' Comment: Specific comments There are numerous mis-spellings, grammatical and punctuation errors throughout the manuscript that should be corrected. I have highlighted a subset of these encountered in the first half of the manuscript here, but the entire manuscript needs careful attention and correction of these.

Authors' Response: We thank the reviewer for his/her grammar revision. We have corrected all of them and revised the entire manuscript.

Reviewers' Comment: Additionally, the ms would benefit from more general written description of trends in the results (or state that there are no trends). Currently the reader is left largely to pick their way through the massive, tiny-font tables.

Authors' Response: The reviewer is right. We have given more information (data ranges) to ease reading and interpretations of given results.

Reviewers' Comment: Title: should be "trace metal concentrations" Authors' Response: Corrected

Reviewers' Comment: P2, L2: what does it mean for an ecosystem to be "ecologically regulated"? Authors' Response: We meant that it hosts a particular and not random microbial (neuston) community. We have removed these words and now the text reads: "Characterized by a high abundance of microorganisms (called neuston and ranging from bacteria to larger siphonophores (Wurl et al., 2017)), the SML constitutes a par-

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ticular marine ecosystem.”

Reviewers' Comment: P3, L15: should be “underlying” Authors' Response: Done

Reviewers' Comment: P4, L15: are the fine or the coarse particles <40 μm ? Authors' Response: We have modified the sentence to avoid confusion. The text now reads: “This inlet was developed to sample particles with an aerodynamic diameter inferior to 40 μm (Rajot et al., 2008).”

Reviewers' Comment: P4, L19: year for Rupprecht & Patashnick? Authors' Response: We have clarified the Rupprecht & Patashnick is a company.

Reviewers' Comment: P4, L24: what is meant by “the cruise smoking”? Authors' Response: We have modified the sentence. It now reads: “A sampling strategy was used to avoid contamination by the ship's fumes.”

Reviewers' Comment: P4, L18: how was the sample collected off the glass plate? With a water or acid rinse? If so, how was dilution of original sample estimated? Authors' Response: The sample is collected from both sides of the glass plate directly into sampling bottles by using a Teflon wiper located in a PVC system (see attached pictures R2). Reviewers' Comment: P5, L22: double citation (also check for other instances of this) Authors' Response: We have removed all double citations along the manuscript.

Reviewers' Comment: P6, L4: dissolved samples were not irradiated? Was a particulate CRM analyzed? What was the digestion approach for the particulate/total phase? How long were samples acidified for? Authors' Response: Dissolved fraction samples were not irradiated. We are aware that organic ligand and DOM are also present in the dissolved fraction. However, unlike other analytical methods where UV digestion is a critical step (e.g. polarography, or method using particulate chelating resin), in the method used here (liquid-liquid extraction using APDC-DDDC), the UV radiation is not considered a critical step. In the case of the total fraction we decided to include the UV step to guarantee a full cell breakdown and the complete digestion of samples. As

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far as these coauthors know CRM for particulate metals in seawater are not available. For the total phase UV digestion we used an UV system consisting in one UV (80 W) mercury lamp that irradiated the samples (contained in quartz bottles) during 30 min. All samples (dissolved and total) were acidified and stored for at least 1 month prior to analysis. It has been now specified in the manuscript. The text now reads: “All samples were acidified on board to $\text{pH} < 2$ with Ultrapure-grade HCl in a class-100 HEPA laminar flow hood. The metals, (i.e. Cd, Co, Cu, Fe, Ni, Mo, V, Zn and Pb) were stored for at least 1 month prior to analysis.”

Reviewers' Comment: P7, L4: I assume this should be 0.5 μm Authors' Response: Yes, corrected.

Reviewers' Comment: P8, L28: here and later the text refers to “previous studies” but only one study is cited Authors' Response: The reviewer is right. It has been corrected in the manuscript.

Reviewers' Comment: P9, L3: is it standard deviation or error presented here and in other parentheses? Authors' Response: It is standard deviation. It has been specified along the manuscript.

Reviewers' Comment: P10, L18: in the discussion of residence times the ms refers to particulate metals, but the methods only describes collecting a dissolved (filtered) and a total (unfiltered) fraction. So, how can the behavior of the particulate fraction be isolated and determined? Please explain the assumptions made to do this, so they can be evaluated. Authors' Response: We assumed that the metal in the total fraction is strongly influenced by lithogenic/aerosol material. We were aware that Total fraction also include metals from other pools (e.g. microbial and organic material) and perhaps, assuming this, we were overestimating the residence time. However, our residence time were of the same order that those calculated by Ebling and Landing (2017) using reactive and refractory particulate concentrations, and therefore making of our assumption feasible. We have specified this assumption in the manuscript, that

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now reads: “For the calculations of the residence times throughout our different stations we used simultaneous empirical measurements of total metal concentrations in the SML (assuming that the metal in the total fraction is highly influenced by material from aerosol dust) and metal aerosol fluxes”

Reviewers’ Comment: P11, L4: what does “dynamic” mean here? Authors’ Response: We meant physical properties. We have modified the sentences that now reads: “...other variables (linked to physical processes, photochemistry or biological activity) probably affected the residence time of this and the other metals in the SML.”

