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A numerical simulation study of dissolved organic carbon accumulation in the northern Adriatic Sea

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[1] A mechanistic explanation for the accumulation of dissolved organic carbon (DOC), observed in coastal seas such as the Northern Adriatic Sea, is proposed here on the basis of numerical simulations of the marine ecosystem dynamics carried out with a coupled biogeochemical-circulation model. The biogeochemical model is based on the European Regional Seas Ecosystem Model (ERSEM) upgraded with a more detailed representation of the DOC-bacteria interactions and resolving different level of DOC lability/refractivity. The circulation model is the Adriatic Sea implementation of the Princeton Ocean Model. The analysis of simulations confirms the important role of the Po river nutrient input on the ecosystem dynamics and highlights the presence of a strong across-shelf trophic gradient that, affecting the Bacterial Growth Efficiency (BGE), could be a key factor for the DOC accumulation. The simulations show the importance of circulation features in modulating the exchanges between areas having different trophic structure such as the western coastal strip, strongly influenced by the Po river runoff, and the open sea areas in the centre of the northern Adriatic sub-basin. The DOC produced in the high energy system of the Po runoff coastal strip, characterized by high BGE, is transported toward the open areas, which is a more oligotrophic environment with lower BGE. In this area the DOC turnover time is strongly increased giving rise to the DOC accumulation.

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1. Introduction

[2] Although the dynamics of dissolved organic carbon (DOC) in the Adriatic Sea is thought to be involved in important and extreme phenomena such as near anoxic and anoxic events [*Pettine et al.*, 1999] and the formation of massive mucillaginous aggregates [*Degobbis et al.*, 1999], the observations on the distribution and variability of DOC and its important components are still limited [*Pettine et al.*, 1999]. Despite this lack of data, a general overview about DOC behaviour and concentration in the Adriatic Sea, can be derived from the literature. The presence of a seasonal cycle in the northern basin, with spring-summer concentration increase of a factor of 2, was observed by *Pettine et al.* [1999, 2001] who found that total DOC concentration varied in the range of 74–281 μmol L^{-1}, in June, and 53–123 μmol L^{-1} in February. This increase was related to the freshwater DOC input and nutrient discharges (that increase the marine primary production), mainly from the Po River [*Giani et al.*, 2005].

[3] The seasonal increase in DOC concentration was also reported by *Fonda Umani et al.* [1997] and *Faganeli and Herndl* [1991] who found seasonal variations ranging from 66–154 μmol L^{-1}, during the autumn and winter, up to 500 μmol L^{-1}, in summer, near the Slovenian part of the Gulf of Trieste. Recently the MAT project [*Giani et al.*, 2005] monthly monitored for hydrology and DOC the sections A, B and C of Figure 1. The analysis of DOC data indicated a general spring-summer increase of the DOC pool, from the winter values, of about 70 μmol L^{-1} for sections B and C while the seasonal increase for the northern section (A) was on average 48 μmol L^{-1}.

[4] The seasonal pattern in DOC accumulation observed in the northern Adriatic basin is similar to that observed in other coastal basins such as the Baltic Sea [*Zweifel et al.*, 1995], or in open sea areas such as the north western Mediterranean [*Copin-Montegut and Avril*, 1993] and the Sargasso Sea [*Carlson et al.*, 1994].

[5] The seasonal DOC accumulation could be due to an enrichment in refractory compounds either discharged by rivers or resulting from abiotic chemical interactions and/or from biological processes [*Azam et al.*, 1993, 1999]. The lack of orthophosphate and the low nutritional quality of organic substrate could be a factor to explain such DOC accumulation. Increase in freshwater residence time, the onset of strong vertical stratification and specific circulation structures characterizing the summer period circulation, are

