Dear Editor,

please find below our answers to the reviewers' comments.

The main suggestion posed by the three reviewers is to better exploit model results in order to give a quantification of the processes that causes the spatial-temporal variability of alkalinity (section 3). In the new version of the manuscript we carefully revised the results section by adding a new sub-section (3.4) and three new figures dedicated to the quantification of the biological (Fig. 7) and physical (Fig. 8) contributions to the alkalinity rate of change. We completed the analysis of the alkalinity processes by computing fluxes at the straits between sub-basins and producing a budget for alkalinity in the Mediterranean Sea. Figure 5, which was poorly readable, has been revised. This new figure (Figure 6 in the new manuscript) has been simplified and labels have been made more readable.

Further, as requested by reviewers #2 and #3 we performed the calculation of alkalinity-salinity regression based on the observations, which is coherent with our conclusions. The section 3.2 has been revised according to the new findings. However, we would like to say that there is still space for an analysis based entirely on observations since our dataset might be no exhaustive. Some recent datasets are not included in our work. To this point, two reviewers (#1 and #2) claimed for the inclusion of additional observations to be used in our analysis. We would like to stress that we used all the data we were able to gather. The data listed in Table 2 have been gathered by exploring: the Perseus web dataset, the Pangea webservice and the SeaDataNet (OGS-NODC) database. We selected data collected after 1998 in order to be consistent with the period of the simulation.

We are aware of some recent campaigns (for example: from MedSea project) but those data are not available to us. Then, as suggested by the reviewers, we explored the possibility to use an old dataset (MEDAR/MEDATLAS 2002). We compared MEDAR dataset with the one listed in Table 2. Results of the comparison (Figure 1 at the end of this document) show large discrepancies (differences of up to 100 μmol kg-1) between the two datasets in several areas of the Mediterranean Sea. Further, it is worth to note that data acquired before the adoption of the release of Dickson CRM (certified reference material DOE 1994) might be affected by large discrepancies. Therefore, we believe that an analysis between the two datasets would deserve a specific study that goes beyond the scope of the present paper. According to these considerations we propose not to include the MEdar/Medatlas dataset in our analysis.

Other suggestions raised by reviewer#2 about abstract and introduction have been carefully taken into account.

Finally, reviewer #1 suggested to include results about DIC dynamics in the paper (which is, indeed, a variable of our model). However, since we have not received a similar commitment also by the other reviewers and the editor, we would prefer to focus this paper on the analysis of alkalinity in the Mediterranean (on the quantification of the biological and physical sources of its variability, and on the analysis of alkalinity and salinity relationship), leaving to a next paper the analysis of the carbonate system of the Mediterranean Sea.

The following table reports our detailed answers (right column) to the reviewers' comments (left column).

A revised manuscript is also uploaded. We provide a marked-up manuscript version showing the changes made (we used the track changes in Word).

We hope that the revision will meet the high standard of Biogeosciences publications.

Best regards,

Gianpiero Cossarini and Co-authors

	REVIEW1 of Cossarini et al. (2014)	
	This work deals with the spatial and temporal modelization of alkalinity in a particular marginal sea, the Mediterranean. This landlocked area with a particular CO2 system is suffering a particularly high human pressure and with regard to the oceanic system, physical, chemical and biological drastic changes have been reported. There is now a major concern about the impacts of ocean acidification in the structure and functioning	We thank the reviewer for her/his comments that helped us to improve the manuscript. Our manuscript meant to be not only a model for alkalinity but also to: a) provide an updated space and time climatology of alkalinity for the whole Mediterranean Sea; this is important per se, given that this variable is useful also in experimental studies, and fills a gap given that data are sparse and can not return an unbiased

	of ecological systems, with several international projects going on. Therefore, in order to predict future changes, apart of the observational and experimental efforts, the modeling community is integrating the CO2 system in 3D transport-biogoechemical models adjusted to the particular MedSea circulation as a first step for a higher objective. This work models TA in the MedSea, compares the results from the model with the gathered data in the area. The results are fairly good but the general objective is meagre. In my opinion, despite presenting interesting results, this work is too short or weak, lacking of entity to be published in a high rank journal as BGD. I propose major revision.	representation of 3D alkalinity fields. b) stress that alkalinity can not be derived by global (not site specific) regressions versus salinity c) discuss an alkalinity budget for the Mediterranean Sea. We carefully revised several parts of the manuscript in order to study the alkalinity variability in the Mediterranean Sea and to improve our analysis of the processes that affect this important parameter. In particular, the result sections have been improved (see new sections 3.3 and 3.4) providing a more thorough analysis about the processes that drive alkalinity spatio-temporal variability (new figures 7 and 8). An alkalinity budget is also included along with estimations of fluxes through Gibraltar and Sicily straits.
	General Comments 1) Regarding TA:	
R1-01	General Comments 1) Regarding TA: - I miss a better quantification of the processes affecting its variability, they are commented, roughly quantified in Fig. 5 but it seems that the authors could go a little bit further. In the Conclusions is particularly stated that the model would help to understand how different factors contribute to defining spatial gradients and seasonal variability…. It would be nice to get a better quantification of all these processes as they are differentiated in the 3D transport model.	Thank you. This important point has been addressed. In the new manuscripts, the quantification of physical and biological processes affecting alkalinity has been better presented and analyzed. In particular, the section 2.1 (pag 12875, model description) has been revised including a better explanation of the processes reproduced by the OPATM-BFM model. Further, results sections have been revised: the revised section 3.3 focuses on the temporal variability of alkalinity and a new section (3.4, pages 12880-12881) explains and quantifies the physical and biological factors that drive the spatio-temporal evolution of alkalinity. Fig. 5 has been substituted by 4 new figures, that show: the temporal variability of alkalinity in Mediterranean Sea (new Fig. 5), the mean seasonal profiles (Fig. 6), the quantification of the rate of change of alkalinity due the biological (Fig. 7) and physical (Fig. 8) processes. Finally, conclusions have been revised according to the new findings described in section 3 (conclusion section, pag. 12881).
R1-02	why not using the MEDAR/MEDATLAS data?	The data listed in Table 2 have been gathered by exploring: the Perseus web dataset, the Pangea webservice and the SeaDataNet (OGS-NODC) database. We used all the datasets that were freely available to us. We selected data collected after 1998 in order to be consistent with the period of the simulation. According to the reviewer#1 suggestion, we have checked for alkalinity data also in the MEDAR-MEDATLAS 2002 DATABASE (MEDAR Group, 2002 - MEDATLAS/2002 database. Mediterranean and Black Sea database of temperature salinity and bio-chemical parameters. Climatological Atlas. IFREMER Edition (4 Cdroms)). However, up to our ability in exploring this dataset, we have found that most of the data refer to the period 1980-1990 (and few to the period 1990-1995). We performed a comparison between MEDAR/MEDATLAS dataset and the one listed in tables 2 of our manuscript. Results of the comparison (Figure 1 at the end of this document) show large differences (up to 100 μmol kg-1) between the two

		datasets for several areas of the Mediterranean Sea (e.g. in the Ionian Sea, in the Adriatic Sea, in the Tyrrhenian Sea, and in the north Aegean Sea). Further, according to Louanchi et al (2009) alkalinity data acquired before the release of Dickson CRM (certified reference material DOE 1994) might be affected by large discrepancies. An analysis of data consistency of the two periods is beyond the scope of the present manuscript and it would deserve a dedicated study. Given the above considerations, and the fact that our simulation is focused on the first part of 2000 decade we decided not to include the Medar/Medatlas dataset. A comment on this point has been added to the section 2.3 (pag. 12876).
R1-03	the variability of TA in the MedSea was commented in Schneider et al. (2007) and more thoroughly in the recent Álvarez et al. (Oc. Sc. 2014).	We accept and incorporate this suggestion in the manuscript. In particular, results of our model are consistent with the data described in the works by Scheinder et al. (2007) and Alvarez et al., (2014). This is shown in figures 2 and 3 that report the simulated and observed spatial variability of alkalinity and the skill assessment of the model results. Our findings are consistent with the description of variability of Alkalinity given by those authors (for example: the west to east alkalinity gradient, the role of LIW in moving westward high alkalinity water, the impact of the MAV carrying low alkaline water eastward). We revised the results section, by adding appropriate comments that confirm the consistency of our results with the findings of those previous papers.
R1-04	given the low DIC/TA ratio, the CO2 chemistry is particularly resistant to the CO2 input from the atmosphere, this is quantified in Álvarez et al. (2014) but is a direct consequence of the CO2 chemistry, i.e., general knowledge for CO2 chemists.	Even if the model (and the simulations) describes the carbonate system and DIC dynamics, in this manuscript our choice is to focus on alkalinity and on the empirical alkalinity-salinity relationships. As it is well known, alkalinity is a master variable for the resolution of the carbonate system, but, differently from DIC, it is not influenced by the atmospheric CO2 invasion (Wolf-Gladrow et al., 2007). Therefore we believe that models should have some skill in reproducing this parameter, before being used to investigate the carbonate system dynamics. For this reason, we prefer not to add too much material in a single manuscript. In this paper our main concerns are the analysis of the good performance of our model in reproducing the alkalinity in the Mediterranean, the quantification of the biological and physical sources of its variability, the analysis of the spatial and temporal variability of alkalinity and the analysis of alkalinity and salinity relationship in the Mediterranean Sea.
R1-05	The work by Louanchi et al. (Decadal changes in surface carbon dioxide and related variables in the Mediterranean Sea as inferred from a coupled data diagnostic model approach, ICES journal, 2009) should be cited in the introduction	We appreciate the indication about this literature reference; we have added it in the introduction. Although, it is worth to note that Louanchi et al (2009) compute alkalinity using the same salinity-alkalinity relationship of Scheinder et al. (2007). This reinforces the relevance and necessity of our study whose results update the alkalinity estimations in the Mediterranean Sea.
R1-06	The recent work by Takahashi et al. (Mar Chem, 2014) should also be cited as they present a TA climatology with several TA vs salinity regressions and all the marginal seas are missing.	We thanks for the suggestion about this very recent and interesting literature, we have added it in the introduction (pag 12872).
R1-07	- Figure 5: very difficult to see, the numbers and the	Thank you for this important suggestion. Figure 5 and

