## Interactive comment on "Reviews and Syntheses: Ocean acidification and its potential impacts on marine ecosystems"

Authors: K. M. G. Mostofa et al.

Dear Prof. G. Herndl, Associate Editor, Biogeosciences,

First of all, thank you very much for providing two good and constructive reviews for our paper. We have received some thoughtful comments from the second referee that were very helpful to improve the quality of the manuscript. For your kind information, we have used blue color for new additions in the manuscript.

Our responses to referee comments are mentioned below:

### Anonymous Referee #2

Ocean acidification potentially influences marine organisms and hence ecosystems. The effects could be manifold and in particular are driven by direct  $CO_2$  enrichment and/or the subsequent reduction in pH, e.g. affecting calcium carbonate saturation state etc. Mostofa et al discussed mechanistic insights into a variety of OA-dependent processes and pH changes, and focused especially on processes taking place at different time scales with potentially detrimental effects on marine organisms as well as ecosystems and their services. Indeed the topic is attractive, timely, and can raise important issues. However, in my opinion the authors could have done a better job in summarizing and conceptualizing recent findings.

### Ans: Thank you very much for your true evaluation on the manuscript.

The manuscript lacks some important literature and in particular I miss some good graphics representing linkages of different environmental drivers, processes and cycles related to ocean acidification and on potential OA effects on aquatic ecosystems in the future ocean. For me, the structure of the review is not clear, e.g. there is no clear distinction between natural and anthropogenic OA and related processes.

Ans: Creative and very thoughtful comment for this manuscript. According to the first part of these comment we have designed a new Figure (Fig. 6) to provide necessary information (please see the Fig. 6). Please see the detailed specific comments.

For the second part of the comment, as suggested we have added in Chapter 2: "......(*i*) Increasing dissolution of atmospheric  $CO_2$  to seawater: Anthropogenic ocean acidification; (*ii*) input of  $CO_2$  plus DIC upon mineralization of PP influenced by elevated atmospheric  $CO_2$ : Natural ocean acidification; (iii) enhanced PP and respiration due to the effects of global warming and other processes: Natural ocean acidification, and (iv) direct acidification and stimulation of PP by atmospheric acid rain: Natural and anthropogenic ocean acidification." in page 7, lines 19-23.

As accordingly,

Chapter 2.1 was modified with new addition as "2.1 Increasing dissolution of atmospheric  $CO_2$  to seawater: Anthropogenic ocean acidification" in page 8, lines 4-5

Similarly, Chapter 2.2 was modified as "2.2 Input of CO<sub>2</sub> plus DIC upon mineralization of PP influenced by elevated atmospheric CO<sub>2</sub>: Natural ocean acidification" in page 8, lines 22-23

Chapter 2.3 was modified as "2.3 Enhanced PP and respiration due to the effects of global warming and other processes: Natural ocean acidification" in page 11, lines 16-17

Chapter 2.4 was modified as "2.4 Direct acidification and stimulation of PP by atmospheric acid rain: Natural and anthropogenic ocean acidification." in page 8, lines 300-301 in Supplementary Material.

We have also added "Anthropogenic global warming could also enhance the natural acidification process." as a starting sentence in Chapter 2.3: "2.3 Enhanced PP and respiration due to the effects of global warming and other processes" in page 11, lines 18-19.

We have also clearly mentioned these "Natural and anthropogenic acidification processes" in the respective processes in the new Figure 6 (Please see Figure 6).

### Specific comments:

P4, L6 "anthropic activities" I guess you mean "anthropogenic activities", however, studying Greek philosophy is never disadvantageous!

Ans: As suggested we have been replaced "anthropic activities" by "anthropogenic activities" in page 4, line 11.

P4, L13ff Furthermore, while the global oceans are net sinks of atmospheric CO2, particular locations such as the sub-Antarctic zone during winter and the equatorial oceans are actually net CO<sub>2</sub> sources to the atmosphere (Takahashi et al., 2002, 2009; Cai et al., 2010; Zhai et al., 2014).

I would be more careful with this statement since we are far away from understanding the C sink/source function of the ocean: None of the cited studies can calculate a full budget throughout a year or even several decades, in particular when including the deep sea.

