

RESEARCH ARTICLE

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Key Points:

- Carbon budget in the northern Adriatic Sea was calculated for February 2008
- Results are consistent with previous estimates of NAd winter oligotrophy
- The correct assessment of the BBL role in carbon cycling needs further study

Supporting Information:

- Readme
- Text S1

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The carbon budget in the northern Adriatic Sea, a winter case study

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Abstract This paper presents a winter carbon budget for the northern Adriatic Sea, obtained through direct measurements during two multidisciplinary cruises and literature data. A box model approach was adopted to integrate estimates of stocks and fluxes of carbon species over the total area. The oligotrophy at the basin scale and the start of primary productivity well before the onset of spring stratification were observed. In winter, the system underwent a complete reset, as the mixing of water masses erased any signal of previous hypoxia or anoxia episodes. The northern Adriatic Sea was phosphorus depleted with respect to C and N availability. This fact confirms the importance of mixing with deep-sea water for P supply to biological processes on the whole. Despite the abundant prokaryotic biomass, the microbial food web was less efficient in organic C production than phytoplankton. In the upper layer, the carbon produced by primary production exceeded the fraction respired by planktonic community smaller than 200 μm . On the contrary, respiration processes prevailed in the water column below the pycnocline. The carbon budget also proved that the northern Adriatic Sea can be an effective sink for atmospheric CO_2 throughout the entire winter season.

1. Introduction

The Adriatic Sea, and especially its northern basin, is certainly one of the most studied regions of the Mediterranean for environmental, geographical, historical reasons that define its great economic and cultural value for all bordering countries: Italy, Slovenia, Croatia, Bosnia-Herzegovina, Montenegro, Albania, and Greece. Physical features and water masses of the Adriatic Sea are well known [Cushman-Roisin *et al.*, 2001], and they define a circulation pattern that is primarily controlled by horizontal density and salinity gradients which are derived from the mixing of southeast high-salinity waters and northwest riverine waters.

The Po River, with its load of nutrients and allochthonous organic and inorganic carbon, is the principal continental source, contributing with about $44.5 \text{ km}^3 \text{ yr}^{-1}$ of fresh water input [Cozzi and Giani, 2011] and $13 \times 10^6 \text{ Mg yr}^{-1}$ of sediments [Syvitski and Kettner, 2007] that greatly influence the carbon budget of water masses over the 100 m isobath [Frignani *et al.*, 2005]. The resulting western low-salinity surface layer spreads onshore or offshore in relation to the intensity of river discharge and of available energy for mixing. Similarly, the cyclonic Adriatic current confines active sedimentation areas near the coast and south of the Po River mouth [Ravaioli *et al.*, 2003], where both particulate and dissolved organic (POC and DOC) and inorganic carbon (PIC and DIC) can be buried in, or released by bottom sediments.

In spring, when the surface stratification is set up, nutrient inputs from both river discharges and atmospheric precipitation can, under favorable irradiance conditions, give rise to phytoplankton blooms, which make the northern Adriatic Sea a very productive area and a site of carbon uptake. In addition, during summer and fall, the simultaneous occurrence of water column stability and biomass accumulation can sometimes lead to conditions of hypoxia or anoxia in near-bottom waters and coastal zones in proximity of the Po River delta. In recent decades eutrophic phenomena have diminished [Giani *et al.*, 2012] while outbreaks of massive mucilage aggregates (caused by the uncoupling between organic C production and prokaryotic C demand) [Fonda Umani *et al.*, 2007] increased. DOC production/accumulation plays a substantial role in the

environmental preconditioning of mucilage outbreaks [Giani *et al.*, 2005]. The development of a “closed” circulation in summer due to formation of an anticyclonic gyre and stable vertical stratification of the water column seem to be essential environmental conditions for mucilage formation and accumulation to nuisance levels [Supić *et al.*, 2004; De Lazzari *et al.*, 2008].

All these factors underline the importance of processes taking place in the Adriatic Sea and their role across the entire Mediterranean area: first, the Adriatic Sea is site of dense water formation and of CO₂ dissolution from the atmosphere, and second, the continental shelf pump in the shallow and highly productive northern Adriatic Sea plays an important role in carbon cycling and ocean acidification. Dense waters form in the northern Adriatic Sea under the dominant influence of strong and cold winds like the Bora [Boldrin *et al.*, 2009] thus allowing annual bottom water ventilation and renewal [Russo *et al.*, 2005]. This mechanism is responsible for the CO₂ sequestration and acidification of deep waters [Luchetta *et al.*, 2010] and, together with the deep convection occurring in the southern Adriatic [Civitaresse and Gacic, 2001], makes this an important contributor to the Eastern Mediterranean Deep Water and to the whole Mediterranean circulation, and it is expected to have an impact on climate variability [Marty *et al.*, 2002] and biogeochemical characteristics [La Ferla and Azzaro, 2004].

This paper focuses on the carbon budget of northern Adriatic Sea estimated during winter conditions. Two multidisciplinary cruises were carried out in February 2008 (water column hydrological and biological parameters) and October 2008 (sediment parameters). In order to improve our knowledge of the biogeochemical functioning of the northern Adriatic Sea, a box model approach has been adopted to integrate experimental measurements of stocks and fluxes of carbon species over the whole area. This approach permits an overview of the studied environment that can be compared with the outputs of numerical models. Moreover, this box model highlights some lacks of knowledge about both processes and stocks used during this approach, making their assessment goals for future work. A similar approach, starting from experimental data, has been proposed by Najjar *et al.* [2010] for a preliminary synthesis of the carbon budget over Eastern USA continental shelf.

2. Material and Methods

2.1. Sampling Strategy and Analyzed Parameters

Seawater physical, chemical, and biological parameters were measured at 32 stations (Figure 1). The sampling design was developed in order to: (i) quantify stocks and fluxes of C cycling in the northern Adriatic Sea, from the Gulf of Trieste, in the north, until the 100 m isobath in the south and (ii) compute the water exchange with the central Adriatic basin across the southern open border.

Sediments were instead sampled over a different set of stations because of the different spatial and temporal scales involved in the sedimentary processes (Figure 1).

All field measurements were performed during two cruises: the first (14–27 February 2008, cruise VECSES1), mainly concerning seawater and sediment samplings, was carried out on board of R/V *Urania*, while the second (9–15 October 2008, cruise VECTOR632) was devoted to the study of early diagenesis processes and benthic flux data on board of R/V *Dallaporta*.

Hereafter, a brief description of sampling procedures and analyzed parameters is reported. Further details relative to analytical methods can be found in the supporting information.

2.1.1. Physical Seawater Properties

Profiles of seawater pressure, temperature, and salinity were measured along the water column using a conductivity-temperature-depth (CTD) Seabird SBE 911-plus probe. The probe was equipped with sensors for measuring fluorescence (Chelsea Aqua 3), dissolved oxygen concentration (SBE 43), the ratio between photosynthetically active radiation (PAR), along the water column and surface PAR value (Biospherical/Licor), and light transmission. Corresponding profiles of water density excess ($\sigma = \text{in situ water density} - 1000 \text{ kg m}^{-3}$) have been calculated using Java Ocean Atlas as a function of pressure, temperature, and salinity. Two types of acoustic Doppler current profilers (Ocean Surveyor 75 kHz, cell size 16 m; and Workhorse 300 kHz, cell size 8 m), mounted on the ship hull, measured current velocity profiles along the ship's track. Due to the large vertical cell size and the surface and bottom “blind” layers of the acoustic instrumentation, very few cells were valid for current measurements in this shallow region (see supporting information for details).