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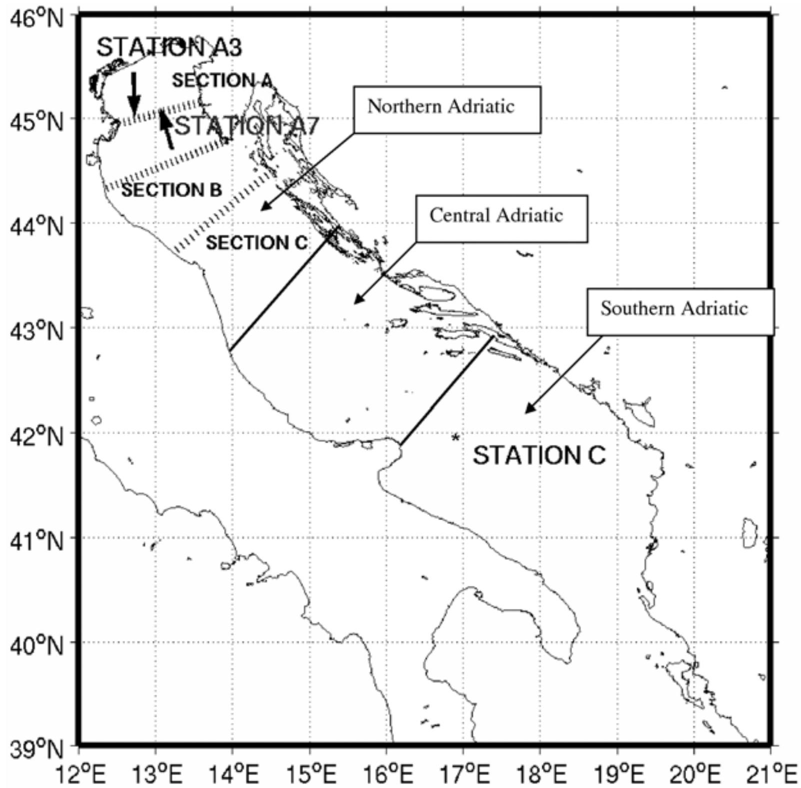

Figure 1. The model domain and observational sections of the MAT project. Section A and stations A3 and A7 are used for the comparison between observations and simulations (see Figures 6, 7, and 9). Stations A3, A7 and C are also used for simulations analysis in order to compare different trophic conditions. Sections B and C are mentioned in to the text.

also factors which could favour the accumulation of riverine organic matter as well as the occurrence of abiotic interactions which may lower the degradation rate of the organic substrate [*Keil and Kirchman*, 1994; *Pettine et al.*, 1999]. *Thingstad et al.* [1997] have proposed a theoretical model to explain DOM accumulation. According to this theory, bacterial carbon consumption may be limited by bacteria-phytoplankton competition for nutrients and by bacterial predators, respectively controlling growth and biomass of bacteria.

[6] In this paper we use numerical simulations to explore the process of DOC accumulation in the northern Adriatic basin, as described by *Giani et al.* [2005]. The numerical simulations are referred to as 'perpetual year' simulations because the circulation is forced to follow a perpetual seasonal cycle every year due to the coarse resolution of the hydrodynamics model and the repetition of the atmospheric forcing functions [*Zavatarelli and Pinardi*, 2003].

[7] The ecosystem simulations are produced by the coupling of such a three dimensional circulation model with a biogeochemical model derived from the European Regional Seas Ecosystem Model, ERSEM [*Baretta et al.*, 1995; *Polimene et al.*, 2006b]. The model has been validated in a previous paper for the major biogeochemical bulk properties [*Polimene et al.*, 2006b]. In this paper, the simulations are further validated against available DOC observations and, then, explored to investigate the DOC dynamics in the Northern Adriatic basin and the factors leading to DOC accumulation in this region.

2. Coupled Physical-Biogeochemical Model

[8] The three-dimensional ecosystem numerical model used is a coupled biogeochemical-hydrodynamic model. The biogeochemical pelagic model is a development of the European Sea Ecosystem Model (ERSEM [*Baretta et al.*, 1995; *Vichi et al.*, 2004, 2007; *Blackford et al.*, 2004]), to which we added the bacteria-DOC sub-model described by *Polimene et al.* [2006a]. Following this work, DOC was subdivided in three broad and distinct classes/state variables (the labile, the semi-labile and the semi-refractory DOC), each of them corresponding to different degrees of lability and having different production pathways. It should be stressed that the three classes of the model DOC cover only the labile and the semi-labile DOC pool, consequently the truly refractory DOC, that (having a turnover time of 100–1000 yr) is not involved in the seasonal DOC accumulation, is not considered.

[9] The model grid has an horizontal resolution of approximately 5 km while in the vertical the model uses a 21 σ levels defined as $\sigma = (z - \eta)/(H + \eta)$, where H (x, y) is the bottom topography and η(x, y, t) is the free surface elevation. The sigma layers have a logarithmic distribution near the surface and the bottom. The full model implementation is described by *Polimene et al.* [2006b] while the description of the coupling between the biogeochemical and

