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Biogeosciences Discussions

Interactive comment on "Longitudinal variability of the biogeochemical role of Mediterranean aerosols in the Mediterranean Sea" *by* E. Ternon et al.

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Interactive comment on "Longitudinal variability of the biogeochemical role of Mediterranean aerosols in the Mediterranean Sea" by E. Ternon et al. Anonymous Referee #1

General comments on the manuscript

I feel this represents a missed opportunity. The manuscript represents an interesting experiment but key measurements appear not to have been made. In particular the authors have no determined the amount of bioavailable phosphate and nitrate & ammonium which was leached from the aerosol samples into the microcosms. This is the

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critical driving parameter for their experiments. At one point they estimate a value from literature values but this is a very poor substitute for the actual values.

PLEASE SEE RESPONSE IN SPECIFIC COMMENT #2

They have calculated a value for anthropogenic P based on P/Al for natural unpolluted crustal rocks. However this value is far from fixed. We have data which shows a very large range of values for P/Al for rocks in the Saharan dust source region. As such it is not possible therefore to calculate enrichment factors in this simplistic manner.

PLEASE SEE RESPONSE IN SPECIFIC COMMENT #12 ('Discussion')

Finally I am unhappy about the relationship of this manuscript to other manuscripts in the series. There are a series of manuscripts from the BOUM cruise which are referred to as in preparation. These often contain crucial information related to this manuscript and vice versa. It would be much better to submit these all to a single dedicated volume so that all could be considered together.

All the papers related to the BOUM cruise have been referred in our manuscript as 'this issue': indeed, a special issue is in preparation (please check at http://www.biogeosciences-discuss.net/special_issue63.html). Of course, as all the manuscripts were not ready at the exact same time, some of the papers are still with the editors (T. Moutin and L. Prieur) before they agree to be published in BGD. The editors recommended to make as most as possible cross-referencing, and this is what we did in our manuscript. The only paper mentioned as 'in preparation' is not related to the BOUM cruise (Ridame et al. DUNE experiment).

Specific comments:

#1 Aerosol sampling: Insufficient detail is given of how the aerosols were actually sampled.

Details of the aerosol sampling were added to the method section. "This sampling device (see Wagener et al., 2008 for further details) was made by a "box" that achieved

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an integrative sampling during the cruise. The “box” was attached on the front desk of the ship to a 7 m-high mast in order to avoid any contamination from the engine exhaust stack. Local wind direction and speed were measured continuously close to the sampling box using a wind anenometer. Depending on the wind conditions, the box operated either in a “sampling” mode or a “protection” mode. “Sampling” mode (air pumped through the filters) was activated only if wind was oriented in a 90° open angle upwind at a speed higher than 2 m.s-1. “Protection” mode (no air pumped, box closure, filters protected) was activated if wind conditions could generate samples contamination.”

#2 If samples still exist then the authors could potentially still measure Leachable inorganic P and inorganic N and thus solve my major problem with this manuscript.

We agree with the fact that some key measurements are missing. For the reasons exposed below, phosphate, nitrate and ammonium concentrations in seawater were not available for this experiment. Literature data were used as this was the only way to make estimations of bioavailable nutrients released by aerosols in the microcosm, and the manuscript clearly mentions that these estimations have to be taken with precautions. During summer in the Mediterranean Sea, inorganic P as well as inorganic N in some cases, that are potentially released by aerosols in seawater, may be under detection limit of classical methods of measurements (classical spectrophotometry) and should be measured with the LWCC method: we did use such method on board but unfortunately we did encounter several analytical problems resulting in non workable data-set. This was very disappointing as all the samples have been used on board and no additional leaching experiment could be done in the lab: this is the reason why we choose to refer to literature data. We emphasize in the manuscript on this quite poor quantitative way to interpret the data (although this approach have been widely used in quite recent papers), and in the present version we also added the following paragraph to section 4.2.2: “As leachable inorganic P and N concentrations at nanomolar levels were not available for the BOUM cruise and that no filter was left after the cruise to

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perform those analyses in the laboratory, literature data had to be used to estimate inorganic P and N potentially released by the aerosol samples. Although this method is based on rough calculations it still provides orders of magnitude of the atmospheric nutrients input to the seawater potentially released from our sampled aerosols."