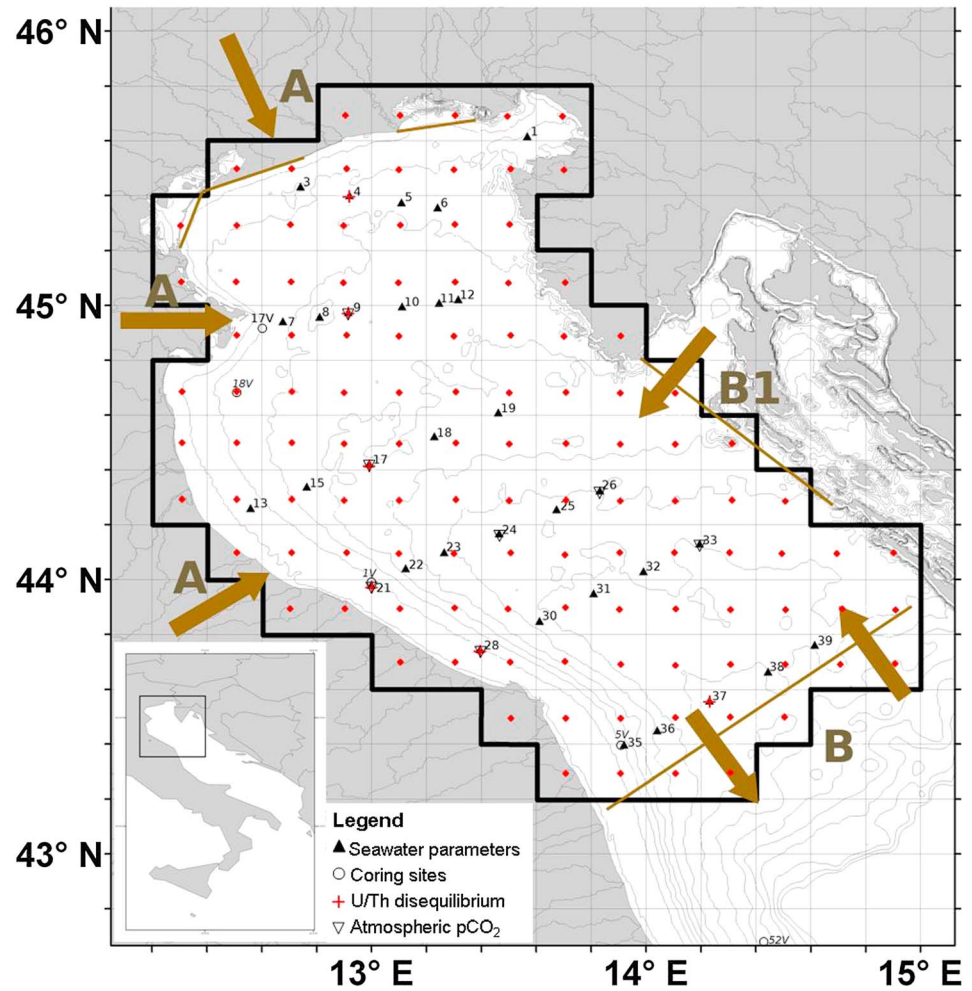


Figure 1. Map of the sampling stations (black triangles = hydrological stations; white circles = sediment samplings) and display of the box subdivision with the virtual grid centers (red squares). Physical boundaries of the study area are also shown (straight lines), together with river inputs (A), input and output across the southern open border (B), and inputs from the east Croatian islands' line (B1).

2.1.2. Chemical Seawater Parameters

Hydrocasts were performed at 32 hydrological stations, sampling seawater at 3–13 discrete depths, depending on bottom depths. Water sampling was carried out by means of a carousel rosette General Oceanics mod. SA1–241 equipped with 24 Niskin bottles of 10 L capacity. Chemical parameters for the definition of the carbon cycling in the northern Adriatic Sea included the following: total alkalinity, pH, and carbonate system species, i.e., CO₂ partial pressure and activity, HCO₃ and CO₃ concentrations, DIC, saturation states for Aragonite (Ω_{arag}) and Calcite (Ω_{calc}), DOC, and POC. Other chemical parameters such as dissolved oxygen, nutrients (NO₃, NO₂, NH₄, PO₄), and Si(OH)₄ were sampled in support of chemical and biological determinations (see supporting information for details).

2.1.3. Biological Seawater Parameters

Several biological parameters were measured from hydrocast samples, in order to provide estimates of biological stocks and transfer processes for the carbon balance in the northern Adriatic Sea. Details of analytical procedures are reported in the supporting information which represents an essential integration to the paper. The following parameters were quantified: phytoplankton abundance and biomass, chlorophyll-*a* (chl-*a*), microzooplankton abundance and biomass, heterotrophic prokaryotic biomass (including archaea and bacteria), particulate and dissolved primary productivity, prokaryotic heterotrophic productivity, extracellular enzymatic activity, and electron transport system respiratory activity. Values of actual prokaryotic heterotrophic productivity (as real rate), actual exoenzymatic activity, and total community

respiration (with its splitting up among prokaryotic, phytoplankton, and microzooplankton fractions) have then been respectively calculated (see again the supporting information).

2.1.4. POC Vertical Fluxes

The sedimentary flux of POC was estimated at six of the 32 hydrological stations (Figure 1), through the direct measurement of dissolved and particulate ^{234}Th on large volume filtrations and the definition of ratios between the inventories of measured POC and total ^{234}Th (see supporting information for details).

2.1.5. Sediment POC and PIC Accumulation

Gravity cores were collected by means of the SW104 corer [Magagnoli and Mengoli, 1995] at five stations along the western, muddy side of the central and northern Adriatic Sea, between the Po River submerged delta and the Mid-Adriatic Depression (Figure 1).

2.2. Cell and Box Subdivision and Grid Interpolation for the Water Column

In order to evaluate total stocks and fluxes of carbon species, the study zone has been divided in 114 cells of $0.2 \times 0.2^\circ$ of latitude and longitude. The surface sea area of each cell has been calculated, as well as its mean depth, using the General Bathymetric Chart of the Oceans (GEBCO) One Minute Grid bathymetry (version 1.00) extracted with "GEBCO Centenary Edition software interface" (<http://www.bodc.ac.uk/gebco>). Subsequently, the water volume has been computed in each cell and the position of its geographic center was defined, obtaining in such way a regular virtual grid of 114 stations (Figure 1).

The values of temperature, salinity, and water density excess (σ), measured by CTD in 32 stations at selected levels (0, 5, 10 m, etc.), were horizontally interpolated adopting the SURFER software package (Golden Software, Inc.). Then, the interpolated values were assigned to the centers of the 114 cells at the same levels. Thus, each cell was characterized by its vertical properties, which were subsequently used to derive its average hydrological characteristics. From the T - S diagram it was possible to distinguish, if present, an upper mixed layer from a deep mixed layer, on the basis of seawater density: $\sigma < 29.0$ for the upper mixed layer and $\sigma > 29.0$ for the deep mixed layer (Figure 2).

The chemical and biological parameters measured in the hydrological stations were first linearly interpolated to obtain regularly 5 m spaced vertical profiles, then, similarly to physical parameters, horizontally interpolated with the SURFER package over the virtual grid of 114 cell centers.

Summarizing, the final result of this procedure has been to set up of a grid of physical, chemical, and biological values, regularly spaced both in the vertical direction, every 5 m, and on the horizontal plane, every 0.2° of latitude and longitude. Subsequently, amounts and weighted mean values of these parameters were calculated in the upper mixed layer and in the deep mixed layer of each cell, as well as their total amount in the upper mixed layer (box 1) and in the deep mixed layer (box 2) over the whole study zone.

2.3. Evaluation of Riverine Inputs

Riverine inputs flowing into the northern Adriatic Sea (A, Figure 1) are derived from Cozzi and Giani [2011] and Frignani *et al.* [2005]. The loads of organic and inorganic carbon for many of the minor rivers flowing in the northern Adriatic Sea are poorly studied or sometimes unknown. In this case our estimates were derived from average values or concentrations from nearby rivers.

The cumulated discharge of freshwater during February 2008 has been estimated on the basis of the mean daily flows. The discharge F of each nutrient has been estimated by assuming a linear relationship between the concentration and the water flow:

$$F \text{ (Mmol m}^{-3}\text{month}^{-1}\text{)} = C_d 10^{-9} \cdot Q_{\text{month}}$$

where C_d = daily concentration of species expressed in $\mu\text{mol L}^{-1}$ (measured or from literature) and Q_{month} = cumulative water discharge in February 2008 obtained as the sum of the daily mean discharges expressed in $\text{m}^3 \text{month}^{-1}$. Monthly flows and POC and DOC inputs from rivers can be found in the supporting information.

2.4. Evaluation of Across-Border Transports

The measured current profiles across the open southern boundary did not extend over the entire area of section B (Figure 1). Moreover, the measured vertical resolution was also low. Therefore, in order to estimate currents at the entire section B, we used numerically modeled daily current velocity values. Northern Adriatic

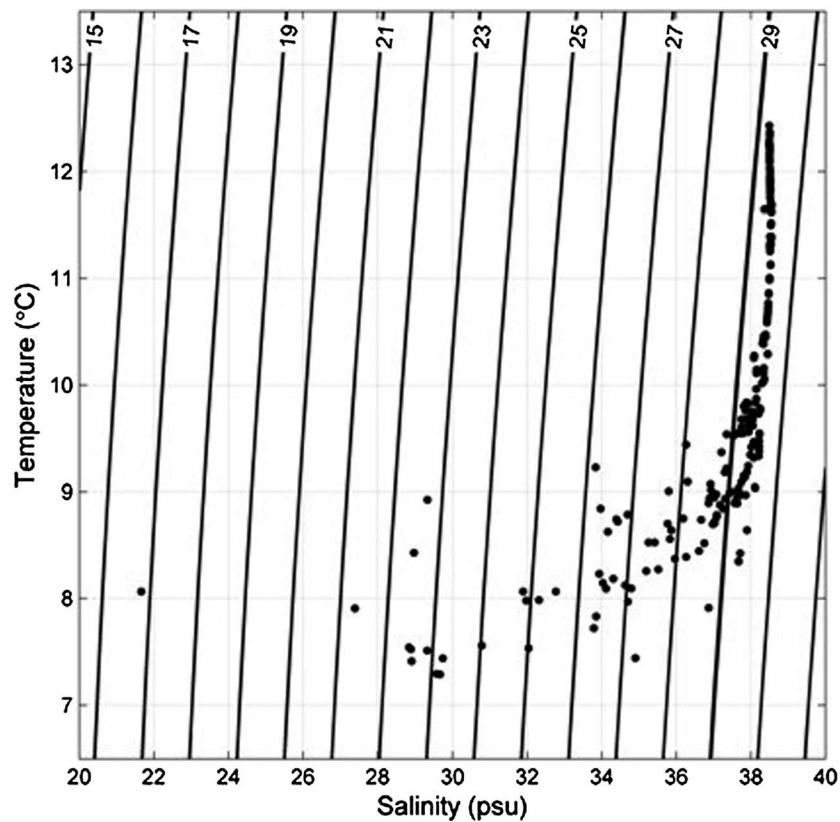


Figure 2. T/S diagram of all hydrological stations with highlighted the isopycnal line of $\sigma = 29.0$ separating the upper mixed layer and the deep mixed layer.