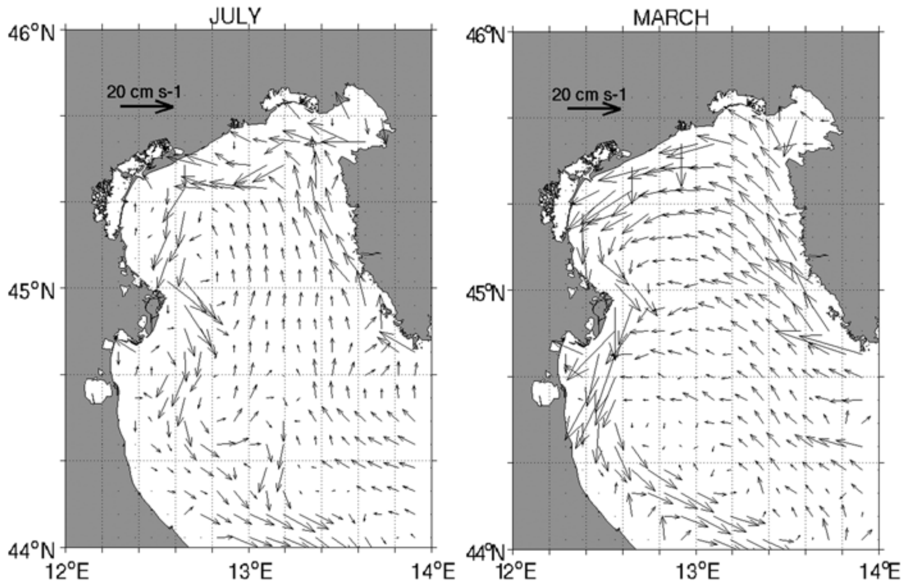

Figure 2. Velocity, monthly averaged, surface fields (cm s^{-1}).

physical model is detailed in *Zavatarelli et al.* [2000]. The model domain with the Adriatic sub-basins definition and the locations used for simulations analyses and comparison with observations are represented in Figure 1.

2.1. Biogeochemical Initial Conditions

[10] The initial conditions for the nutrients have been estimated from the ABCD dataset [*Zavatarelli et al.*, 1998] climatological winter averages and are assumed to be horizontally homogeneous but vertically variable. Initial condition for phytoplankton, zooplankton and bacteria biomass have been taken from the initial conditions for the ERSEM North Sea model [*Baretta et al.*, 1995]. Semi-labile and semi-refractory DOC was initialised with low constant concentration (20 μmol/L) while all the components (C, N, P) of the labile DOM were initialised to zero.

2.2. Biogeochemical External Input Fluxes

[11] Only few chemical families in the model are considered to have external inputs. Rivers are considered to be a source of dissolved inorganic nutrients and thus an external input to the model. The nutrient loads were specified at the mouth of each river and were parameterized as surface fluxes, as for salinity. The rivers considered and the rivers mouth locations are described by *Zavatarelli and Pinardi* [2003]. The monthly mean river runoff data were obtained from *Raicich* [1994, 1996] monthly climatologies, while the mean river nutrient loads were taken from *Degobbis and Gilmartin* [1990] who estimated them for the Po river. For the other rivers the annual mean load, for each nutrient, was supposed to be a fraction of that one of the Po river, respectively 20% for the Albanian rivers 10% for the Istrian rivers and 50% for all the others.

[12] Concerning the lateral open boundary in the Ionian Sea we used the same open boundary condition scheme implemented for temperature and salinity by *Zavatarelli and Pinardi* [2003].

2.3. Physical Circulation Structures

[13] The physical model implementation gives rise to a perpetual year simulation, i.e., the model is forced with repeated atmospheric forcing seasonal cycle until a steady repeating cycle in temperature, salinity and currents is obtained. The repeating seasonal cycle of the circulation is documented in *Zavatarelli and Pinardi* [2003] and will not be reproduced here. The model is capable to reproduce the major structures of the circulation such as the Western Adriatic Coastal Current (WACC) and the cyclonic circulation gyres in the central and southern Adriatic Sea.

[14] The coarse model resolution does not allow the development of a fully turbulent flow field, meaning in particular three-dimensional quasi-geostrophic turbulence or a mesoscale circulation, but it allows for internal instabilities to occur. The flow field is varying from month to month, repeating the same monthly circulation every year. One of such repeating structures of the circulation is the periodic detachment of the WACC from the coastal strip and its meandering toward the central areas of the Adriatic.

[15] Figure 2 shows the monthly mean circulation for July and March, the two opposite seasons central months. During March the circulation is strongly cyclonic with an intense WACC on the Italian side. The Po river runoff waters are confined in the western coastal strip (not shown). In July instead the circulation around the Po delta is weaker and a cyclonic recirculation exists in front and south of the Po river that tends to exchange waters of river origin toward the centre of the basin. We will see that this cyclonic recirculation is a very important part of the ecosystem response leading to DOC accumulation in the centre of the basin.

