Biogeosciences Discuss., 9, C6764–C6797, 2012 www.biogeosciences-discuss.net/9/C6764/2012/ © Author(s) 2012. This work is distributed under the Creative Commons Attribute 3.0 License.



## *Interactive comment on* "CO<sub>2</sub> exchange in a temperate marginal sea of the Mediterranean Sea:

# processes and carbon budget" by G. Cossarini et al.

G. Cossarini et al.

gcossarini@ogs.trieste.it

Received and published: 22 December 2012

In this section we reply to all the remarks raised by reviewer#2 (reported in capital letters). A general reply has been added to the main page of the interactive discussion, along with a supplementary file containing the new Appendixes A and B and the new section 3.2.

REVIEWER #2

##GENERAL COMMENTS MANUSCRIPT "CO2 EXCHANGE IN A TEMPERATE

C6764

MARGINAL SEA OF THE MEDITERRANEAN SEA: PROCESSES AND CAR-BON BUDGET" BY COSSARINI ET AL. PRESENTS A STUDY ON CO2 AIR-SEA EXCHANGE AND CARBON BUDGET IN THE ADRIATIC SEA DURING TWO YEARS, 2007 AND 2008, USING A 3D CARBONATE-BIOGEOCHEMICAL-PHYSICAL MODEL. THE AUTHORS CONCLUDE THAT THE ADRIATIC SEA ACTED AS A SINK OF CO2 FOR THE ATMOSPHERE DURING THE 2 STUDIED YEARS CHARAC-TERISED BY DIFFERENT WINTER AND SUMMER CONDITIONS. ACCORDING TO THE AUTHORS, THE FORMATION OF DENSE WATER IN THE NORTHERN REGION IN WINTER AND ITS SOUTHWARD FLOW ARE THE DOMINANT PRO-CESSES EXPLAINING THE UPTAKE OF ATMOSPHERIC CO2 BY THE BASIN. THE MODEL RESULTS PRESENTED HERE COULD BE A GREAT CONTRIBUTION TO OUR UNDERSTANDING ON THE COASTAL REGION IN CO2 EXCHANGE AND CARBON CYCLE, ESPECIALLY GIVEN THE FEW MODELLING EFFORTS UNDER-TAKEN SO FAR IN AIR-SEA CO2 EXCHANGE. HOWEVER, I WILL NOT REC-OMMEND THIS MANUSCRIPT FOR PUBLICATION UNTIL MAJOR AND MINOR POINTS OF CONCERN ARE ADDRESSED IN A REVISION. A MAJOR ISSUE OF CRITIQUES CONCERNS THE VALIDATION OF THE COUPLED MODEL. THE COM-PARISON OF MODEL RESULTS WITH DATA IS NOT SUFFICIENTLY EXTENDED TO ALLOW A CONFIDENCE IN MODELLING RESULTS FOR THE COMPUTATION OF AIR-SEA CO2 EXCHANGE AND CARBON BUDGET. THE REVIEWERS HAVE YET NO ACCESS TO THE RESULTS OF THE PHYSICAL MODELLING OF 2007 AND 2008 (DESCRIBED IN QUERIN ET AL., 2012) AND THEIR VALIDATION WITH OBSERVATIONS (FORMATION AND SPREADING OF DENSE WATER, TEMPERA-TURE, WATER COLUMN STRUCTURE). THE VARIABLES AND FLUXES OF THE BIOGEOCHEMICAL AND CARBONATE MODELS ARE COMPARED WITH OBSER-VATIONS ON DIFFERENT PERIODS. A COMPARISON WITH 2007 AND 2008 OB-SERVATIONS WHEN AVAILABLE (SURFACE CHL, SEA SURFACE CO2 IN THE GULF OF TRIESTE) WOULD BE USEFUL TO VALIDATE THE MODEL. ADDITIONAL COMPARISONS WITH DATA, IF AVAILABLE, RELEVANT FOR THE AIR-SEA CO2

# EXCHANGES (RESPIRATION RATES OR NET COMMUNITY PRODUCTION, DIC PROFILES) WOULD ALSO BE USEFUL TO MAKE THE MODEL ESTIMATES MORE ROBUST.

As stated at the beginning of this reply (general comments), the new Appendix B reports the validation of the model simulation. In particular, the MODIS chlorophyll satellite data (Volpe et al., 2012) have been used to assess the ability of the model to simulate the temporal trend and the horizontal surface gradients of the primary producers. Three climatological datasets (Zavatarelli et al., 1998, Solidoro et al., 2008, Cossarini et al., 2012) has been used to validate the seasonal dynamics, the vertical differences and the main spatial differences among the north-to-south and the west-toeast gradients of DIP and chlorophyll-a. Literature data have been used to assess the consistency of the model to simulate relevant ecosystem processes (e.g. primary and bacterial production, sinking rate) and other model variables (DOP, pCO2, alkalinity and DIC). The nighttime radiometer (AVHRR) data from satellite NOAA-18 processed by the OGS-SIRE (SIstemi REmoti) group have been used for the comparison with simulated sea surface temperature. The comparison is presented in the section 3.2 of the paper by Querin et al. In particular, it is shown that the model simulates the remote sensed wintertime SST fields over the entire basin fairly well, reproducing the main spatial features (the recirculation structure in the NA induced by a Bora event; the instabilities along the frontal structure of the Western Adriatic Current - WAC).

BELOW IS A LIST OF SOME GENERAL POINTS, ON WHICH I WILL COME BACK IN FOLLOWING SPECIFIC AND TECHNICAL COMMENT SECTIONS: - THE DESCRIP-TION OF THE COUPLED MODEL SHOULD BE MORE DETAILED.

A more detailed description of the coupled model and the list of the biogeochemical model parameterizations have been added in the new Appendix A. Further, additional details will be added to section 2.2 and 2.3 to account for the other reviewers' comments.

C6766

- ESTIMATES OF FLUXES AT THE OTRANTO STRAIT ARE QUESTIONABLE CON-SIDERING THE PROXIMITY OF THE STRAIT TO THE BOUNDARY AND THE FORC-ING METHOD AT THIS BOUNDARY.

Our estimation of carbon fluxes at the Otranto Strait are indeed boundary conditions, and not results of the model simulation. Besides, as described in the point referred to the boundary conditions (see one of the next point), our boundary conditions are computed by a validated physical-biogeochemical model (Lazzari et al., 2012) and therefore we assume they are consistent. In the new version of section 4.4 we indicate clearly that the values of fluxes at the Otranto Strait are not a direct result of the simulation, but they are boundary conditions. However, we believe that the estimates of POC and DIC fluxes are an interesting information to be reported in order to understand and compare the magnitude of the terms that constitute the carbon budget in the Adriatic Sea.