Sea current patterns for the month of February have been modeled by ROMS (Regional Ocean Modelling Systems) [Shchepetkin and McWilliams, 2005] kindly provided by Aniello Russo. The description of the model with all its details can be found in Russo et al. [2009]. Within the northern Adriatic Sea current pattern, just values along section B have been extracted, in order to calculate the exchange of water mass, heat, carbon, and nutrients across the southern border B (Figure 1). Model results have been first compared with the direct measurements obtained during the cruise (see section 2.1.1). Model current values across transection B (Figure 1) have been interpolated over a finer grid with a 200 m horizontal step and a 1 m vertical step. This enabled us to calculate the volume transport avoiding bias due to the coarse division of the box model. Daily values have then been averaged to obtain a value representative for the entire month of February.

Table 1. Physical and Chemical Parameters of the Study Area as Upper Mixed Layer (UML), Deep Mixed Layer (DML), and Total Northern Adriatic Sea (Total), Consisting in 114 Cells Covering the North Adriatic Basin ($G = 10^9$; $P = 10^{15}$, According to the SI Units)

	Units	UML	DML	Total
Total surface	km ²	13,622	29,370	33,836
Volume of seawater	Gm ³	135.147	1,374.948	1,510.095
Mass of seawater	Pg	138.962	1,415.387	1,554.349
Seawater temperature	°C	8.71	11.10	10.89
Salinity	psu	36.35	38.41	38.23
Seawater density	kg/m ³	1,028.22	1,029.41	1,029.30
Total alkalinity	μmol/kg	2,705.5	2,655.9	2,660.4
pH (situ)	total scale	8.201	8.164	8.167
fCO ₂	μatm	305.1	326.4	324.5
Ω aragonite	ratio	3.19	3.20	3.20
Ω calcite	ratio	5.01	5.00	5.01

Table 2. Mean Values and Standard Deviation of Atmospheric Parameters Measured During the Cruise of R/V *Urania*

	Units	Replicates	Mean Values for the Period 16–19 February 2008
Air temperature	°C	7	6.9 ± 2.8
Barometric pressure	hPa	7	1,031.7 ± 4.4
Atmospheric pCO ₂	µatm standard	13	399.8 ± 4.4

Mass/nutrients/heat transports have finally been evaluated interpolating the measured values over the same spatial grid and multiplying them by the velocity perpendicular to the transect area. In order to obtain mass transports of salt and heat loss, salinity and temperature have been multiplied by density and by density × specific heat, respectively. Once the water volume transport had been evaluated across section B, the river runoff by tributaries denoted by A (Figure 1) was added. Then the imposition of volume conservation in the area, permitted the calculation of inflow from the eastern border B1 (Croatian Island line, Figure 1), assigning to this partial volume of seawater the same physical and chemical features as for the easternmost cell of the southern B border.

2.5. Atmospheric pCO₂

Air pCO₂ was measured in duplicate at seven stations (Figure 1) [S. Piacentino, personal communication, 2008] to obtain a north–south direction trend. The mean air pCO₂ value was then used to establish the thermodynamic disequilibrium of pCO₂ at the atmosphere-sea surface interface.

3. Results

The general strategy employed was based on the LOICZ_IGBP (Land Ocean Interaction Coastal Zone–International Geosphere Biosphere Program) approach, at least in its initial guidelines. First, the physical boundaries of the system of interest have been defined to calculate their extent as a sum of cell areas and volumes. Second, total upper mixed layer (box 1) and deep mixed layer (box 2) water volumes have been also calculated (Table 1) taking into account the thickness of the two layers in each cell. Some average physical and chemical characteristics of the studied basin (seawater temperature, salinity, density, total alkalinity, pH (situ), CO₂ fugacity (fCO₂), apparent oxygen utilization, Ω_{arag}, and Ω_{calc}) have been also calculated dividing the sum of total quantities of each cell by the volume or mass of the seawater of the upper mixed layer and the deep mixed layer in the studied area (Table 1). The meteorological conditions (air temperature, barometric pressure) during the R/V *Urania* cruise, which were recorded at several stations together with the atmospheric pCO₂ and their mean values, are reported in Table 2.

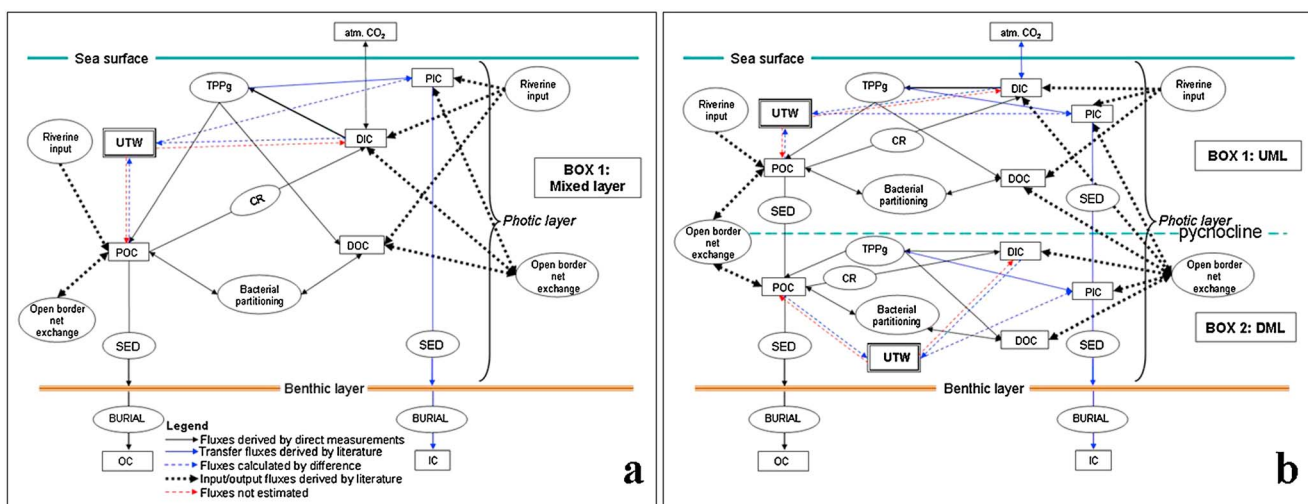


Figure 3. Conceptual models of the carbon cycling: (a) mixed—not stratified water column; (b) stratified water column where an upper mixed layer (UML) and a deep mixed layer (DML) can be defined. UTW = upper trophic web. SED = sedimentation. TPPg = gross total primary production. CR = community respiration.

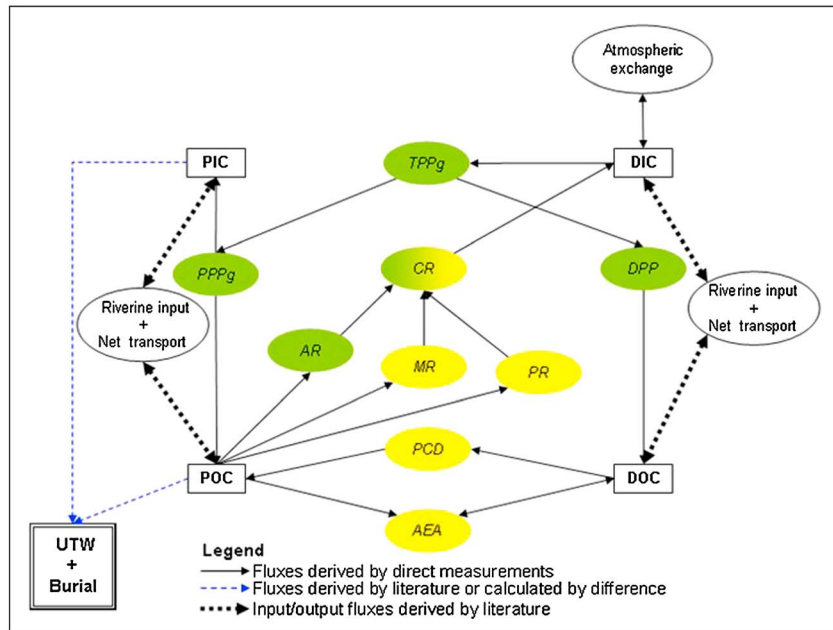


Figure 4. Conceptual model of the carbon cycling: total primary production and bacterial partitioning enlargement. PPPg = gross particulate primary production. DPP = dissolved primary production. PCD = prokaryotic carbon demand. AEA = actual exoenzymatic activity (as sum of leucine-aminopeptidase and β -glucosidase assays). AR = autotrophic respiration. PR = prokaryotic respiration. MR = microzooplankton respiration. DIC = dissolved inorganic carbon. DOC = dissolved organic carbon (labile and refractory). POC = particulate organic carbon (autotrophic biomass, prokaryotic biomass, microzooplankton biomass, detritus). PIC = particulate inorganic carbon. UTW = upper trophic web.