2.4. Coupled Model Spin-Up

[16] The circulation model is coupled with the Biogeochemical Fluxes Model (BFM, http://www.bo.ingv.it/bfm) at the start of the fourth year of integration, where the seasonal cycle in the hydrodynamics is stabilized. The BFM is then coupled with the hydrodynamics for 4 additional years during which the dissolved inorganic nutrients reach a repeating seasonal cycle starting from the uniform initial condition specified above [*Polimene et al.*, 2006b]. The results discussed in this paper are obtained only from the

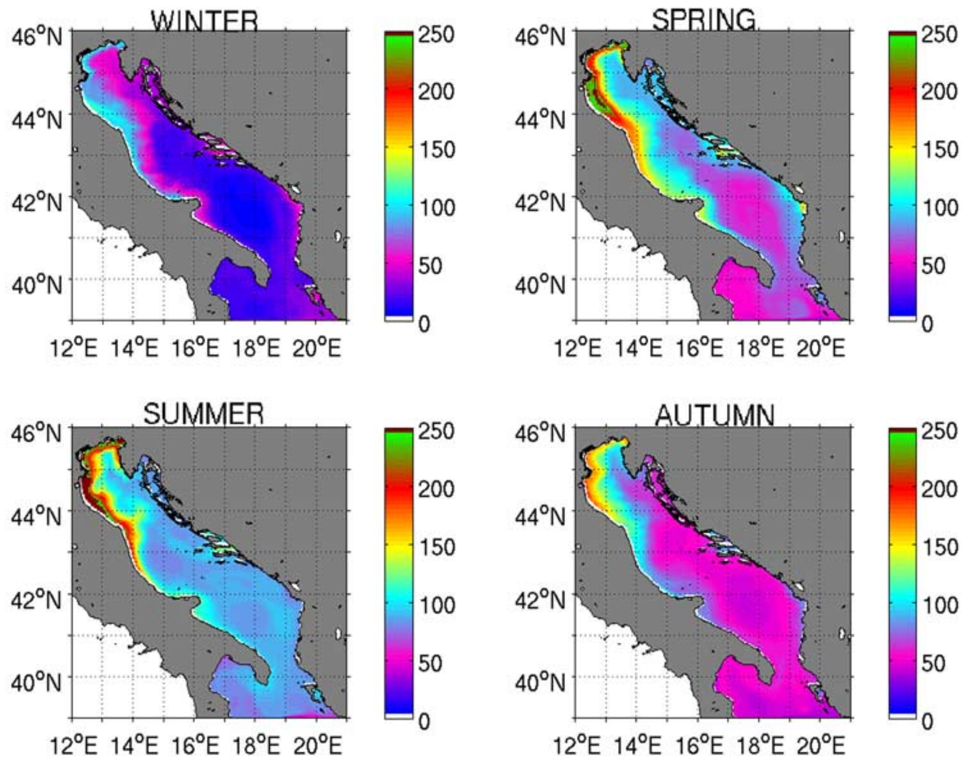

Figure 3. Surface, seasonally averaged, simulated total DOC (μmol L^{-1}) distribution.

fourth year of integration of the coupled model where the seasonal cycle is stabilized.

3. Results

3.1. DOC Horizontal Distributions

[17] Figure 3 shows the surface seasonal averages of the total DOC (the sum of the three DOC state variables resolved by the model) concentrations. The DOC winter values range from 25 μmol L^{-1} in the southern part of the basin and in the central area of the central basin, to 100 μmol L^{-1} along the Italian coasts, in the northern and central basin.

[18] During spring, DOC increases along the whole northern and western coasts, reaching values higher than 200 μmol L^{-1} in the north-western part of the basin. In the southern basin the DOC concentration is around 100 μmol L^{-1} in the coastal areas and 50 μmol L^{-1} in the open sea. In summer, the DOC concentration increases all over the basin reaching the values of about 100 μmol L^{-1} even in the open waters of the southern Adriatic. In autumn the concentration returns to the value of 50 μmol L^{-1} in the southern basin and in the eastern part of the central basin. In the north western basin concentrations higher than 150 μmol L^{-1} are still present in the coastal area.

[19] Figure 4 shows the monthly averaged time series of the simulated surface concentrations of semi-labile and semi-refractory DOC and the gross primary production for grid point corresponding to the location reported in Figure 1. Locations called "Station A3" and "Station A7" correspond to the MAT sampling stations along section A (Figure 1): station A3 is very close to the Po river delta area while station A7 is in the centre of the northern basin. Location called "station C" is representative of the southern basin open water.

