

# Scenarios of trophic web changes in Mediterranean carbonate ecosystem

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## Abstract

Mediterranean ecosystem is described by means of chemical and biological interactions including potential carbon dioxide leaks into the marine environment. The bottom-up synopsis is based on the following subsystems in terms of the carbon dioxide contents, sources and sinks: macrobenthos in the aerobic and anaerobic zones, biogeochemical cycles of the food web up to the higher trophic levels, seagrass growth and marine carbon geochemistry.

The geochemical methods quantify complex impacts of different events, giving a critical pH of 7 or less, under which the ecosystem responses change. Recovery of the ecosystem from high carbon dioxide leak is outlined.

**Keywords:** Seawater carbonate system, Carbon Capture and Storage, *Posidonia oceanica*, Marine food web, Mediterranean ecosystem

## 1. Introduction

The response of the sea to carbon dioxide additions is an important issue for addressing both potential environmental impacts originated by events of carbon leaks and possible forecasted ecosystem modifications due to an increasing of the carbon in the biosphere.

In particular, evaluations of CO<sub>2</sub> marine transfers at the two boundaries, i. e. air-sea and sea-sediment fluxes, are important, but difficult to carry out because of the dynamics of the carbon dioxide, which is resolved in terms of geochemical knowledge, and of physical preconditions, such as turbulent diffusion, advective transport, and sea-state (Wanninkhof, 1992). More specifically, on one hand, the benthic layers have biological components, connected to the present benthic organisms, and geochemical ones, impacted by the active marine chemical species (Boudreau, 1996; Blackford, 2002); on the other, the seawater ecosystem is connected to the dynamics of the sub-basin dynamics and general circulation (Lenhart et al., 1995; Roussenov et al., 1995).

The aim of this work is to schematize the carbon cycle, putting in dynamic link the two parts of the ecological system, dynamics of the carbon cycle in sediment layers and related changes of the trophic web with emphasis on seagrass, connected through

geochemical characteristics.

The link between these two subsystems has been reckoned by simultaneously describing both the profile of the dissolved inorganic carbon, which, in addition to modulating marine acidity, is one of the major nutrients for primary producers, and that of total alkalinity, which is determined by superimposing carbonate contribution on the other nutrient alkalinities, modulated by the variability of the thermohaline field and by the geometry of the sediment.

The approach is geochemical and emphasis is given to acidic conditions as controlled by the seawater field of mass. Such a model is also capable of giving additional information about response of the ecological system to Carbon Capture and Storage (CCS), about potential impact of carbon leaks and seepages and subsequent recovery of the ecosystem.

The advantage of choosing an approach so general and integrated ensures that the results of this numerical approach, based on medium-term time scales of temperate ecosystems, are consistently applicable to different forcing of different ecosystems, modifying appropriately environmental boundary conditions. This approach can achieve proper results provided to redefine the responses of involved biological communities from experimental data collected in the stations of the application area. The technicalities introduced in this work for integrating the marine ecosystem with the geochemical environment are: the modifications of the acidic environment acting on the biological communities and their survival (Pörtner et al., 2004); the modifications and adaptations of the biomass responses to a changing environment, particularly in terms of growth; the boundary conditions of a specific environment, in this case the Mediterranean ecosystem.

The relative growth of the *Posidonia oceanica* seagrass, dominant and, presently, declining species in Mediterranean (Borum et al., 2004), has been studied focussing on the CO<sub>2</sub> buffered signal based mainly on primary production and basal and activity

respirations. Carbon leaks and seepages, as well as lateral inflows, have been treated considering additions to the available dissolved inorganic carbon.

The feasibility test of the ecosystem has been performed in mixed mesocosm, where the water column is the site of the primary production of the seagrass and of the recirculation into dissolved inorganic carbon of the organic carbon stored by the plant and then distributed to the four biological compartments. These variables have been designed in order to close the trophic cycle up to the higher description levels of the ecosystem. Demersal fish have been included, representing major predators of the seagrass meadows (Verlaque, 1990), and, at the same time, particular attention has been given to description of the biological species in the sediment where, in addition to the aerobes and anaerobes, meiobenthos and feeders are included (Danovaro et al., 2002).

These species reside in sediment where the organic carbon is at disposal and represents an intermediate compartment between the inorganic carbon and the refractory compartment, which has the longer remineralization time and is designed to characterize the formations of long-term maintenance, which in Mediterranean environment are named matte (Mateo et al., 1997).

The following section deals with the geochemistry in medium- and long-term evolutions and with extensions to leakage transients of the seagrass life in Mediterranean realistic nutrient levels. Continuous update of the seawater pH triggers the speciation of carbon into bicarbonate, carbonate and, consequently, the internal buffer factors and carbon budgets are estimated in the results section at different levels of carbon additions. Some hypotheses about the overall system behaviour in different scenarios are outlined in the discussion section.

## **2. Materials and Methods**

### **2.1 Determination of the seawater carbonate system**

This geochemical description estimates variabilities of the  $pH$  and  $pCO_2$  due to bicarbonate and carbonate ions, independently evaluated, boric acid and seawater

dissociation. The National Bureau of Standards acidity units are selected for consistency with the geochemical and laboratory experiments discussed in this work.

Starting from the analysis of the total dissolved inorganic carbon,  $TCO_2$ , given by

$$TCO_2 = (CO_{2(aq)}) + (HCO_3^-) + (CO_3^{2-}) \quad (2.1)$$

and substituting in it  $K'_{Cl}$ , the apparent dissociation constant of carbonic acid (Mehrbach et al., 1973),

$$(HCO_3^-) = K'_{c1} (CO_{2(aq)}) / a_H$$

the following expression describes the dissolved carbon dioxide concentration,  $CO_{2(aq)}$ , sum of the hydrate  $CO_2$  and carbonic acid concentrations

$$(CO_{2(aq)}) = (2TCO_2 - A_c) / (2 + K'_{c1} / a_H) \quad (2.2)$$

where  $A_c = (HCO_3^-) + 2(CO_3^{2-})$  and  $a_H$  are, respectively, the carbonate alkalinity and the activity of the hydrogen ion.

Restarting from the equation of the total carbon (2.1) and substituting in it, this second time, the definition of the apparent dissociation constant of bicarbonates

$$(CO_3^{2-}) = K'_{c2} (HCO_3^-) / a_H$$

it follows that the total carbon results expressed as follows:

$$TCO_2 = (CO_{2(aq)}) (1 + K'_{c1} / a_H + K'_{c1} K'_{c2} / a_H^2) \quad (2.3)$$

After elimination of the dissolved carbon dioxide concentration from equations (2.2) and (2.3), the following quadratic equation is obtained, determining the value of the activity of the hydrogen ion in terms of the total dissolved inorganic carbon concentration and carbonate alkalinity:

$$A_c a_H^2 + (K'_{c1} A_c - TCO_2 K'_{c1}) a_H + (A_c - 2TCO_2) K'_{c1} K'_{c2} = 0 \quad (2.4)$$

On the other hand, the value of the carbonate alkalinity is obtained after estimating both water dissociation and borate contributions. The water dissociation constant

$$K'_w = (H_{sw}^+) (OH^-),$$

as given by Millero (1995), based on combined results (Hansson, 1973; Culberston and Pytkovicz, 1973; Dickson and Riley, 1979), and the expression for the seawater scale hydrogen,  $H_{SWS}^+$ , in function of the total hydrogen ion activity

$$(H_{SWS}^+) = (H^+) + (HF) + (HSO_4^-) = a_H / f_H$$

are used to evaluate  $A_w$ , the alkalinity due to seawater dissociation as:

$$A_w = (K'_w f_H / a_H) - (a_H / f_H) \quad (2.6)$$

The borate alkalinity,  $A_B$ , due to boric acid is

$$A_b = \frac{K'_b}{K'_b + a_H} TB \quad (2.5)$$

where  $TB$  is the total boron (Culkin, 1965; Millero, 1982)

$$TB = (H_2BO_3^-) + (H_3BO_3)$$

and  $K'_B$  is the apparent dissociation constant of the boric acid (Lyman, 1956; Peng et al., 1987).

Consequently, seawater dissociation and borate alkalinities are subtracted from the total alkalinity

$$A_c = A_T - A_w - A_B \quad (2.7)$$

and carbonate alkalinity is obtained.

The solution for positive values of  $a_H$  is determined by equation (2.4) through the following expression

$$a_H = \frac{K_{c1}}{2_c} \left[ \left( \frac{TCO_2}{A_c} - 1 \right) + \sqrt{\left( \frac{TCO_2}{A_c} - 1 \right)^2 + 4 \frac{K_{c2}}{K_{c1}} \left( \frac{2TCO_2}{A_c} - 1 \right)} \right] \quad (2.8)$$

while other root of the quadratic equation must be discarded, because the radicand is always greater than  $TCO_2 - A_C$ , producing for this second root a negative, unrealistic value for  $a_H$ .

In the case of acidic seawater,  $TCO_2 > A_C$ , an increase of carbonate alkalinity produces a decreasing  $a_H$ , i. e. a stabilizing effect. The same is also shown true in alkaline seawater. The solution of this system for the activity of the hydrogen ion and carbonate alkalinity results in performing in the order (2.5) and (2.6), (2.7) and, finally (2.8); in fact, an

increase of the activity of the hydrogen ion produces a stabilizing effect at the every step of the calculation. The reverse effect, in the case of a decrease of  $a_H$ , is symmetrical.