- THE USE OF TWO DIFFERENT ATMOSPHERIC MODELS FOR WIND AND HEAT AND WATER FLUXES FORCING REDUCES THE RELIABILITY OF THE ESTIMATES OF AIR-SEA CO2 EXCHANGES.

As specified in the reply to reviewer #1, in the present configuration of the MITgcm model, the wind acts adiabatically on ocean currents whereas total heat fluxes are provided by the Mediterranean Forecast System (MFS) model. MFS total heat fluxes can be considered a good approximation for surface fluxes (Oddo and Guarnieri, 2011) because of the relatively low spatial variability of air temperature, irradiance and humidity compared to wind direction and speed. Given the aim of this study (reproducing the formation and spreading of dense water), the wind stress obtained from the MFS model ( $1/16^{\circ}$  and daily) would not be sufficiently spatially and temporally fine, therefore ALADIN ( $0.03^{\circ} \times 0.02^{\circ}$ , three hour frequency) guarantees the necessary accuracy in describing the wind field. Some peculiar wind driven circulation features (e.g. double gyre circulation induced by Bora wind in Northern Adriatic sub-basin) require relatively high-resolution wind forcing to be properly reproduced (Querin et al., 2012). There-

fore, we believe that the atmospheric forcings are not inconsistent when simulating the physical processes at the surface (heat exchanges, wind stress and piston velocity).

- THE COMPARISON OF ATMOSPHERIC CONDITIONS 2007 AND 2008 WITH CLI-MATOLOGY SEEMS QUESTIONABLE. THIS HAS IMPLICATIONS ON THE DISCUS-SION AND CONCLUSION OF THE STUDY.

One of the main goals of the present modelling experiment is to test how different winter conditions influence the efficiency of the carbon pump in the Adriatic Sea. Two case studies have been analysed (winter 2006/2007 and winter 2007/2008, i.e.: a "mild" and a "normal" winter condition, respectively) in order to show how the occurrence of mild winter conditions over the Adriatic Sea can lead to lower dense water production rates, and to lower efficiency of the carbon continental pump. We use an 11 years climatology (2000-2010) as a reference term in order to better highlight the differences between the two simulated cases. The total heat flux (spatially averaged over the northern Adriatic Sea surface) in the period from November to February was -114 and -131 W/m2 in AW06/07 and AW07/08, respectively. The anomalies with respect to the climatology 2000-2010 are +32 and +15 W/m2. The following plot (Fig. R2\_F1), that reports the cumulative anomalies of total heat flux for the two periods, clearly shows the higher positive anomaly of the winter 06/07 compared to the anomaly of the winter 07/08.

Here Fig. R2\_F1

Fig. R2\_F1. Trend of the cumulative anomalies of the total heat flux over the northern Adriatic Sea for the two years. The anomalies are computed with respect to the climatology 2000-2010.

In the plot, we consider the period starting from November since the autumn cooling represents the phase of pre-conditioning for the formation of the dense waters. See Querin et al. (2012) for additional details on the phases of the dense water formation and spreading. Other authors (Oddo and Guarnieri, 2011; Cardin et al, 2012) have already reported the relatively mild winter conditions of 2007 and the relatively cold

C6768

winter conditions of 2008 and their influence in the water characteristics and dynamics in the Adriatic sea. The section 3.1 will be changed in order to - indicate more clearly the period over which the mean anomaly is computed; - better specify that winter 2007 was milder with respect to 2008, that climatology serves as a reference term, and that the 2008 was characterized by almost normal winter conditions; - explain that the mild winter 2007 causes a reduced formation of dense water, whereas during winter 2008 the formation of dense water occurs as it is usually expected for the Adriatic Sea.

- THE AUTHORS SHOULD DISCUSS THE DIFFERENT SOURCES OF UNCER-TAINTY IN THEIR ESTIMATES BASED ON MODELLING.

Our results show that the evolution of surface pCO2 (and CO2 exchanges) simulated by our model is sensitive to the spatial and temporal variability of the surface temperature, and that the interannual difference in winter surface heat fluxes causes a difference in the dense water transport from the northern shelf to the interior of the Adriatic Sea (the southern Adriatic pit). Clearly, the estimates of absolute values of the CO2 solubility and the equilibrium of carbonate system are affected by uncertainties, which fall back on the computation of the CO2 air-sea exchanges. In fact, these results are affected by uncertainty in model estimates of temperature, DIC, alkalinity (Zeebe and Wolf-Gladrow, 2003) as well as by uncertainty in model boundary conditions (e.g.: atmospheric pCO2 values). Still, insofar model errors are systematic, it is reasonable to assume that the projections of the differences between 2 simulated years does provide some indication of potential changes. Anyway, we tried to constrain our simulations to the few available experimental observations. Among them, we considered the data of alkalinity and DIC gathered during 2008, even if it was not possible to incorporate them in the manuscript, since we were able to see them as as personal communication only. but these data were not made available for our study Based on these data, the new simulation was obtained by performing a spin up run and by adjusting ICs and BCs, since we noticed the partial inadequacy of the Scheinder et al. (2007) relationship to estimate alkalinity from salinity in the Adriatic Sea, and, consequently, the DIC from

alkalinity. Difference between the previous and the present simulations are of the order of 1% and 1-2% for alkalinity and DIC, respectively. Therefore, at the present stage, the largest uncertainty in estimating CO2 exchange fluxes occurs in the prediction of reliable values of DIC and alkalinity for the whole basin. As an example a change of 1% in the alkalinity (~25 mmol/m3) caused a change of almost 10% in the annual mean values of pCO2. However, it is worth to stress that this factor affected in the same way the two simulated years, whereas the relative difference of the efficiency of the carbon pump between the two years is primarily due to the difference in the heat flux conditions between the years. The largest impact in the computation of DIC and alkalinity is played by the initial conditions and the boundary conditions at the Otranto Strait. Also, the input from the rivers is characterized by large uncertainties, however their impact is more local. As reported previously, the lack of an accurate representation of benthic processes can also be a source of error, because it leads to underestimate a source of CO2 in the water column. However, since the very scarce quantitative information on these parameters and fluxes for the Adriatic Sea, we can only speculate on their importance. These concepts will be included in the discussion section.