[20] In station A3 the potential primary production shows two peaks in spring and autumn clearly related to the Po river runoff. The maximum value in spring is 100 mg C m^{-3} d^{-1}, while in September-October the maximum value is 500 mg C m^{-3} d^{-1}. The distribution of the semi-labile DOC is weakly related to the gross primary production with two relative maxima, one in spring (around 80 μmol L^{-1} in May) and the second one in autumn (around 100 μmol L^{-1} in October).

[21] The 'semi-refractory' DOC shows a quite constant value throughout the year (around 30 μmol L^{-1}) with a small increase (around 5 μmol L^{-1}) from June to October. In station A7 the gross primary production cycle is also marked by two peaks in spring and autumn, but with the values remarkably lower than in the station A3 (around 60 mg C m^{-3} d^{-1}). The semi-labile DOC reflects the gross primary production distribution with two maxima in June and October (70–80 μmol L^{-1}). The values are slightly lower with respect to the A3 station. The annual cycle of the gross primary production at the station C shows only one maximum in May with a value of 65 mg C m^{-3} d^{-1}. The maximum of 'semi-labile' DOC is reached in July when the simulated value is 65 μmol L^{-1}. The 'semi-refractory' DOC concentration shows a mild seasonality (only 5 μmol L^{-1} the increase between the minimum, in March, and the maximum, in October) and during winter is higher than the semi-labile DOC.

3.2. DOC Vertical Distribution

[22] The semi-labile and semi-refractory DOC annually averaged profiles in the northern, central and southern Adriatic (see Figure 1) are shown in Figure 5.

[23] In the northern basin, the semi-labile DOC reaches 80 μmol L^{-1} in the surface, and decrease constantly with