	profiles. The equivalence of the letters is not commented in the caption.	section 3.3 have undergone a radical revision (see comments on point R1-01). In the new version of the manuscript, the new figures 7-8 and the new section 3.4 (Pag. 12881) depict the temporal and spatial evolution of the biological and physical terms of alkalinity equation. These terms (the partial derivatives of the alkalinity of OPATM-BFM model) are now introduced appropriately in the revised section 2.2 (pag 12874).
R1-08	2) Suggestions This paper would greatly be improved if in addition to the quantification of the processes affecting TA, some results about DIC are also included. This is hinted in the methods section, DIC is mentioned as a new state variable in the OPATM-BFM (section 2.1). Why not presenting the results?.	Please, see comment on point R1_04. Further, since we have not received a similar commitment by the other reviewers and by the editor, we would prefer to focus this paper on the analysis of alkalinity in the Mediterranean (the quantification of the biological and physical sources of its variability, and the analysis of alkalinity and salinity relationship), leaving to a next paper the analysis of the carbonate system of the Mediterranean Sea.
	REVIEW2 of Cossarini et al. (2014)	
R2-01	The paper by Cossarini et al. uses a model of the Mediterranean to infer information on the distribution of total alkalinity. The paper is, in principle, interesting but it lacks in-depth analysis of the results, and of the concept of alkalinity. The model seems to reproduce observations reasonable, although more efforts should be made to verify this particularly for critical regions close to major estuaries. The model thus provide the means of a more thorough analysis of the Mediterranean Sea alkalinity budget and processes. This potential is not used to its full extent, far from it. I think that the manuscript can be publishable in BG, but major revision would be needed, see below.	We thank the reviewer for her/his interesting and challenging comments. According to the reviewer's suggestions we have enlarged the discussion and interpretation of model results. In particular, the result sections have been improved (see new section 3.3 and 3.4) providing a more thorough analysis about the processes that drive alkalinity spatio-temporal variability. An alkalinity budget is also included along with estimations of fluxes through Gibraltar and Sicily straits. See specific points on this revision. Regarding the assessment of the model in reproducing alkalinity in critical regions close to major estuaries, we believe that the model resolution (1/8 degree) is too rough to fully resolve coastal processes and the available dataset is not appropriate to validate the model on coastal areas.
	Major concerns:	
R2-02	Abstract lines 5-6: It is such an elementary statement (statement is repeat several times in the ms) that it does not belong in the abstract, if at all it should be phrased differently; it is well known that the alkalinity in the Med is high compared to the Atlantic, nothing new there. If the model did not reproduce this it would be disastrous, at least.	The abstract has been revised (See pag. 12871). In the new version, the sentences about the difference between Atlantic and Mediterranean sea have been deleted. A short note about the peculiar difference of the Mediterranean Sea respect to the Atlantic Ocean is now present only in the introduction. Further, some sentences of the abstract have been rephrased to better explain the focus and the main findings of the paper.
R2-03	Introduction: The alkalinity definition and its dependence on various processes that effect alkalinity is poorly described and discussed. Alkalinity is not a simple function of salinity for a number of reasons; the authors tries to, but do not succeed, in conveying this message. This section needs to be greatly expanded.	Thank you for this important suggestion. This part of the introduction has been revised and enlarged (pag. 12872). We explain that: - alkalinity is a measure of the capabilities of sea water to buffer acidification; - alkalinity is operationally defined as the sum of weak bases dissolved in seawater and empirically measured as the amount of protons buffered by seawater up to a reference pH level; - salinity is used to proxy alkalinity but different regional seas present different responses to ocean acidification also as a consequence of specific alkalinity conditions; - further, salinity cannot track the occurrence of biological processes that also modifies alkalinity; - therefore we propose the possibility of an alternative approach by using process-based numerical models

R2-04	Section 2.2: There are additional data sets available in public databases (and in MedSea internal data bases) for DIC and Alkalinity that can be used for initialization of the model. Particularly there is an almost complete lack of data in the western basin, despite the availability of data there. This does not seem justified. A list of data is provided by the authors in table 2; why are these not used?	The data listed in Table 2 have been gathered by exploring: the Perseus web dataset, the Pangea webservice and the SeaDataNet (OGS-NODC) database. Up to our knowledge, we used all the datasets that were freely available to us. We selected data collected after 1998 in order to be consistent with the period of the simulation, and to avoid possible problem of inconsistency of data (see also comment is R1-02). In particular, the MEDAR/MEDATLAS dataset was not used because data cover a period before 1995 (see comment in R1-02), and data of the MedSea 2013 cruise are not currently available for this manuscript. The initializzation was made using the Meteor2001 dataset. This dataset is the closest in time to the start of the simulation and gives a basin wide view of alkalinity in Mediterranean Sea covering the entire east to west gradients. The spin up of the simulation (see section 2.2 on model setup) adjusts the initial conditions to the model dynamics.
R2-05	Section 3: There is an almost complete lack of discussion of several potentially essential processes that are responsible for the observed distribution and variation of TA, both spatial and temporal. What about remineralization in the water column, on the benthos, sedimentation, budgets? This model frame-work has the potential to shed insight to many of these processes. The framework of a model allows for discussion on these themes; I would like to see this potential used by the authors.	We thank for this comment that helped us to improve the manuscript. The quantification of physical and biological processes impacting alkalinity has been enlarged and better presented in the new version of the manuscript. In particular, the new section 3.4 is dedicated to quantify and discuss the physical and biological factors that affect the spatial and temporal evolution and variability of alkalinity. Two new figures provide a quantification of the rate of change of alkalinity due the biological processes (Fig. 7) and physical (Fig. 8) along the vertical axis in the different sub-basins and seasons. The section ends with a budget analysis of alkalinity for the Mediterranean Sea.
	Minor comments:	
R2-06	Abstract, line 4: I suggest that the authors use the word “observations” (or “observational”) rather than “experimental” here, and in other places in the ms where they refer to observations of alkalinity (or other properties).	The word “observations” has been used instead of experimental throughout the text.
R2-07	Abstract lines 8-10: There are not only west-east gradients, also north-south gradients (although mostly of secondary importance). This could be rephrased to reflect the influence on regional phenomena or processes.	The sentence has been rephrased according to the reviewer’s suggestion.
R2-08	Abstract line 20: This statement is wrong; which has clearly been shown by others (Álvarez et al., 2014;Palmiéri et al., 2014). Also a statement that “which might indicate a higher buffer capacity” cannot be written in a paper; the buffer capacities can easily be calculated based on elementary chemistry of the carbonate system, the authors should do these calculations themselves rather than speculate, particularly when the speculations can be easily proven to be not correct.	The abstract has been revised. The statement at line 20 has been removed.
R2-09	Abstract line 11: Why is dense water formation in the western Med not mentioned in this context?	The abstract has been revised. This statement does not belong to the abstract anymore.
R2-10	Abstract line 16: This is poorly phrased. There is always some fresh water influence (otherwise little S variability). I think the authors want to say that in some areas the freshwater from major rivers has	Abstract has been revised. The sentence has been clarified.