- THE MANUSCRIPT GENERALLY SUFFERS FROM POOR READABILITY: SOME SENTENCES ARE AWKWARD; IT SEEMS THAT SOME FIGURES AND TABLE ARE POORLY REFERRED.

The manuscript and figure references have been checked and corrected.

#### ##SPECIFIC COMMENTS

#SECTION 2 - MOVE THE SITE DESCRIPTION FROM SECTION 2 TO THE INTRO-DUCTION SECTION WHERE THE ADRIATIC SEA IS PARTLY DESCRIBED.

We agree to move the site description in the introduction section.

- A DESCRIPTION OF THE COUPLED MODEL IN AN APPENDIX SECTION WOULD CONSIDERABLY HELP THE READING AND UNDERSTANDING OF THE

C6770

### MANUSCRIPT.

The new appendix A contains a more detailed description of the coupled model. Equations and parameterizations of the biogeochemical model have been also added.

- COULD YOU GIVE THE VALUE OF THE FRACTION OF SINKING MATERIAL REACHING THE BOTTOM THAT IS REMINERALISED IN THE SEDIMENT? ARE BOTH INORGANIC NUTRIENTS AND DIC RELEASED IN THE WATER COLUMN?

Yes, both phosphorus inorganic nutrient and DIC are released in the water column and from the sunk organic matter accumulated at the bottom layer. The formulation of the respiration processes for DIC and of the mineralization for DIP in the model formulation is reported in the appendix A. However, the model does not explicitly account for a sediment layer (which entraps the organic material that reaches the bottom), and the organic matter that reaches the bottom is subjected to remineralization, lateral transport and resuspension. As we have already answered to reviewer#1, we agree that sediment processes can affect the carbon cycle in shallow areas and the model parameterization (a first order kinetic of sinking organic matter) is very rough and possibly inadequate. Unfortunately, state of the art is not very advanced on that, and the examples of fully coupled pelagic-benthic modules are very few (e.g. Vichi et al., 2003 [1D model], Brigolin et al., 2011 [limited coastal area model]). Even fewer are the validated benthic pelagic models. And basically no example exists of application of validate pelagic-benthic models to large 3D basins. On the other hand, the experimental information on the spatial distribution of a number of benthic parameters required to a proper initialization of a basin scale 3D model is presently not available for Adriatic Sea as well. Because of this, the choice of a first-order approximate parameterization might be (as in many other studies) unavoidable.

- WAS THE CALIBRATION OF THE BIOGEOCHEMICAL MODEL DONE USING OB-SERVATIONS IN THE ADRIATIC SEA?

The original model by Cossarini and Solidoro (2008) has been developed using data

collected in the northern Adriatic Sea. The present version of the model, which is an upgrade of the original model, has been empirically calibrated using data of the Adriatic Sea (see appendix A for addition details on the model formulation). Observations used in the present work are presented in Appendix B.

- THE AUTHORS ESTIMATE THE FLUX OF DIC AT THE OTRANTO STRAIT IN SEC-TION 4.4. HOWEVER THE FORCING AT THIS DOMAIN LIMIT APPEARS QUES-TIONABLE CONSIDERING THE USE OF TWO DIFFERENT HYDRODYNAMIC MOD-ELS. THE USE OF 1/16\_INGV MODEL FOR THE PHYSICAL SIMULATION ON ONE SIDE AND THE USE OF OPATM FOR THE PHYSICAL/BIOGEOCHEMICAL SIMULA-TION ON THE OTHER SIDE COULD BE A SOURCE OF INCONSISTENCY IN THE FLUXES AT THE BOUNDARY.

There are not two Mediterranean models for the physical fields. The two listed models constitute the Mediterranean Forecasting System (MFS) within the MyOcean infrastructure. The INGV model generates the physical 3D fields (U, V, W, S, T, viscosity and diffusivity), that are subsequently used by the OPATM-BFM model to simulate the transport and the reaction of the biogeochemical variables. The INGV model is a NEMO-OPA version 3.2 (Madec et al., 2008), which has been implemented in the Mediterranean at 1/16 deg. horizontal resolution and 72 unevenly spaced vertical levels (Tonani et al., 2008, Oddo et al., 2009). The OPATM-BFM is a coupled transportbiogeochemical model. The transport of tracers is resolved by the OPATM model (a modified version of the OPA 8.1 transport model) which uses the physical 3D fields (daily data) provided by the INGV model in off-line mode. The domain is based on a 1/8° horizontal resolution grid and 72 unevenly spaced vertical levels, which matches with the grid of the physical model. The off-line coupling, which is part of the MFS of the MyOcean infrastructure, is explained in Lazzari et al., 2010. This paper provides also the validation of the coupled model for the Mediterranean Sea. Section 2.3 will be changed to provide a better explanation of the sources of the boundary conditions (for physical and biogeochemical variables) at the Otranto Strait. The new text will be

C6772

changed as follows:

Initial conditions (ICs) and boundary conditions (BCs) at the Otranto strait for physical and biogeochemical variables are provided by the MyOcean Mediterranean Forecasting System (MFS). The MyOcean-MFS consists of the physical NEMO-OPA model (Tonani et al., 2008) and the transport-biogeochemical OPATM-BFM model (Lazzari et al., 2009). Velocity, salinity and temperature fields are provided on a 1/16° horizontal resolution, with 72 unevenly spaced vertical levels and daily temporal resolution, whereas biological and chemical fields are provided at 1/8° horizontal resolution. The fields are linearly interpolated on the Adriatic model domain (ICs) and on the Otranto Strait (BCs).

- THE USE OF TWO DIFFERENT ATMOSPHERIC MODELS (ALADIN FOR WIND DATA AND MFS FOR HEAT FLUXES AND WATER FLUXES) COULD GENERATE INCONSISTENCY IN AIR-SEA CO2 EXCHANGES.