3.1. The Conceptual Ecological Model

As far as stocks and fluxes for carbon budget estimation in the northern Adriatic Sea are concerned, a simplified conceptual model describing carbon cycling in the water column down to the benthic layer and seabed is here proposed both in presence of a single mixed layer (i.e., only deep mixed layer, Figure 3a) or two stratified layers (upper mixed layer and deep mixed layer, Figure 3b). In addition, some processes, such as those relating to the bacterial partitioning of organic carbon, are better detailed in Figure 4. However, the model presented is a compromise between the theoretical complexity and our experimental capability to measure these fluxes in a single step. According to these limitations, reservoirs and fluxes depicted are mainly reflecting the work carried out during the oceanographic cruises but some estimates are based on literature data. The gaps particularly regard the riverine advection of DIC, PIC, DOC, and POC from Apennine rivers. In seawater, the main gaps concern the benthic boundary layer and in particular its prokaryotic activity on POC and DOC that accumulate there following the sedimentary processes. Prokaryotic activity on POC, which accumulates in the benthic boundary layer before its partial burial, in turn involves the following: the benthic production of DIC, DOC, the lowering of pH, and the triggering of the buffer effect of PIC. Nevertheless, these fluxes are included in the general model description because they can explain a significant amount of the carbon budget of the northern Adriatic Sea, but remain unresolved in the benthic boundary layer for a lack of both specific measurements and availability of literature data.

3.2. Stock Estimates and Mean-Weighted Concentrations

Stocks and average concentration values in the upper mixed layer, deep mixed layer, and total water masses are reported in Table 3. Before the onset of the highly productive spring period, the northern Adriatic Sea basin is well oxygenated (mean dissolved oxygen = 292 and 273 $\mu\text{mol L}^{-1}$ in the deep mixed layer and in the upper mixed layer, respectively, Table 3) and with an average negative apparent oxygen utilization both in the upper mixed layer ($-5.5 \mu\text{mol L}^{-1}$, Table 3) and the deep mixed layer ($-3.9 \mu\text{mol L}^{-1}$, Table 3). This oversaturation is consistent with primary production already being active within the entire water column. It also indicates that winter mixing has erased any possible previous

Table 3. Stocks and Average Concentrations of Chemical and Biological Parameters in February 2008^a

Parameter	Units	UML	DML	Total
Salt content	Tg	5,053	54,364	59,417
	g kg ⁻¹	36.4	38.4	38.2
Dissolved oxygen	Gmol-O ₂	39	376	415
	μmol L ⁻¹	292	273	275
Apparent oxygen utilization	Gmol-O ₂	-0.74	-5.4	-6.1
	μmol L ⁻¹	-5.5	-3.9	-4.1
DIC	Gmol-C	335	3,336	3,671
	μmol kg ⁻¹	2,413	2,357	2,362
CO ₂	Gmol-C	1.9	19	21
	μmol kg ⁻¹	14	14	14
HCO ₃	Gmol-C	304	3,011	3,315
	μmol kg ⁻¹	2,186	2,127	2,133
CO ₃	Gmol-C	30	306	335
	μmol kg ⁻¹	213	216	216
PO ₄	Mmol-P	4.5	80	85
	μmol L ⁻¹	0.03	0.06	0.06
Dissolved inorganic nitrogen	Mmol-N	873	2,061	2,934
	μmol L ⁻¹	6.5	1.5	1.9
Total phytoplankton biomass	Mmol-C	713	1,592	2,305
	μmol L ⁻¹	5.3	1.2	1.5
Autotrophic picoplankton	Mmol-C	370	1,130	1,500
	μmol L ⁻¹	2.7	0.82	0.99
Autotrophic nanoplankton and microplankton	Mmol-C	343	463	805
	μmol L ⁻¹	2.5	0.34	0.53
Total calcareous phytoplankton	Mmol-C	78	104	182
	μmol L ⁻¹	0.57	0.06	0.12
PIC from calcareous phytoplankton	Mmol-C	33	44	76
	μmol L ⁻¹	0.24	0.03	0.05
Microzooplankton	Mmol-C	11	64	75
	μmol L ⁻¹	0.08	0.05	0.05
Prokaryotic biomass	Mmol-C	473	2,273	2,745
	μmol L ⁻¹	3.5	1.7	1.8
Total DOC	Gmol-C	11	91	103
	μmol L ⁻¹	83	67	68
Total POC	Gmol-C	1.6	5.0	6.5
	μmol L ⁻¹	12	3.6	4.3

^aDerived values (i.e., not directly measured) are reported in italics. UML = upper mixed layer; DML = deep mixed layer; total = total northern Adriatic Sea.

hypoxia conditions and is an evidence of the reset capability of the northern Adriatic Sea basin toward its progressive eutrophication from 1 year to the next [Franco, 1983].

Average concentrations of dissolved inorganic nitrogen (Table 3) account for a riverine input that is confined in the upper mixed layer (6.5 μmol L⁻¹ with respect to 1.5 μmol L⁻¹ in the deep mixed layer). A similar difference is not shown by phosphorus. On the contrary, the higher concentration estimated in the deep mixed layer (0.06 μmol L⁻¹ with respect to 0.03 μmol L⁻¹ in the upper mixed layer) seems to indicate a southern input from deep waters. The low continental phosphorus inputs from rivers are confined in the coastal areas that are not resolved by the present cell subdivision. N/P availability ratios (195 in the upper mixed layer and 26 in the deep mixed layer) confirm the phosphorus deficiency of the northern Adriatic Sea [Socal *et al.*, 2008; Solidoro *et al.*, 2009; Giani *et al.*, 2012]. However, the photic zone gets a large amount of P through the upper mixed layer mixing with the deep mixed layer, with a contribution of 80 Mmol-P over a total amount of 85 Mmol-P (Table 3). These results are in good agreement with those reported in literature for the northern Adriatic Sea during winter conditions [Faganeli *et al.*, 2009; Luchetta *et al.*, 2010]. Particularly, they confirm the depletion of P with respect to N, especially in the upper mixed layer that is influenced to the greatest extent by riverine inputs. A similar riverine influence affects DIC and HCO₃ concentrations that are higher in the upper mixed layer than in the deep mixed layer (Table 3). These findings confirm the inverse ratio with salinity already pointed out in the northern Adriatic Sea [Luchetta *et al.*, 2010] and the importance of riverine advectons for the carbonate system and the capacity of surface layers to absorb atmospheric CO₂.

Total phytoplankton biomass exceeds the prokaryotic stock in the upper mixed layer (713 Mmol-C and 473 Mmol-C, respectively, Table 3) while the opposite characterizes the deep mixed layer and the total northern Adriatic Sea water masses (prokaryotes: 2273 and 2745 Mmol-C in the deep mixed layer and total, respectively; phytoplankton: 1592 and 2305 Mmol-C in the deep mixed layer and total, respectively, Table 3). Averaged concentrations of total phytoplankton (5.3 , 1.2 , and $1.5 \mu\text{mol-C L}^{-1}$ in the upper mixed layer, the deep mixed layer, and total, respectively, Table 3) and prokaryotic biomass (3.5 , 1.7 , and $1.8 \mu\text{mol-C L}^{-1}$ in the upper mixed layer, the deep mixed layer, and total, respectively, Table 3) define a $C_{\text{phyto}}/C_{\text{prok}}$ ratio of 1.5 , 0.7 , and 0.8 in the upper mixed layer, the deep mixed layer, and total water masses, respectively. Mean values of biomasses, POC and DOC for the upper mixed layer, the deep mixed layer, and total are consistent with those reported by *Puddu et al.* [1998], supporting the reliability of our computation. However, considering prokaryotes, previous studies in northern Adriatic Sea highlighted low seasonal variability in their abundance, and high variability in biomass due to increasing cell sizes in June 1996–1997 [*La Ferla et al.*, 2001; *La Ferla and Leonardi*, 2005]. The POC living fraction (defined as the sum of microzooplankton, phytoplankton, and prokaryotic biomasses, Table 3) in the upper mixed layer and in the deep mixed layer represents the 75–79% of the total, respectively; the remaining fraction is detritus. DOC is by far the dominant carbon fraction (11 and 92 Gmol-C, respectively compared to 1.6 and 5.0 Gmol-C of POC in the upper mixed layer and the deep mixed layer, Table 3) leading to DOC/POC ratios of 7.1 and 18 in the upper mixed layer and the deep mixed layer, respectively.

3.3. Carbon Fluxes Between Biogeochemical Reservoirs

According to the reservoirs defined in the conceptual model (Figures 3 and 4) and the stocks specified in section 3.2 and Table 3, total C fluxes (as Mmol-C d^{-1}) have been calculated and reported in Table 4 together with their surface-specific values (as $\text{mmol-C m}^{-2} \text{d}^{-1}$). These latter have been calculated by combining the total fluxes with their respective seawater surfaces. As for stocks, this procedure has been adopted to provide a more straightforward comparison with the available literature data. Indeed, the values from the present research fit very well with winter primary production values previously observed in the Adriatic Sea [*Socal et al.*, 2002; *Pugnetti et al.*, 2004, 2005], confirming the low-carbon production in the upper mixed layer and in the deep mixed layer during February 2008. Total primary production products are mainly represented by POC, DOC production being a lower fraction in both of the analyzed layers (31 and 15% in the upper mixed layer and in the deep mixed layer, respectively).