It can be seen that the same behaviour is true considering other environmental contributions to total alkalinity, because all those alkalinities are expressed similarly to the borate alkalinity. Thus, extended descriptions are applicable to other geochemical systems considering the proper environmental alkalinity contributions. All chemical components can be straightforwardly solved after superimposing, the following, if applicable, terms to the total alkalinity: the phosphate, the silicate, the sulphide, the ammonia, the sulfate, the hydrogen fluoride and nitrous acid alkalinities (Wolf-Gladrow et al., 2007). This scheme, as reported in this section and implemented in the ecosystem model, permits an evaluation of  $pH_{NBS}$ ,  $pH_{NBS} = -\log_{10}(a_H)$  and  $pCO_2$  through  $CO_2$  solubility in seawater (Weiss, 1974),  $pCO_2 = \alpha_S CO_{2(aq)}$ , for controlling both carbon fluxes toward and from the atmosphere and biogeochemical pressures.

## 2.2 Impacts on food web

The responses by species to changed conditions of the seawater geochemistry have been synthesized starting from the results obtained by two meta-analyses (Hendriks et al., 2010; Kroeker et al., 2010).

The fundamental features of *Posidonia oceanica* seagrass are at the base of the present Mediterranean ecosystem scheme and their properties are given heretoafter for what regards environmental forcing. *Posidonia Oceanica* (L.) Delile, 1813, is perennial aquatic plant with rhizomes and root fibers, with hermaphrodite, spike-shaped united, free (not enclosed in a sheath) flowers, with one ovary and no perianth, and completes the overall life cycle in the marine ecosystem (Abel et al., 1963). This species is dominant in the Mediterranean coastal waters, where it forms the climatic ecosystem; the analogies and differences among this species and the others present in this basin, *Cymodocea nodosa*, *Zostera marina* and *Zostera noltii*, consist in biological response and produced oxygen and, respectively, in higher production and slower recovery times (Borum et al., 2004).

According to the first meta-analysis (Hendriks et al., 2010), the seagrass growth effect levels to an increased CO<sub>2</sub> were analyzed in all-treatments scenario from 11 treatments of *Zostera marina*: 2 from Thom (1996), 4 from Zimmerman et al. (1997) and 5 from Palacios and Zimmerman (2007); the former were used also in the limited scenario. The conclusion of this meta-analysis was that growth rates may increase more than 500% in the all-treatments scenario and by 50%, when pH decreases from the controls of 8.1–8.2 down to values around 7.5. The respective results about metabolic effect levels, including one treatment of *Posidonia oceanica* and two treatments of *Cymodocea nodosa* by Invers et al. (1997), gave similar increased levels of photosynthesis and net apparent productivity, with found effect levels slightly lower than in the case of the previous growth effect.

In the second meta-analysis (Kroeker et al., 2000), the treatments were taken from Invers et al. (1997) and Hall-Spencer et al. (2008): one *Posidonia oceanica* treatment was taken from the second paper and contributed to the overall growth meta-analysis; the first paper contributed 3 treatments about *Posidonia oceanica*, 5 treatments about *Cymodocea nodosa* and 4 treatments about *Zostera noltii* to photosynthesis meta-analysis. Two works about eelgrass (Thom, 1996; Zimmerman et al., 1997) were taken into account for the deviations, but excluded from the meta-analysis. The overall growth gave significant differences between calcifiers and non-calcifiers, with the latter positively and similarly affected than in the previous results; on the other hand, photosynthesis effects showed no significant effects with negative mean effects on calcifiers, while neutral non-calcifying organisms are positively affected in the unweighted, fixed effects analysis.

As a conclusion of both meta-analyses, the seagrass growth is positively affected by increasing carbon dioxide and this higher growth rate is quantified in the model at the level of 87.5% for seawater acidification of one unit in pH.

The fish impacts were considered by the first meta-analysis using 45 survival treatments taken from the papers of Parra and Yúfera (2002) and Kikkawa et al. (2003). Hendriks et

al., (2010) considered also influences of one high CO<sub>2</sub> treatment on *Sparus aurata* from the results by Michaelidis et al. (2007), giving a reduction from 1 to 0.92 in metabolism; anyway, no treatments were taken into account for growth.

The second meta-analysis extended the results to larval and juvenile stages; the growth was developed by means of 4 treatments (Munday, 2009b), while the survival was based on 2 treatments, each on different adult fish species (Munday, 2009a). In these two experiments, neutral pH of 8.15 decreased down to 7.80; results made it clear that a decrease in growth and an increase in mortality are not found; anyway, these results cannot be extended to higher concentrations of CO<sub>2</sub>, as occurs in marine sites with natural emissions of carbon dioxide and is observed in other experiments focused on fishes, applying an increasing content of carbon dioxide to the later stages of development. The other cited papers by Kroeker et al. (2010) analyzed the consequences of acute toxicity for evaluating the survival of different species in the case of , respectively, adult and juvenile specimens (Hayashi et al., 2004a; Kikkawa et al. ,2006); demonstrated that impacts are guided by the carbon dioxide concentrations in the ecosystem, while the pH levels could be misleading (Hayashi et al., 2004b); put in evidence that no impacts on the mobility appear as increasing the acidity in the range of the above-cited papers (Melzner et al., 2009).

Summarizing, these two meta-analyses are not conclusive about the impacts of elevated CO<sub>2</sub> concentrations on the growth of fish; therefore we have considered two reviews about this topic, which explicitly discussed growth effects on juveniles and adult stages. The considerations about these two reviews and related papers are summarized in Appendix; here we point out that an evaluation for high concentrations in the ecosystem is required, because of influences on cardiac output, on ventilatory response, as well as on metabolism, as also seen in the latter case from the meta-analyses discussions (Ishimatsu et al. 2005, Melzner et al., 2009).



The limitation of the fish growth to increased aquatic carbon dioxide has been designed in Appendix according to controlled experiments, giving the following dependence on total carbon dioxide.

$$k_{gr}^i = k_{mgr}^i (-0.0116 \cdot CO_{2(aq)} + 1.07)$$

Experience in aquaculture intensive exploitations confirm these results that, exceeding 10 mgCO<sub>2(aq)</sub>, modifications in growth and metabolic fish functions could be induced. The other species are not considered impacted by carbon dioxide: in fact, different studies demonstrate that community responses must be carefully analyzed in terms of all environmental parameters and actual taxa.

Crustaceans, not covered by the first meta-analysis, have a behaviour with non-significant positive effects in the second meta-analysis, anyway not covered by experiments regarding the taxa under consideration in this study. Moreover, there are crustaceans less sensitive to increased acidification (Spicer et al., 2007). In this study no carbon dioxide effect has been arbitrarily assumed on crustaceans.

The response of sea urchins was discussed by the two meta-analyses only in terms of embryos; anyway, there are recent studies about different sea urchin taxa in sites of specific interest in the Mediterranean Sea (Calosi et al., 2013). These studies confirm some abilities of these species in regulating their extracellular fluids, but the framework is still to be completed because a lot of attention must be paid in the quantification of the biological interactions with different geochemical processes in the sediment hosting sea urchins (Widdicombe et al., 2013). For these reasons no impacts on sea urchin growth has been here hypothesized.

Molluscs are the most controversial regarding the impact of an increase of carbon dioxide, as conflicting responses were obtained comparing the growth of the shell with respect to that of the soft tissue, with the latter apparently less affected under hypercapnia (Klok et al., 2014). Also in this case, no impacts on mollusc growth has

been hypothesized; we mean that this uncertainty is less important for developing the model with respect to others, because suspension feeders are not predators of the seagrass.

Future studies will have high influence on modeling and environmental studies like the present one, in particular those analyzing in different treatments main grazers of seagrasses besides *Sarpa salpa*, like *Idotea* spp. and sea urchin *Paracentrotus lividus*.

### 2.3 The food web forcing

Seagrass growth depends on sea surface sun irradiance,  $I_{sur}$ , expressed in  $ly\ d^{-1}$  units; the irradiance has been optimized according to monthly averages at 42°N and 30°N latitudes of the total, direct plus diffuse, sun irradiance (Kimball, 1928). These data, covering entire Mediterranean Sea, have been converted into  $ly\ d^{-1}$  multiplying the original data units in  $gcal\ cm^{-2}\ minute^{-1}$  by the factor 1437.9. The photoperiod,  $ph(jday)$ , where  $jday$  is the julian day of the specific year, has been included in the optimizing calculation, taking into account the effective day length and averaging the effect of the bright and dark hours.