	higher alkalinity than the Med, causing a negative S/TA relationship.	
R2-11	Page 12873, line 3: remove the word “potentially”	Comment refers to page 12872. Done
R2-12	Page 12873, line 8: Why “ad hoc” studies?	“Ad hoc” has been substituted by “specific”.
R2-13	Page 12873, line 14: Add reference to Takahashi et al. (2014).	Done
R2-15	Table 1: Is the alkalinity of the Tyrrhenian that high? I do not think so, correct or explain.	In the new version of the manuscript, Table 2 refers to the alkaline discharges from rivers and watersheds. Values of this table are correct. Tyrrhenian value is assumed from data reported in Table 2 of Copin-Montegut (1993), which refers to observations gathered by Petine et al. (1985). In particular, our value of rivers and runoff of the Tyrrhenian sub-basin is derived from data values of rivers Tiber and Arno of tables 2 of Copin-Montegut (1993). However, it is worth to note that, despite the pretty high values of those rivers, their freshwater discharges are very low and therefore their impact on alkalinity of this sub-basin is pretty small.
R2-15	Table 2. Please add information on the average TA content of the main rivers, not only the discharge. This is important to understand the intercept of the TA/S relationship.	In the new version of the manuscript, Table 2 refers to the alkaline discharges from rivers and watersheds. The values of the concentration of freshwater alkalinity of major rivers are equal to the concentration of the freshwater discharges of the entire watershed (sub-basin). The discharges from rivers are given to indicate the quota of the major rivers to the total discharge in a given sub-basin. We revised the format of the new Table 2.
R2-16	Figure 5. These figures need different scales to be readable. Also the legend needs to explain where these selected points are (ref to Figure 1).	Figure 5 has been simplified and revised. The new figure (now Figure 6) shows the mean annual profiles and the profiles of the winter and summer range. Further, labels have been resized and the indication of the selected points has been added.
R2-17	Figure 4: This is probably the highlight of the manuscript. It would be very interesting to see a similar plot made based on observational data. For this the authors probably need to explore the Med-Atlas collection as well as those already listed in Table 2. Deviations between model and observations needs to be discussed in more detail, and such a figure could be a vehicle for doing so. References: Álvarez, M., Sanleón-Bartolomé, H., Tanhua, T., Mintrop, L., Luchetta, A., Cantoni, C., Schroeder, K., and Civitarese, G.: The CO2 system in the Mediterranean Sea: a basin wide perspective, Ocean Sci., 10, 69-92, 10.5194/os-10-69-2014, 2014. Palmiéri, J., Orr, J. C., Dutay, J. C., Béranger, K., Schneider, A., Beuvier, J., and Somot, S.: Simulated anthropogenic CO2 uptake and acidification of the Mediterranean Sea, Biogeosciences Discuss., 11, 6461-6517, 10.5194/bgd-11-6461-2014, 2014. Takahashi, T., Sutherland, S. C., Chipman, D. W., Goddard, J. G., Ho, C., Newberger, T., Sweeney, C., and Munro, D. R.: Climatological distributions of pH, pCO2, total CO2, alkalinity, and CaCO3 saturation in the global surface ocean, and temporal changes at selected locations, Marine Chemistry, 164, 95-125,	Following the reviewer’s suggestion we propose an alkalinity-salinity regression computed on the observations. The new regression is based on observations distributed across the Alboran (alb), Southwestwest (sww), southwesteast (swe), Ionian (Ion) and Levantine (Lev) sub-regions. Observations consist of 194 surface values (mean values of the surface layer 0-50m) extracted from the datasets listed in Table 2 of the manuscript. The new regression is consistent with model results. The small difference between the two regressions is investigated and it reflects likely a model overestimation of the Ionian values. Model and observation regressions differ from the one proposed by Schneider et al., 2007. The discrepancy reflects the different sampling location and number of points used by the two works. Further, we compute also seasonal regressions based on model results that highlight the uncertainty of the alkalinity-salinity regression due to the temporal variability of the parameters. The section 3.2 has been revised according to the new findings and a new table has been added. The new Table 3 reports parameters, errors and significance of the regressions based on model results, on observations and the regression published by Schneider et al., 2007.

	http://dx.doi.org/10.1016/j.marchem.2014.06.004, 2014.	
	REVIEW3	
R3-01	This manuscript presents modeling experiments that describe the spatial-temporal evolution of alkalinity in the Mediterranean Sea using a 3-D transport biogeochemical carbonate model. The simulation experiments cover the period 1999-2004. Model results facilitate to understand, how the deferent biogeophysical processes contribute in describing the spatial gradients and also the seasonal variation of alkalinity. Overall, the study is well written and presents a relevant development. The experiments are carefully described. The experiments indicate that the regression between salinity and alkalinity varies from region to region and highlight that it's potential to use one equation to reconstruct alkalinity values over the entire Mediterranean as long as marginal seas and regions influenced by fresh water inputs aren't thought-about. I think that the manuscript can be recommended for publication with some additional discussions/clarifications considering my comments bellow. Overall, this should only require a minor revision of the manuscript.	We thank the reviewer for his encouraging comments.
R3-02	P 12875 l 20 – p 12876 l 5: The description of the carbonate model is rather complicated. Please rewrite it. It seems that for the estimation of alkalinity only BFM and salinity are required. Why the authors call it carbonate module?	We agree with this comment. Alkalinity evolution depends on physical processes (transport, boundaries exchanges and net evaporation) and biological processes (nutrients utilization/release by the biological components), which are included in the OPATM-BFM model. The alkalinity, along with DIC (another variable of the BFM model), is the input parameter of the carbonate module that has been coupled with the BFM and is used to compute the CO2 air-sea exchanges. However, the carbonate module is not strictly requested to compute the alkalinity terms. According to this comment, we have revised the section 2.2 to describe properly the alkalinity formulation of the BFM model (pag. 122874).
R3-03	P12877 l 10: how long was the spin up period?	The spin up period consists of 5 years (first year was repeated and the first three years of the simulation, 1998-2000, were not considered for the calculation of the results). For the calculation used in the manuscript, we have considered model results of the period 2001-2004.
R3-04	P2878 l 6 – p12878 l 16: This information is known also from the data. The model results should provide more detailed information. It would be interesting if the authors could expand this section discussing the model results in comparison with the observations.	Following the suggestion of reviewers #2 (point R2-17) and #3 we propose a new regression computed on the observations. The new regression is based on observations distributed across the Alboran (alb), Southwestwest (sww), southwesteast (swe), Ionian (Ion) and Levantine (Lev) sub-regions. Observations consist of 194 surface values (mean values of the surface layer 0-50m) extracted by the datasets listed in Table 2 of the manuscript. The new regression is consistent with model results. The small difference between the two regressions is investigated and it reflects likely a model overestimation of the Ionian values. Model and observation regressions differ from the one proposed by Schneider et al., (2007). The discrepancy reflects the different sampling location and number of points used by the

		two works. Further, we compute also seasonal regressions based on model results that highlight the uncertainty of the alkalinity-salinity regression due to the temporal variability of the parameters. The section 3.2 has been revised accordingly to the new findings and a new table has been added. The new Table 3 reports parameters, errors and significance of the regressions based on model results, of the one based on observations and the regression published by Schneider et al. (2007).
R3-05	P12878 l20 - P12878 l25: "The thermohaline . . ..less variability" How the authors identify these characteristics? It should be also beneficial to further demonstrate the role of the treromohaline circulation by calculating the water fluxes among different regions of the Mediterranean	Results of MED16 model simulation (which represent the physical forcings of our run) reproduce satisfactorily the thermohaline basin wide circulation, and water mass fluxes are validated in correspondence of several straits including Gibraltar Strait and Sicily Channel (Beranger et al, 2005). According to the validated circulation (Beranger, 2005), the surface gradient of alkalinity is driven by the propagation eastward of the Atlantic water. In turn, the LIW closes the termohaline cell at the layer 200-600 m (Beranger, 2005) and it is responsible for the west-to-east alkalinity gradient at the intermediate layer (Fig. 2b). These findings are also supported by the calculated alkalinity fluxes at the Sicily strait for the surface layer and the intermediate and deep layers. A description of the alkalinity fluxes at the Sicily strait (along with the ones at the Otranto straits and between Aegean Sea and eastern Mediterranean Sea) has been added in the new version of the manuscript (pag 12877).
R3-06	P12879 l 15: Since alkalinity depends on evaporation and the Atlantic water inflow, a comment would be useful to show that the water budget E-P is consistent ensuring that there is not significant drift in the alkalinity.	According to the results of Beranger et al. (2005), the hydrological cycle is consistent with data. A sentence about consistency of the hydrological cycle has been added in the section 2.2 (pag. 12875)
R3-07	P12881 l 18: I cannot follow the calculation of the biological contribution. Please explain	Following also the suggestion of the reviewers #1 and #2 the section 3.3 has been carefully revised and a new section 3.4 (pag. 12881) has been added in order to explain and quantify the contributions of physical and biological processes to the alkalinity variability. See also comments to points R1-01 and R2-05.
R3-08	Figure 5. Please report the selected points in the figure 5 caption.	Figure 5 of previous version of the manuscript (now Fig.6 in the new version) has been revised. The indication of the selected points is now specified in the caption of new Fig 6. and the location of points is displayed in the new Figure 5

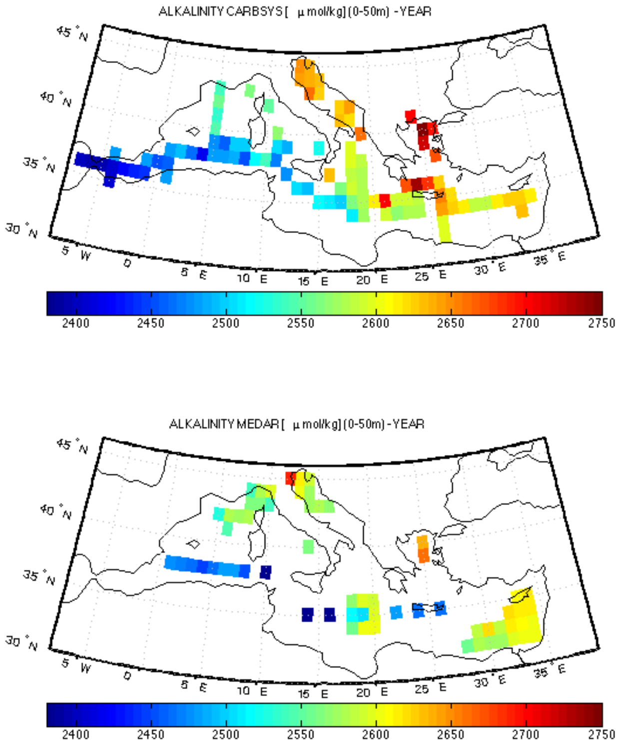

Fig. 1. Maps of alkalinity at 1x1 degrees of resolution calculated on datasets listed in Table 2 of the manuscript (upper panel) and on the MEDAR/MEDATLAS dataset (lower panel). Values of alkalinity at each bin of 1 x 1 degrees are computed following the same rule explained in section 2.3 of the manuscript.