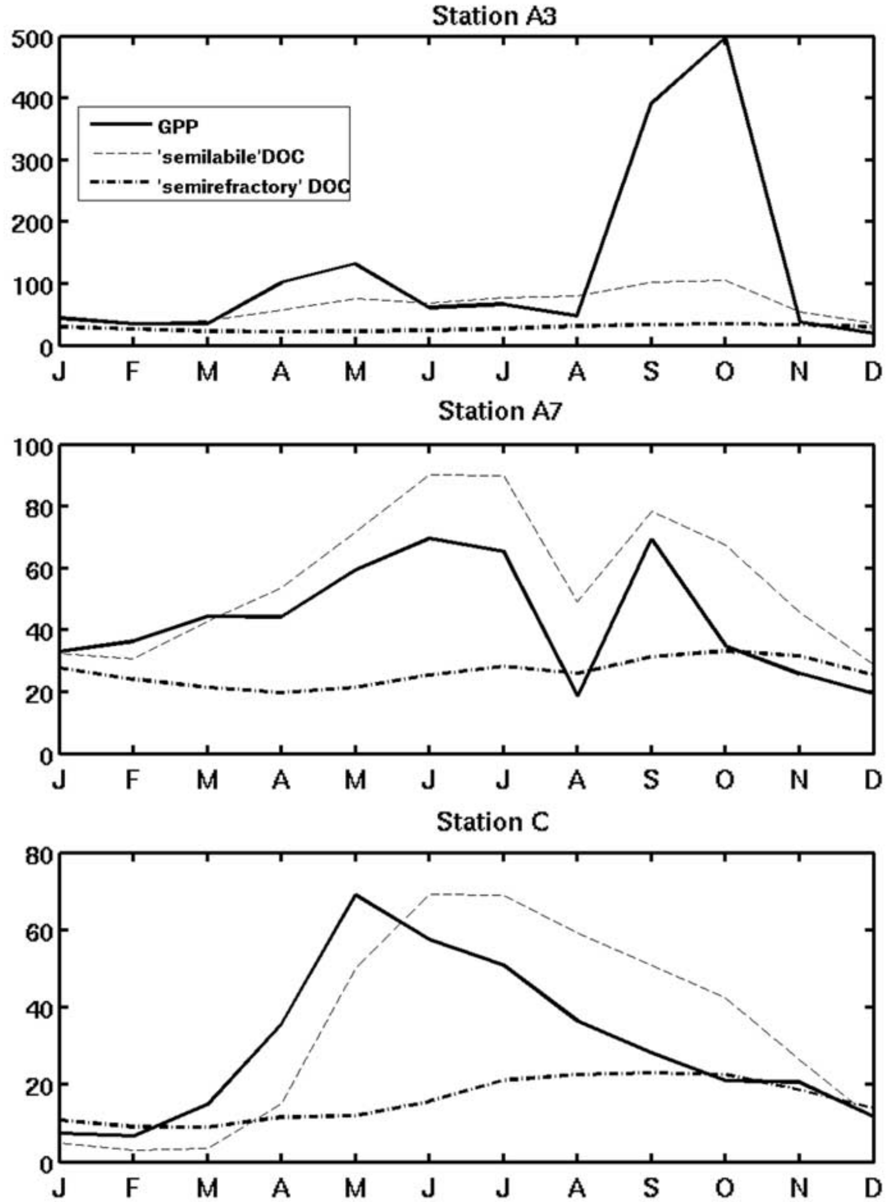

Figure 4. Yearly cycle of simulated surface, monthly averaged, semi-labile, semi-refractory DOC (μmol L^{-1}) and gross primary production (mg C m^{-3} d^{-1}) in stations A3, A7 and C.

depth reaching a value of 20 μmol L^{-1} at the bottom. Conversely the semi-refractory DOC shows a quite constant vertical profile (about 30 μmol L^{-1}). In the central basin the semi-labile DOC concentration decreases from the surface value of 40 μmol L^{-1} to about 10 μmol L^{-1} at 50 meters depth and then remains vertically constant. The semi-refractory DOC concentration is about 20 μmol L^{-1} near the surface and decrease gently till the bottom where the value is around 10 μmol L^{-1}.

[24] The semi-labile and semi-refractory DOC profiles, in the southern basin, do not change significantly in terms of both behaviour and amount with respect to the central basin.

3.3. DOC Distribution Along the Section A and Comparison With Data

[25] In this section the simulated, monthly averaged, DOC concentrations along section A are analyzed and compared (Figure 6) with data monthly sampled in a three years period (1999–2002) during the MAT project. In order to compare observations with climatological simulations data collected from 1999 to 2002 were monthly averaged. Both model and observational data were averaged over the water column.

[26] In winter, the simulated DOC concentrations range from 70 to 100 μmol L^{-1}, in the area close to the Italian coast while are almost constant (around 70 μmol L^{-1}) in the eastern part of the section. These values are in good agreement with observations in the zone of the section A closer to the Italian coast, while, on the eastern side, the model tends to underestimate the observed data. From March to June the concentrations increase everywhere along the section, but the west-east gradient is still evident with higher values (150–160 μmol L^{-1}) on the western part of the section.

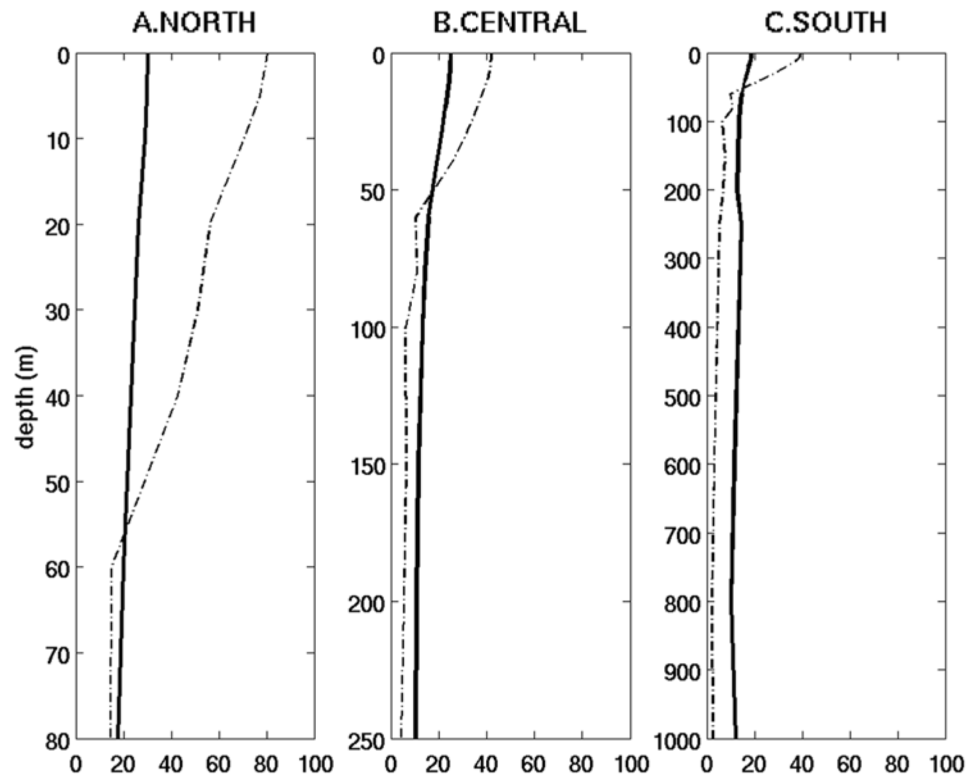

Figure 5. Simulated vertically profiles of yearly averaged semi-labile (dotted line) and semi-refractory (bold line) DOC (μmol L^{-1}) averaged on the North (a), Central (b) and Southern (c) Adriatic sub basins.