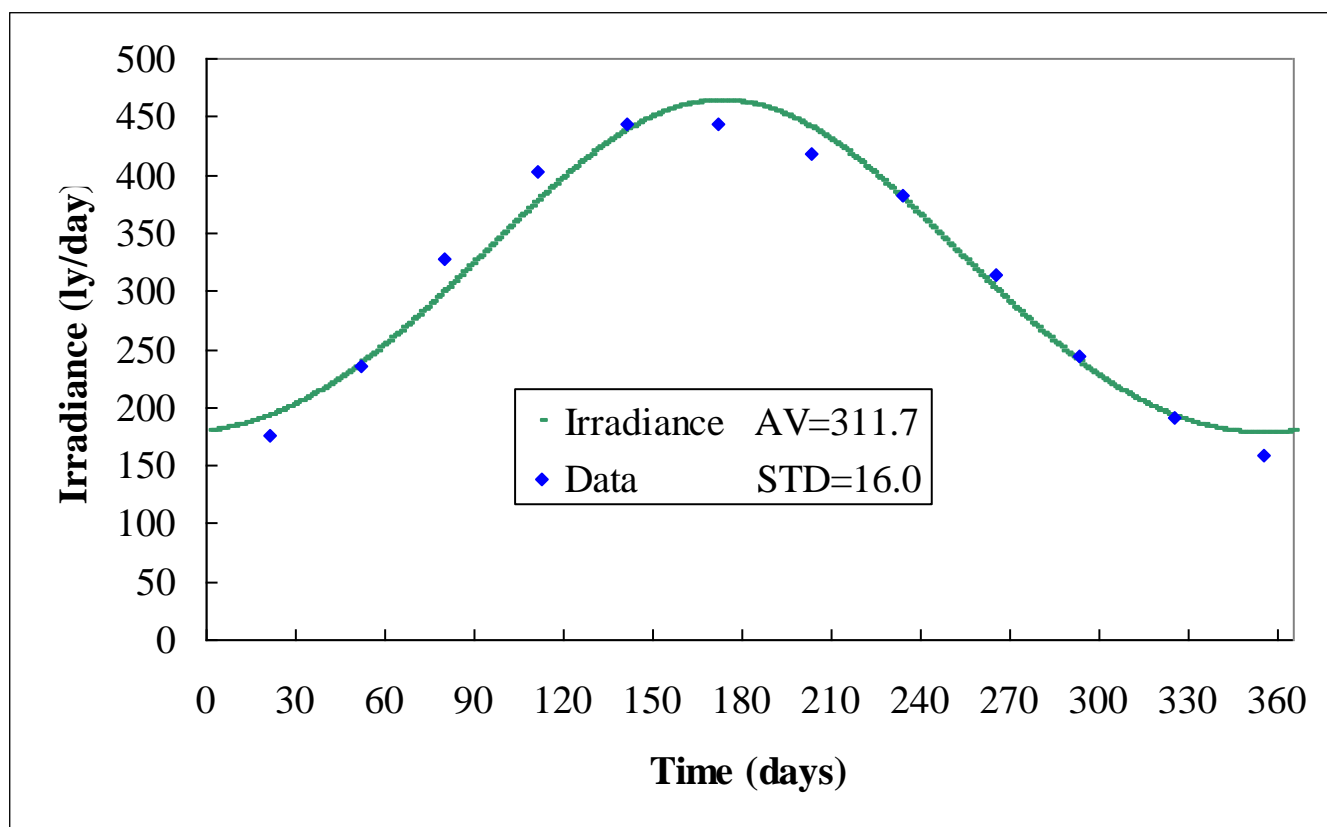


Figure 1.

The optimized solar irradiances has as an annual average of 311.6 ly day<sup>-1</sup>, equal to the energy contents in the data, and standard deviation of 16.0 ly day<sup>-1</sup>, with respect to the data (Figure 1). This optimized formulation for the sea surface irradiance gives the evolution of the photosynthetic available radiation (PAR),  $I_{sur}$ , expressed in ly day<sup>-1</sup>, by means of the reflected light,  $ref$ , and long wave radiation,  $lwr$ , fractions and has been used for estimating the seagrass growth limitation in depth,

$$I_{PAR}(jday) = ph(jday)(1 - ref)(1 - lwr)I_{sur}$$

where the parameter values have been kept, as well as the photoperiod, as in Crispi and Pacciaroni (2009).

Validity of this optimized formula for temperate areas is therefore assured for climatological studies, as the present one; it could be useful, in the cases of seasonal studies, trimming with Mediterranean site data anomalies of these climatological values for the extreme season values of December and January in winter and June and July during summer. Our final formulation incorporates the average cloud coverage per month by means of the formula:  $I_{sur} = I_0 (1 - 0.071C)$  where  $I_0$  is the total incoming radiation with a clear sky (Sverdrup et al., 1943) and  $C$  is decimal fraction of the sky covered by clouds, where scale in oktas is transformed as *clouds-in-oktas*/8.

The primary production happens mainly in the leaves of the seagrass, but with a significant part in the rhizomes: this quota varies from 5–6% in deeper plants to 9–10% in shallower ones (Pergent et al., 1994). It is limited by  $I_{sur}$  through light limitation factor depending on depth

$$f_L(jday, z) = ph(jday) \frac{I_{PAR} e^{-k_z z}}{I_{opt}} e^{1 - I_{PAR} e^{-k_z z} / I_{opt}}$$

where  $z$  is the depth of the seabed.

Consequently, the daily seagrass primary production,  $PP_{daily}$ , is modulated by the photoperiod and annual gross primary production can be expressed in terms of a 24-hours illuminated biomass production,  $\overline{PP}_{daily}$ , as

$$PP_{annual} = \frac{1}{2} \cdot \overline{PP}_{daily} \cdot 365$$

It gives the used following expression of the daily gross primary production, in case of constant temperature and depth, as in the numerical experiments

$$PP_{daily} = \frac{PP_{annual}}{365} \left( 1.0 - 0.25 \cdot \cos \frac{2\pi(jday + 10)}{365} \right).$$

The space limitation of the plant acts in function of the seagrass biomass (Verhagen and Nienhuis, 1983) and limits only above the optimum quota:

$$\left\{ \begin{array}{l} f_s = \exp \left[ - \left( \frac{BIO - 750}{\sigma} \right)^2 \right] \leftarrow BIO > 750 \text{ gDWm}^{-2} \\ f_s = 1 \leftarrow BIO \leq 750 \text{ gDWm}^{-2} \end{array} \right.$$

Here  $BIO$  is the biomass of the seagrass in g dry weight per square metre obtained starting from biomass in carbon,  $CAR$ , and using the specific contents found in the northwestern Mediterranean by Havelange et al. (1997).

Seagrass losses are quantified in terms of basal and activity respirations, exudation and blade fall in the following ways. The total respiration,  $rer$ , is given by

$$rer = k_r \cdot CAR + 0.05 \cdot (1 - k_r) \cdot PP_{daily} \cdot CAR ;$$

where the first term is the basal respiration and the second one is the activity respiration. The net primary production is evaluated considering the carbon uptake minus the total respiration of the seagrass, sum of the basal plus the activity terms.

The seagrass exudation,  $per$ , is given at the rate

$$per = k_e \cdot CAR$$

which applies to carbon exudation by means of the exudation to uptake ratio,  $k_e$

The blade fall rate,  $plr$ , is given by

$$plr = k_l \cdot CAR$$

and, similarly, the mortality rates of the other biological compartments are given by

$$mor_i = k_i \cdot C_i$$

where index i goes from the index 1 to 6 along the other biological compartments: fish, meiobenthos, deposit feeders, suspension feeders, aerobic bacteria and anaerobic bacteria. The sloppy feeding for the first compartment, Table 1, has been kept 80% from the seagrass and 60% for the other compartments according to Havelange et al. (1997). The model describes four species; one pelagic fish, grazing on seagrass, and three benthic species, meiobenthos and deposit and suspension feeders.

Functional forms of predation are being discussed from experimental data taking into account bites on the leaves by fish, meiobenthos, deposit feeders (Cebrián et al., 1996). The preference food matrix is presented in Table 1 and exhibits moderate complexity, fitting quite well with biological benthos descriptions. The following prevalent species have been taken into account from surveys about grazing of seagrass: fish species, *Sarpa salpa*; meiobenthos, *Idotea baltica*; deposit feeder, *Paracentrotus lividus*.

Table 1

<b>Food</b>	<i>Meiobenthos</i>	<i>Deposit Feeders</i>	<i>Suspension Feeders</i>	<i>Aerobic Bacteria</i>	<i>Anaerobic Bacteria</i>	<i>Seagrass</i>	Organic C	Refractory C
<b>Fauna</b>								
<i>Fish</i>	<b>0.8 (0.4)</b>	<b>0.5 (0.4)</b>	<b>0.8 (0.4)</b>			<b>0.8 (0.2)</b>		
<i>Meiobenthos</i>			<b>0.1</b>			<b>0.8</b>		<b>0.1</b>
<i>Deposit Feeders</i>				<b>0.2</b>	<b>0.2</b>	<b>0.2</b>	<b>0.1</b>	<b>0.3</b>
<i>Suspension Feeders</i>				<b>0.5</b>			<b>0.3</b>	<b>0.2</b>

The grazing by *Sarpa salpa* fish,  $C_1$  in carbon units, is given by the following expression

$$gra_{16} = k_{gr}^1 \cdot \frac{PRE(1,6)C_1}{k_1 + PRE(1,1)C_2 + PRE(1,2)C_3 + PRE(1,3)C_4 + PRE(1,6)CAR} CAR$$

where  $PRE(1,6)$  is the preference (Table 1) of the *Sarpa salpa*, grazing on the seagrass biomass,  $CAR$ .