Biogeosciences Discuss., 11, 12871–12893, 2014
www.biogeosciences-discuss.net/11/12871/2014/ doi:10.5194/bgd-11-12871-2014

Space-time variability of alkalinity in the Mediterranean Sea

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Received: 1 August 2014 – Accepted: 20 August 2014 – Published: 3 September 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The paper provides a basin scale assessment of the spatial distribution of alkalinity in the Mediterranean Sea. The assessment is made by integrating the available observations in a 3-D transport-biogeochemical model.

The results indicate the presence of complex spatial patterns: a marked west-to-east surface gradient of alkalinity is coupled to secondary negative gradients: 1) from marginal seas (Adriatic and Aegean Sea) to the eastern Mediterranean Sea and 2) from north to south in the western region. The west-east gradient is related to the mixing of the Atlantic water entering from the Gibraltar Strait with the high alkaline water of the eastern sub-basins, which is correlated to the positive surface flux of evaporation minus precipitation. The north to south gradients are related to the terrestrial input and to input of the Black Sea water through Dardanelles. In the surface layers, alkalinity has a relevant seasonal cycle (up to 40 µmol kg^{-1}) that is driven by physical processes (seasonal cycle of evaporation and vertical mixing) and – to a minor extent – by biological processes. A comparison of alkalinity vs. salinity indicates that different regions present different relationships: in regions of freshwater influence, the two quantities are negatively correlated due to riverine alkalinity input, whereas they are positively correlated in open sea areas of the Mediterranean Sea.

1 Introduction

The dissolution of atmospheric CO_2 mitigates the effects of the atmospheric concentration of fossil carbon emissions but causes acidification in marine water. Observations of ocean acidification have already been recorded, and evidence suggests that this phenomenon is occurring at an unprecedented rate. A number of studies indicate that ocean acidification might impact the structure and functioning of ecological

systems, with cascading consequences on socio-economic activities (Rodrigues et al., 2013; Turley and Boot, 2011; Melaku Canu et al., 2014). In this context alkalinity is a very relevant concept, because it is a measure of the capabilities of sea water to buffer acidification. In fact, a number of chemical compounds are dissolved in sea water, including carbonate and bicarbonate ions, boron and other weak bases, which can combine with free protons. Total alkalinity is operationally defined as the sum of these weak bases (Zeebe and Wolf-Gladrow, 2001), and empirically measured as the amount of protons buffered by seawater up to a reference pH level. Therefore, different regional seas present different responses to ocean acidification also as a consequence of specific alkalinity conditions, a fact that might call for specific studies. As an example, in the Mediterranean Sea - a landlocked, relatively small, highly dynamic ecosystem with high anthropic pressure in the coastal areas - the existing data indicate that alkalinity is significantly higher than in the Atlantic Ocean, and that a west-east spatial gradient is

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present. Thus, the alkalinity concentration increases moving from the Atlantic Ocean to the western basin of the Mediterranean and reaches its maximum values in the eastern basin (Schneider et al., 2007; Touratier and Goyet, 2011; Alvarez et al., 2014). This pattern clearly indicates that it is not possible to address the study of this basin by relying only on the results of global studies.

Global climatology has been produced for pH and alkalinity (Lee et al., 2006; Takahashi et al., 2014), often based on the use of empirical site-specific regressions between alkalinity and temperature and salinity data. In the open sea environment, alkalinity often correlates with salinity and temperature (Lee et al., 2006; Takahashi et al., 2014). The underpinning process is that evaporation (and precipitation) concentrates (or dilutes) all compounds that contribute to alkalinity. The regression coefficients, however, change with the nature and relative composition of these compounds and can vary over different regions. Furthermore, salinity cannot track the occurrence of biological processes that also modify alkalinity, such as nutrients uptake, mineralization, nitrification and denitrification (Wolf-Gladrow et al., 2007). Nonetheless, salinity based empirical relationships are widely used to reconstruct the spatio-temporal distribution of alkalinity from existing data sets and to infer conclusions on pH state and trends.

Several regression relationships have been proposed for the Mediterranean Sea (Schneider et al., 2007; Copin-Montegut, 1993) and indicate different reconstructions. In addition, regressions based on local areas exist (Santana-Casiano et al., 2002;

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Huertas et al., 2009), some of which indicate a negative correlation between alkalinity and salinity in regions of freshwater (river) input (Luccheta et al., 2010). Few data, however, are available for the Mediterranean Sea, and as such, in this important basin the statistical spatial interpolation and extrapolation of existing information are critical.

Process based on numerical models represent an alternative to the use of empirical regressive models. In process-based numerical models, alkalinity and dissolved inorganic carbon (DIC) are considered explicit state variables (master variables used to solve the carbonate system) that are transported by physical processes and modified by chemical and biological processes (Wakelinken et al., 2012; Prowe et al., 2009; Artioli et al., 2012; Turi et al., 2013; Fiechter et al., 2014). Also this approach is not free from criticalities, as it implies the need to explicitly parameterize the major known relationships among DIC, alkalinity and the biogeochemical processes, and to define exactly which chemical compounds are considered in the definition of the alkalinity. The boundary and initial conditions of the area considered must be estimated as well. The advantage of this approach is that once a numerical model exists, it can be used to interpolate existing observations and to make projections on future states.

Many studies were carried out to numerically simulate the carbonate system in the global oceans (Orr et al., 2005). In the Mediterranean Sea, box modeling estimates were made by d'Ortenzio et al. (2008), who used an array of decoupled 1-D water column biogeochemical models forced by satellite observations, and by Louanchi et al. (2009) who used a coupled data-diagnostic model approach to estimate trend in carbonate variables over last decades. An high resolution circulation model coupled with CO_2 module adopting a perturbation technique was used by Palmieri et al. (2014) to estimate the anthropogenic CO_2 in the Mediterranean Sea. However, in all these publications alkalinity was derived from a salinity regression, in agreement with Scheinder et al. (2007). In contrast, in this manuscript, we dynamically simulated alkalinity, by introducing a new full state variable in an existing state-of-the-art biogeochemical model of the Mediterranean Sea (Lazzari et al., 2012). We also use the extended model to integrate, in a coherent framework, the available measures of alkalinity within the Mediterranean Sea and along its boundaries with the aim of deriving a space–time climatology of alkalinity. The model results are then used to explore the space–time variability of this important parameter and assess specific relationships between alkalinity and salinity for different regions of the Mediterranean Sea. The impact of different processes, like biological uptake, on alkalinity spatial and temporal variability is also addressed.

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2 Model and data for the Mediterranean Sea

2.1 Biogeochemical and carbonate system coupled model

The biogeochemical modelling system of the Mediterranean Sea (OPATM-BFM) used in the present study is a 3-D transport reaction model. It is capable of resolving the large-scale variability and seasonal cycle of nutrients and primary producers (Lazzari et al., 2012).

The transport of dissolved and particulate matter is resolved using the OPATM transport model (Lazzari et al., 2010), offline forced by dynamic field that is reproduced by the hydrodynamic general

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circulation model MED16 OGCM (Béranger et al., 2005).

The transport is computed with a horizontal resolution of 1/8 o (approximately 12 km) and with a vertical z-coordinate discretization that is coarser at the bottom layers and more refined at the surface layers (13 levels in the 0–200 m layer, 7 layers in the 200– 600 m layer and 23 levels in the 600-bottom layer).

The dynamics of the biogeochemical properties are described by the BFM model, a biogeochemical model that describes the cycles of nitrogen, phosphorus, silica and carbon through biotic (4 phytoplankton pools, heterotrophic bacteria, 2 microzooplankton, and 2 mesozooplankton pools) and abiotic (detritus, labile, semi-labile and refractory dissolved organic matter, dissolved inorganic compounds) components as a function of temperature and light (Lazzari et al., 2012).

The OPATM-BFM was upgraded by implementing a carbonate system module that requires two new state variables: dissolved inorganic carbon (DIC) and alkalinity.