[27] From June to November the concentrations near the Italian coast are permanently high (130–160 μmol L^{-1}) but, at the same time, it is evident that in the central of the section other maxima occur, reaching 130 μmol L^{-1} in July and September–October. Maxima located in the central of the section are also present in the observations in April and June–July. In November and December the simulated DOC

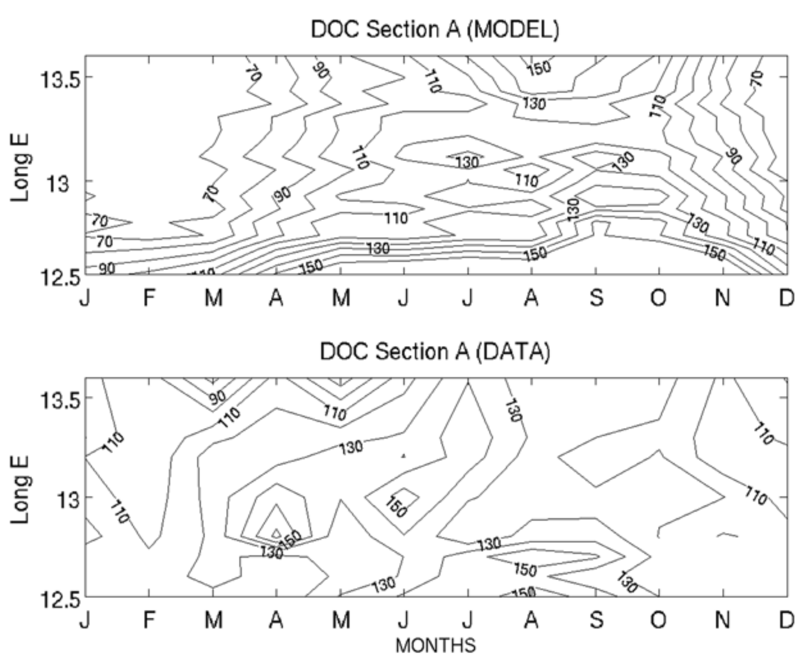

Figure 6. Annual time series of simulated monthly averaged total DOC concentrations (μmol L^{-1}) along section A and data sampled along the same section during the MAT project. Data plot is made by monthly averaging three years (1999–2002) observations. Both observational and simulated values are averaged over the water column.