Ans: We agree with the referee's comments. So we have deleted this sentence from introduction in page 4, lines in between 19-20.

Introduction in general: I miss a statement on the possibility that Ocean Acidification could be also increase in primary productivity, but this could be strongly related to temperature changes (see Holding et al. 2015, Nature Climate Change). There are many more references stating that increasing CO2 concentrations can also increase primary production in the long-term run (greenhouse effect), at least at CO2 levels expected in the near future.

Ans: As suggested, we have added "Recent studies demonstrate that ocean acidification under elevated  $CO_2$  and temperature levels could increase primary productivity of specific species (Holding et al., 2015; Coello-Camba et al. 2014; Li et al., 2012). Additionally, such specific species-based primary productivity is also found to increase either by enhanced seawater  $CO_2$  level (Kim et al., 2006; Olischläger et al., 2013) or elevated temperature alone because of the effects of global warming (Yvon-Durocher et al., 2015; Lewandowska et al., 2012)." in the Introduction in Page 5, lines 1-6.

P6, L4: "This review will provide an insight into the mechanisms of the ocean acidification..." Sentence sounds a bit strange.

Ans: We added "a general overview of the ocean acidification...." instead of "an insight into the mechanisms of the ocean acidification ...." in page 7, line 3.

Chapter 2.3: reference from Holding et al. 2015 is missing in addition to others.....

Ans: As suggested we have added the references in the appropriate places in Chapter 2.3 in page 11, line 22.

Chapter 3: Here, I would expect an overview of different ocean sites which respond differently. Depending on the respective buffer capacity, the system reacts more or less pronounced.

Ans: According to this comment, we have added at the end of chapter 3 "Finally, different regions or ecosystems are expected to give different responses to ocean acidification (Gattuso et al., 2015). Unfortunately, little has been documented on geographical comparisons on this aspect." in page 18, lines 22-25. And cited additional reference reflects this point.

Gattuso, J.-P., Magnan, A., Billé, R., Cheung, W. W. L., Howes, E. L., Joos, F., Allemand, D., Bopp, L., Cooley, S. R., Eakin, C. M., Hoegh-Guldberg, O., Kelly, R. P., Pörtner, H.-O., Rogers, A. D., Baxter, J. M., Laffoley, D., Osborn, D., Rankovic, A., Rochette, J., Sumaila, U. R., Treyer, S., and Turley, C.: Contrasting futures for ocean and society from different anthropogenic CO<sub>2</sub> emissions scenarios. Science 349, 4722.1-4722.10, 2015.

P13, L21ff: The matter of upwelling of CO2 rich deep water is a different story and should be discussed with care in an own chapter.

Ans: Thank you for your comment to write an own chapter about "upwelling of  $CO_2$  rich deep water". Considering the manuscript length, we did not lengthen our manuscript again. This should remain in future work.

P16, L1, Pt.1 needs some references, otherwise it remains quite speculative.

Ans: As suggested we have added the references "(Cai et al., 2011; Bate et al., 2013; Zhai et al., 2013; Byrne et al., 2010; Zhai et al., 2014)." in page 19, lines 10-11.

P16, L8, Pt.2: I don't necessarily agree with this statement since coastal water in general has a higher buffer capacity related to its higher trophy. Be more specific.

Ans: According to this comment, we have revised this sentence with addition of several references which mentioned freshwater influences. The new addition includes "Coastal seawater, particularly in locations that are highly influenced by terrestrial river freshwater inputs, is at risk of substantial acidification, to a higher extent compared to the open oceans (Zhai et al., 2014; Thomas et al., 2009; Bate et al., 2013; Barton et al., 2014; Cai et al., 2011; Cai, 2011; Bauer et al., 2013; Hu et al., 2015)." to replace "Coastal seawater from all over the world is at risk of substantial acidification, to a higher extent compared to the open other open oceans." in page 19, lines 15-19.

P18, L3ff: I miss an evaluation of acidification effects on heterotrophic microorganisms (e.g. Grossart et al. 2006; Piontek et al. 2010) and potential feedback mechanisms.