Alkalinity evolution is driven by physical and biological mediated processes and boundary conditions fluxes:

$$\frac{\partial ALK}{\partial t} = \frac{\partial ALK}{\partial t}_{bio} + \frac{\partial ALK}{\partial t}_{trsp} + \frac{\partial ALK}{\partial t}_{EmP} \qquad (1)$$

In particular, according to its explicit conservative expression (Wolf-Gladrow et al., 2007), the total alkalinity dynamic is affected by the biological processes that alter the concentrations of NO_3^-, PO_4^{3-} and NH_4^+ (bio term in equation 1). Nitrification, NH_4^+ uptake and the release of both NO_3^- and PO_4^{3-} by the phytoplankton and bacterial groups decrease alkalinity by an equivalent amount of moles. On the other hand the the uptake of NO_3^- and

PO_4^{3-} and the NH_4^+ release by phytoplankton and bacteria and the denitrification increase alkalinity (Wolf-Gladrow et al., 2007). The evaporation minus precipitation flux at the surface affects alkalinity by producing either a concentration or a dilution, (EmP term in equation 1). Alkalinity is then advected and diffused by the tracer transport model, which integrates the exchanges with Atlantic buffer and the input from river discharges (trsp term in equation 1).

In turn, alkalinity – together with DIC and temperature – determines seawater pH, dissolved CO_2 (pCO2) and, eventually, DIC exchange at the air–sea interface (Orr et al., 1999).

2.2 Model setup

The present run covers the 1998–2004 period; the physical and biogeochemical setups are extensively detailed by Béranger et al. (2005) and Lazzari et al. (2012) and are briefly reported here. The atmospheric forcings are from the ERA40 reanalysis (Uppala et al., 2005), and from the ECMWF analysis. Net evaporation (0.7 m/y) and water balance considering fluxes at Gibraltar Strait are consistent with current knowledge (Béranger et al., 2005). The initial conditions of physical variables are based on the MODB4 climatology (Brankart and Brasseur, 1998), and those of the nutrients are based on the Medar-Medatlas datasets (Crise et al., 2003). The nutrient loads (nitrates, phosphates and silicates) are from the terrestrial inputs derived from the paper of Ludwig et al. (2009). The atmospheric inputs of phosphates and nitrates are also included, considering a mean annual value for the eastern and western Mediterranean Sea (Ribera d'Alcalà et al., 2003). A buffer area in the Atlantic Ocean is used to simulate the boundary at the Strait of Gibraltar, as detailed by Béranger et al. (2005) and Lazzari et al. (2012).

Regarding alkalinity and DIC, three mean profiles are computed from data of Meteor51 cruise (Schneider et al., 2007) and used to uniformly initialize the western Mediterranean Sea (alb, nwm, sww, swe and tyr sub-basins in Fig. 1), Ionian-Adriatic Seas (ion, adn and ads in Fig. 1) and Levantine (lev in Fig. 1). The Aegean Sea (aeg) is initialized with a mean profile that is computed from the Sesame-Aegean dataset (Table 1). A Newtonian dumping term regulates the Atlantic buffer zone that is outside the Strait of Gibraltar (atl in Fig. 1), where the alkalinity and DIC concentrations are relaxed to the mean profiles derived from the data published by Huertas et al. (2009) and Dafner et al. (2001).

The terrestrial inputs of alkalinity are computed as the products of freshwater flows, as given by Ludwig et al. (2009), and the terrestrial concentration of alkalinity per water mass, estimated from each of the 10 macro coastal sectors used by Ludwig et al. (2009), based on previously obtained data (Copin-Montégut, 1993). Table 2 reports the mean alkalinity values at the macro coastal areas and the annual loads, including the quota of the most relevant rivers. The Dardanelles inputs are considered in the same way but based on previous information (Somot et al., 2008; Copin-Montégut, 1993). Atmospheric CO2 is

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set according to the trend shown at the Lampedusa station (Artuso et al., 2009).

To smooth artificial effects of discontinuous initial conditions, before starting the actual biogeochemical simulation a spin up period (5 years) was run by using atmospheric forcing typical of the period.

2.3 Reference dataset for comparison

A reference dataset of alkalinity observations (Table 1) has been gathered for model initialization and validation. More than 4200 alkalinity measurements, collected through Pangea, SeaDataNet and Perseus database services, refer to several campaigns and research cruises (Table 1) in the period 1999–2011. This period is consistent with the time window of the simulation and allows to avoid possible problems of inconsistency with older data (Louanchi et al., 2009). Given the inhomogeneity of the spatial-temporal coverage of data, average climatology profiles have been computed for a grid of $1^{\circ} \times 1^{\circ}$ for the year and the four seasons. The $1^{\circ} \times 1^{\circ}$ bins at any given quota are considered empty when less than 4 measurements were present, or when the range of variability of the data was larger than 40 %.

3 Results and discussion

3.1 Spatial variability of alkalinity

The physical and biogeochemical results of the present simulation have been extensively presented and validated by Béranger et al. (2005) and Lazzari et al. (2012), respectively. Here, we focus on the alkalinity time and space variability in the Mediterranean Basin. The results show that the Mediterranean Sea is characterized by alkalinity values that are much higher (100–150 μmol kg^{-1} higher) than those observed in the Atlantic Ocean at the same latitude (Lee et al., 2006). The results indicate a strong surface west-to-east gradient (Fig. 2a), with values ranging from 2400 μmol kg^{-1} near the Strait of Gibraltar to 2700 μmol kg^{-1}, as simulated in the upper ends of the eastern marginal seas (Adriatic and Aegean Seas). These features are in agreement with the recent experimental findings (Schneider et al., 2007, Touratier and Goyet, 2011; Alvarez et al., 2014). The west-to-east gradient is a permanent structure recognizable at all depths, but less marked in the maps of the intermediate and deep layers (Fig. 2). Indeed, the range of variability of alkalinity for the deepest layer spans from 2560 μmol kg^{-1} of the Alboran Sea to 2620 μmol kg^{-1} of the Levantine sub-basin (2650–2670 μmol kg^{-1} in the deeper layers of the Adriatic and Aegean Seas). At the surface, alkalinity dynamics are driven by three major factors: the input in the eastern marginal seas (the terrestrial input from Po and other Italian rivers and the input from the Dardanelles, see Table 2), the effect of evaporation in the eastern basin, and the influx of the low alkaline Atlantic water. The thermohaline basin wide circulation modulates the intensity and the patterns of the spatial gradients. Intermediate and deep layers show lower dynamics and less variability. The Adriatic and Aegean Seas recharge the Levantine intermediate and deep waters as is shown by the calculated fluxes at the boundaries of these sub-basins. On average, the Otranto strait accounts for a northward flux of 8.18 x 10^{12} mol y^{-1} at surface (0-200m) and a southward flux of 8.21 x 10^{12} mol y^{-1} at the intermediate and deep layers. The Aegean sea import 35.9 x 10^{12} mol y^{-1} from the eastern Mediterranean Sea at the 0-200m layer but it export 36.5 x 10^{12} mol y^{-1} to the intermediate and deep layers of Levantine and Ionian sub-basins.

The excess of alkalinity in the intermediate and deep layers of the eastern sub-basins is then spread towards the western sub-basins by the thermoaline cell Mediterranean circulation. At the Sicily channel, the eastward surface flux (0-200) of 48.3 x 10^{12} mol y^{-1} is more than counterbalanced by a westward flux of 56.9 x 10^{12} mol y^{-1} at the intermediate and deep layers, which results consistent with the spreading of the Levantine Intermediate Water described by Alvarez et al. (2014).

The model reconstructions of horizontal gradients at the different depths are quite consistent with the reference values (Fig. 2). High correlation values and low relative root mean square error values (depicted in the Taylor diagram of Fig. 3) quantitatively

confirm the good performance of the model in reproducing the mean annual fields. Higher relative errors (normalized bias and RMSE) are registered at the deepest layers (Fig. 2d and symbol e in Fig. 3), where the effect of input of high alkaline water from the Aegean and Adriatic to the Ionian Sea and Levantine regions appears to be partly underestimated. However, considering the absolute values, the bias and RMSE are quite low: 10.4 μmol kg^{-1} and 14.6 μmol kg^{-1}, respectively. These values are significant

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only because of the low variability in these layer (standard deviation equals to 15.8 µmol kg^{-1}). The bias error is pretty low for all the layers expect for the surface one. The model performance at surface is worsened by an overestimation of values (about 20 µmol kg^{-1}) in the Ionian and western part of Levantine sub-basins.

3.2 Alkalinity vs. salinity regression

It has been recognized that several relationships between alkalinity and salinity are appropriate for different sub-basins of the Mediterranean Sea, given the different sources of alkalinity and water mass dynamics (Schneider et al., 2007; Touratier and Goyet, 2011; Luchetta et al., 2010). The results of the present simulation allow for the basin-wide quantification of these regressions and for the investigation of the rationale of their differences (Fig. 4).