The other grazing functions are analogous and these four feeding species close the food web taking into account the different high level trophic presences in seawater and the sediment. Any of these four compartments represent specific species and moreover communities subjected to the same environmental pressures. In the following their different behaviours are followed: the advantage of this approach is the ability to trace the medium-term evolution of the total system in the case of changing conditions, pH and nutrients, and in extreme circumstances, to follow the behaviour of extant species. Finally, the two bacteria compartment are modelled by taking up dissolved organic carbon; the main differences between aerobes and anaerobes originate as subjected to either deposit feeders or suspension feeders grazing strategies.

### **3. Results**

#### **3.1 Control responses**

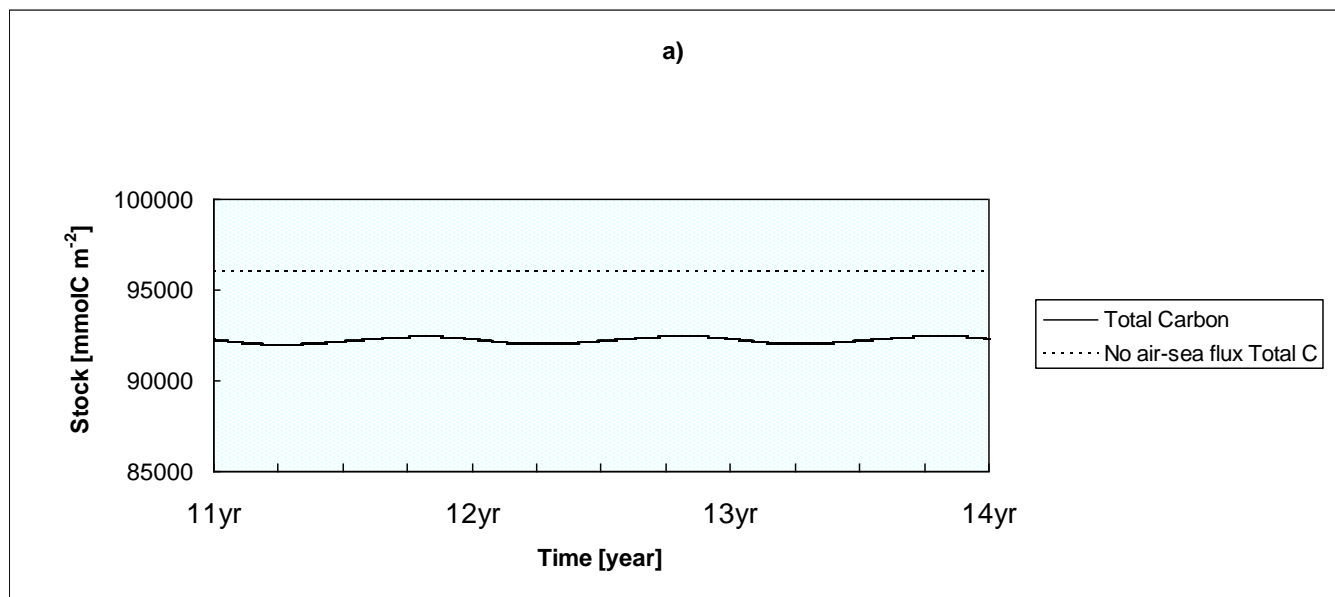
The feasibility test of the ecosystem has been performed in numerical experiments with seawater 7 m depth and sediment 0.5 m thick, with a sediment porosity of 0.6.

The temperature and salinity are kept constant and all environmental parameters are scaled to these averaged values in the Mediterranean Sea by Manca et al. (2004). Biological respiration and remineralization parameters have been taken constant because of these nearly optimal values for temperatures, as well as the geochemical dissociation constants.

Standing stocks in the ecosystem during the three-year simulation after 11 years of spin-up of all compartments are shown in Figure 2. Total Carbon inside the marine ecosystem, dissolved inorganic carbon (DIC) and seagrass biomass are shown in the case of air-sea flux simulation and no-flux one, i. e. in the closed marine ecosystem; no carbon leaks are considered in both cases. The formulation of air-sea fluxes by

Wanninkhof and McGillis (1999) has been selected because of strong adherence with global results in the cases of long-term analyses; the average winds in the Mediterranean basin have been taken into account (Castellari et al., 1998; Lavagnini et al., 2005) and average volumetric parts of CO<sub>2</sub> in atmosphere measured at Lampedusa Island have been selected (Chamard et al., 2001).

The total carbon, Fig. 2a, shows remarkable stable values along the simulations in both cases. As expected, the no-flux evolution maintains a constant total carbon because no fluxes are present, but also the air-sea flux simulation exhibits remarkable stability of the carbon contained in the overall system. Main differences are: a lower average value in the air-sea flux simulation with respect to the no-flux case and, moreover, there are slight oscillations of the total carbon in the air-sea flux case demonstrating a lower standing stock of the total carbon contents at early spring, and maxima in the autumn season.



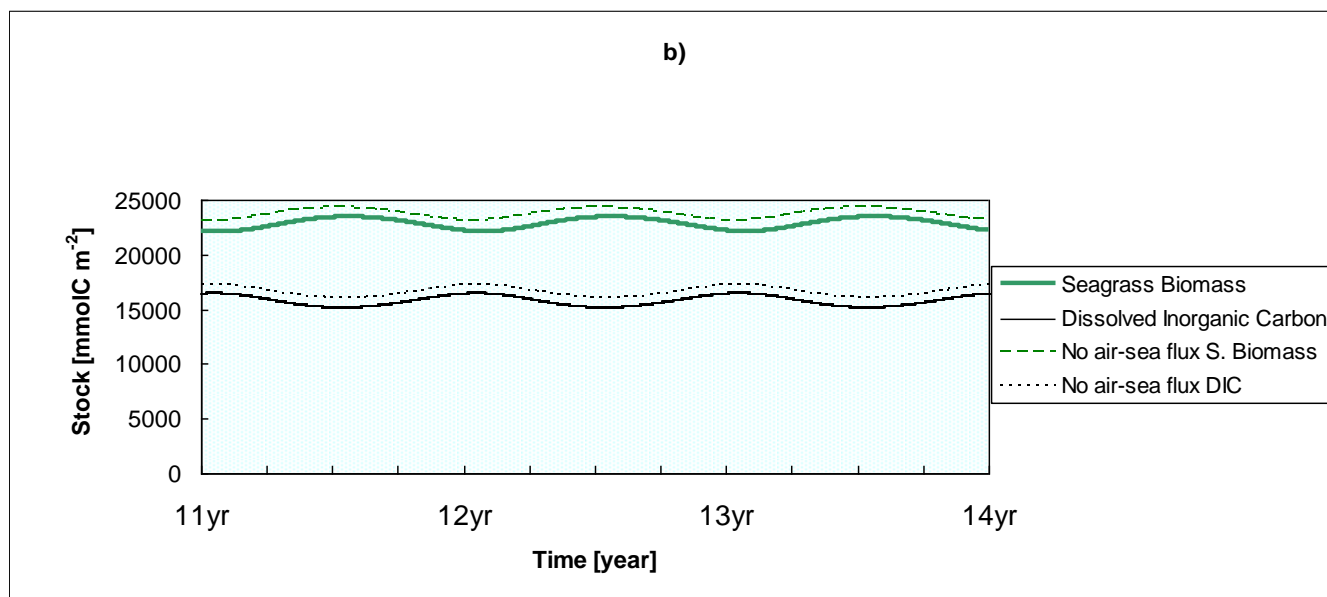


Figure 2

DIC, Fig.2b, follows a similar evolution in both cases. The no-flux evolution shows higher contents of carbon with respect to the air-sea flux values, both behaving with oscillations from maxima in winter to minima in summer. The oscillations are reversed for seagrass biomass, with minima in winter and maxima in early summer; here a more complex dependence on time is noted in terms of distance between the air-sea flux and no-flux responses.

Table 2 reports the average values obtained in the ten years from 11 to 20 by the seagrass and fish biomasses, total carbon of the system, refractory carbon and pH. The statistics give yearly oscillations of the total carbon about one third of that obtained by plant biomass. The seagrass biomass of 806.3 gDW m<sup>-2</sup>, using the Havelange et al (1997) ratio of 0.34 gC per gram of Dry Weight (gDW), is slightly lower than that reached in the no-flux simulation. This average value is in reasonable accord, also in this case slightly lower, to the *Posidonia oceanica* biomass measured in spring and summer by Barrón et al. (2006) in Magalluf Bay, 859.0 and 880.5 gDW m<sup>-2</sup> respectively, at similar depth and sediment characteristics; the time variations appear lower than those measured during the above study.



Fish biomass of the air-sea numerical experiment is on average  $0.85 \text{ gC m}^{-2}$ , slightly lower than the observed stock of  $0.8 \text{ gC m}^{-2}$  reported for *Sarpa salpa* biomass in Revellata Bay (Houziaux, 1993; Havelange et al., 1997); it is also lower than that obtained in the no-flux numerical experiment. The fish production is  $0.6 \text{ gC m}^{-2} \text{ yr}^{-1}$  of the same order than that reported in Revellata Bay,  $1.2 \text{ gC m}^{-2} \text{ yr}^{-1}$  (Velimirov, 1984; Havelange et al., 1997). The overall seagrass consumption made by the three grazers of the *Posidonia oceanica* reaches  $10.2 \text{ gC m}^{-2} \text{ yr}^{-1}$ .