Ans: Very thoughtful and creative comment. As suggested we have added: "ocean acidification could indirectly enhance heterotrophic bacterial activities with increasing bacterial protein production and growth rate at elevated pCO<sub>2</sub> levels (Grossart et al., 2006; Endres et al., 2014; Baragi et al., 2015); higher bacterial abundance has been reported under high  $pCO_2$  treatments (Endres et al., 2014; Tait et al., 2013), which could consequently accelerate respiration processes and increase the respiratory CO<sub>2</sub> production in the future ocean (Piontek et al., 2010)." in page 22, lines 18-23 to page 23, line 1.

P19 Chapter 5.2: I suggest to cutting down a bit to have the review more concise. The matter of ROS has been already addressed above.

Ans: As suggested we have deleted "Note that increasing amounts of  $NO_2^-$  and  $NO_3^-$  may be expected in coastal waters, as explained in earlier sections, although the parallel increase in the concentration of dissolved organic matter (DOM) as HO<sup>•</sup> scavenger would produce a partial or even total compensation (Maddigapu et al., 2010)." from page 24, line 13.

And also

"Furthermore, in oceanic water, bromide anions can act as major HO<sup>•</sup> scavengers to give the Br<sup>•</sup> radical, which would mainly react with a bromide ion to yield the dibromide radical anion (Br<sub>2</sub><sup>-•</sup>) (De Laurentiis et al., 2012; Mostofa et al., 2013c). Br<sub>2</sub><sup>-•</sup> is a moderately strong oxidant ( $E_{Br_2^{-•}/2Br^{-}} = 1.63 \text{ V } vs$ . NHE) and a brominating agent (Neta

et al., 1988; Nair et al., 2001), which is able to promote the formation of bromoderivatives that are usually persistent and toxic pollutants (Steen et al., 2009)." from 24, line 21.

### Deleted references linked with above Text are:

- De Laurentiis, E., Minella, M., Maurino, V., Minero, C., Mailhot, G., Sarakha, M., Brigante, M., and Vione, D.: Assessing the occurrence of the dibromide radical (Br<sub>2</sub><sup>•</sup>) in natural waters: Measures of triplet-sensitised formation, reactivity, and modelling. Sci. Total Environ., 439, 299-306, 2012.
- Maddigapu, P. R., Minella, M., Vione, D., Maurino, V., and Minero, C.: Modeling phototransformation reactions in surface water bodies: 2, 4-Dichloro-6-nitrophenol as a case study. Environ. Sci. Technol., 45, 209-214, 2010.
- Nair, V., Panicker, S. B., Augustine, A., George, T. G., Thomas, S., and Vairamani, M.: An efficient bromination of alkenes using cerium (IV) ammonium nitrate (CAN) and potassium bromide. Tetrahedron, 57, 7417-7422, 2001.
- Neta, P., Huie, R. E., and Ross, A. B.: Rate constants for reactions of inorganic radicals in aqueous solution. J. Phys. Chem. Ref. Data, 17, 1027-1284, 1988.
- Steen, P. O., Grandbois, M., McNeill, K., and Arnold, W. A.: Photochemical formation of halogenated dioxins from hydroxylated polybrominated diphenyl ethers:OH-

PBDEs) and chlorinated derivatives:OH-PBCDEs). Environ. Sci. Technol., 43, 4405-4411, 2009.

P22, Chapter 5.4. Please add that there is a potential interaction between OA and toxic phytoplankton blooms. For example, there are studies in the Baltic Sea which demonstrate that OA has a clear impact on growth and toxicity of diazotrophic cyanobacteria such as Nodularia and Aphanizomenon (e.g. Wannicke et al. 2013).

Ans: Thank you very much for your additional information in that regards. Yes, we have also found more references (Jin et al., 2015; Olli et al., 2015; Fu et al., 2012) regarding this issue. We have checked the reference papers (Wannicke et al. 2012, Endres et al., 2013 and Unger et al., 2013: who authored each other in: Part 1, Part 2 and Part 3) and we did not find Wannicke et al. 2013, but the respective information belongs to Endres et al., 2013. Note that among two diazotrophic cyanobacteria (Nodularia and Aphanizomenon), only Nodularia is highly toxic (Olli et al., 2015).