The relationship computed using the model grid points of the pelagic areas (points with depths greater than 200 m) is somehow consistent with the one computed on observations (Table 3), and supports the conclusion that at a basin scale, the effect of evaporation and the end term of Atlantic water are the major drivers for alkalinity spatial dynamics. However, a close analysis reveals that the Mediterranean regression is the average of several regressions: one computed for the eastern sub-basins (ion and lev), a second one computed for the western sub-basins (alb, tyr, sww and swe), and two more for the eastern marginal seas (Adriatic and Aegean Seas). Results, therefore, highlight that the two main sub-basins are affected by different sources of interference. The western regression has a higher correlation and lower dispersion values for residuals and lower regression coefficient values compared with the eastern sub-basin. Therefore, the latter is characterized by the presence of more intense sources of variability. Negative correlations between salinity and alkalinity are observed in the marginal seas, where the changes in salinity no longer can be related to evaporation processes, but they track the input of alkalinity at zero or low salinity from rivers and the Dardanelles. The Adriatic Sea regression shows the highest dispersion in coefficient values and error of residuals

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as a consequence of the higher variability generated by the local and topographic effects. Further, for the nwm sub-basin, the effect of inputs from Rhone and Ebro rivers generates a negative correlation, but this effect remains confined only in the Gulf of Lion. Other local effects can produce deviations from the general relationship, as for example, the coastal areas of the Gulf of Gabes and the far eastern coastal areas of the Levantine sub-basin, where local sources of terrestrial inputs are associated with high rates of evaporation flux and thus produce the orange and red clusters lying above the Mediterranean Sea regression (dashed thick line).

Our regressions update the findings of the Schneider et al. (2007). The steeper slopes and the less negative intercepts of our regressions reflects the fact that our data cover the whole Mediterranean basin from Gibraltar to the end of Levantine sub-basin. Difference between our model and observation regressions is not statistically significant, but the lower slope of the model regression likely reflects the model overestimation of Ionian points (Fig. 2). Given the relative weight of this sub-basin to the total number of gridpoints of the Mediterranean domain, the Ionian model overestimation, indeed, causes the raise of the lower left end of the regression line (Fig. 4). Seasonal variability of the basin wide regression leads to an uncertainty of the slope and intercept estimates of about 6% and 30%, respectively (Table 3). The slope increases during summer and decreases during winter (Table 3) reflecting the differential impact of different factors in the different sub-basins throughout the year.

3.3 Temporal variability of alkalinity

A marked seasonal cycle is simulated in the surface layer (Fig. 5): the range of the mean annual variation of surface alkalinity varies from approximately 10–15 µmol kg^{-1} for the Alboran and the North western regions, to up to 50 umol kg^{-1}, in the Balearic region, in the Aegean Sea, in patches of the southern western region and in the Sicily channel. The extent of seasonal variability is consistent with available observations, as shown by the high values of the skill indexes depicted in the Taylor diagram for the seasonal comparison (symbols in Fig. 3). Vertical profiles (Fig. 6) are generally characterized by large variability at surface, minimum values between the surface and 100 m, a sharp increase until 200–250 m and almost stationary values below 400– 500 m (Fig. 5), but important differences between the eastern and western profiles highlight the presence of different forcings, water mass dynamics and confinements in each area.

The largest fluctuations are observed in the transition areas between different sub-basins, where the

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surface circulation modifies the patterns of the horizontal gradients throughout the year (e.g. Balearic area, edges of the Sicily channel, and northern and eastern Ionian Sea, Fig. 5). On the other hand, mesoscale dynamics and horizontal transport of the low alkaline Atlantic water generates the patches of large annual fluctuations in the southwestern Mediterranean Sea (Fig. 5). These large fluctuations are mainly confined to the first 50 meters of the water column (Fig. 6b, d-f). High annual range of seasonal cycle is simulated for the southern and central Aegean Sea, where the influence of the Dardanelles boundary and of seasonal cycle of surface enrichment and mixing is significant.

In the western Mediterranean Sea two areas are characterized by a low range (15-20 μmol kg^{-1}) of the annual cycle at surface: the Alboran and the northwestern sub-basins. In the first area, the impact of the constant boundary condition at the Atlantic boundary buffer area limits the seasonal oscillation. In the second area, a high vertical ventilation causes an exceeding vertical homogenization of the water column below 20-30m throughout the year (Fig. 6a): the lower limit of the range of the graph at surface (blue line in Fig. 6a) has values of 2580 μmol kg^{-1} which seems as an overestimation with respect to the lower limit of observations at the Dyfamed station reported by Copin Montegut and Begovic (2002).

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In the southwest Mediterranean Sea (Fig. 6c,d), the mixing of Levantine water (below 400 m) and the Atlantic water (upper layer) generates a zone (between 150 and 400 m) that is characterized by large temporal variability. Moving eastward, to points e and f of Fig. 6, the modified Atlantic water generates a minimum at 50–100 m in the summer, when evaporation produces a surface lens of high alkaline concentration (red lines in Fig. 6). During winter the profiles tend to be more homogeneous (blue lines in Fig. 6). Below the modified Atlantic water, the intermediate Levantine water, characterized by alkalinity values of 2610–2620 μmol kg^{-1}, shows low seasonal variability and decreasing values moving westward, as also pointed out by Alvarez et al. (2014). This layer is recharged by the high alkalinity values and dense water that are generated in the Adriatic and Aegean Seas and subsequently deepens in the Levantine and Ionian sub-basins.

In the Levantine and Ionian sub-basins, the seasonal cycle of summer evaporation and winter mixing produces large excursion at surface (up to 40-45 μmol kg^{-1}) and a mean seasonal variability of more than 30 μmol kg^{-1} in the first 50–100 m (Fig. 5 and 6h).

3.4 Impacts of biological and physical processes on alkalinity variability.

According to the synthetic equation (1), Figures 7 and 8 report the mean annual cycle of the monthly rate of variation of alkalinity due to biological and physical (transport plus evaporation minus precipitation) processes for the selected sub-basins. The contribution of evaporation minus precipitation is added to the physical plots in Fig. 8.

The physical contribution exceeds by 5-8 times the biological one, however in the surface layers of the water column, biological processes significantly contribute to the annual variability (Fig. 7) by increasing alkalinity during winter-spring period. The largest impact of biology is in the nwm region whereas eastern sub-basins are less impacted (Fig. 7). The high rate of plankton production causes a large uptake of NO_3^- and PO_4^{3-} (which exceed the NH_4^+ uptake) during the first half of the year, triggering an increase of alkalinity that can be higher than 0.05 μmol m^{-3} d^{-1} in the first 50–100 m of the water column. During summer, the productivity decreases (Lazzari et al., 2012), and in the layer below 100–120 m, the mineralization of NO_3^- (through processes of mineralization of NH_4^+ and subsequent nitrification) and of PO_4^{3-} generally prevails. At these depths, biology contributes negatively to alkalinity throughout the year even if at lower rate (blue area in Fig. 7). The relevance of biological processes in contributing

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to the alkalinity dynamics decreases from the northwestern to the eastern regions, according to the well-known decrease in the Mediterranean trophic gradient (Lazzari et al., 2012). The depth at which the positive impact of biology on alkalinity becomes zero increases eastward from 80–100 m to 120 m of the eastern sub-basins (Fig. 7), according to the deepening of the deep chlorophyll maximum from west to east (deep red spots in summer of plots of Fig. 7). This indicates that biology contributes to the high temporal variability of the surface values in the western sub-basins and that, together with physical processes, it contributes to the increase in alkalinity in the subsurface layer in the eastern sub-basins.

The term of surface evaporation minus precipitation, which is generally positive for the Mediterranean Sea, contributes to increasing the surface alkalinity, with an average rate that ranges from 6 mmol m^{-2} d^{-1} in the western sub-basins to 7 mmol m^{-2} d^{-1} in the eastern sub-basins (Fig. 8 upper panel). During

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summer, the increase of alkalinity due to the concentration process can reach values up to 0.3 mmol m^{-3} d^{-1} in the first 30-50 meters (Fig. 8 lower panel). The autumn and winter vertical mixing drives a homogenization of the water column by decreasing surface values and increasing subsurface values. In the southern Adriatic Sea (ads) and Aegean Sea (aeg), these effects of recharging the deeper layers below 200-300 are particularly visible during the autumn-winter vertical ventilation. The different pattern shown for the sww sub-region and partly to swe sub-region is related to the impact of the lateral transport of low alkaline water from the Atlantic that contrasts the increase due to evaporation at surface.

An alkalinity budget is then compiled in order to quantify sources and sinks: the input from rivers and from Dardanelles amount to 0.9 x 10^{12} mol y^{-1} and 1.15 x 10^{12} mol y^{-1}, respectively. The simulated net flow at Gibraltar is an export of alkalinity equals to 3.1 x 10^{12} mol y^{-1}. Compared to the findings of Schneider et al. (2007) who estimated a net alkalinity outflow at Gibraltar of 0.8 x 10^{12} mol y^{-1}, our estimation is almost 4 times bigger and closer to the estimate of 2.43 x 10^{12} mol y^{-1} given by Copin-Montègut (1993). Biological processes act as a source of alkalinity in the 0-100m layer (+0.52 x 10^{12} mol y^{-1}) and as a sink of alkalinity in the intermediate and deep layers (-0.47 x 10^{12} mol y^{-1}). A basin scale budget of mass of proton acceptor compounds contributing to alkalinity, therefore, sums up to an annual loss of about 1 x 10^{12} mol y^{-1}, equivalent to 0.3 mol m^{2} y^{-1} or - assuming that most processes are confined in the upper 300 meters - of about 1 mmol/m^{3} y^{-1}, i.e. not too far from a steady state.