The total carbon flux released through actual exoenzymatic activity (Table 4) was calculated by the regression analysis of the available enzymatic data with the main environmental variables (i.e., leucino-aminopeptidase with salinity, $r^2 = 0.735$, and β -glucosidase with temperature, $r^2 = 0.359$, $n = 65$), to infer the enzymatic data for the unsampled stations. The enzymatic activity rates were higher in the deep mixed layer than in the upper mixed layer for both leucino-aminopeptidase and β -glucosidase. This result is due to the larger volume of seawater considered in the deep mixed layer compared to the upper mixed layer (Table 4). Conversely, in terms of surface-specific carbon fluxes, in the upper mixed layer mean leucino-aminopeptidase activity rates exceeded those found in the deep mixed layer, while β -glucosidase showed high activity rates in the deep mixed layer, in agreement with the ability of this enzyme to partially decompose refractory organic polymers that are more abundant at greater depths. In the upper mixed layer, the prevalence of leucino-aminopeptidase over β -glucosidase resulted in leucino-aminopeptidase/ β -glucosidase ratios > 1 (not reported in the table), which suggest that in this layer, microbial decomposition was mostly of proteic, labile, and organic substrates. Conversely, in the deep mixed layer, β -glucosidase prevailed over leucino-aminopeptidase, resulting in leucino-aminopeptidase/ β -glucosidase ratios < 1 ; this indicates that in this layer, a preferential decomposition of polysaccharides, compared to proteins, occurred.

The mean flux of carbon released by actual exoenzymatic activity, calculated as the sum of leucino-aminopeptidase and β -glucosidase (Table 4), was quantified as 2.9 and $4.1 \text{ mmol-C m}^{-2} \text{d}^{-1}$ in the upper mixed layer and in the deep mixed layer, respectively. Globally, we estimated that leucino-aminopeptidase and β -glucosidase together were able to hydrolyze, per day, as much as 0.31% and 0.13% of the carbon from the total POC + DOC pool in the upper mixed layer and in the deep mixed layer, respectively. It should be underlined that these percentages are exclusively based on the hydrolysis of peptide bond adjacent to a free-amino group (leucino-aminopeptidase) and a variety of β -D glucoside substrates (β -glucosidase); consequently, hydrocarbons with other than β 1–4 bonds and structural complex proteins cannot be

Table 4. Mean Carbon Fluxes Estimated in February 2008^a

Parameter	Units	UML	DML	Total
CO ₂ air-sea flux	Mmol-C d ⁻¹	-	-	92
	mmol-C m ⁻² d ⁻¹			2.7
Total primary productivity	Mmol-C d ⁻¹	197	382	579
	mmol-C m ⁻² d ⁻¹	14	13	17
Dissolved primary productivity	Mmol-C d ⁻¹	62	61	123
	mmol-C m ⁻² d ⁻¹	4.5	2.1	3.6
Calcareous dissolved primary productivity ^b	Mmol-C d ⁻¹	15	14	29
	mmol-C m ⁻² d ⁻¹	1.1	0.46	0.86
Particulate primary productivity	Mmol-C d ⁻¹	135	322	457
	mmol-C m ⁻² d ⁻¹	9.9	11	14
Calcareous particulate primary productivity ^c	Mmol-C d ⁻¹	32	69	101
	mmol-C m ⁻² d ⁻¹	2.4	2.4	3.0
Calcareous particulate primary productivity ^d	Mmol-C d ⁻¹	14	29	43
	mmol-C m ⁻² d ⁻¹	0.99	0.99	1.3
Foraminifera PIC production	Mmol-C d ⁻¹	-	-	1.2
Prokaryotic heterotrophic productivity ^e	Mmol-C d ⁻¹	63	34	97
	mmol-C m ⁻² d ⁻¹	4.6	1.2	2.9
Community respiration	Mmol-C d ⁻¹	43	496	539
	mmol-C m ⁻² d ⁻¹	3.2	17	16
Phytoplankton respiration	Mmol-C d ⁻¹	22	201	224
	mmol-C m ⁻² d ⁻¹	1.6	6.9	6.6
Prokaryota respiration	Mmol-C d ⁻¹	21	287	308
	mmol-C m ⁻² d ⁻¹	1.5	9.8	9.1
Microzooplankton respiration ^f	Mmol-C d ⁻¹	0.25	8.1	8.4
	mmol-C m ⁻² d ⁻¹	0.02	0.28	0.25
Actual exoenzymatic activity	Mmol-C d ⁻¹	39	122	161
	mmol-C m ⁻² d ⁻¹	2.9	4.1	4.7
Leucino-aminopeptidase actual activity	Mmol-C d ⁻¹	35	51	86
	mmol-C m ⁻² d ⁻¹	2.6	1.7	2.5
β -glucosidase actual activity	Mmol-C d ⁻¹	4.4	71	75
	mmol-C m ⁻² d ⁻¹	0.32	2.4	2.2
PIC sedimentation	Mmol-C d ⁻¹	-	-	44
POC sedimentation ^g	Mmol-C d ⁻¹	44	411	455
	mmol-C m ⁻² d ⁻¹	3.2	14	13
POC net burial	Mmol-C d ⁻¹	-	-	24
PIC net burial	Mmol-C d ⁻¹	-	-	1.2
DOC benthic release ^h	Mmol-C d ⁻¹	-	-	106
DIC benthic release ^h	Mmol-C d ⁻¹	-	-	89
DOC riverine input	Mmol-C d ⁻¹	-	-	30
POC riverine input	Mmol-C d ⁻¹	-	-	22
DIC riverine input	Mmol-C d ⁻¹	-	-	285
DOC outflows ⁱ	Mmol-C d ⁻¹	-	-	59
POC outflows ⁱ	Mmol-C d ⁻¹	-	-	11
DIC outflows ⁱ	Mmol-C d ⁻¹	-	-	311

^aDerived values (i.e., not directly measured) are reported in italics. UML = upper mixed layer; DML = deep mixed layer; total = total northern Adriatic Sea.

^bFrom coccolithophorides and foraminifera.

^cEstimate of coccolithophorides and foraminifera particulate primary productivity as total carbon.

^dEstimate of coccolithophorides and foraminifera particulate primary productivity as particulate inorganic carbon (PIC).

^eNet prokaryotic heterotrophic production as real rate.

^fDue to plankton <200 μ m.

^gFrom U/Th disequilibrium.

^hFrom reactive sediment.

ⁱNet transport across the open borders (south and east).

hydrolyzed by such enzymes. It is also important to note that some biases may affect the quantitative assessments of the amount of microbially decomposed organic matter. Indeed, many other different enzymes (other proteolytic enzymes, α -glucosidases, phosphatases, etc.), which were not assayed during the current investigation, could contribute to carbon release [Hoppe *et al.*, 2002a]. Moreover, ectoenzymes and extracellular enzymes remain active for several days after the death of the microorganism responsible

for their production, and an important fraction of the total enzyme pool present in waters is constituted by enzymes attached to dead bacterial cells [Vives-Rego *et al.*, 1985]. Therefore, it is reasonable to presume that the global rates of POC hydrolysis (and consequent DOC production) could be higher than those estimated in this study where only leucino-aminopeptidase and β -glucosidase were taken into consideration.

The total mean flux of calculated prokaryotic heterotrophic productivity was consistent with the fluxes observed in the 0–100 m depth photic layers ($1.4\text{--}2.5\text{ mmol-C m}^{-2}\text{ d}^{-1}$) at the South Adriatic central station AM1 during the 2007 seasonal survey [Azzaro *et al.*, 2012].

Previous studies in northern Adriatic Sea showed a seasonal variability of respiration rates suggesting a more efficient remineralization during warm periods than in cold ones [La Ferla *et al.*, 2006]. Moreover, different scenarios were observed between low- and high-salinity systems, probably reflecting the availability of organic material spread with the river discharge. In our case study, similar mean community respiration values in the upper mixed layer and in the deep mixed layer were detected (Table 4), but in the deep mixed layer, the flux of C remineralized by prokaryotes was higher than that by $<200\text{ }\mu\text{m}$ plankton. In the deep mixed layer (taking into account the high volume of seawater, Table 1), the mean carbon fluxes were more than 10 times higher than in the upper mixed layer.

The prokaryotic growth efficiency (as the ratio between prokaryotic heterotrophic productivity and prokaryotic carbon demand, this latter defined as the sum of prokaryotic heterotrophic productivity and prokaryotic respiration) was 0.24, similar to the value routinely adopted in oceanic studies in the absence of experimental data [Hoppe *et al.*, 2002a]. Nevertheless, the prokaryotic growth efficiency varied widely between 0.75 and 0.11 in the upper mixed layer and in the deep mixed layer, respectively.

As for POC vertical fluxes through the water column, Giani *et al.* [2001] report an estimate of $71\text{--}97\text{ g-C m}^{-2}\text{ yr}^{-1}$, measured in the northern Adriatic Sea through sediment trap deployments. In our study case the estimated vertical fluxes ($59\text{ g-C m}^{-2}\text{ yr}^{-1}$ equivalent to $13\text{ mmol m}^{-2}\text{ d}^{-1}$, Table 4) imply a slight underestimation. However, the comparison is close when considering all the uncertainties in the calculation methods (see supporting information). In addition, estimates from sediment traps tend to be higher than U/Th derived ones, as a consequence of additional lateral inputs [Giuliani *et al.*, 2007]. The difference between POC vertical flux through the water column (455 Mmol-C d^{-1} , Table 4) and POC amount buried in sediments (24 Mmol-C d^{-1} , Table 4) leaves more than 430 Mmol POC available daily for biological benthic processes (i.e., carbon demand of both plankton and prokaryotic stocks and for the benthic fauna). However, the lack of a specific flux measurement inside the benthic boundary layer does not permit us to further investigate this issue.