So according to this comment, we have added "Ocean acidification or elevated  $CO_2$  could increase the toxic algal blooms, involving for instance the diazotrophic cyanobacterium *Nodularia spumigena* (Endres et al., 2013; Olli et al., 2015). They could also increase the accumulation of toxic phenolic compounds across trophic levels in phytoplankton grown under elevated  $CO_2$  concentrations (Jin et al., 2015). Ocean acidification combined with nutrient limitation or temperature changes could considerably enhance the toxicity of some harmful groups (Fu et al., 2012). Correspondingly," in page 27, lines 6-12.

The next sentences are well adjusted with above addition in the TEXT, such as "Correspondingly, harmful algal blooms are expected to increase in coastal waters because of increasing WT and eutrophication (Anderson et al., 2008; Glibert et al., 2010; Mostofa et al., 2013a), which would enhance net primary productivity that is the essential backdrop for the development of such blooms. The same phenomena are ......."

P41, Fig 1: I suggest to link processes of OA with the different chapters given in the text. Currently this is not really clear. I miss a summarizing figure of potential effects of OA. I general, I miss a thorough evaluation of potential ecological and biogeochemiocal consequences of future OA.

**Ans**: According to this comment, we have provided a short summary based on the recent results opening in a new Chapter in pages 29-32.

**"6 Potential ecological and biogeochemical consequences arising from future ocean** acidification" An overview of the potential upcoming ecological and biogeochemical consequences, linking different environmental drivers, processes and cycles related to acidification in the future ocean is provided in Figure 6. Recent study demonstrated that different types of tropical cyclones (hurricanes and typhoons) could increase significantly in oceans and on land over the 21<sup>st</sup> century (Lin and Emanuel, 2016). Extreme daily rainfall is thought to increase with temperature in some regions (Chan et al., 2016 and reference therein). Watersheds with high precipitation induce higher riverine discharge rates (Bauer et al., 2013) and, for instance, a single tropical storm can export approximately 43% of the average annual riverine DOC (Yoon and Raymond, 2012). Similarly, on decadal timescales, single large, cyclone-induced floods can transport 77–92% of particulate organic carbon from mountainous regions (Hilton et al., 2008). Correspondingly, enhanced human activities due to increasing population will unquestionably jeopardize Earth's natural systems. Soil erosion is gradually intensified in regions where forests are converted into croplands (Ito, 2007), and humans have increased the sediment transport by global rivers through soil erosion by 2.3±0.6 billion metric tons per year (Syvitski et al., 2005). Potential changes in erosion rates in the Midwestern United States under climate change is predicted and runoff could increase from +10% to +310% (along with soil loss increase from +33% to +274%) in 2040-2059 relative to 1990-1999 (O'Neal et al., 2005). The transfer of OM or organic carbon from the terrestrial soil to the oceans via erosion and riverine transport could significantly affect the coastal oceans (Hilton et al., 2008; Bauer et al., 2013; Galy et al., 2015). Particulate organic carbon (POC) export from the terrestrial biosphere into the oceans is mostly controlled by physical erosion, which is thus predicted to become the dominant long-term atmospheric CO<sub>2</sub> sink under a fourfold increase in global physical erosion rate at constant temperature (Galy et al., 2015).

Such enhanced input of OM with raising temperature under future global warming conditions will drastically impact on the ocean acidification that is concomitantly linked with other biogeochemical processes (Jin et al., 2015; Mora et al., 2013). Moreover, temperature regulates important abiotic and biotic processes that can alter water throughput, flow paths, dissolution rates and watershed carbon stocks (Bauer et al., 2013) as well as stratification period or euphotic zone (Fig. 1; Mora et al., 2013; Huisman et al., 2006; Jöhnk et al., 2008). In addition, elevated temperature under global warming conditions could potentially enhance the proliferation of harmful Cyanobacteria in surface water (Paerl and Huisman, 2008; Jöhnk et al., 2008). The overall ecological and biogeochemical consequences of future ocean acidification under forthcoming global warming conditions in oceans could severely impact on coastal seas, with a spreading of anoxic dead zones and a frequent occurrence of toxic dinoflagellate blooms (Jackson, 2008). Possible evolutions could involve expanding hypoxia in the deeper water layers (Wannicke et al., 2012; Stramma et al., 2008); changes in food-web dynamics (Fabry et al., 2008; Wannicke et al., 2012); changes in the biogeochemical cycling dynamics of C, N, and P (Keeling et al., 2010; Wannicke et al., 2012; Toseland et al., 2013; Unger et al.,