As already specified in this reply, the wind acts adiabatically on ocean currents whereas total heat fluxes provided by the MFS model can be considered a good approximation for surface fluxes [Oddo and Guarnieri, 2011] because of the relatively low spatial variability of air temperature, irradiance and humidity compared with wind direction and speed. Given the aim of this study (reproducing the formation and spreading of dense water), the wind stress obtained from the MFS model ( $1/16^{\circ}$  and daily) would not be sufficiently spatially and temporally fine, therefore ALADIN ( $0.03^{\circ} \times 0.02^{\circ}$ , three hour frequency) guarantees the necessary accuracy in describing the wind field. Some peculiar wind driven circulation features (e.g. double gyre circulation induced by Bora wind in Northern Adriatic sub-basin) require high resolution wind forcing to be properly reproduced (Querin et al., 2012). Therefore, we believe that the atmospheric forcings are not inconsistent in simulating the physical processes at the surface (heat exchanges, wind stress and piston velocity bulk formula). Text of section 2.3 will be changed as following:

Regarding the surface atmospheric forcing, daily total heat and evaporation-minus precipitation fluxes are provided by the Mediterranean Forecast System (MFS) model, which can be considered a good approximation for surface fluxes (Oddo and Guarnieri, 2011) because of the relatively low spatial variability of air temperature, irradiance and humidity. Wind data - that in the present configuration of the MITgcm model acts adiabatically on ocean currents - are provided by the high resolution atmospheric models ETA006 and ALADIN. The proper simulation of some peculiar wind driven circulation features of Adriatic Sea requires wind fields of spatial and time resolution higher than those provided by MFS. Additional details on the atmospheric forcing are given in Querin et al. (2012).

- THE AUTHORS SHOULD SPECIFY THAT NO ATMOSPHERIC INPUT (EXCEPT FOR CO2) IS PRESCRIBED AND HOW THIS COULD CHANGE THE RESULTS OF THE STUDY.

No direct atmospheric inputs are considered in the model. To our knowledge, no information on alkalinity deposition is available for the Adriatic Sea. The atmospheric deposition of nutrients can have a perceptible impact in sustaining the productivity in very oligotrophic areas (like the Eastern Mediterranean Sea, Lazzari et al., 2012) and, therefore, in modifying the carbonate system variables. However, for the present simulation, we consider that the nutrient depositions have negligible effects in the Adriatic Sea dynamics when compared to the effects due to the river discharges. Finally, the model takes into account the variation of concentration due to the effect of evaporation and precipitation, which impact on the sea surface height. In particular, evaporation leads to an increase of concentration within the surface layer, whereas precipitation, which is assumed to have a concentration equal to zero, implies dilution. In this way, the total mass of the system (water and tracers) is conserved.

- COULD DENITRIFICATION PROCESS, NOT TAKEN INTO ACCOUNT IN THIS STUDY, MODIFY THE ORGANIC CARBON REMINERALISATION AND AIR-SEA CO2 EXCHANGE?

C6774

To our knowledge, denitrification process can alter the budget of alkalinity, increasing of 1 mole of alkalinity per mole of nitrate converted to N2. In turn, alkalinity affects the solution of the carbonate equilibrium and the CO2 exchange. The effect of denitrification is balanced by N2 fixation and remineralization, even if these processes can occur in different areas and periods (Wolf-Gladrow et al., 2007). The model does not consider the nitrogen cycles, but the rate of change of alkalinity includes the contribution of nitrogen changes by using a coefficient based on the Redfield ratio (see parameterization in Appendix A). Further, denitrification affects directly the budget of DIC by producing 5 mole of CO2 per 4 mole of NO3- consumed (Wolf-Gladrow et al., 2007). The model simulates only aerobic bacterial respiration (see Appendix A). Anaerobic respirations are not considered, however they occur when oxygen is depleted, which is a condition quite rare in the water column of the Adriatic Sea for the recent years.

#SECTION 3.1 - COULD THE AUTHORS EXPLAIN HOW THEY OBTAIN THE LAST DECADAL CLIMATOLOGY?

The total heat flux climatology has been computed by averaging the MFS data for the period 2000-2010. Data consist of a reanalysis of the physical dynamics of the Mediterranean Sea (Tonani et al., 2008). A better explanation will be added to section 3.1.

- THE AUTHORS DESCRIBED WINTER 2008 AS SIMILAR TO A "MEAN WINTER". I DON'T SEE THIS SIMILARITY: ACCORDING TO FIGURE 3, 2008 IS WARMER THAN THE CLIMATOLOGY BETWEEN MID- DECEMBER AND MARCH. THE NET POSITIVE HEAT FLUX ANOMALY IN WINTER 2008 WITH RESPECT TO THE CLI-MATOLOGY APPEARS EVEN MORE IMPORTANT THAN THE ONE OBTAINED IN SUMMER 2008 AND MENTIONED BY THE AUTHORS L7-9 P10339.

See also the point on this issue in the general comments. The climatology is used only as reference term to highlight the fact that 2007 has a larger deviation from the mean condition (climatology) than 2008. Winter 2008 is more similar to the mean

winter conditions. The difference in the total heat flux in 2008 is of +15W/m2 (for the period November 2007- February 2008), whereas the positive mean anomaly of 2007 is + 32W/m2 (for the same period). We agree with the suggestion of the reviewer and we will not refer winter 2008 as "normal condition", but rather as "more similar to the normal condition than 2007".

- THE AUTHORS SHOULD DESCRIBE THE RESULTS OF COMPARISON BETWEEN MODEL OUTPUTS AND OBSERVATIONS REGARDING THE FORMATION AND SPREADING OF DENSE WATER. MEANWHILE THE MANUSCRIPT BY QUERIN ET AL (2012) IS PUBLISHED, COULD THEY SEND THE LAST VERSION OR RELEVANT EXTRACTS TO THE REVIEWERS?

Querin et al., 2012 paper has been attached to this reply.

- THE AUTHORS DESCRIBE WEATHER CONDITIONS AND PHYSICAL DYNAMICS ONLY FOR THE NORTHERN ADRIATIC WHILE THEY STUDY, IN THE FOLLOW-ING SECTIONS, BIOGEOCHEMICAL AND CARBON EXCHANGE IN THE WHOLE BASIN. VARIABILITY IN WINTER HEAT FLUXES AND OPEN OCEAN CONVECTION INTENSITY THAT WOULD OCCUR IN THE SOUTHERN ADRIATIC SEA BETWEEN 2007 AND 2008, COULD INDUCE DIFFERENCES IN BIOGEOCHEMICAL PRODUC-TIVITY DURING WINTER AND SPRING IN THIS REGION. BESIDES, THE DIFFER-ENCE IN SUMMER HEAT FLUXES BETWEEN 2007 AND 2008 FOR CA AND SA IS ALSO DISCUSSED IN SECTION 4.4.