The PIC vertical flux was determined by the combined contribution of coccolithophorides and planktonic foraminifera sedimentation. As for POC, just a limited fraction (less than 3%) of sedimenting PIC (44 Mmol-C d^{-1} , Table 4) is buried in sediments (1.2 Mmol-C d^{-1} , Table 4). The rest accumulates in the benthic boundary layer and takes part in several chemical processes such as the PIC buffering action toward pH lowering following the intense bacterial activity of POC mineralization.

3.4. CO₂ Exchange Between Atmosphere and Sea Surface

CO₂ exchange at the atmosphere-seawater interface was computed according to Ho *et al.* [2006], taking into account the $p\text{CO}_2$ values in the surface water (interpolated in each of 114 boxes), the seawater temperature and salinity, the atmospheric $p\text{CO}_2$, and the wind speed. Results, integrated on the total area, are summarized in Table 4. Although there is a mean thermodynamic disequilibrium of $84.5\text{ }\mu\text{atm}$, the actual mean flux of CO₂ from atmosphere to sea was set as $92.1\text{ Mmol-C d}^{-1}$, with an average surface-specific value of $2.7\text{ mmol-C m}^{-2}\text{ d}^{-1}$, in good agreement with the mean annual flux of $6\text{ mmol-C m}^{-2}\text{ d}^{-1}$ measured by Cantoni *et al.* [2012] and Turk *et al.* [2013] in the upper part of the northern Adriatic Sea.

3.5. Carbon Advection From Riverine Inputs

River advection of dissolved and particulate organic carbon and dissolved inorganic carbon is summarized in Table 4. These fluxes were not measured during this project and have been retrieved from literature (see details in the supporting information) but still present some significant lacks. Indeed, riverine advection, in general (and minor river flow rates in particular), represents a well-known gap for the northern Adriatic Sea on the whole and define some open questions. Noticeably, Apennine rivers, even if characterized by

lower flows, seem to transport significant loads of dissolved and particulate matter with respect to the much larger Po River [Frignani *et al.*, 2005; Tesi *et al.*, 2013].

No data have been found on pH and inorganic carbon system from continental runoff, and also, this fact represents a serious omission in our carbon balance. The DIC advection reported in Table 4 has been extrapolated from the values of the Isonzo River [Szramek *et al.*, 2011], but this approach allows just a rough estimation of the flow magnitude. No PIC data were found, and riverine pH values are few and reported without indications of the measured scale and temperature.

3.6. Transport Across the Open Southern and Eastern Borders

DOC, POC, and DIC exchanges at the southern and eastern borders of the study area are summarized in Table 4. A negative budget (i.e., export exceeds import) has been found for all parameters considered (Table S3.1 in the supporting information). To check these estimates, mean concentrations have been calculated both in entering and exiting fluxes (Table S3.2 in the supporting information), dividing the total masses involved by respective water volumes. The resulting concentrations were consistent with those reported in the literature [Degobbis *et al.*, 2005; Giani *et al.*, 2005; Krasakopoulou *et al.*, 2011].

4. Discussion

February 2008, when the present investigation took place, was coincident with a postconvective winter period in the northern Adriatic Sea, before the start of the usual spring water stratification and the onset of maximum productivity. This period is characterized by the presence of scarce biomass or oligotrophic conditions and high CO₂ levels in seawater, due to its major solubility in the cold winter water. Therefore, the carbon budget of this period can be considered as a suitable baseline in order to (i) verify the possibility of the northern Adriatic Sea acting as a “continental shelf pump” for CO₂ sequestration, from the combined effect of solubility and biological pumps, and (ii) define the degree of eutrophication that sometimes occurs during spring-summer. Among the few studies about this topic, some researches of the microbial C biogeochemistry showed different trophic regimes in different areas and seasons [Giani *et al.*, 1999; La Ferla *et al.*, 2002, 2005, 2006; Fonda Umani *et al.*, 2007; Fuks *et al.*, 2012]. During the PRISMA 2 project (1996–1998), the trophic balance appeared to move toward autotrophy in winter when a positive C budget resulted. opposite scenario occurred in summer when the trophic balance moved to heterotrophy with a negative C budget.

The winter conditions in the northern Adriatic Sea are generally favorable for vertical convection and mixing, as summarized by Gačić *et al.* [2001]. Therefore, the greatest portion of the study zone resulted in a homogenous deep mixed layer, characterized by $\sigma > 29.0$ from surface to bottom (Figure 2) and by small depth variations of temperature and salinity (ranging between 8.8–12.5°C and 37.5–38.5 practical salinity unit (psu), respectively). However, some areas, under the influence of fresh water discharge (either near the coast, or offshore), had a two-layer structure, the upper mixed layer and the deep mixed layer. The upper mixed layer, with σ values < 29.0 , exhibited high-salinity variability with values ranging between 21.0 and 37.5 psu. Only few coastal and shallow cells were characterized by a single homogenous upper mixed layer, as their σ values were < 29.0 from surface to bottom.

4.1. Northern Adriatic Sea Trophic Status and Related Phenomenology

In the past, the northern Adriatic Sea trophic status has been the focus of several Italian and international research projects and scientific debates [Franco and Michelato, 1992; Hopkins *et al.*, 1999; Giani *et al.*, 2005]. The descriptions of the basin stressed the presence of a coastal eutrophic zone characterized by high peaks of carbon production and an offshore oligotrophic area with relatively low biological activity; however, little information on the mean evaluation of the carbon cycle in the basin was presented [La Ferla and Azzaro, 2001; Giani *et al.*, 2005; La Ferla *et al.*, 2006]. Our results partially fill this gap, in the way that they refer to a particular month of the year (February) and provide estimates for the total northern Adriatic Sea water mass and the upper mixed layer and deep mixed layer subdivisions (Tables 1 and 3).

In the upper mixed layer, the total phytoplankton biomass (i.e., the sum of picophytoplankton, nanophytoplankton, and microphytoplankton size classes), expressed in Mmol-C, resulted in a higher value than the corresponding prokaryotic biomass (Table 3). Conversely, in the deep mixed layer and in total (i.e., considering the upper mixed layer and the deep mixed layer together), the heterotrophic biomass exceeds the

phytoplanktonic one, in disagreement with a previous study in the northern Adriatic Sea [La Ferla *et al.*, 2005] where bacterial carbon biomass was always lower than the phytoplanktonic C biomass (derived from chl-*a* estimates). In fact, the phytoplankton represented the 84% to 66% of the microbial biomass in February 1997–1998 and June 1996–1997, respectively [La Ferla *et al.*, 2005]. Fuks *et al.* [2012] found that, both under oligotrophic conditions and in eutrophic events, chl-*a*-derived biomass in the northern Adriatic Sea was always higher than the prokaryotic one, the two being almost equal only at surface during oligotrophic conditions. In the Gulf of Trieste (the northeastern part of northern Adriatic Sea), Fonda Umani *et al.* [2012] found prokaryotic biomass higher than microbiomass only in summer. In some other areas of the Mediterranean basin, such as in the northwestern Mediterranean Sea, it was found that prokaryotic biomass was lower than micro biomass in the deep chlorophyll maximum but not at surface [Pedrós-Alió *et al.*, 1999]. In the Aegean Sea the Cphyto/Cprok ratios oscillated between 0.5 and 2.3 linked mainly to variation observed as consequence of different trophic conditions [Siokou-Frangou *et al.*, 2002]. The same happened in the Tyrrhenian Sea (Cphyto/Cprok ratio range: 0.2–1.6) [La Ferla *et al.*, 2010]. Our ratios fell in the range reported for other oligotrophic seas.

Phytoplankton production determined in the total northern Adriatic Sea is about 5 times higher than the prokaryotic one (Table 4). The ratio between prokaryotic heterotrophic productivity and total primary productivity can be considered in assessing the relative importance of prokaryotes versus phytoplankton in channeling organic carbon along the trophic web. This ratio varies greatly over time and space, but usually it is low in the open oceans (about 0.1), whereas it can be high in estuaries [Pradeep Ram *et al.*, 2007] or in lakes (0.3–0.5) because of the input of terrestrial organic carbon [Kirchman, 2012]. Indeed, in coastal and estuarine systems, substrates for bacterial growth can derive from sources such as river borne material, terrestrial runoff, anthropogenic loads [Almeida *et al.*, 2005]. In our study, this ratio showed a shift in the deep mixed layer and the upper mixed layer from a classic autotrophic metabolism to an increasing importance of the heterotrophic one, linked to the dynamics of estuarine environments (0.1 and 0.3, respectively). Such a difference is even more notable considering the ratio between prokaryotic and phytoplankton production normalized for their respective biomasses: 0.1 and 0.5 in the deep mixed layer and in the upper mixed layer, respectively. Since the ratios between total primary productivity and total phytoplankton biomass result similar in the deep mixed layer and in the upper mixed layer (0.24–0.28 d⁻¹, respectively), the normalized prokaryotic heterotrophic productivity/total primary productivity ratio appear to be constrained from the prokaryotic specific production rate that widely varies between the two layers (i.e., prokaryotic heterotrophic productivity/prokaryotic biomass = 0.02–0.13 d⁻¹, in the deep mixed layer and in the upper mixed layer, respectively).