4 Conclusions

In this paper, we used a calibrated state-of-the-art 3-D transport-biogeochemical-carbonate model to integrate the observations of alkalinity collected over the last decade into a single picture. The study returns a coherent picture of the space–time evolution of this parameter, which is crucial for properly assessing the impacts of ocean acidification.

Different factors (e.g., ingression of low alkaline water from Atlantic Ocean, surface concentration due to evaporation in the eastern sub-basins, and input from rivers and Dardanelles) shape a basin wide west to east gradient coupled with north to south gradients in the marginal seas (Adriatic and Aegean) and in the western sub-basin. As a consequence, the regression between salinity and alkalinity strongly varies from region to region and highlights that it is possible to use a single equation to reconstruct alkalinity values over the whole Mediterranean Sea only if marginal seas and regions of freshwater influence are not considered. The regression equations for each of these regions, treated separately, were also computed. A range up to 40 µmol kg-1 of the seasonal cycle should be considered typical at surface in several parts of the Mediterranean Sea. Different processes trigger the alkalinity variability in different regions: seasonal cycle of summer concentration due to evaporation and winter vertical mixing in the eastern sub-basins, intense biological processes in the northwestern sub-region and horizontal transport in the southwestern sub-regions.

Acknowledgements. This study was supported by the EU projects MEDSEA (grant agreement n. 265103) and OPEC (grant agreement n. 283291).

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Table 1. List of available alkalinity datasets for the Mediterranean Sea.

Name	Area	Period	Reference
Meteor51	Mediterranean Sea	June 2001	Schneider et al., 2007
Meteor84	Mediterranean Sea	April 2011	Tanhua et al., 2012
Prosope	Western Mediterranean and Ionian Sea	1999	Bégovic and Copin, 2013
Boum2008	Mediterranean Sea	June-July 2008	Touratier et al., 2012
Sesame Egeo	Aegean Sea	April, September 2008	http://isramar.ocean.org.il/PERSEUS_Data
Sesame Regina Maris Sesame Garcia del cid	Alboran Sea	April, September 2008	http://isramar.ocean.org.il/PERSEUS_Data
Sesame Adriatic	Adriatic and northern Ionian Sea	April, October 2008	http://isramar.ocean.org.il/PERSEUS_Data
CARBGIB 1-6	Gibraltar Strait, Alboran Sea	2005-2006	Huertas, 2007a
GIFT1-2	Gibraltar Strait, Alboran Sea	2005-2006	Huertas, 2007b
Dyfamed	Gulf of Lions	2001-2005	Copin-Montégut and Bégovic, 2002

Table 2. Alkalinity mean annual discharges for the Mediterranean sub-basins and quota of the discharges due to major rivers (second column). Values of alkalinity concentration in the terrestrial input of the given sub-basins (third column) are derived from Copin-Montégut (1993).

Sub-basins and major rivers	Alkalinity discharges [Gmol y^{-1}]	Alkalinity concentration [mmol m^{-3}]
Alboran (alb)	12	2960
southwest west (sww) and southwest east (swe)	23	2960
northwest Mediterranean (nwm)	251	2960
Ebro	*31*	
Rhone	*163*	
Tyrrhenian Sea (tyr)	104	5675
northern Adriatic Sea (adn) and southern Adriatic Sea (ads)	319	2700
Po	*182*	
Ionian Sea (ion)	36	2200
Aegean Sea (aeg)	1265	2620
Dardanelles	*1150*	
Levantine (lev)	79	2200
Nile	*32*	

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Table 3. Coefficients of the alkalinity vs salinity linear regression of the surface layer (mean 0-50m) computed for the model results (year and seasonal averages) and for observations of dataset listed in Tab. 1. Coefficients of Schneider et al. (2007) regression are also reported.

$Alk = a \cdot Sal + b$	a	b	R2	RMS(resid)	n.data	p
Model, mean layer 0-50m, year	85.4 (± 4.8)	-656.9 (± 183.4)	0.91	18.8	>5000	<0.001
Observations of Table 2 datasets, mean layer 0-50m	88.7 (± 7.5)	-834.5 (± 282.5)	0.90	27.7	198	<0.001
Schneider et al. (2007), observations of Meteor 51/2	73.7 (± 3.0)	-285.7(± 114.9)	0.98	8.2	15	
Model, mean layer 0-50m, winter	83.1 (± 3.8)	-582.8 (± 145.1)	0.94	13.7	>5000	<0.001
Model, mean layer 0-50m, spring	81.7 (± 4.3)	-528.9 (± 163.1)	0.93	16.5	>5000	<0.001
Model, mean layer 0-50m, summer	85.0 (± 5.8)	-648.2 (± 223.2)	0.88	24.1	>5000	<0.001
Model, mean layer 0-50m, autumn	86.4 (± 5.7)	-701.9 (± 219.5)	0.89	22.5	>5000	<0.001

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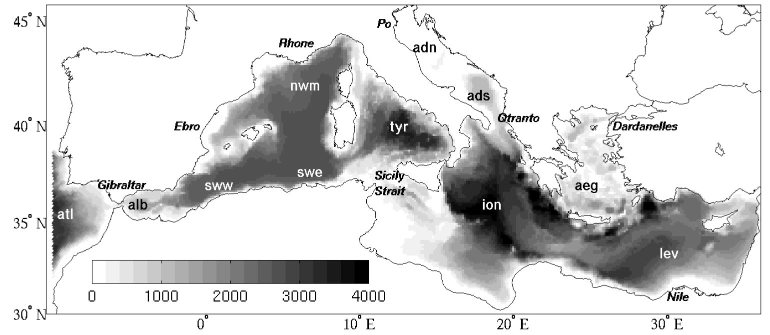

Figure 1. Map of the Mediterranean Sea domain reporting the sub-basins indication (atl, Atlantic buffer zone; alb, Alboran; nwm, northwest Med; sww, southwest west; swe, southwest east; tyr, Tyrrhenian Sea; ion, Ionian Sea; adn, northern Adriatic Sea; ads, southern Adriatic Sea; aeg, Aegean Sea; lev, Levantine), the location of principal rivers and straits.

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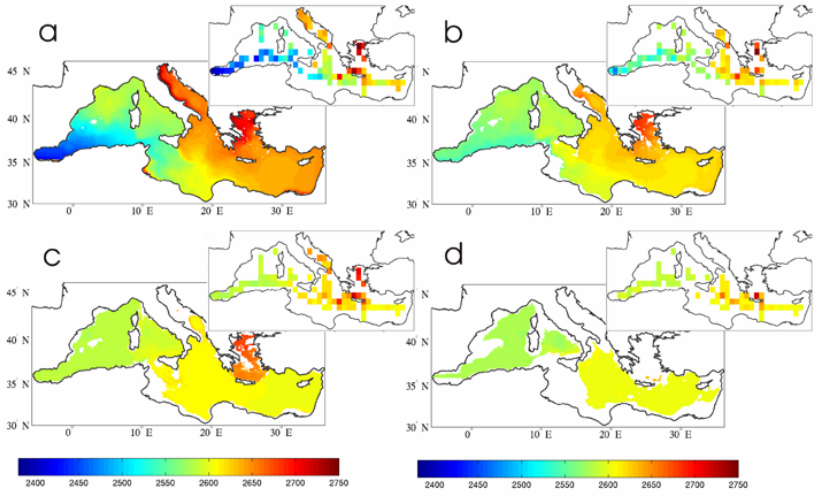

Figure 2. Alkalinity maps for selected layers: surface (a), 100–200 m (b) 400–1500 m (c) 1500–4000 (d). Model maps refer to the average of the simulation. Maps of 1o x 1o annual climatology are reported in the upper right corner of each selected layer.

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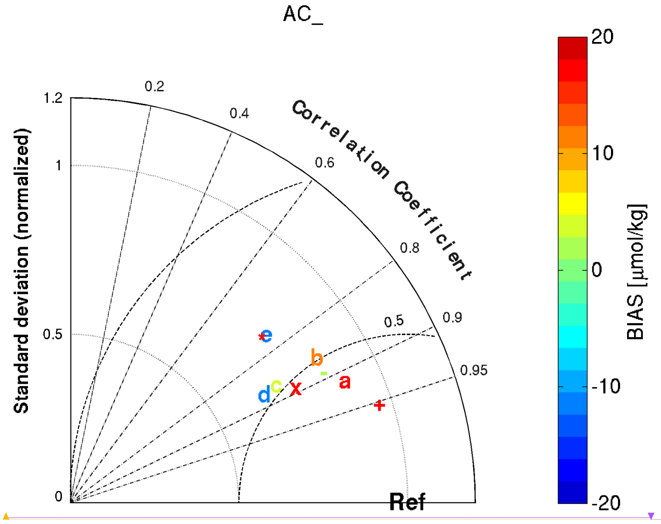

Figure 3. Taylor diagram of alkalinity of the mean annual model and observation fields for the following layers: surface (a), 50–100 m (b), 100–200 m (c), 200–1500 m (d), and 1500–4000 m (e) and for the following seasons at the surface layer: winter (+), spring (-) summer (x), autumn (*). The color of symbols and the bar report the bias (mean model-observation error).