Physical conditions for central and southern sub-basin have been discussed in Querin et al. 2012 (find the paper in attachment to this reply). In particular, the simulation results (see Fig. 8 in Querin et al.) show that in the central Adriatic Sea (plot b), the mixed layer depth can reach the bottom only during cold years (2008). Moreover, Fig. 4, 6 and 8 in Querin et al. show how the deep convection affects the southern Adriatic Sea in February 2008 (but not in winter 2007). The convection occurs after a preconditioning phase that lasts for a couple of months. The previous year did not

C6776

show the formation of the deep vertical mixing chimneys typical of the open ocean convection. In winter 2008, the more intense open ocean convection generates a larger vertical flux of nutrients, and a stronger cooling of the surface layer. This phenomena can be noticed in Fig. 5 of section 3.2 of the present paper, which shows the evolution of DIP and CHLA in one point of the central part of the southern Adriatic sea. The section 3.1 will be enriched by these remarks.

- A COMPARISON WITH OBSERVED TEMPERATURE AT DIFFERENT POINTS OF THE MODELLING DOMAIN WOULD BE RELEVANT TO VALIDATE THE MODELLED SOLUBILITY OF CO2.

A comparison of sea surface temperature is presented in the paper by Querin et al., that the editor and the reviewers can find in attachment. In particular, Fig. 7 (in Querin et al.) shows the remarkable difference in temperature between the two winter periods, especially on the northern shelf, where the average surface temperature in mid-February 2007 is approximately 11.5°C but in mid-February 2008 is approximately 10°C. In February and March, the SST difference between the two years varies from 1.5-2°C in the northern region to 0.5°C in the southern region. In brief, the SST differences decrease to zero moving from the northern shelf down to the Otranto Strait.

#SECTION 3.2 - A COMPARISON OF MODEL RESULTS WITH SATELLITE MAPS FOR 2007 AND 2008 YEARS AT DIFFERENT SEASONS, INSTEAD OF THE COM-PARISON WITH THOSE PRESENTED BY BARALE ET AL. 2005, WOULD GIVE MORE CONFIDENCE IN MODELLING RESULTS.

Modelled surface chlorophyll-a has been compared with MODIS satellite data; the comparison is reported in the new appendix B. The section 3.2 has been changed; the new version is focused on the description of the ecosystem dynamics simulated by the model, and the reference to Barale e al. 2005 has been deleted.

- THE CO2 EXCHANGE DUE TO BIOLOGICAL PROCESSES DEPENDS NOT ONLY ON PRIMARY PRODUCTION RATE BUT ALSO ON RESPIRATION RATES AND ON THE STRUCTURE OF THE WATER COLUMN (STRATIFIED OR WELL MIXED). HOWEVER, NO COMPARISON WITH DATA ON THE STRATIFICATION OF THE WA-TER COLUMN AND ON THE RESPIRATION RATES IS PRESENTED.

The physical dynamics are discussed in the paper by Querin et al., which shows that the mixed layer depth (MLD) greatly varies in the three sub-basins during the 2 years (Fig. 8 in Querin et al.). In the present paper we show how the northern dense water formation and spreading contribute to the downwelling of the organic carbon into the interior of the deep southern Adriatic pit. In order to account for the vertical structure of the water column, we computed the vertical fluxes of carbon component at two depths (90 and 180 meters). The second one was chosen because the mixing processes seldom reach deeper layers (Fig. 8 in Querin et al.). Further, other details on ecosystem dynamics have been added to the manuscript. Remineralization and respiration of the organic matter occur during the sinking and downwelling transport contributing to the accumulation of DIC in the water column. The new section 3.2 (attached to the general comment section of this interactive discussion) reports the maps of primary production and total respiration. The section shows that in the western part of NA the primary production is higher than the respiration (making this part of the Adriatic sea a prominent zone for the biological carbon pump), whereas in southern Adriatic pit the respiration prevails during summer stratification.

#SECTION 3.3 - A COMPARISON OF MODEL RESULTS WITH OBSERVATIONS OF PCO2 AND CO2 EXCHANGE AT THE VIDA POINT (TURK ET AL, 2012) WOULD CONTRIBUTE TO A VALIDATION OF THE CARBONATE MODEL RESULTS.

Appendix B contains a plot with the time series of pCO2 at a point representative of the Gulf of Trieste. The observed values shown in Figure 2 of Turk et al., 2010 are quite well reproduced by the model. Besides, the model reproduces the observed differences between the two years (lower values of April-May 2008 and higher values in autumn 2008 with respect to the previous year), that are due to the discussed differences of the specific weather conditions of the two years.

C6778

- DOES PCO2 DECREASE TO 200-250 PPM IN WINTER IN THE WHOLE ADRI-ATIC SEA? THE PCO2 IN WINTER IN THE SA PRESENTED IN D'ORTENZIO ET AL. (2008) IS AROUND 350 PPM. COULD YOU COMPARE SIMULATED SA PCO2 WITH RESULTS OF D'ORTENZIO ET AL. (2008, FIG10) FOR THE DIFFERENT SEA-SONS? IT WOULD BE NICE TO SEE MAPS OF ANNUAL OR SEASONAL PCO2 AND CO2 EXCHANGE.

Table B5 in Appendix B reports the comparison of the seasonal values of pCO2 for the central part of the southern Adriatic Sea. Modelled values are in good agreement with the estimation proposed by d'Ortenzio et al., 2008. Besides, Fig. R2\_F2 reports the maps of seasonal values of pCO2 and CO2 exchange for 2008. In order to keep the number of figures to a reasonable value, we would not add these maps in the manuscript unless reviewers think that we should. The maps show the main spatial and temporal differences which are discussed in the section 3.3 of manuscript and are synthesized in Fig. 6 and Table 2 of the manuscript.

Here Fig. R2\_F2

Fig. R2\_F2. Maps of mean seasonal values of pCO2 at surface (left plots) and of CO2 exchange (right plots) for 2008.

#SECTION 4.2 - THE DEFINITION OF ADRIATIC DENSE WATER (REFERENCED AS 'ADDW'), BEING RHO>1029.5 KG/M3, IS CONFUSING AND SEEMS INAPPRO-PRIATE WITH THE FOLLOWING DESCRIPTION OF THE SPREADING OF DENSE WATER: THE ISOLINE 1029.5 AND THUS THE ASSOCIATED ADDW WATER MASS ARE ONLY VISIBLE FOR MARCH 2008 ON FIG 8 (I.E. FIG 8.B), WHEREAS THE AUTHORS DESCRIBE THE FLOW OF ADDW MASS IN THE WHOLE BASIN.