The refractory carbon gives an annual flux of  $200.5 \text{ gC m}^{-2} \text{ yr}^{-1}$  of the ecosystem toward the benthos. This value is reasonably higher than the experimental outcome of  $139 \text{ gC m}^{-2} \text{ yr}^{-1}$ , in site 10 m depth, obtained by Dauby et al. (1995) in the Bay of Calvi, because of the higher net primary production of the seagrass,  $273.8 \text{ gC m}^{-2} \text{ yr}^{-1}$ , in the model with respect to the experimental production of *Posidonia oceanica* in the same site,  $204 \text{ gC m}^{-2} \text{ yr}^{-1}$  (Dauby et al., 1995; Bay, 1984). Here it should be noted that the carbon content in the deposited matter in the Bay of Calvi was found 33%, very near to the ratio inside the seagrass, which is on average 34% as reported above: this is an indicator of deposited matter made mainly of seagrass blades and scarcely of  $\text{CaCO}_3$ -rich material.

Matte formations in seven Mediterranean stations at the northwestern coast and in the Tyrrhenian Sea were estimated with an average carbon accumulation rate of  $57.8 \text{ gC m}^{-2} \text{ yr}^{-1}$  and average depth of 5 m (Mateo et al., 1997). Combining the above results with the model's annual flux should suggest a deposition in such formations of about 30% of the total refractory carbon originated by the ecosystem and residing in the matte for centennial or longer turnover times.

The variation of pH is about 0.38 around 8.24, obtained as model's acidity average. This yearly excursion is remarkably similar to that obtained by Frankignoulle and Bouquegneau (1990) in a station 8 m depth in the Bay of Calvi by using experimental values covering all seasons. Model's results are affected by a positive shift of about 0.15 in the pH values with respect to the data, while the variabilities are in keeping with standard deviation of 0.1 (0.09 in the daily average data). The no-flux average response

gives lower pH values, in keeping with climatological values in the Mediterranean basin (Maillard and MEDAR Group, 2001; MEDAR Group, 2002) and slightly lower, 0.05, than the average in the above-cited station.

Table 2

	Average	Minimum	Maximum	St. Dev.
<b><i>Posidonia oceanica</i></b>	22845.0 (23780.0)	22106.0 (23084.0)	23479.0 (24383.0)	472.0 (415.0)
<b>Fish</b>	71.0 (72.5)	66.6 (67.1)	75.7 (78.5)	2.6 (3.3)
<b>Total C</b>	92198.8 (95979.2)	91889.0 (95979.2)	92465.4 (95979.2)	160.5 (0.0)
<b>Refractory C</b>	53318.0 (55358.0)	53105.0 (55119.0)	53468.0 (55576.0)	87.0 (111.0)
<b>pH<sub>NBS</sub></b>	8.24 (8.04)	7.99 (7.80)	8.37 (8.20)	0.09 (0.11)

The reasonability of the values in the system has been controlled in every phase of this medium- to long-term numerical experiments and understood in terms both of realistic situations under experimental analysis and potential scenarios considered by CCS recommendations. Examples of these shifts of the responses, to be controlled by means of field data, are lateral inputs of carbon into the system and modifications of the boundary conditions for the total alkalinity.

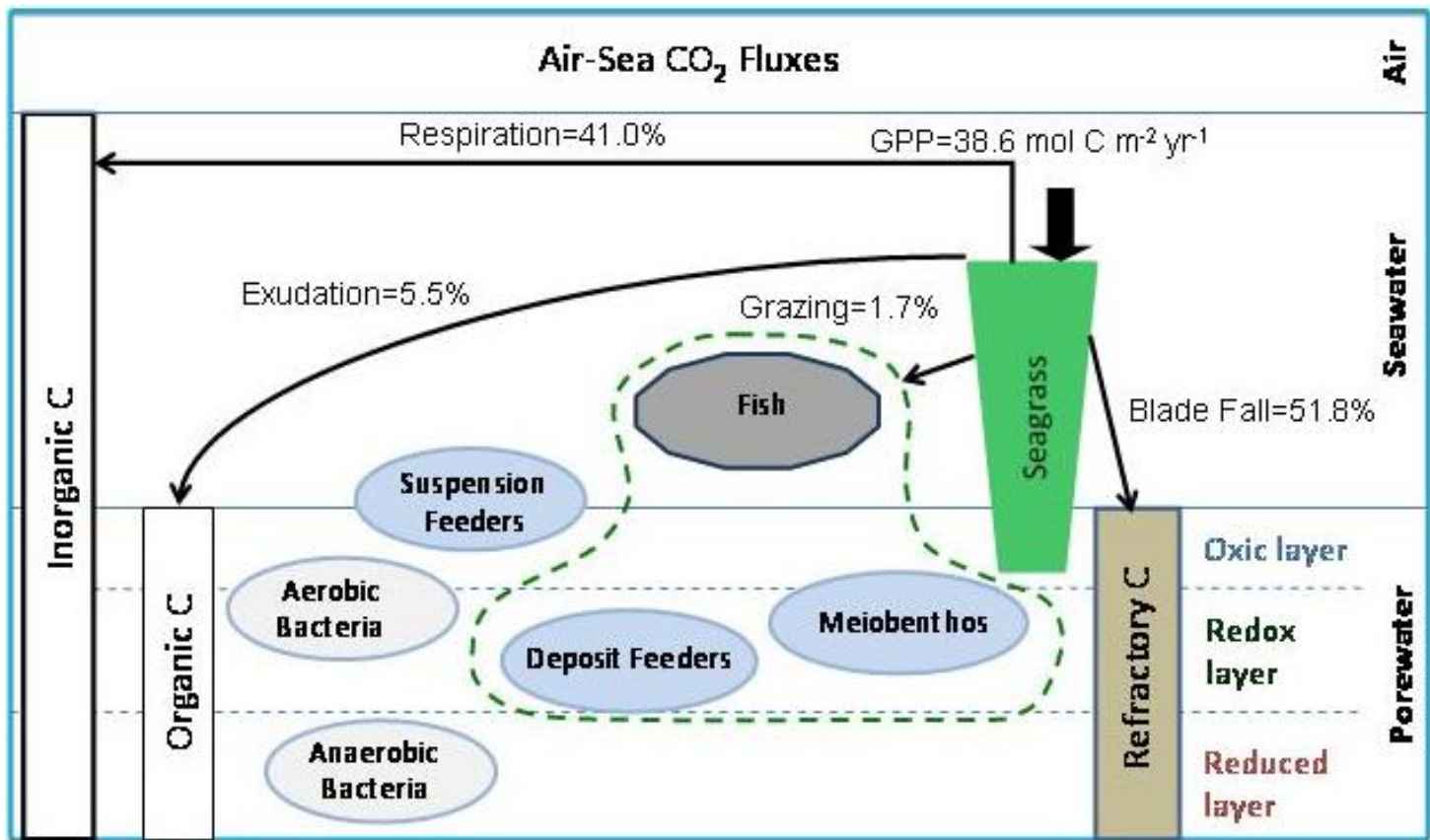


Figure 3

Figure 3 shows the fluxes originated by the seagrass gross primary production, GPP, embedded in the overall ecosystem schematics, in which are resolved the three components of the carbon; the refractory, the organic and inorganic carbon. The biological fluxes can be appreciated considering the percentages, in terms of gross primary production of the seagrass going into specific compartments. The dominant one is that into the refractory carbon, due to seagrass fall of the leaves: in the flux simulation this value is 51.8% more than one half of the GPP, evaluated in 58.6 molC m<sup>-2</sup> y<sup>-1</sup>. Another consistent part of the GPP, 41%, goes in respiration of the seagrass, returning the carbon to the ecosystem. Total grazing, intended as the sum of the three grazing removal from seagrass biomass by fish, meiobenthos and deposit feeders, and exudation are 5.5% and 1.7%, respectively. Secondary production yields 5.6 gC m<sup>-2</sup> yr<sup>-1</sup>, equivalent to 2% as transfer efficiency from the seagrass to higher trophic levels.

On average, the gross primary production is  $1.69 \text{ gC m}^{-2} \text{ y}^{-1}$  per each gC of seagrass biomass present in the ecosystem; net primary production is lower, about  $0.73 \text{ gC m}^{-2} \text{ y}^{-1}$  per each gC of seagrass biomass. These values are consistent with an average net primary production of about 40 in the same units produced on a basin average by Mediterranean phytoplankton.

In this model's ecosystem, the net primary production of the seagrass is twice or more than that of other autotrophs, while the specific net production is less 2% of the phytoplankton one. This suggests, also by numbers, that *Posidonia oceanica* is the dominant species in Mediterranean coastal ecosystems.

Moreover, these values appear in keeping with phenomenological seagrass net primary production results in the order of magnitude of  $100 \text{ g C m}^{-2} \text{ year}^{-1}$  at 10 m depth. In 7 m depth site, the gross primary production has been estimated in a range between 338.4 and  $472.8 \text{ g C m}^{-2} \text{ year}^{-1}$  (Barrón et al., 2006), while net primary production was five time lower in the same site, from 39.6 to  $104.4 \text{ g C m}^{-2} \text{ year}^{-1}$ .

Model's values result even higher because the ecosystem can possibly sustain higher net primary production because of absence of other autotrophs as competitor of the seagrass.