2013; Olli et al., 2015; Baragi et al., 2015); changes in metabolic pathways (Jin et al., 2015); increases in coral susceptibility to disease, pathogen abundance and pathogen virulence (Maynard et al., 2015); negative consequences up to mortality for various marine organisms, particularly for the shell-forming ones (Haigh et al., 2015; Doney et al., 2009); structural changes in phytoplankton communities (Dutkiewicz et al., 2015) and in some marine keystone species (Waldbusser et al., 2014; Barton et al., 2012); setting up of the Lilliput effect that causes organisms to evolve towards becoming smaller and exploit related physiological advantages (Garilli et al., 2015); increasing appearance of harmful marine species (e.g., Nodularia spumigena sp., Olli et al., 2015; Jackson, 2008; Paerl and Huisman, 2008) and of toxic compounds (e.g. of the phenolic type, Jin et al., 2015); alteration of fish populations through habitat modification (Nagelkerken et al., 2016), as well as increasing global redistribution of marine biodiversity (Molinos et al., 2016). Finally, such ecological and biogeochemical changes in the oceans could have profound consequences for marine biodiversity, ecosystem-services or processes, and seafood quality with deep implications for fishery industries in the upcoming decades (Doney et al., 2009; Mora et al., 2013; Jin et al., 2015)."

# Corrected responses of the first referee's comment over similar comments from the second referee

According to distinguished second referee's comments, we have got some references provided by second referee and also ourselves, which are directly linked with ocean acidification and harmful algal blooms for the chapter 5.4. So we have revised Chapter 5.4 and in that chapter we have revised two comments provided by first distinguished referee and our responses are as follows:

2. I am concerned about the confusing use of direct and indirect evidence to support relationships proposed in the review. Specifically, I think that section "Stress caused by algal or red-tide toxins and pathogens" lacks direct evidence.

Ans: According to the comments of the second referee, we have found more references in that issues and we have revised the text accordingly. Please find our revision in the earlier comment.

4. P10961 line 10, "Elevated PCO<sub>2</sub> causes bacterial community shifts" is incorrect. The influence of higher CO2 and lower pH on ocean microbial community has not been completely verified in terms of significance. For example, some studies observed there is little effect of pCO2 treatments (380, 540, 750, 1,120, and 3,000  $\mu$ atm) on microbial diversity (Joint et al., 2011; Tait et al., 2013).

Ans: According to this comment, we have deleted this sentence and revised newly additions from several recent reference papers which showed similar results with each other. We read the reference paper of Joint et al. (2011), but this work is a Perspective Article and they also asked for future researches.

Our new addition in that respect is: "Ocean acidification/elevated  $CO_2$  could indirectly affect bacterial activity and abundance (see section 5.1; Grossart et al., 2006; Allgaier et al., 2008; Endres et al., 2014; Baragi et al., 2015; Witt et al., 2011; Tait et al., 2013). However, the abundance of different bacterial communities could respond differently (increase, remain unchanged or even decrease) under the effect of global warming (Allgaier et al., 2008; Witt et al., 2011; Baragi et al., 2015)." in page 28, lines 18-23.

Furthermore, to concentrate the more research in that issue, we have added at the end of this Chapter 5.4 the following sentence "Finally, more experimental researches are warranted to find out links and mechanisms between harmful algal blooms and ocean acidification/elevated CO<sub>2</sub>." in page 29, lines 18-20.

#### **References added newly**

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Thank you.

Sincerely Yours, Mostofa

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