Reviewers’ Comment: P11, L7: this is an example of the selective explanation of elemental behaviors. Is the influence of wind on just Co, or Co and Ni? Additionally, why would wind effect only one or two of the metals? Would wind not have the same physical transport or diffusion and mixing effects on all metals? Please provide some additional discussion of this very selective effect. Authors’ Response: We agree with the reviewer. In deed the reviewer is right in his/her comment. We realized that we made a mistake in the residence time calculation because we used the aerosol metal flux of the first station (station 1) to estimate the residence time of all stations. We have revised and corrected all calculations and now residence time is calculated using the aerosol flux of each station (calculated using the aerosols concentration (table 1) and assuming a deposition velocity of 0.1cm/s). Recalculated residence time are of the same order of magnitude than before, however we changed some part of the discussion. In the previous version residence time of Co was very well correlated with wind speed, which opened the question on the lack of effect of wind speed on the other metals. Now the relative low wind speed during our campaign (9 ± 4.99 knots) did not affect the residence time of metals in the SML. It has been indicated in this section.

Reviewers’ Comment: P11, L11: it should be “nucleic acid” Authors’ Response: Corrected

Reviewers’ Comment: P11, L13: the methods for characterizing all of these separate

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biological groups needs to be provided and justified: why were these groups characterized? Authors' Response: We have focused the discussion in the most representative microbial community in the SML (i.e. Bacteria; High nucleic acid-content bacteria: HNA; Low nucleic acid-content bacteria: LNA; pico-phytoplankton). We have removed the different phytoplankton groups from the text since discussion about their abundance is speculative with the existing data.

Reviewers' Comment: P11, L24: how is SML fraction different from T-SML? Authors' Response: We meant microbial abundance in the SML and reactive elements in the T-SML. We have modified the sentence to avoid confusion. Now the sentence reads: "Microbial abundance in the SML and reactive elements (i.e. Cu, Fe, and Zn) in the T-SML showed the same longitudinal gradients in this study,..."

Reviewers' Comment: P12, L2: bacterial assimilation would result in no change in T-SML, which includes both dissolved and particulate fractions. Authors' Response: The reviewer is right. This argument is valid only for the dissolved fraction, we have now removed the T-SML and the sentence now reads: "Bacteria could efficiently assimilate the fraction of Cu, Fe and Zn available, favouring a decrease in the D-SML fraction (Table 1-2)."

Reviewers' Comment: P12, L23: why would regeneration in the east only be active for Co, when many other bioactive metals are also remineralized actively? Authors' Response: The regeneration of biogenic particle is probably active for many other metals, however it only has been suggested in the Mediterranean Sea for Co.

Reviewers' Comment: P13: I think there is inadequate support for the conclusion that Ni is inhibiting growth in the surface waters, particularly given the lack of relationship with primary production and chl a Authors' Response: We agree and we have toned down the conclusion. Unfortunately, we don't have Chl-a and primary production measurements in the SML not even in the first meter of the sea surface to confirm our hypothesis (available Chl-a and primary production data are from 5 meter depth).

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Reviewers' Comment: P14, L13: how can there be a 'major difficulty of mobility' (a strange term, I feel) for Fe when the residence times are only a few minutes (table 3)?
Authors' Response: We agree. We have changed the word "mobility" by "diffusion".

Reviewers' Comment: Fig S2: please include the year in the date in the caption
Authors' Response: Done

Reviewers' Comment: Fig S3: the figure does not match the caption
Authors' Response: The reviewer is right. Figure S3 (now Figure S4) has been changed with rainfall rates from the radar European composite product that are geo-referenced allowing to plot the position of the FAST station. The figure caption has been changed consequently and now reads: "Accumulated rainfall during the night between June 3rd and 4th 2017 (00h00 – UTC) and position of R/V at the Fast Station. The rainfall rates are estimated from the radar European composite products provided by the Odyssey system." We really thank to the reviewer for all these comments and the many errors detected.

Please also note the supplement to this comment:

<https://www.biogeosciences-discuss.net/bg-2019-290/bg-2019-290-AC2-supplement.pdf>

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2019-290>, 2019.

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Pictures R2. SML system used during Pacetime campaign.

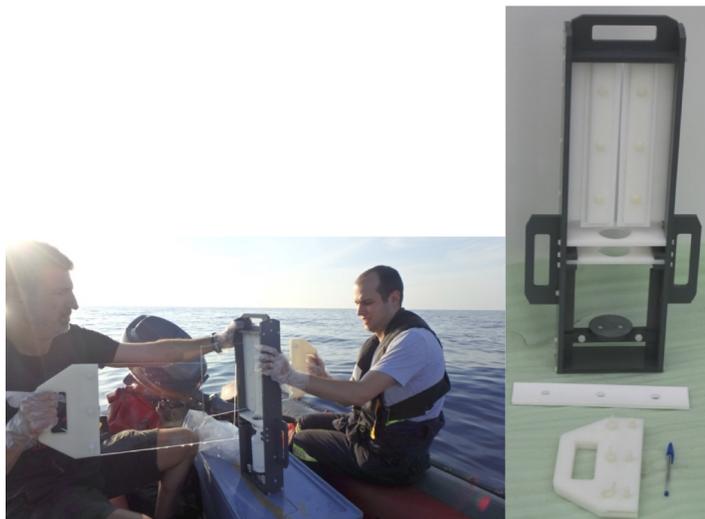


Fig. 1.

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