### **3.2. Responses to carbon dioxide leaks**

Two different leaks of carbon dioxide have been applied to the set-up of the model including air-sea fluxes and the results of both cases is here compared to those obtained in the air-sea flux simulation. The chosen leaks are  $1.5 \mu\text{molC m}^{-2} \text{ s}^{-1}$ , equivalent to  $2.1 \text{ kg m}^{-2} \text{ yr}^{-1}$  inflow of carbon dioxide into the  $\text{CO}_2$  leak ecosystem response, and  $3.0 \mu\text{molC m}^{-2} \text{ s}^{-1}$ , i. e.  $4.2 \text{ kg m}^{-2} \text{ yr}^{-1}$  of additional carbon dioxide in the case of high leak simulation. Both leaks have been applied to the ecosystem in long-term numerical experiments and, at the same time, the proper boundary conditions are taken into account. Both leaks are in keeping with the diffuse seepages chosen by Blackford et al. (2008) for long-term simulations: carbon dioxide inflows, consistent with their Seepage-low, were observed during observations of CCS pilot sites, while the Seepage-high treatment was introduced for testing potential environmental modifications in a scenario

subjected to a higher, hypothetical carbon dioxide inflow, one hundred times the real seepages experienced in CCS sites till now.

Chosen leaks of the present work are intermediate with respect to the above-mentioned values and represent two potential scenarios of ecosystem response: our CO<sub>2</sub> leak is less than the average of the two former seepages and our high leak is about two third of their Seepage-high treatment. Analogously, natural sites have been continuously studied for the evaluation of ecosystem behaviour in presence of carbon dioxide inflows from volcanic vents into the water column. In Mediterranean sites of current experimental interest, the natural sites of higher carbon emission contribute with additional diffuse sources even higher than 100 μmolC m<sup>-2</sup> s<sup>-1</sup> (Hall-Spencer et al., 2008; Steinbrückner, 2008), i. e. higher than our high leak.

Table 3

	Average	Minimum	Maximum	St. Dev.
<b><i>Posidonia oceanica</i></b>	25628.6 (25962.7)	24935.9 (25289.7)	26226.6 (26539.3)	442.8 (427.4)
<b>Fish</b>	64.6 (25.4)	62.7 (18.7)	66.4 (33.4)	1.1 (4.2)
<b>Total C</b>	104610.9 (106890.9)	103483.1 (105616.8)	105501.0 (107835.8)	512.4 (537.3)
<b>Refractory C</b>	59491.4 (60158.9)	58919.0 (59451.9)	59884.3 (60616.4)	278.2 (335.9)
<b>pH<sub>NBS</sub></b>	7.16 (6.88)	7.13 (6.86)	7.19 (6.90)	0.02 (0.01)

The performances are higher when considering the seagrass biomass in the case of the leak simulation, in Table 3, with respect to the no-leak one, reported in Table 2. The increase of the average biomass is evident, about 3 molC m<sup>-2</sup>. Another point is that seagrass biomass increases are not linear as introducing new carbon, in fact a plateau is reached and an increase of one tenth is obtained in averaging biomass after doubling the leaked carbon in the second experiment, value in parenthesis of Table 3.

The behavior of the fish is different, because in the carbon leak the fish biomass does not increase in presence of an even higher primary producer, on the contrary fish biomass exhibits some decrease in biomass. Anyway, the big shift in the ecosystem response happens in presence of the high-leak simulation, with average values of the fish biomass dropped toward one third of the reference simulation in Table 2. This cut-off of the fish biomass and the slight decrease experimented in the CO<sub>2</sub>-leak case, suggests that the value of about 7 in pH is the edge between an ecosystem functioning near to the reference situations occurring in the Mediterranean and ecosystem subjected to a shift in the functioning and, possibly, of the biological components.

The value of total carbon does not increase proportionally to the amount of the CO<sub>2</sub> injected into the system because of leaks. We found an increase of 6 molC m<sup>-2</sup> of total carbon for each kg of carbon dioxide per year entered into the pristine ecosystem, but only of 1 molC m<sup>-2</sup> for each additional kgCO<sub>2</sub> entered into the system in the high-leak case. This result constitutes a threshold in the case of carbon leaks reaching 5–6 μmolC m<sup>-2</sup> s<sup>-1</sup> and, when subjected to these very high leaks, the capacity of the ecosystem to incorporate new carbon ends. This threshold value is consistent with that level beyond which the ecosystem undergoes a change. As might be expected, these values should be taken in consideration on average and on long-term applications to similar marine ecosystems.

The capacity of the refractory organic carbon is in line with the above-mentioned behavior of total carbon content in the ecosystem, with 50% percent of the total carbon leak taken up by the refractory compartment in the CO<sub>2</sub>-leak numerical experiment, but only with about 30% of incorporated carbon from additional new carbon in the high-leak simulation.

The average value of the pH is more than 7, 7.16, in the first carbon leak experiment; while the pH level is reduced to a smaller value, 6.88, in the high-leak one, giving a first indication that acidity of the order of 7 represents the value of sill not to be overcome for

maintaining ecological resilience and, in any case, being able to adequately treat the biological compartments by means of short-term recovery.

### 3.3 Potential recovery of the ecosystem

Recovery of the original ecosystem situation has been also investigated, starting after fifteen years of the high-leak numerical experiment.

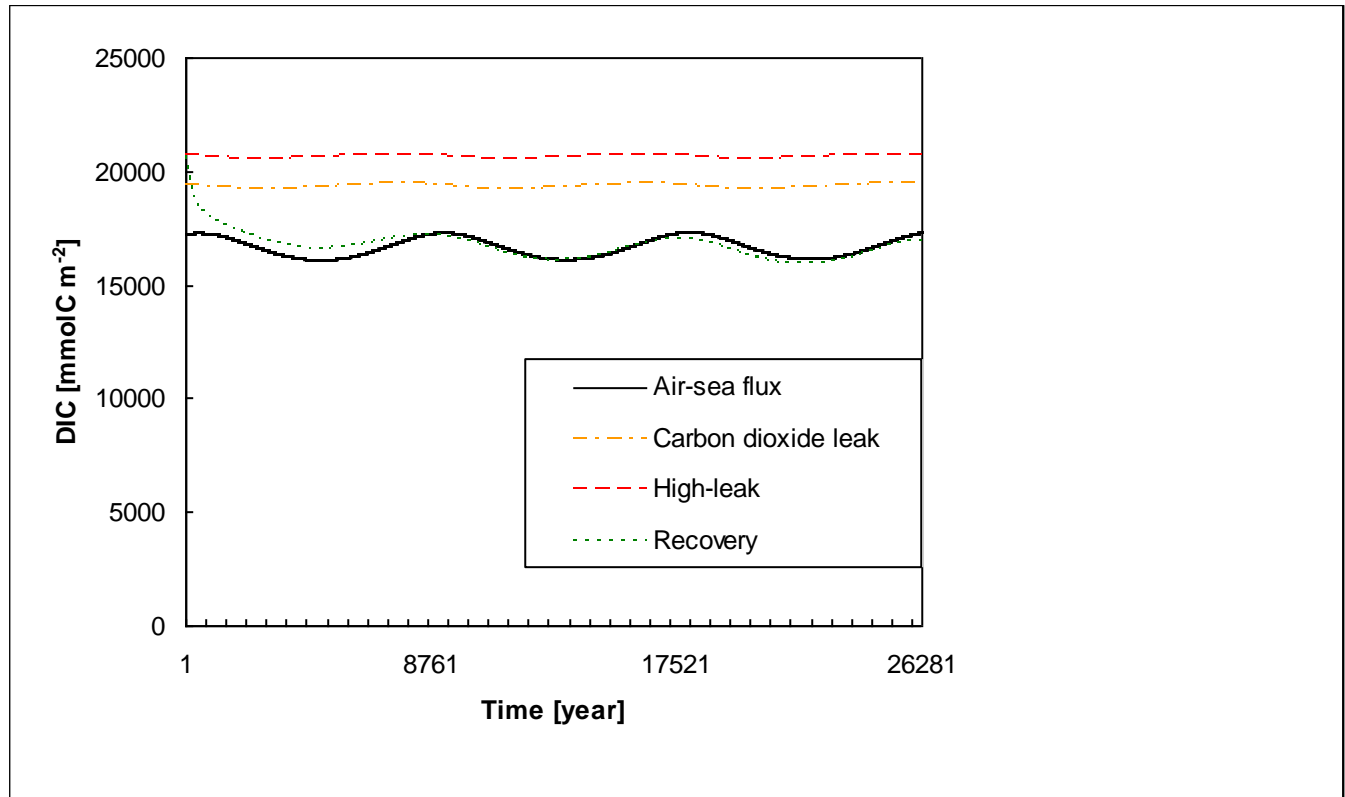


Figure 4

After fifteen year of the simulation, the leak is shut down and the ecosystem is put free to evolve toward the reference situation depicted for years 12–14 in Fig 2b, full line, without carbon leaks. Figure 4 shows the final part of the DIC from fifteen- to twenty-year evolutions of the air-sea and recovery simulations, placed next to the  $\text{CO}_2$ -leak and high-leak ones. The DIC of the recovery starts from the highest values reached in the last evolution and reaches after about 1–2 years the previous values of the reference simulation, full line in Fig. 4. The total carbon, not shown, requires more time for its

recovery, and in these five years is intermediate between the average values in the high-leak and the air-sea flux target simulation.

