Comments by Maurizio Ribera d'Alcala and our responses

Referee report for the manuscript bg-2020-411: **Influence of atmospheric deposition on biogeochemical cycles in an oligotrophic ocean system** by *France Van Wambeke, Vincent Taillandier, Karine Desboeufs, Elvira Pulido-Villena, Julie Dinasquet, Anja Engel, Emilio Marañón, Céline Ridame, Cécile Guieu*

This paper is clearly one among several contributions for a special issue of BG illustrating and discussing the results of the basin scale experiment PEACETIME, carried out during summer 2017 in the Mediterranean sea to assess the impact of atmospheric depositions on the functioning of plankton food web in the basin. Therefore it describes a small set among the numerous processes that have been studied during the cruise, namely, the weighted support to phytoplankton and heterotrophic bacteria production and nutrient assimilation in the surface layer by different forms of bioavailable Nitrogen (N) and Phosphorus (P).

The obvious focus is on the forms derived by the atmospheric deposition. This is just a piece of a mosaic whose whole picture, I assume, will be published either in this special issue or somewhere else. The key question behind the experiment was the extent to which and by which mechanisms atmospheric deposition modulates biogeochemical processes in the basin. This is also reflected in the title and the manuscript addresses a key phase: the first processing of new nutrients in the surface layer. Therefore the results represent the short time response, even though they likely embed also responses due to processes occurring over some time before the event (see below).

To better dissect the processes in the surface layer the authors divide it in two sublayers, the Mixed Layer (ML) proper which is the layer directly affected by air sea interactions and, therefore, the entry point of atmospheric inputs, and a second layer spanning from the ML Depth and the depth of the nutriclines (N or P) identified as the depth of the 'heaviest' isopycnal with Dissolved Inorganic Nitrogen (DIN) or Phosphorus (DIP) values equal to zero. The latter determined by extrapolation in DiX-density diagrams. Considering what is reported in Table S1 I assume that the zero value is obtained plotting the concentration determined with the segmented flow analyzer (a clarification on line 333 would help).

This allowed them to discriminate among the different sources or sinks of surface DiX to better identify the weight of the atmospheric component. Different N and P chemical forms where analyzed and linked to the different sources and sinks, namely DIN derived from N-fixation, DIN from atmospheric inputs, in situ Total Dissolved Nitrogen (TDN) and Total Hydrolizable Aminoacids (TAA) for Nitrogen and DIP from atmospheric inputs, total Dissolve Organic Phosphorus (DOP), and its labile component.

Three stations were sampled for longer times, namely those where wet deposition events were occurring or had occurred just before sampling, which allowed, with the caveat of advective processes going on, of better reconstructing the vertical dynamics of N and P in relation to pico-plankton, the dominant component in the sampled area, activity. The main outcome of the paper is a quantification of the fraction of N-demand and P demand by pico-planktonic autotrophs and heterotrophs supplied by the atmospheric inputs as compared with the other sources of recycled or existing forms. An additional outcome is the difference in the N and P dynamics in the surface layer after input which may hint to a differential response of the picoplankton community to the supply of the two elements as well as to particle scavenging.

The paper contains many useful data and tries to condense a big experimental effort. The need to present them in full, makes the text a bit heavy to read (e.g., section 3.1). In the discussion the authors make the commendable effort to examine all the possible processes, already reported in the literature, which may explain the patterns they observed but this, at the end, does not provide the reader with an answer, or at least the answer preferred by the authors.

The fact that in such large experiments with so many scientists involved, there is a need to divide the informations in many papers weaken a bit some of them because many questions that arise reading one are likely answered in other papers of the same fact that is one piece of a large picture, and because the methods used are robust.

We thank the referee for his constructive comments. To summarize changes made on the revised version: we moved some of the information in the supplement section (the enrichment experiment), we added a new table (S2), and we shortened the text and reorganized some of the discussion. See all our response in blue and citations of parts of the revised version in italics. A .doc version with tracking changes will help to visualize all the changes provided.

My suggestion to make the paper more punchy are the following:

1. Let the tables to summarize the data and shorten the description highlighting the most significant result. The text is definitely long.
As far as possible, unnecessary citation of numbers when the data are also reported on tables were removed.
The M&M, results and figures referring to the enrichment experiment have been moved in the supplement. In the supplement section, we also added a table (Table S2) reporting the stocks and fluxes at ION and FAST Stations. Section 3.3 has been reorganized in a more logical order; section 3.4 has been shortened, as well as the discussion. All in all, the ms is now reduced by a hundred lines (~2 pages).

2. Do not include the enrichment experiments. They do not add too much unless you discuss them integrating them with the other information.
The methodology and result description of the enrichment experiments have been moved to the supplementary section, as well as Fig 6.

3. Discuss what are your conclusions about the significant variability among the different sites having in view the possible impact at basin scale. The present conclusions discuss other aspects.
We think that a snapshot of 10 short stations at a given single period of the year is not enough information to discuss inter-basin variability or impact at the basin scale. Nevertheless, we added a sentence in the discussion showing that the longitudinal dry atmospheric deposition was less variable than biological fluxes within the ML.
We restricted the discussion (which is already very dense) to the contributions of the dry atmospheric flux to the biological needs of phytoplankton and heterotrophic bacteria, as well as on the short term effects of rain, which could have been observed in any part of the basins.