4.2. Northern Adriatic Sea Microbial Loop

The measured detrital fraction of POC measured (21–25% of the total) is one of the lowest detected in the Mediterranean Sea. In the northwestern Mediterranean Sea the detrital pool was in the range 33–83% of POC with a mean of about 50% [Van Wambeke *et al.*, 2001], similar to that found in the oceanic euphotic zone [Cho and Azam, 1990]. In the central Mediterranean Sea the detrital POC range varied between 43 and more than 90%, and in the northern Adriatic Sea in February 1997–1998 and June 1996–1997 it oscillated from 43 to 70%, respectively [La Ferla *et al.*, 2005].

Concerning the mathematical calculations applied to infer enzymatic activity rates, the variability in potential enzymatic activity patterns has always been explored in relation to environmental variables, as enzyme activity rates provide information on the initial response of the microbial community to environmental changes [Hoppe *et al.*, 2002b; Cunha *et al.*, 2010, and references therein]. Several studies have found salinity to be one of the most important physicochemical parameters affecting microbial metabolism. In a first study performed from spring to autumn 1995 in coastal sites close to the Po River delta (northwestern Adriatic Sea), within the PRISMA 1 research program, Caruso and Zaccone [2000] reported that temperature affected positively, although not significantly, leucino-aminopeptidase activity patterns (Pearson's correlation coefficient $r = +0.83$). Nevertheless, during the successive PRISMA 2 research program (1996–1998) it became evident that in the northern Adriatic Sea the main factor driving the microbial activity, even more than temperature, was salinity, which correlated inversely with leucino-aminopeptidase activity rates throughout the year and particularly in the northern area ($r =$ from -0.75 to -0.94 , $P < 0.01$); conversely, temperature related with enzymatic rates to lower significance levels ($r =$ from $+0.49$ to $+0.61$, $P < 0.01$) [La Ferla *et al.*, 2001].

Significant negative correlations of leucino-aminopeptidase versus salinity values are in agreement with the peculiar hydrological features of the Adriatic Sea [Artegiani *et al.*, 1997; Monticelli *et al.*, 2014] and stress the importance of freshwater supply by river inputs in providing fresh organic matter substrates fuelling microbial metabolism, as also pointed out by the detection of higher extracellular enzymatic activity rates within the surface layers (depth: 0–10 m). More recently, Caruso [2010] confirmed salinity as the main environmental factor which affected enzyme patterns in the northern Adriatic Sea. The rates of proteolysis correlated negatively with salinity (along the Po coast, $r = -0.771$, $P < 0.01$, as well as along the eastern side, $r = -0.833$, $P < 0.01$). Also, alkaline phosphatase rates were negatively affected by salinity ($r = -0.811$, $P < 0.01$) along the western side, indicating that the trophic supply from the Po River enriches the surface layer with new organic polymers which stimulate microbial metabolism. Similar patterns have also been found by Celussi and Del Negro [2012] in shallow northern Adriatic Sea waters, where significant direct and indirect correlations versus temperature and salinity have been reported for both leucino-aminopeptidase ($r = +0.45$ and -0.52 , $P < 0.001$, respectively) and alkaline phosphatase ($r = +0.43$ and -0.46 , $P < 0.001$, respectively). Due to the importance of external input in the Adriatic basin [Cozzi and Giani, 2011], inverse relationships with salinity suggest that a fraction of organic matter on which enzymes act is of riverine origin, both in its dissolved and particulate phase.

The influence of frontal systems between saltier and more diluted waters also extends southward, like in the central Adriatic basin; in the Manfredonia Gulf area, Monticelli *et al.* [2014] found a positive significant relationships of β -glucosidase versus temperature ($r = +0.45$, $P < 0.001$), and a negative one versus salinity ($r = -0.54$, $P < 0.0001$); moreover, alkaline phosphatase was positively related to temperature ($r = +0.33$, $P < 0.01$) and leucino-aminopeptidase negatively related to salinity ($r = -0.43$, $P < 0.002$).

From the estimated rates for organic polymers decomposition by exoenzymatic activities, prokaryotic production, and mineralization processes, the microbial community living in the northern Adriatic Sea basin in February 2008 appeared to be very active in the mobilization of carbon. In the deep mixed layer and total northern Adriatic Sea (Table 4), the amount of carbon released by exoenzymatic hydrolysis exceeded that incorporated into new prokaryotic biomass by the process of prokaryotic heterotrophic productivity (i.e., actual exoenzymatic activity/prokaryotic heterotrophic productivity ratios were 3.5 and 1.6, respectively), thus increasing the pool of DOC available to other organisms in the trophic web. A similar uncoupling between enzymatic hydrolysis and uptake was also found during previous investigations performed in the same season in the northern Adriatic Sea [La Ferla *et al.*, 2001]. Unlike the deep mixed layer, in the upper mixed layer, the ratio between actual exoenzymatic activity and prokaryotic heterotrophic productivity was 0.6, thus indicating that in this layer, prokaryotic heterotrophic productivity was more active than enzymatic hydrolysis, reinforcing the concept that other sources of organic carbon, of allochthonous origin, sustain the prokaryotic growth in the northern Adriatic Sea. In fact, besides the above mentioned process (DOC production from POC decomposition), other sources of low molecular weight biologically available DOC come from viral lysis, sloppy feeding, or may be introduced into the ecosystem by rain, and fog events. In this work, the amount of DOC present in rain waters was not analyzed, but according to a conservative value for coastal areas ($2 \text{ g-C m}^{-2} \text{ yr}^{-1}$) [Willey *et al.*, 2000], it is possible to assume an input of about $15.2 \text{ Mmol-C d}^{-1}$ into the entire northern Adriatic Sea which corresponds to about half of the river DOC inputs. DOC is consumed by picoplanktonic respiration [Middelboe *et al.*, 2006; Willey *et al.*, 2000; Mazzoleni *et al.*, 2010; Saba *et al.*, 2011]; therefore, from the total values of assessed C fluxes, the amount of carbon required for the production of new prokaryotic biomass was balanced by the DOC produced by photosynthetic process in upper mixed layer (i.e., dissolved primary productivity/prokaryotic heterotrophic productivity = 1.0), while it was higher in the deep mixed layer and total northern Adriatic Sea (dissolved primary productivity/prokaryotic heterotrophic productivity = 1.8 and 1.3, respectively). The relationships between the microbial processes implicated in the DOC cycle, as production versus consumption ((dissolved primary productivity + actual exoenzymatic activity)/prokaryotic carbon demand = prokaryotic heterotrophic productivity + prokaryotic respiration) were 0.7, 1.2, and 0.6 in total northern Adriatic Sea, in the upper mixed layer, and in the deep mixed layer, respectively. Therefore, prokaryotic DOC needs were fully covered/satisfied by enzymatic and photosynthetic activities only in the upper mixed layer; conversely, if the “classical” V_{max} approach had been used to estimate C fluxes, higher enzymatic activity rates would have been obtained (not shown in Table 4), indicating that a significant surplus of DOC would have been produced.

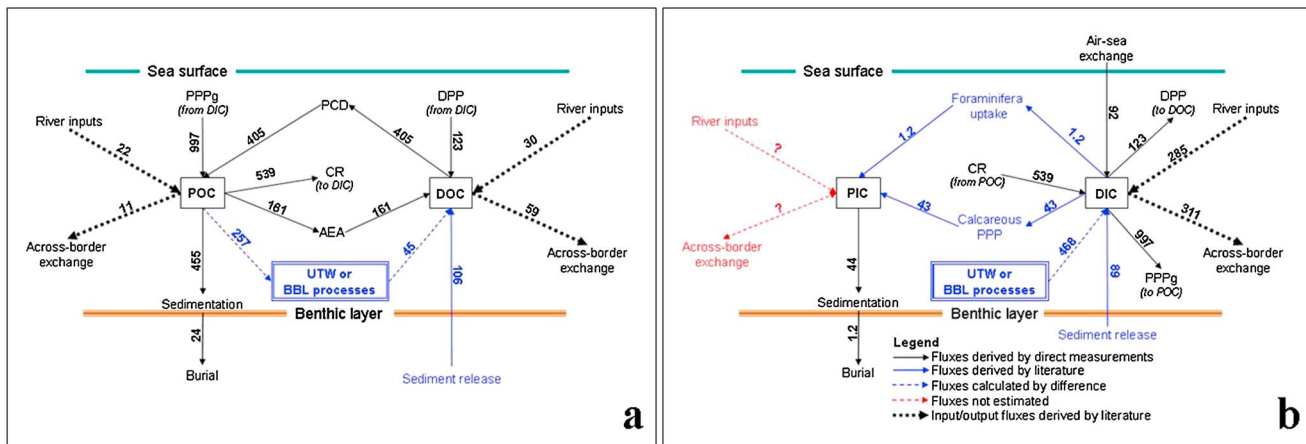


Figure 5. Carbon budgets in the northern Adriatic Sea on February 2008: (a) POC and DOC; (b) PIC and DIC. Flux values are in Mmol d^{-1} (see Table 4). BBL = benthic boundary layer. For other acronym explanations see Figures 3 and 4.