This scenario of ecosystem recovery is solely potential, because this evolution is based on a hypothetical result after 15 years in continuous conditions of high acidity. This simulation is so long-term that different geochemical variables could be different in terms of variability of the physics, changes of temperature and salinity, of modified boundary conditions, in the sediment or at the interface, and of the biology, with dominance of other species and absence of some species structured in the chosen description.

Comparison with real observations should be incorporated along the evolution of the perturbed environment and for recovering the ecosystem; we have done such a comparison with different surveys performed in different Mediterranean sites and this examination does not produce any relevant anomalies of the geochemical variables in any simulation, thus reducing the uncertainties in the geochemical method results.

#### **4. Discussion**

The model's results obtained by these numerical experiments ought to be considered preliminary because of simplified boundary conditions. They should be subjected to more refinement of the benthic chemical interactions. Oxygen and nitrogen species introduce complexity in biogeochemical descriptions like nitrogen and phosphorus cycling. Hydrogen sulphide and magnesium calcite take into account concurrent biomass growth, epiphyte role and impact of seawater acidity on sea urchins.

These simulations in the choice of limited complexity in the description of the ecosystem show the consistency in the long-run of the geochemical system characterizing carbon dioxide aquatic species and related variables. The generality of the method assure convergence of the chosen geochemical methods and model's results



confirm that it can be successfully used for environmental and management purposes, i. e. for addressing different situations externally forced as well as semi-closed systems, spanning from few weeks up to several years. The latter simulations are deemed possible, but at the price of controlling environmental conditions, possibly eroding dissolved inorganic carbon profiles and thus generating a shift of the seawater acidity in the ecosystem model. For overcoming this major shift, the carbonate concentrations ought to be controlled by experimental profile data.

Moreover, in the cases of temporal variabilities of the field of mass, there is need to control the apparent dissociation constants, water solubility constants and piston velocities of the air-sea exchanges. Complex vertical and horizontal geometries must be adequately followed through the physical characteristics of ecosystems, like temperature and salinity profiles, for giving rise to the seawater circulation and tracers dynamics. Finally, other chemical species, considered important in the involved biogeochemical processes, may take a straightforward role in the proposed algorithm.

The feasibility of the benthic food web we have designed in Mediterranean ecosystem with average values and conditions for the growth of the dominant species is shown in the long-run with consistent values of the overall carbon system. Biomasses of the seagrass primary producer are in keeping with dry weight measures in sites at similar depth, giving generally higher values and reduced seasonal variability, in line with the mean condition of temperature. Fish compartment shows, at the same time, reasonable results according to wet weight measures; anyway other variables, firstly biological parameters in terms of seagrass production and partition of the growth, and presence of the involved communities, such as sea urchins and suspension feeders, should be verified in terms of acquired data in the ecosystem to guarantee control and possibly correction of the model's results during long-term simulations. In fact, the real conditions can be modified by external loads and altered by external conditions at the large boundary.

The evolution of the simulated ecosystem presents features in keeping with observed coastal surveys in terms of order of magnitude of the primary productions of the seagrass and secondary one of the fish and of a reasonable shift of the pH toward higher values in the case of air-sea fluxes without carbon leaks.

The critical values for the ecosystem are reasonable and are given comparing the no input simulations with the high-leak scenario. Significant deviations appear in the case of pH less than 7 and this is a result of the overall integrated model, considering also that the impact on fish has been resolved in term of the sum of hydrate carbon dioxide and seawater carbonic acid.

Another difference between data and model appears in the average pH, while the natural variability is in keeping with the data. The variabilities seem to cooperate to obtain averages more similar to the experimental situation observed by (Frankignoulle and Bouquegneau, 1990), because we acknowledge a lower pH and other values are in keeping. Thus in the Bay of Calvi, some lateral input or benthic carbon inflow should be introduced in the model for giving a consistent description of that coastal ecosystem: local fluxes of  $100\text{--}150 \text{ nmolC m}^{-2} \text{ s}^{-1}$ , about one tenth of the  $\text{CO}_2$ -leak, should induce higher values of pH, obtained after filtering out diel variabilities, and this hypothesis ought to be carefully controlled through air-sea carbon fluxes.

For these specific applications, the recovery is recognized possible but it is not very fast, requiring about two years for recovering values similar to the pristine carbon system and reassessing, after about five years from the excessive carbon intrusion events, biomasses in line with the no  $\text{CO}_2$  input ecosystem. Thus, the total carbon reaches rapidly its bulk contents, but biological species require consistent time lag for completing their recovery.

In any case, the assured stability of the geochemical methods, that guides all the components of the ecosystem, does not assure that also other components of the ecosystem would be well represented automatically; in our opinion they should require surveys in the sites of interest and laboratory analyses.

Further improvements of the ecosystem model should be the shading by phytoplankton, which has been considered at this developmental stage and at least in one-dimensional approach, and the proper limitations by nutrients other than carbon, considering also nitrogen and phosphorus.

The time-dependent description of the *Posidonia oceanica* growth, given in this work, and the realistic interaction with the environment, reported after the cited experimental works, suggest the numerical introduction of three additional, but potentially important, effects of physical forcing. They are: diel evolution of the photosynthetic available radiation and their impacts, adaptation of the seagrass to new optimum light depending on the seasonal temperature variability and vertical migration of the necton.

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## **Appendix**

The marine higher trophic levels, in particular species of demersal and benthopelagic fish, are affected by increases in the concentration of CO<sub>2(aq)</sub> and corresponding increases in the partial pressure of carbon dioxide. Cardiac failure is the primary disturbance induced by high CO<sub>2</sub> levels and another is enhanced ventilation for removing accumulated CO<sub>2</sub> (Pörtner et al., 2004).

The two cited meta-analyses (Hendricks et al, 2010; Kroeker et al., 2010) base their results on studies of the effects of carbon dioxide on embryos and larvae; therefore, we have also considered experiments on postsmolts and juvenile fish, followed during their growth in controlled seawater environments, with the objective of characterizing quantitatively the impact on adult individuals.

As a result of the effects found in these experiments, different fish species exhibit reductions in their growth rates at high carbon concentrations; in reality, these generalized effects emerge from review papers about this topic on fish both in open and at coastal seas, on fish that feed on plankton and at seabed, on saltwater and freshwater fish species (Ishimatsu et al., 2005; Melzner et al., 2009).

The compartment in the ecosystem model has bentopelagic behavior and then it is discussed starting from effects found in herds in seawater in the cases of *Salmo salar* L. postsmolts (Fivelstad et al., 1998) and *Anarhichas minor* Olafsen juveniles (Foss et al., 2003). The salinities of these experiments were 34 for the former and 33 for the latter, near to the ocean average salinity and somewhat lower than that in the Mediterranean Sea; salinities were kept constant during the experiments and continuously maintained by seawater influx.

The *Salmo salar* experiment (Fivelstad et al., 1998) has been analyzed in the present work by using the results of Forsberg (1995) obtained in relation to the weight and temperature and regardless of the photoperiod, for what regards the control group exposed to 1.3 mg CO<sub>2</sub> l<sup>-1</sup>. This group exhibited a metabolic rate of 0.0109 d<sup>-1</sup> according to the average growth observed along the 43 days of the experiment. This metabolic rate has been modulated to achieve the specific growth rate observed in the treatment group with 10.6 mg CO<sub>2</sub> l<sup>-1</sup>, without mortality, and in the two groups treated with CO<sub>2(aq)</sub> concentrations equal to 26.0 and 44.0 mg CO<sub>2</sub> l<sup>-1</sup>, in which the mortalities reached, respectively, levels of 1% and 4.3 %.

These modulations have been performed making them proportional to the average oxygen consumptions observed in the respective experiments: in fact this behaviour was

attested by statistical proportionality of oxygen consumption to the average fish exudation of CO<sub>2</sub> (Thorarensen and Farrell, 2011).

Figure A1 shows the growth rates for the four considered concentrations, after normalization to the growth rate as obtained in the control group, and they are respectful