Additional comments

l.215-218 "*The concentrations used were averages from PILS-IC analysis obtained during the occupation of each short station, and averages between two successive casts during site occupations, except for ST1 where concentrations were issued from filter by IC analyses after water extraction.*"

It is not clear to me why for dry deposition it was taken a quasi-instantaneous value instead of an estimate of the deposition during a few hours before the sampling.

PILS-IC measurements have a time-resolution of 70 min. for NO3 analysis and ~30 min. for NH4 analysis. The ship occupied each short station during a few hours (on average 0.33 ± 0.13 days). In order to compare atmospheric deposition and bulk in situ nutrient stocks in the water column at the same time but also at the same place, we didn't use the instantaneous measurements before cast for estimating dry deposition, but we considered the average PILS data acquired during the occupation of the short stations. For example, for station 5 from 16/05 at 4:00 to 16/05 at 11:00, we averaged the PILS data for this period, that comprises 6 measurements for NO3 and 11 measurements for NH4. For long stations, TYR, ION and FAST, we integrated PILS data from the arrival at the station and the first cast, then over the time interval between each cast (that comprises on average about ~15 measurements for NO3 and ~30 for NH4).

We modified the M&M section to make this point clearer.

It would be interesting to mention here the variability of dry deposition along the cruise track which, should be part of the Fu et al. (in preparation) paper and to discuss how representative are quasi-instantaneous values. Likewise for filter samples. This aspect is indeed considered only for the stations that were sample for many days because of wet deposition events (see l.628-632)

The concentrations and fluxes from dry deposition (DIP on filters, NO3 and NH4 from PILS-IC) are not instantaneous but integrate measurements over the few hours of occupation of the short duration station. DIP is derived from one filter sampling aerosols during the whole occupation of the short duration station and consequently with no possible access to a shorter time-variability. In contrast, as the PILS-IC technique allows to determine NO3 and NH4 in aerosols every 70 and 30 minutes respectively, for these parameters the short term time-variability is accessible. It is quantified in the sd cited on Table 2, which is calculated from the variability of the NO3 and NH4 concentrations solubilized from aerosols during the occupation of the short duration stations. This information is now detailed in the legend of Table 2.

The variability of NO3 concentration solubilized from aerosols is also visible on Figure 1.

I am also wondering, not being an expert, if the ions solubilization efficiency and time of aerosol particles in PILS is the same than that of sea water.

PILS-IC is one of the most used device for online measurement of water-soluble inorganic ions in atmospheric aerosol particles. PILS-IC is a method which is optimised to extract water-soluble fraction of N species in aerosols (water being ultrapure water), whatever the type of particles (Orsini et al., 2003). Dissolution experiments from atmospheric aerosols show that the solubilities of nitrate and ammonium are similar in seawater or pure water, i.e. 100% (e.g. Chen et al., 2006). Under these conditions, we considered that the NO3 and NH4 values obtained by aerosols solubilisation by PILS-IC are comparable to the DIN values brought by the dry deposition of these aerosols in sea water.

Orsini, D. A., Ma, Y., Sullivan, A., Sierau, B., Baumann, K., and Weber, R. J., Refinements to the Particle-Into-Liquid Sampler for Ground and Airborne Measurements of Water Soluble Aerosol Compositions. Atmos. Environ., 37:1243–1259, 2003.

Chen, Y., J. Street, A. Paytan, Comparison between pure-water and seawater soluble nutrient concentrations of aerosols from the Gulf of Aqaba, Mar. Chem., 101, 141-152, 2006.

l.258 space after (...Dickson)
done

Line 333 : Considering what is reported in Table S1 I assume that the zero value is obtained plotting the concentration determined with the segmented flow analyzer (a clarification on line 333 would help).
Yes it is, we wrote ‘micromolar’ concentrations

l.345 For what I understood the advective flux is an entrainment/detrainment mechanism sensu *Cullen, J. J., Franks, P. J., Karl, D. M., & Longhurst, A. L. A. N. (2002). Physical influences on marine ecosystem dynamics. The sea, 12, 297-336*. If true, an additional sentence may better clarify which processes the authors refer to.
Right, the term ‘advection’ has been used as complementary to ‘diffusion’, however the advective flux is associated to entrainment/detrainment *sensu* Cullen et al. (2002). The following sentence has been added to clarify the underlying mechanism of vertical advection, in the revised version:
‘The advective flux F_{ADV} corresponds either to the entrainment of deeper water in the mixed layer by erosion of the near-surface pycnocline, or to the detrainment of waters below the mixed layer by restratification, depending on the variations of wind stress and solar heating (Cullen et al., 2002). It is expressed by the variation …’

The reference Cullen et al. (2002) has been added in the revised manuscript.