We agree that the reference to rho (potential density)>1029.5 kg/m3 does not indicate the AdDW. It was used to help the reader to identify the core of the dense water in the plot. Besides, during the southward spreading, the core of dense water dilutes with the surrounding water and its density decreases. This can be seen in the following plots d

and f. The sentence will be changed as follows:

"During March 2008 (Fig. 8b), a core of dense water (identifiable by the isopycnal 1029.5) flows on the bottom of the slope, whereas during March 2007 (Fig. 8a), dense water flow is much less clear. Consequently, in 2007 a large part of the C-rich water layer is shallower and mainly confined to the western side of the slope. It is important to note that in 2008, the C-rich water is moved towards the bottom by the downwelling of dense water. Besides, the organic carbon content of the dense water core is 5-10 mmolC/m3 higher than that of the adjacent water masses and of the water occupying the bottom of the slope during the previous year."

- IT WOULD ALSO BE NICE TO SEE VERTICAL SECTIONS OF DIC.

Fig. R2\_F3 shows the simulated seasonal vertical profiles of DIC for the central part of the southern sub-basin (spatial average over an area (10 x 10 grid points) around the site indicated in Fig. 1). The figure shows that the profile is almost stationary from the 200 m down to the bottom. The sub-surface layer (around 150 meters) shows an accumulation due to respiration in summer and autumn, and the surface layer values vary due to the effect of biological processes and of exchanges at the air-sea interface (outgasing in summer and autumn, adsorption in winter). We would not add this figure in the manuscript unless reviewers suggest to do so. Because of the uncertainty on initial conditions and the impossibility to validate the profiles, the focus of our analysis is to show the relative changes among the different periods instead of showing the absolute values.

Here Fig. R2\_F3

Fig. R2\_F3. seasonal profile of DIC [umol/kg] for the central part of the southern pit during the two years.

- A CORE OF DENSE C-RICH WATER MASSES (LESS DENSE AND C-RICH THAN IN 2008) IS ALSO VISIBLE ON THE BOTTOM OF THE SLOPE FOR 2007 IN CA

C6780

REGION (FIG. 8C), CONTRARY TO WHAT IS SUGGESTED BY THE AUTHORS L25-26 P10345.

We agree that the differences in the carbon concentration distribution between the two years are not very well noticeable. However the most evident difference is the matching of the core of dense water with POC distribution, that is visible in 2008 but not in 2007. The sentence will be changed as follows:

"In the CA region, in 2008, the C-rich water lies at the bottom of the slope and it is associated with a core of dense water, whereas in 2007 the C-rich water is associated to lighter water. (Figs. 8c and d)"

Please consider that figure 8 has been redrawn with the new results that are reported in Fig. R2\_F4.

Here Fig. R2\_F4

Fig. R2\_F4: new figure 8. Distribution of POC (filled contour) and density (isolines) in the 44.03°, 43.16° and 41.53° latitude sections (see their position in Fig. 1). The average data for March, April and June, for the three sections are presented. Arrows indicate the zonal-vertical components of velocity (vertical velocities are amplified). The northward (cross) and southward (dot) velocities are reported for the absolute intervals 0-0.02 (small symbols), 0.02-0.04 (medium symbols) and >0.04 m/s (large symbols).

#SECTION 4.3 - ARE THE DOC FLUXES INCLUDED IN THE ORGANIC CARBON FLUXES DESCRIBED IN SECTION 4.3 AND PRESENTED ON FIG 9?

Organic carbon vertical flux accounts for living and non living organic carbon. Only the labile DOC is included in the sum of Corg flux of Figure 9. Because of the short length of the simulation, the model simulates only the labile part of the DOC, which constitutes 10-30% of the total DOC (Giani et al., 2005, De Vittor et al., 2008; Cossarini et al., 2012). The largest part of DOC consists of refractory organic carbon, whose dynamics have longer time scales than that simulated, and indeed is not included in the Corg

flux. Therefore, Corg flux accounts for all the components of organic carbon which can be subjected to remineralization and respiration in the deep layer in the time frame of the simulation. The new figure 9 is reported below (Fig. R2\_F5) together with the new caption.

Here Fig. R2\_F5

Fig. R2\_F5. New figure 9. Vertical transport (sum of the advective, diffusive and turbulent transport) of DIC and organic carbon (sum of living and non living particulate organic carbon and of labile DOC) and sinking rate of POC and phytoplankton. Western part of the CA at a depth of 90 m (a), western part of the SA at 90 m (b) and 180 m (c) and the central part of the SA at 180 m (d). Positive values indicate an upward flux.

- L 11-12 P10346: IS SINKING TAKEN INTO ACCOUNT IN THE VERTICAL FLUXES OF ORGANIC CARBON PLOTTED ON FIG 9?

In Fig. 9. "sink Corg" accounts for the sinking of POC and phytoplankton groups (see new caption of Fig. 9). The sentence is rewritten as follows: "The effect of the deepening of the AdDW is assessed by computing the spatial mean of the sink and of the vertical transport flux of inorganic and organic carbon over the western part of the CA and SA at 90 meters depth and over the western and central parts of the SA at 180 m depth (Fig. 9). The vertical transport of organic carbon considers POC and phytoplankton groups. The depth of 180 meters was chosen because the mixing processes seldom reach deeper layers (see Fig. 8 of Querin et al., 2012)."

- L 24 P10347: COULD YOU GIVE THE VALUE OF THE FRACTION OF ORGANIC CARBON REACHING THE BOTTOM?

The fraction of organic carbon reaching the bottom greatly varies among the domain (Fig. R2\_F6). Table B4 in Appendix B reports the comparison of the modelled sinking values with literature data for a few selected areas. It must be reported that the sunk material on the last layer is not entrapped in sediment and can be re-suspended by

C6782

vertical transport processes. Therefore, for the shallow area (where transport dynamics are stronger), the figure may represent an overestimation of the effective fraction of organic carbon reaching the bottom. Further, since the contribution of POC input form the rivers the fraction values can be higher than 1 in the coastal zone.

Here Fig. R2\_F6

Fig. R2\_F6. Ratio between sinking of POC on the bottom layer and the primary production (integrated over the water column).

- THE COMPARISON OF SIMULATED AND OBSERVED (BOLDRIN ET AL., 2002) ORGANIC CARBON VERTICAL FLUXES WOULD BE MORE RELEVANT IF DONE AT THE SAME DEPTHS (150 M AND 1050 M), SAME PERIOD (POST-OPEN-CONVECTION) AND SAME LOCATION (L26 P10347-L2 P10348).