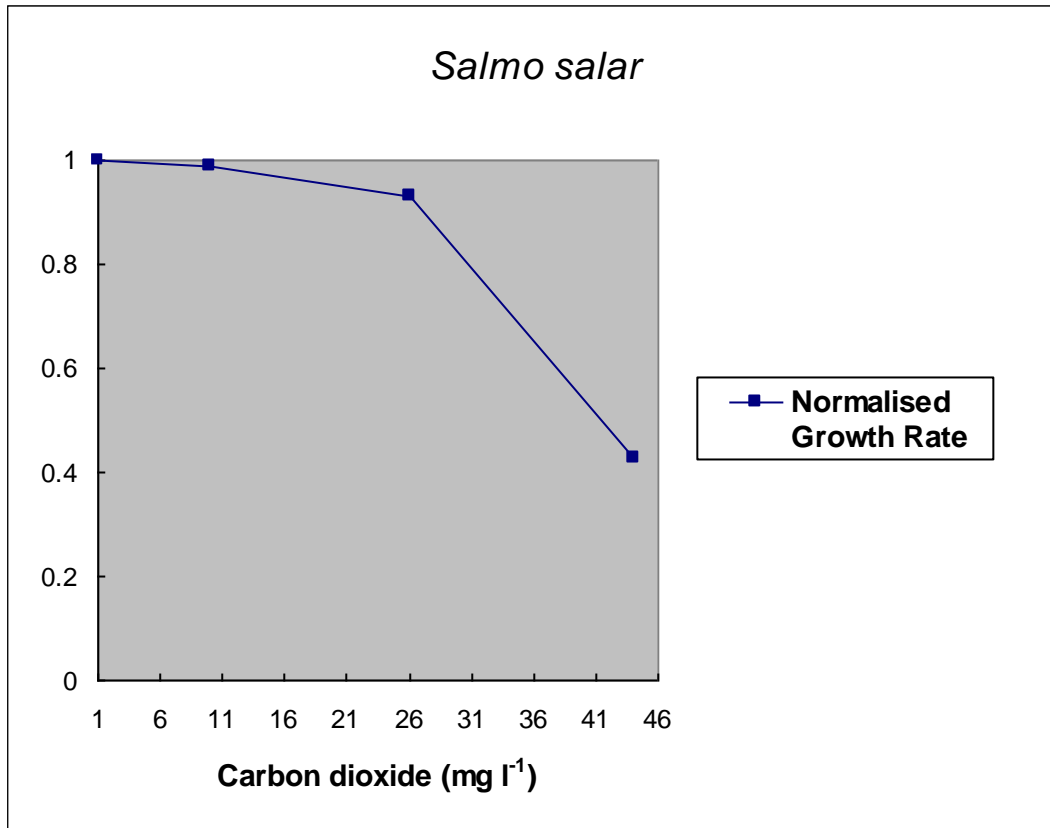


Figure A1

to the specific growth rates measured in the open flow system groups. The behavior of the normalized growth rates exhibit a decrease progressively more pronounced up to an effect of approximately 45% cut of the growth in correspondence to the highest concentration of 44.0 mg CO<sub>2</sub> l<sup>-1</sup>. It should be noted that the deviations from the reference value in the cases of the two intermediate concentrations are reduced, but still appreciable; their significance remain to be confirmed taking into account a number of replicates higher than the two performed during the experiment by Fivelstad et al. (1998).

The *Anarhichas minor* results have been analyzed according to a pattern of growth without mortality, since mortalities were not found in the four duplicate groups (Foss et al., 2003). The selections of individuals covered by the protocol provided on days 0, 28, 49, 70 have been taken into account. As reference data, the total food consumptions have been considered, understood as the total of the food ingested during the three experimental periods, one of 28 days and the other two of 21 days, and treated with respect to the control group reared at  $1.1 \text{ mg CO}_2 \text{ l}^{-1}$ . The daily growth rates have been calibrated with respect to the total food consumptions in each of the three duplicate groups at 18.1 , 33.5 and 59.4  $\text{mg CO}_2 \text{ l}^{-1}$ . Finally, the exudation rates have been controlled by referring them to the average values of the daily food rates found in the four treatments and the final behavior has been optimized in relation to the reference value of the daily food rate found in the control group.

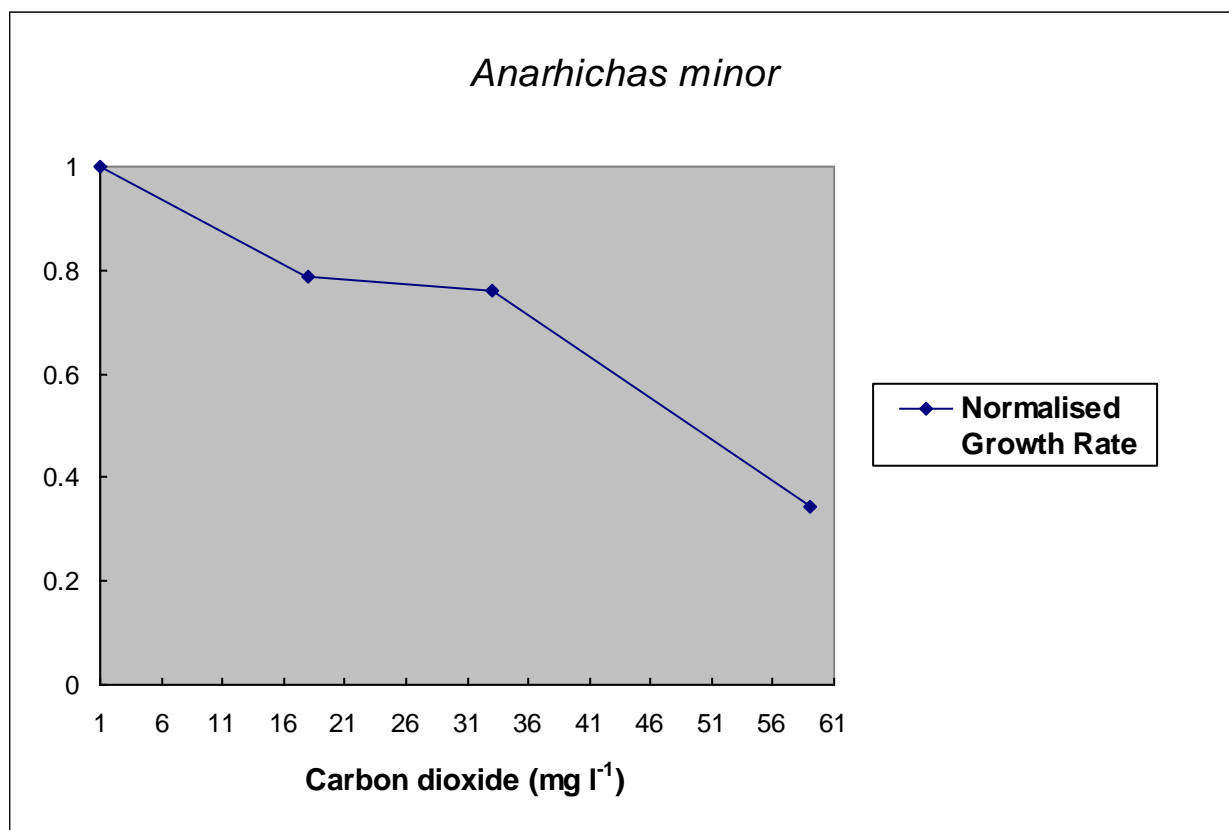


Figure A2

Our analysis, shown in Figure A2, is respectful to the specific growth rates measured in these shallow raceway experiments (Foss et al, 2003).

The regression, made considering the pool of all the normalized growth rates, gives the regression of the growth rate for the fish,  $k'_{gr}$  with respect to  $CO_{2(aq)}$

$$k'_{gr} = k'_{mgr} (-0.0116 \cdot CO_{2(aq)} + 1.07)$$

where  $k'_{mgr}$  is the maximum growth rate. The coefficient of correlation is -0.93. Growth rates greater than one have been normalized to the maximum growth rate.

Results by Smart et al. (2001) and by Cock and Pick (1999), reviewed by Ishimatsu et al. (2005; Table 2) for determining the impact of the carbon dioxide, respectively, on the trout and the salmon, have been also evaluated, giving similar results when increasing carbon dioxide. These growths have not been used in the regression, because they are related to freshwater species and therefore not representative of the ranges of salinity found in both coastal and deep-sea marine waters. Moreover, some results about a typical Mediterranean Sea fish, *Sparus aurata*, gave, as reported in impacts on food web section, effect levels of the fish metabolism similar, if not greater, than the normalized growth rates here estimated.

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## Figures captions

Figure 1. Optimized  $I_{\text{sur}}$  radiation, full line, and the monthly averaged data, diamonds; averages, AVE, is the same in the data and in the interpolating line, and STD is the standard deviation between data and interpolation.

Table 1. Food web matrix: Preferences of faunal species are given in the food web matrix and efficiencies are indicated in parentheses.

Figure 2. Three-year evolutions of the Total Carbon, higher plate a), Seagrass Biomass and Dissolved Inorganic Carbon, lower plate b), after the eleventh year with atmospheric fluxes, thin and thick full lines, and without atmospheric exchanges, dotted and dashed lines.

Table 2. Averages of vertically integrated Seagrass and Fish biomasses, Total Carbon, Refractory Carbon standing stocks,  $\text{mmolC m}^{-2}$ , and pH during the ten-year after the eleventh year simulation; no air-sea flux statistics are in parentheses.

Figure 3. Food web schematics with biochemical flux percentages of the gross primary production in the case of the air-sea simulation; the seawater geochemistry is depicted aside, vertical bars.

Table 3. Averages of vertically integrated Seagrass and Fish Biomass, Total Carbon, Refractory Carbon standing stocks,  $\text{mmolC m}^{-2}$ , and pH in the ten years after the eleventh in the cases of CO<sub>2</sub>-leak and high-leak.

Figure 4. Evolution of the Dissolved Inorganic Carbon during the three-year simulation from 16 yr to 18 yr after recovery at the end of the fifteenth year of the high-leak simulation; air-sea, CO<sub>2</sub>-leak and high-leak evolutions are also shown in the same years.

Figure A1. Normalized growth rate of *Salmo salar* L. in the case of the four treatments of seawater carbon dioxide, CO<sub>2(aq)</sub>, at 1.3, 10, 27, 44  $\text{mgC l}^{-1}$ .

Figure A2. Normalized growth rate of *Anarhichas minor* Olafsen in the case of the four treatments of seawater carbon dioxide, CO<sub>2(aq)</sub>, at 1.1, 18.1, 32, 59  $\text{mgC l}^{-1}$ .