l.441-443 It is a little confusing putting together the rates of opposite processes, the demand, which is the theoretical intake given certain compositional ratios, and the increase in availability. Since the sentence that follows clarifies the point I would remove the part of the sentence realated to the release rate or I would write “*... (hprokN demand), which is confronted by an in situ LAP…)*
done

l.629 this phrase may be misleading. Indeed what is measured is not the integral but the time-space weighted average of the fluxes.
All this part has been modified in the revised version as we finally calculated DIN and P (PP, DOP, DIP) wet deposition events by multiplying concentration calculated from analysis of collected rain by total precipitation estimated from radar data:
The M&M section 2.2.1 was modified as: *‘In the rains collected onboard the ship, NO3, NH4 and dissolved inorganic phosphorus (DIP) were also determined by ion chromatography after recovery of the dissolved fraction in the samples. Then, the wet deposition fluxes of these nutrients were estimated from the measured concentrations in the dissolved fractions of rains,*

multiplied by the total precipitation. This total precipitation was issued from the hourly total precipitation accumulated during the rain event over the region from ERA5 hourly data reanalysis (Hersbach et al., 2018). Total precipitation was obtained by adding hourly rainfall on the grid-points (0.25° x 0.25°) spanning the ship location, more or less 1° around this central grid-point for integrating the regional variability.'

All the discussion section (the beginning of 3.4 section) reporting risk of underestimation of rain fluxes was consequently removed. Note that the updated rain fluxes considering the total precipitation from radar data do not change the main conclusions of our ms.

Hersbach, H., Bell, B., Berrisford, P., Biavati, G., Horányi, A., Muñoz Sabater, J., Nicolas, J., Peubey, C., Radu, R., Rozum, I., Schepers, D., Simmons, A., Soci, C., Dee, D., Thépaut, J-N.: ERA5 hourly data on single levels from 1979 to present. Copernicus Climate Change Service (C3S) Climate Data Store (CDS). doi: 10.24381/cds.adbb2d47, 2018.

l.447 correct *dominatedby*
done

l.739 and the following. Please rephrase, since you do not *deliver* neither *accumulate* concentrations, as it is more properly written on l.744.
We substituted 'accumulation' by 'variation' and 'delivered' by 'released'. Also the sentences were put in a more logical order as follows:
'At the long duration FAST station, the maximum net variations of NO3 and DIP concentrations within the ML before/after the rainy period reached i) 1520-665 = +855 µmol N m^{-2} *for NO3 (data from FAST+0.24 relative to FAST-0.25 and ii) 283-137 = +144 µmol P* m^{-2} *for DIP (data from FAST+1.05 relative to FAST-0.25). In other terms, based on a mean MLD of 16 m, the net observed increase in the ML are + 9 nM DIP and + 54 nM NO3. As the rain event in the area would have increase by 0.07 nM DIP and 21 nM NO3 concentrations over the whole mixed layer, the net variations observed in the ML are thus higher than the calculated variation in stocks deduced from the N and P concentrations of this rain event (Table 3), in particular for DIP.'*

References
Pulido-Villena et al (2019) is cited on l.243 but is not included in the refs.
Yes this is an error the correct reference is Pulido-Villena et al 2010 which has been added in the ref list.

The following papers are in the References but are never cited in the text

Holmes, R. M., Aminot, A., Kérouel, R., Hooker, B. A,.and Peterson, B. J.: A simple and precise method for measuring ammonium in marine and freshwater ecosystems, Can. J. Fish. Aqua. Sci., 56, 1801-1808, 1999.
Ref removed

Karl, D. M.: Microbially mediated transformations of phosphorus in the sea: New views of an old cycle. Ann. Rev. Mar. Sci. 6: 279–337, doi: 10.1146/annurev-marine-010213-135046, 2014.
Ref removed

Krom, M. D., Herut, B., and Mantoura, R. F. C.: Nutrient budget for the eastern Mediterranean: Implication for phosphorus limitation, Limnol. Oceanogr, 49, 1582-1592, doi: 10.4319/lo.2004.49.5.1582, 2004.

This reference is now cited in the text in substitution to Krom et al., 2010

Krom, M. D., Emeis, K.-C., and Van Capellen, P.: Why is the eastern Mediterranean phosphorus limited? Progress In Oceanography, 85, 236-244, 2010.

Ref removed

Lindroth, P., and Mopper, K.: High performance liquid chromatographic determination of sub picomole amounts of amino acids by precolumn fluorescence derivatization with ophthaldialdehyde, Anal. Chem. 51, 1667–1674, 1979.

Ref removed

Thingstad, T. F., and Rassoulzadegan, F.: Nutrient limitations, microbial food webs, and 'biological C-pumps': suggested interactions in a P-limited Mediterranean, Mar. Ecol. Prog. Ser., 117, 299-306, 1995.

Ref removed

Zhang, J.-Z., and Chi, J.: Automated analysis of nano-molar concentrations of phosphate in natural waters with liquid waveguide, Environ. Sci. Technol., 36, 1048-1053, doi : 10.1021/es011094v, 2002.

The reference is now added in the text in the introduction section when referring to the LWCC technique