The comparison is now shown in appendix B (Tab. B4) and it is performed at the same depths and period.

- THE SENTENCE L9-10 P10348 IS PARTLY REDUNDANT WITH THE SENTENCE L24-25P10347.

Done. Lines from L23p10347 to L02p10248 have been deleted.

- L19 P10348: USE OF "THUS": I DON'T FIND LOGICAL THE LINKAGE BETWEEN THE PREVIOUS SENTENCE AND THIS SENTENCE.

Thus has been deleted

#SECTION 4.4 - "OUR SIMULATION SHOWS NET OUTWARD POC ÏNËĞC' UXES OF 0.2 AND 0.4 TG C YR-1 AND NET OUTWARD DIC ÏNËĞC' UXES OF 3.2 AND 4.8 TG C YR-1 IN THE TWO SIMULATED YEARS." WHAT ABOUT DOC FLUXES? AS MENTIONED BEFORE, THE ESTIMATION OF FLUXES AT OTRANTO STRAIT IS QUESTIONABLE CONSIDERINO THE FORCING AT THE SOUTHERN BOUNDARY.

As specified in the previous points, our model simulates only the labile fraction of DOC

(see Appendix A for additional details on the model parameterization of DOC), therefore we believe that the estimate of the flux at the Otranto strait is not meaningful in light of the model specific definition of labile DOC. As regards the boundary conditions for POC at the Otranto Strait, please see the previous point on this issue. Given that explanation, we believe that the value of POC flux can be an interesting information to be reported in order to judge the relative importance of the different terms that constitute the carbon budget in the Adriatic Sea. However we stress in the new version of the manuscript that the POC flux at the Otranto strait is not a direct result of the simulation but it is a boundary condition.

#CONCLUSION - "THE WINTER DENSE WATER FORMATION IN THE NORTHERN CONTINENTAL SHELF, AS WELL AS ITS SPREADING AND SINKING ALONG THE SLOPE AND INTO THE DEEPER LAYERS OF THE CENTRAL AND SOUTHERN BASINS, ARE THE KEY PROCESSES FOR [. . .] PREVENTING CARBON RE-EXPOSURE AT THE SURFACE DURING THE SUBSEQUENT MIXING PERIOD." THIS IS NOT SHOWN BY THE RESULTS OF THIS STUDY.

We agree, the last part of the sentence has been cancelled. The new sentence is "[...] are the key processes for sequestering C-rich water masses below the mixed layer".

- OBSERVED AND SIMULATED FLUXES (SINK OF ORGANIC CARBON AND BURIAL) INDICATED IN TABLE 1 SEEM TO BE NOT COMMENTED IN THE TEXT.

Table 1 has been moved in Appendix B, which is dedicated to the model validation. Comments on the comparison are written in the Appendix B.

##TECHNICAL CORRECTIONS - REPLACE "DE MADRON" BY ITS ENTIRE NAME "DURRIEU DE MADRON"

Done

- L17 P10333: REPLACE "EQUAL" BY "ESTIMATED".

Done

C6784

- FIG 4: MAPS WITH LABELLED ISOLINES WOULD HELP THE READING.

The maps of simulated surface chlorophyll-a are now shown in Appendix B. The new monthly maps use a more readable colorbar.

- L19 P10339: "DIP CONCENTRATIONS ARE IN THE RANGE 0.1-0.15 MMOL/M3". DO THE AUTHORS REFER TO MODELLED OR OBSERVED DIP CONCENTRA-TIONS? IN TABLE 1, SIMULATED DIP CONCENTRATIONS ARE NOT IN THE RANGE 0.1-0.15 MMOL/M3 EXCEPT FOR SPRING-SUMMER 2007. IN GENERAL, IT IS OFTEN NOT CLEAR IF THE AUTHORS REFER TO SIMULATED OR OB-SERVED RESULTS.

The section 3.2 has been rewritten (see the previous point on this issue). The new section 3.2 describes the relevant simulated ecosystem dynamics, while a new section (Appendix B) shows the validation of the model. The text of new section 3.2 refers to model results. The text of new appendix B clear explains when it refers to simulated results or observed data.

- DIP CONCENTRATIONS IN CA DEEP WATER ARE NOT INDICATED IN TABLE 1 AS SUGGESTED L5-6 P10340.

The comparison between data and model results for DIP has been moved in Tab B2 in Appendix B. Table B2 reports the comparison with observations for the Central Adriatic Sea. Sentence at L5-6 p10340 has been changed.

- L14 P10340: THE "NEARLY" TERM IS EXAGGERATED REGARDING THE MODEL RESULTS.

This sentence has been changed and included in the new section 3.2.

- L16 P10340: DO "THE MAPS" REFER TO FIGURE 4?

This sentence has been changed and included in the new section 3.2.

- L10 AND L22 P10342: IT SEEMS THAT THE AUTHORS REFER TO FIG6 INSTEAD

OF FIG7.

Thanks, the reference to the figure has been corrected.

- ADD "SIMULATED" BEFORE RATE OF CO2 EXCHANGE IN LEGEND OF FIGURE 6.

The term "simulated" has been added to the legend of Fig. 6

- FIG. 7: THE PP -- PR CURVE IS CUT BY THE GRAPHIC BOX' EDGE.

The figure has been redrawn and the legend box has been moved.

- L24 P10344: IT SEEMS THAT THE AUTHORS REFER TO FIG6 INSTEAD OF FIG4.

Thanks, the reference to the figure has been corrected.

- L6 P10345: "COVERS" INSTEAD OF "COVER"?

Done

- L11 P10346: REPLACE 190M BY 180M DEPTH AS IT IS INDICATED ON FIG9?

Done

- L11-12 P10346: REMOVE ONE "SPATIAL" IN THE SENTENCE.

Done

- FIG.9A: THE "CORG FLUX" CURVE IS CUT BY THE GRAPHIC BOX' EDGE.

The figure has been redrawn and the legend box has been moved (Fig. R2\_F5).

- L 28 P10346-L1 P10347: I DON'T UNDERSTAND THE SENTENCE "IT WAS LATER DETERMINED THAT THE LARGEST FRACTION OF CARBON ENTERING THE CA IS TRANSPORTED SOUTHWARD TO THE SA."