#3 Seawater sampling: It is great pity that micrograzers were not also measured in this study.

We certainly agree about the fact that several other measurements could help to better assess the impact of aerosols input to biota. In particular, we agree that micrograzers are important players as recently highlighted in several papers (see for ex. Thingstad et al., 2005, Pulido-Villena et al., 2008). In our microcosm experiment, we were very limited in term of available water volume ('only' 4.5 Liters) and choices had to be made: as primary production/nitrogen fixation measurements are highly water consuming, other major biological parameters such as total chlorophyll and micrograzers could not be measured.

#4 Aerosol addition experiments: The authors state that 'It is noteworthy that due to on-board schedule pressure, aerosol filters used were not necessarily geographically representative of the area where the seawater was sampled.' The author's state there is no problem in doing this. That of course depends on what is the limiting factors when the aerosols are added.

We totally agree with that remark. Hopefully, during the BOUM experiment, Tanaka et al. (see paper in BGD in the special issue) have shown that during the BOUM Cruise, the Mediterranean Sea was N or N-P co-limited at the three tested stations over the three basins (A, B and C stations). Also, as shown, aerosols characteristics were quite stable over the BOUM cruise: the geographical difference should thus not represent an issue to this experiment.

#5 The next paragraph suggests that they have somehow modified the Saharan dust to make it mimic aerosol transport but they do not explain exactly what they have done.

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How was the dust introduced to the microcosms? Was it just added with the filter or was it shaken from the filter. Depending on the answer was their a measure of exactly how much dust was added?

Section 2.2 was modified as following Âń Non-filtered seawater (4.5 L) was immediately amended with two types of aerosols: (1) On-board collected aerosols (CA : Aero 2, 3, 4 and 5, see Fig. 1). Using clean plastic forceps, two whole simultaneously sampled filters were dropped inside two bottles, (2) Saharan dust Analog (SDA, 1 mg.L-1). 4.5 mg of SDA were directly introduced to two other bottles. Dust were weighted before the cruise and kept in clean tubes until the experiment. To ensure that all the SDA was well removed from the tubes, several rinsing with filtered (0.2μm) seawater were performed and the water was poured inside the 4.5 L bottles." And about the protocol: Âń The protocol for preparing the Saharan dust analog (SDA) is fully described in Guieu et al. (2010). Briefly, Saharan analog was produced from (<20 μm) soil collected in Tunisia followed by an appropriate chemical treatment in the laboratory. This protocol to aging Saharan dust mimics the atmospheric uptake of inorganic and organic soluble species on dust during evapocondensation cycling that reproduces the gradients in pH and ionic strength during cloud processing of dust particles (based on Desboeufs et al., 2001). Âż

#6 Acid digestion of aerosol filters What acid was used? More details are needed here so we can understand this manuscript.

This method is fully described in another paper as cited but some details have been added to that section. "Briefly, acid digestion was performed on a whole aerosol filter in "suprapur" acids following two steps: 1.5 mL 65% HNO3, and then 500 μL 65% HNO3 + 500 μL 40% HF. After each treatment, samples were oven heated at 150°C for 5h."

#7 Aerosol metal analysis Can we see the actual precision and accuracy results? It would be very unusual but not impossible to have reference recoveries of 100.0% for all crucial elements.

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This was a mistake and the actual numbers have been added to the manuscript. Actual reference recoveries were added to the text: “Reference material recovery was 101 % 5 % for iron and 96 % % for aluminium (n=11).”