The prokaryotic growth efficiency, as the ratio between prokaryotic heterotrophic productivity and prokaryotic carbon demand [Del Giorgio and Cole, 1998] is the amount of new prokaryotic biomass produced per unit of organic C substrate assimilated. On total values, the ratio was 0.24, in agreement with the mean value previously observed by La Ferla et al. [2001] in the same coastal areas and season, corroborating previous research that assumed a priori a prokaryotic growth efficiency of 0.30 for the ocean [Hoppe et al., 2002a]. Nevertheless, a shift was observed between the upper mixed layer and the deep mixed layer (0.75 and 0.11, respectively). The calculated prokaryotic growth efficiency values suggest a change in the nature and availability of growth substrates and on the relative importance of productive and oxidative processes which occur in the upper mixed layer and in the deep mixed layer. A high value of prokaryotic growth efficiency means high-carbon uptake, while a low value means higher CO_2 release to the ecosystem. In the northern Adriatic Sea, the upper mixed layer seems to act as a sink of CO_2 and the deep mixed layer as a CO_2 source. This finding is highlighted also by the relationships between CO_2 fixed by photosynthesis and CO_2 released by community respiration (total primary productivity/community respiration) that were 4.5 in the upper mixed layer and 0.8 in the deep mixed layer. The same ratio calculated in the whole water column was fairly balanced (≈ 1.1) with an excess of 40 Mmol-C/d ($\sim 7\%$ of the total primary productivity) that was not respired.

4.3. Atmosphere-Seawater CO_2 Exchange and Riverine DIC Advection in the Northern Adriatic Sea

During February 2008, the northern Adriatic Sea had a positive mean difference between atmospheric ($399.8 \mu\text{atm}$) and surface seawater ($305.1 \mu\text{atm}$) of $p\text{CO}_2$, both considered at in situ temperature. Taking into account the particular wind regime during the cruise period (on average 6.8 m s^{-1} over the entire area), it has been calculated an actual flux from the atmosphere to the sea surface of 92 Mmol-C d^{-1} as CO_2 over the entire area, corresponding to a mean flux of $2.7 \text{ mmol-C m}^{-2} \text{ d}^{-1}$ (Table 4). Although wind speed can vary from time to time, our data support the hypothesis of a “solubility pump” acting as sink for CO_2 in the northern Adriatic Sea in winter. Considering the karst nature of many rivers flowing into the northern Adriatic Sea, riverine runoff is potentially an important source to DIC stocks in the area. This condition can explain the great carbonate abundance in coastal sediments, the higher DIC concentration in the upper mixed layer with respect to the deep mixed layer (Table 3) and the inverse trends of total alkalinity/salinity and carbonate alkalinity/salinity ratios [Luchetta et al., 2010]. However, riverine total alkalinity, carbonate alkalinity, and pH measurement are rare or totally absent.

The postwinter sampling period was characterized by an average negative apparent oxygen utilization (indicating the onset of new primary production, Table 3) that contributed to the increase of total alkalinity and pH in the northern Adriatic Sea waters. This increase caused positive effects on the saturation state of carbonates, Ω , as, Ω_{arag} minimum average value (3.19 in the upper mixed layer, Table 1) was well above unity.

4.4. Northern Adriatic Sea Organic and Inorganic Carbon Total Budgets, the Snapshot of February 2008

Figures 5a and 5b depict carbon fluxes between different reservoirs of their marine cycle giving a first synthesis of the carbon budget, i.e., rates of primary and prokaryotic productions, carbon flux to the

sediments, and burial. In this figure, estimates of riverine inputs (A, Figure 1) and exchanges across open borders (B and B1, Figure 1) are included, in order to provide an integrated budget of POC and DOC for the northern Adriatic Sea continental shelf, as summarized in Table 4.

When total northern Adriatic Sea water masses are considered (upper mixed layer + deep mixed layer), particulate primary productivity and prokaryotic heterotrophic productivity were responsible for the formation of 554 Mmol-C of POC every day (Table 4). The balance between POC inputs (i.e., gross particulate primary productivity, riverine inputs, and the prokaryotic carbon production) and outputs (i.e., the loss across the open borders, the community respiration, the actual exoenzymatic activity, and the burial in bottom sediments) showed a positive value of approximately 257 Mmol-C that was available daily for the upper trophic web and benthic boundary layer communities. Biological processes in the water column presumably sustained the large majority of this surplus (Figure 5a), and the importance of prokaryotic and benthic transformation processes in the benthic boundary layer is evidenced by the fact that in February 2008, more than 430 Mmol-C accumulated daily at the water-sediment interface, as just 5.3% of settling POC ($455 \text{ Mmol-C d}^{-1}$, Table 4) was buried in sediments (24 Mmol-C d^{-1}). In synthesis, 18% of daily produced POC was used in the water column, while up to 78% was transformed in the benthic boundary layer by prokaryotes or transferred to upper trophic levels, and just 4% was buried in sediments. This observation underlines the importance of the benthic boundary layer, where the greatest portion of biogenic POC accumulates and is partially channeled in the trophic web.

Contrary to POC, the seawater DOC budget showed a “missing” contribution of $151 \text{ Mmol-C d}^{-1}$, resulting from the balance between inputs (gross dissolved primary productivity, river inputs, and actual exoenzymatic activity) and outputs (across-border outflows and prokaryotic carbon demand, Figure 5a and Table 4). The present budget, however, did not consider the amount of DOC that was actually produced in the benthic boundary layer as the result of microbial POC decomposition processes. This DOC input was probably significant, due to the great portion of POC that accumulated in the benthic boundary layer, and might explain the missing contribution. Part of the observed deficit might also be compensated for by DOC release through POC decomposition in sediments by enzymatic hydrolysis ($106 \text{ Mmol-C d}^{-1}$, Table 4).

DIC represented by far the most abundant carbon fraction (335 Gmol-C in the UML and 3336 Gmol-C in the DML), resulting from the dissolution equilibrium of crustal and biogenic carbonates controlled by pH, community respiration-derived CO_2 and CO_2 exchanged with the atmosphere (Table 4). Flux estimates of DIC considered community respiration, air-sea exchange, and river contribution as inputs, whereas gross particulate primary productivity, dissolved primary productivity, outflows at the open borders, and foraminifera and coccolithophorides uptake were the outputs (Figure 5b). The resulting mass balance showed a deficit of DIC in the seawater equal to $557 \text{ Mmol-C d}^{-1}$ (Figure 5b) that could be compensated for by DIC release from enzymatic POC decomposition in the sediments (89 Mmol-C d^{-1} , Table 4) and by river and biogenic inputs of DIC in the benthic boundary layer. These latter are presumably very important contributions caused, on one side, by the already mentioned karst and dolomitic nature of the continental waters and, on the other, by the probable intense mineralization of organic carbon in the benthic boundary layer. Indeed, the budget of DIC presented here must be considered as relative to the general phenomenology, since it does not take into account that values of pH, Ω_{arag} and Ω_{calc} and DIC stock in the water column can be very different from those measured in the benthic boundary layer. An intense prokaryotic mineralization activity in the benthic boundary layer would cause an increase in the production of CO_2 , with consequent lowering of local pH.

The carbon budget relative to the PIC is biased by the lack of river input estimates and exchange at the open borders (Figure 5b). Therefore, only a rough definition of the level of the magnitude was possible. In synthesis, when considering only the PIC biogenic production by coccolithophorides and planktonic foraminifera (and assuming that due to the shallow water depth of the Northern Adriatic Sea, the entire production reached the benthic boundary layer and the sea bottom), it seems that as much as 97% of PIC produced in the water column (44 Mmol-C d^{-1} , Figure 5b) accumulated in the benthic boundary layer, as just $1.2 \text{ Mmol-C d}^{-1}$ (Figure 5b) was buried in the sediments. This surplus was probably dissolved to buffer the pH lowering mineralization processes in the benthic boundary layer mentioned above.

5. Conclusions

The carbon budget proposed in this paper is based on a box model approach that relies on experimental data, purposely measured during the sampling campaigns or derived from previous research. This approach is not new to the scientific community, but it has never been previously applied in this form in the northern Adriatic Sea. The carbon budget obtained for February 2008 that can be considered representative of a typical winter showed the following:

1. The basin is oligotrophic, and primary productivity starts well before the onset of spring stratification. The system undergoes a reset due to the complete winter mixing of water masses which erase any signal of previous hypoxia or anoxia episodes.
2. The northern Adriatic Sea is a phosphorus-depleted basin with respect to C and N availability. This fact confirms the importance of mixing with deep-sea water for P supply to biological processes on the whole.
3. Despite the abundant prokaryotic biomass, the microbial loop was confirmed as less efficient with respect to the organic C production.
4. The carbon produced by primary production exceeded the fraction respired by community smaller than 200 μm in the upper mixed layer, whereas respiration processes prevailed in the deep mixed layer.
5. During February 2008 and probably throughout the winter season, the northern Adriatic Sea acted as a sink for atmospheric CO_2 .

This carbon balance is far from being complete, as it still shows some data gaps that need to be further investigated. Once these have been addressed, the approach developed in this case study could be used in future research and could be applied to other time periods, to define an annual carbon budget in the Adriatic Sea.

Future implementations of the current approach should include the following: a finer grid of boxes in the coastal zones to better resolve coastal processes and fluxes; concomitant measurements of pH, DIC, and PIC riverine inputs; considering the evaporation and wet deposition; and at last, but not least, quantifying the fluxes and processes relative to the benthic boundary layer. This is probably the biggest gap of the present approach as it highlights some peculiarities of this specific layer that could not be verified. In particular, it prevented us from elucidating the fate of the important accumulation of POC, which occurs in the benthic boundary layer of the northern Adriatic Sea and estimating the consequent DIC and pH decreases as well as the buffer effect of PIC dissolution.

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