The sentence has been changed as following: A fraction of carbon entering the CA is transported southward to the SA by the AdDW that enters the SA at an intermediate

C6786

level and cascades along the Bari Canyon system (as described by Rubino et al., 2010; Querin et al., 2012) during June and July

- L 2 P10347: COULD THE AUTHORS INDICATE THE BARI CANYON ON FIG1?

Fig 1 has been redrawn (Fig. R2\_F7)

Here Fig. R2\_F7

Fig. R2\_F7: New Fig. 1.

- L11 P10348: REMOVE "(WINTER 2008)" FOR A BETTER CONSISTENCY WITH THE NEXT SENTENCE.

Done

- L18 P10348: I DON'T UNDERSTAND THE REFERENCE TO FIG6. DO THE AU-THORS WANT TO REFER TO FIG 5 AFTER "PHYTOPLANKTON BLOOM"?

References have been corrected. The increase of CO2 solubility (and CO2 flux) can be seen in Fig. 6; the phytoplankton bloom can be seen in Fig. 5; and Figs 9 shows the increase in sinking of organic matter in the central part of the SA.

- L7 P10348: THE AUTHORS REFER TO FIG6 INSTEAD OF FIG4?

The reference to the figure has been corrected.

- L8 P10349: REMOVE "UNEXPECTED".

We agree, unexpected has been removed.

- L17 P10349: DO THE AUTHORS REFER TO TABLE 2 INSTEAD OF TABLE1?

This reference is to the table reporting the carbon exchange rates. However, in the new version of the paper this table will be Tab. 1. The table reporting model and data comparison (previous table 1) will be moved to Appendix B.

- L 27 P10351: THE LINKAGE "IN CONTRAST" SEEMS INAPPROPRIATE SINCE

NEGATIVE FLUXES ARE ALSO SIMULATED IN THE EASTERN NA (FIG 6).

"In contrast" has been removed.

- L11-13 P 10352: I DON'T UNDERSTAND THE SENTENCE "BECAUSE THE C-RICH, DENSE WATER OF THE DEEP LAYERS FUELS THE DEEP MEDITER-RANEAN SEA CIRCULATION, CLIMATE CHANGE WOULD POTENTIALLY DE-CREASE THE CAPACITY OF THE ADRIATIC SEA TO ABSORB ATMOSPHERIC CO2."

The sentence has been changed as follows: "Because the C-rich, dense water of the deep layers fuels the deep Mediterranean Sea circulation, climate change would potentially decrease the capacity of the Mediterranean Sea to absorb and stock atmospheric CO2."

### **REFERENCES**:

Cardin, V., Bensi M., Pacciaroni M.: Variability of water mass properties in the last two decades in the South Adriatic Sea with emphasis on the period 2006–2009, Continental Shelf Reserch, doi:10.1016/j.csr.2011.03.002, 2012.

Cossarini, G., Solidoro, C., Fonda Umani, S.: Dynamics of biogeochemical properties in temperate coastal areas of freshwater influence: lessons from the Northern Adriatic Sea (Gulf of Trieste), Estuarine, Coastal and Shelf Science, 115, 63-74, 2012.

De Vittor, C., Paoli, A., Fonda Umani, S., 2008. Dissolved organic carbon variability in a shallow coastal marine system (Gulf of Trieste, northern Adriatic Sea). Estuarine, Coastal and Shelf Science 78(2), 280-290.

Giani, M., Savelli, F., Berto, D., Zangrando, V., Cosovic, B., Vojvodic, V., 2005. Temporal dynamics of dissolved and particulate organic carbon in the northern Adritic sea in relation to the mucilage events. Science of the Total Environment 353, 126-138.

Giordani, P., Helder, W., Koning, E., Miserocchi, S., Danovaro, R., and Malaguti, A.:

C6788

Gradient of benthis-pelagic coupling and carbon budgets in the Adriatic and Northern Ionian Sea, J. Mar. Syst., 33-34, 365-387, 2002.

Hammond, D.E., Giordani, P., Berelson, W.M., Poletti, R.: Diagenesis of carbon and nutrients and benthic exchange in sediments of the Northern Adriatic Sea, Marine Chemistry 66, 53–79, 1999.

Lazzari, P., Teruzzi, A., Salon, S., Campagna, S., Calonaci, C., Colella, S., Tonani, M., Crise A.: Pre-operational short-term forecasts for Mediterranean Sea biogeochemistry, Ocean Sci., 6, 25–39, 2010

Madec, G., Delecluse, P., Imbard, M., and L'evy, C.: OPA 8.1 Ocean General Circulation Model Reference Manual, Note n. 11, Laboratoire d'Oc'eanographie DYnamique et de Climatologie, Institut Pierre Simon Laplace, Paris, France, 91 pp. 1998.

Oddo, P., Adani, M., Pinardi, N., Fratianni, C., Tonani, M., Pettenuzzo, D.: A nested Atlantic-Mediterranean Sea general circulation model for operational forecasting, Ocean Sci. Discuss., 6, 1093–1127, 2009

Oddo P., Guarnirei A.: A study of the hydrographic conditions in the Adriatic Sea from numerical modelling and direct observations (2000–2008), Ocean Sci., 7, 549–567, 2011

Querin, S., Cossarini, G., and Solidoro, C.: Simulating the formation and fate of dense water in a mid-latitude marginal sea during normal and warm winter conditions. Submitted to J. Geophys. Res.-Oceans, 2012.

Tonani, M., Pinardi, N., Dobricic, S., Pujol, I., and Fratianni, C.: A high-resolution freesurface model of the Mediterranean Sea, Ocean Sci., 4, 1-14, 2008.

Turk, D., Malačič, V., DeGrandpre, M. D., McGillis, W.R.: Carbon dioxide variability and air-sea fluxes in the northern Adriatic Sea, J. Geophys. Res.-Oceans, 115, C10043, doi: 10.1029/2009JC006034, 2010

Zeebe R.E., Wolf-Gladrow, D.: CO2 in seawater: equilibrium, kinetics, isotopes. Elsevier Oceanography Series, Amsterdam, The Netherlands, 2003

Interactive comment on Biogeosciences Discuss., 9, 10331, 2012.

C6790



Fig. 1. Fig. R2\_F1



Fig. 2. Fig. R2\_F2

C6792



Fig. 3. Fig. R2\_F3



Fig. 4. Fig. R2\_F4

C6794



Fig. 5. Fig. R2\_F5



Fig. 6. Fig. R2\_F6

C6796



Fig. 7. Fig. R2\_F7