#8 Aerosol phosphorus analysis: What P species is being measured? I can guess it is inorganic P assuming that 1 M HCl is used but that is certainly not Murphy and Riley 1962. It is also rather odd to dilute the samples by 1/10 prior to using a LWCC flow cell to make the measurement. Why not measure undiluted and a normal detection system?

P species measured in aerosols was indeed inorganic P and the LWCC spectrophotometry protocol is based on Murphy and Riley (1962) method. The reason why inorganic P was not measured with classical detection system is that concentrations were very low near the detection limit. At those concentrations, the classical spectrophotometer could not be precise enough. We choose to use the newly improved LWCC system that can detect nanomolar concentrations. “A dilution had to be made as the LWCC system requires 30 mL of sample and the final volume of water added after acid digestion as 10ml”. This last sentence was added to the text.

#9 Section 2.3.5 What is meant by ‘after at least 10 minutes’ ? and less than how long?

The sentence (p8094, l10) was changed into “Samples were incubated at 4°C and then frozen . . .”. For further details about this method, please refer to Obernosterer et al. (2005).

#10 Section 3.2 Did the authors carry out any N fixation blanks? Do they have any idea what is their detection limits for N fixation?

Blanks for N2 fixation were indeed measured during the BOUM cruise at all stations. Results are presented in Bonnet et al., and Ridame et al. which are companion papers. The following sentence was added: “Detection limits for N2 fixation is 0.1 nmol.L-1.d-1 (Bonnet et al., this issue).”

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11 Section 3.3.1 Did they measure chlorophyll changes in this microcosms? I assume the primary productivity was gross primary production.

Primary productivity was indeed gross primary production and Chla was not measured (for the same reason explained in comment # 3). Following the results obtained by Bonnet et al, (2005) our microcosms experiments were performed to look for changes in diversity induced by atmospheric deposition. Both CA and SDA additions favored the small phytoplankton species (in particular synechococcus). The microcosm approach cannot be devoted to follow the changes in the whole assemblage but rather to focus on specific questions: one of our objectives was indeed to investigate "the potential fertilizing effect of new nutrients from aerosols on autotrophic organism diversity and production of autotrophic communities (including diazotrophs)".

Discussion:

#12 Section 4.1 The first section depends on their being a stable and unchanging value for 'crustal' P/Al which applies to all Saharan dust samples. Sadly that is not true. We have data from 10 locations across the Saharan with P/Al ratios which average 0.0134 +/-0.013 (1s). You cannot simply take one value of 0.07 as the background level and assume anything in excess of that is pollution.

Crustal references for P and Al do vary according to the Saharan source region. However, the P/Al values found across those source regions belong to a small domain of values. Several publications normalize their concentration to a reference value way to estimate the anthropogenic contribution of different element in the aerosols (Bergametti et al., 1992; Herut and Krom, 1996; Migon and Sandroni, 1999; Migon et al., 2001...). According to Guieu et al. 2002, Al and P concentrations in the transported dust are more homogeneous than in the fine fraction of the sampled soils in different location of the Sahara (it has to be noted that in this paper, Saharan rains were selected among a 12 years time series to be as much as possible representative of pure Saharan rains. Moreover, the concentrations were recalculated, taking into account the

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loss of the particulate mass due to the dissolution of CaCO3 and the dissolution of P in the rain). The higher level of homogeneity of the transported dust compared to the soils corresponds to the fact that, during a Saharan event that affects a large area of the Saharan desert, the composition of the particles reflects the average composition of the eroded areas (as shown for ex by Bergametti, 1987; Schutz and Sebert, 1987; Pye, 1987). Nevertheless, as the sources emissions can be quite different between the western and the eastern basin, this ratio may be different in the eastern aerosols. Unfortunately we were not able to find the data mentioned (without reference) in the above review but even considering the highest value of the mentioned ratio (0.027) all the Mediterranean data reported on Figure 4 are above this value. We have added to the figure 4 several P/Al from "references": P/Al ratio in the upper crust (Wedepohl, 1995; Taylor and Mc Lennan, 1995) and from Herut et al., 1999b for Saharan aerosols in the eastern Mediterranean. Adding those values show that even though there is indeed some variability of the ratio, all values fit within a quite small domain. The corresponding paragraph was also modified accordingly:: "The (P/Al) ratio of both groups was mostly consistent with results reported for coastal area in Corsica: from 0.03 ("crustal source") to 0.07 ("anthropogenic source") in Bergametti et al. (1992), but well higher than the crustal reference (0.008-0.012 in Wedepohl, 1995; Taylor and Mc Lennan, 1995) and ratio in Saharan aerosol from eastern Mediterranean (Herut et al., 1999b) and "Saharan end-member" in the Western Mediterranean (Guieu et al., 2002)."