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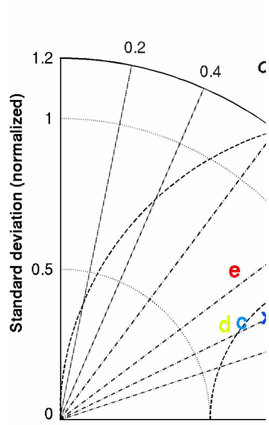

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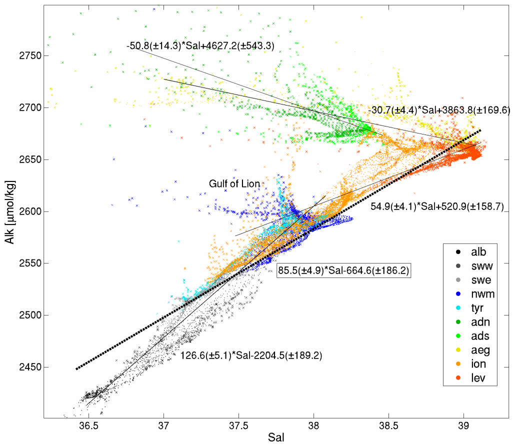

Figure 4. Regressions between salinity and alkalinity at the surface. Colored points belong to the different sub-basins of Fig. 1. Regression for the Mediterranean Sea is shown by a dashed line, and the equation is reported in the black box (95 % confidence intervals of the coefficients are in brackets; $p< 0.001$; $R2 = 0.91$; RMSD = 18.8). The regression uses data from the alb, sww, swe, tyr, ion, lev sub-basins with depths greater than 200 m. Sub-basin regressions are computed for the Adriatic sea (all data; $R2 = 0.45$, RMSD = 32.0), the Aegean Sea (all data; $R2 = 0.77$, RMSD = 9.3), the western Mediterranean Sea (data with depths greater than 200 m; $R2 = 0.95$, RMSD = 11.6) and the eastern Mediterranean Sea (data with depths greater than 200 m; $R2 = 0.74$, RMSD = 13.8).

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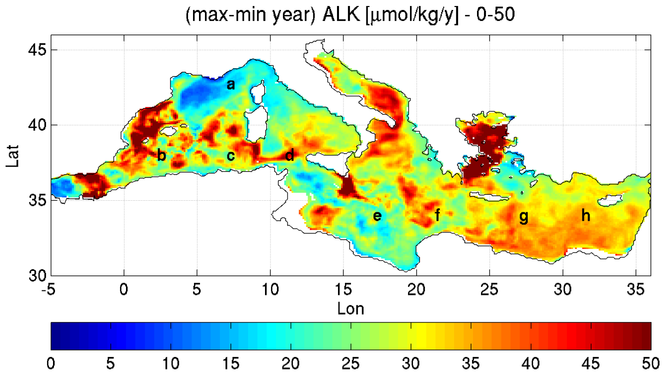

Fig. 5. Map of the mean annual range of alkalinity for the surface layer (0-50m). Letters indicate the coordinates of the profiles given in Fig. 6.

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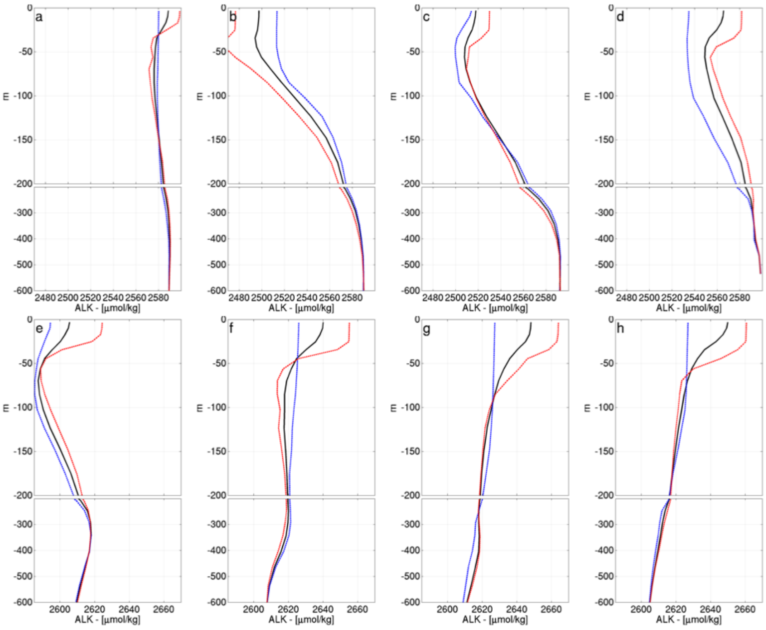

Figure 6. Mean annual vertical profiles of alkalinity (black line) in selected points of the Mediterranean Sea (points in Fig. 5). Mean annual range of variability between winter (blue dashed line) and summer (red dashed line) profiles.

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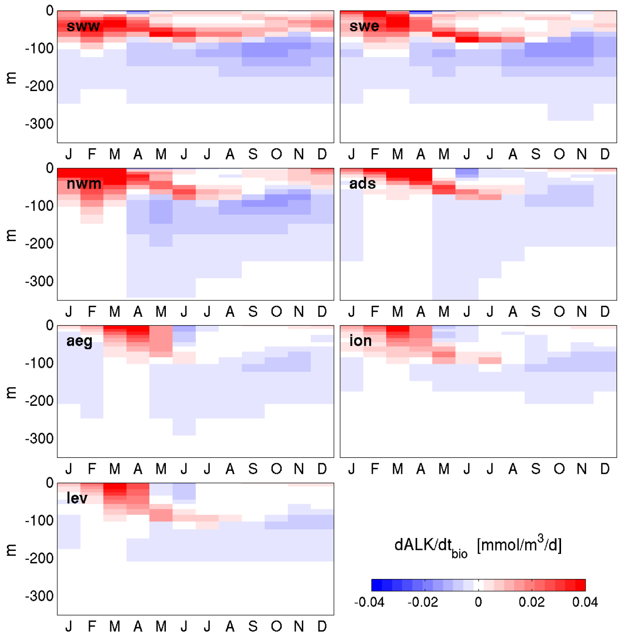

Figure 7. Annual evolution of the mean sub-basin average vertical profiles of the biological term of $\frac{\partial ALK}{\partial t}$ equation. Monthly values are averaged considering only areas deeper than 200m.

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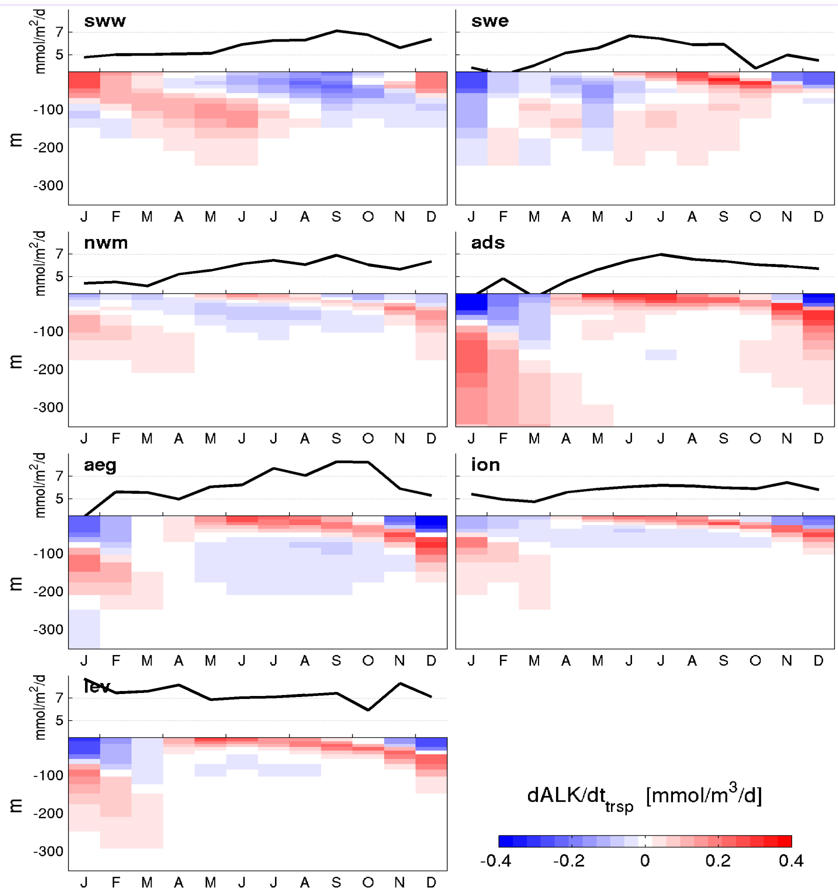

Figure 8. Annual evolution of the mean sub-basin average vertical profiles of the transport term of $\frac{\partial ALK}{\partial t}$ equation (lower panels), and evolution of evaporation minus precipitation term (upper panels). Monthly values are averaged considering only areas deeper than 200m.

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