#13 Section 4.2 The authors correctly calculate a potential nutrient requirement (section 4.2.1) but then never measured the leachable N or P on any samples. They make some general estimate form the literature which can easily be wrong by a factor of 50% or more. Since this was crucial to their experimental design why was it not measured?

P and N nanomolar concentrations are not available for the reasons enounced before and no more sample are available to perform those analyses: making estimates was the only option left and it is clearly said in our manuscript that those estimates are

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rough estimations and have to be considered with caution. Even if huge uncertainties are taken into account, we consider that those calculations still provide information such as “biological N requirements are fully covered by the large N input from both SDA and CA”. This kind of promising experiment needs indeed to be further explored to confirm or invalidate those results.

14 Section 4.2.3 We need to know the speciation of N in the aerosol input to know whether it contains chemical species which might suppress N fixation or not.

N speciation was not determined for CA. In SDA, N specie was NO3-. A recent study shows that for unicellular diazotroph, (such unicellular are encountered in the Mediterranean), the presence of NO3 in seawater does not inhibit the N2 fixation process (Dekeazemaker and Bonnet, submitted to MEPS). Huge uncertainties remain about the inhibition potential of both NH4 and DON concentrations. It seems that to be inhibited, N2 fixation requires high NH4 concentrations, well above those encountered from aerosols dissolution (Mahafey et al., 2005).

#15 In explaining their results, the potential importance of micrograzers is not mentioned.

The very probable importance of micrograzers was mentioned in section 4.4 when considering the biological communities (autotrophic organism and heterotrophic bacterial abundance). We considered that micrograzers do not belong to section 4.2.3 as this part is devoted to explain the P consumption.

#16 Section 4.3 What is a typical midsummer rain? How far east do such rains occur? What is anthropogenic carbonaceous species?

As explained in the manuscript, midsummer rains are characterized by a strong scavenging of all the accumulated aerosols in the air column (Loÿe-Pilot et al., 1990). Indeed during summer very few rains occur in the Mediterranean, aerosols accumulate in the air column. Summer rains are usually associated to storms and torrential rains

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that “clean” the atmosphere from its aerosols. Markaki et al., (2010) showed that rain events in the eastern part of the Mediterranean occurs mainly during the wet season (>95% of the annual rainfall) whereas in the western Mediterranean, rain event are encountered during the dry season, representing up to 30 % of the total annual rainfall. This means that storms and torrential rains would not occur very often in the eastern Mediterranean, most of deposition would mostly be associated to dry deposition in this part of the Mediterranean Sea. The following sentences have been added to Section 4.3: Âń Those events mainly occur in the western part of the Mediterranean Sea, dry deposition being more associated to the eastern Mediterranean summer climate (Markaki et al., 2010). Âż

Anthropogenic carbonaceous species are fly-ashes emitted by heavy fuel oil and coal combustion (Ausset et al., 1999). They are usually concentrated in Zn, Ni, Cd (Desboeufs et al., 2003). To make this clear in the manuscript, the following sentence was added to the corresponding section: “. . . carbonaceous species (fly-ashes emitted by heavy fuel oil and coal combustion in Ausset et al., 1999). . .”

Interactive comment on Biogeosciences Discuss., 7, 8087, 2010.