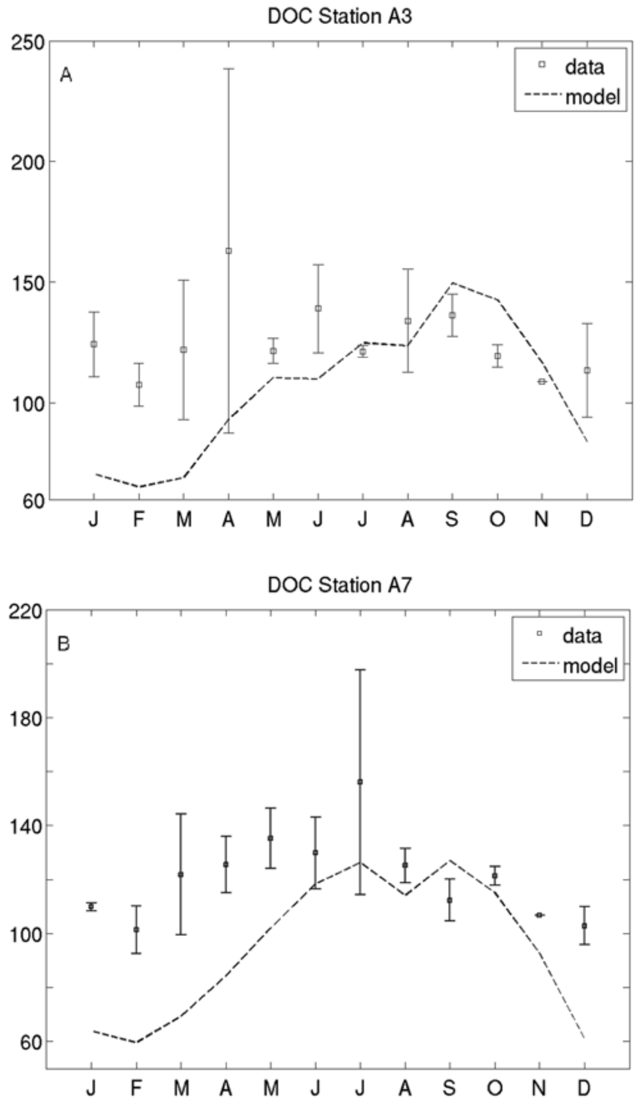

Figure 7. Annual cycle of simulated total DOC (μmol L^{-1}) and comparison with observations. (a) Station A3 and (b) station A7. Both simulated and observed data are averaged over the water column. Three years observations are averaged and plotted with the standard deviation.

concentrations return to the January–February values drawing a seasonal cycle consistent with the observed one.

[28] Figure 7 shows comparison between the annual cycle of observed and simulated DOC (depth averaged) concentrations at stations A3 and A7 (see Figure 1). In both stations, the model underestimates the observations in winter while is in good agreement in summer and autumn. The maximum summer values are well captured by the model especially in station A7.

3.4. Orthophosphate and DIN/ORTHOPHOSPHATE Ratio Along Section A

[29] Figure 8 shows the simulated orthophosphate (depth averaged) concentrations and the dissolved inorganic nitrogen (DIN) to orthophosphate ratio along the section A.

[30] Orthophosphate concentration shows a clear seasonal cycle related to the Po river runoff. The maximum simulated values occur in May and September. Concentrations higher than 0.02 μmol L^{-1} are present only in the coastal area while the central part of the section is orthophosphate depleted throughout the year. The DIN/PO_4 ratio ranges from 50 to 150, with the minimum values near the coasts and the maximum in the center of the section. This means that highly unbalanced conditions for inorganic nutrients exist in the centre of section A which cannot likely sustain a large primary production. Thus the DOC concentrations of Figure 6 in the section A centre have a non local origin, as we will explain in the following section.

4. Discussion and Conclusions

[31] The simulated DOC concentrations, even with a general underestimation, are in qualitatively good agreement with the values reported in literature for some area of the Adriatic Sea [*Pettine et al.*, 1999, 2001; *Giani et al.*, 2005]. The modelled DOC distribution, with the maximum located in the high production area (the north-western part of the basin [*Barale et al.*, 2005; *Polimene et al.*, 2006b]), is reasonable and in agreement with the current knowledge of the DOC dynamics [*Ogawa and Tanoue*, 2003]. A clear seasonal cycle is also well captured by the model and the spring-summer simulated increase, that can double the winter concentration, is consistent with observational findings [*Pettine et al.*, 1999; *Giani et al.*, 2005]. The vertical profiles (Figure 5), with the increase of the semi-labile components in the euphotic zone and the constant concentration of the more refractory DOC trough the water column, are consistent with those reported in literature for the oceanic DOC [*Ogawa and Tanoue*, 2003].

[32] The general underestimation with respect to the data reported in literature could be due to the fact that the model, focusing only on a seasonal time scale, do not consider the so called truly refractory DOC, that is cycled on a time scales ranging from hundreds to thousand of years. Furthermore, important factors such as the DOC riverine input, the UV radiation exposure [*McCallister et al.*, 2004] and the changes in bacterial community structure [*Carlson et al.*, 2002], that are supposed to be important for DOC cycling processes, are not considered in the model.

[33] Despite these limits, the analysis of the different DOC components (Figures 4 and 5) proposed in our implementation, offers a possibility to explain some of the features of the DOC dynamics in the Adriatic basin. The "labile" fraction is a small percentage of the total DOC during the whole year (data not shown). This fraction of DOC ranges from 0 to 4 μmol L^{-1} and is about 1–2 % of the total DOC amount that is a fraction consistent with the fraction reported in literature for the dissolved proteins [*Pettine et al.*, 1999].

[34] The semi-labile fraction of the DOC, that is the main products of phytoplankton and bacteria exudation, is the most abundant in the areas characterized by high productivity, while, in the more oligotrophic zone, as the open water of the southern Adriatic basin, its concentration is equal or less than the semi-refractory DOC (Figure 4).

[35] The semi-refractory DOC surface distribution shows a seasonal cycle less pronounced with respect to the other DOC components and the surface distribution is almost constant throughout the year in the grid point (corresponding

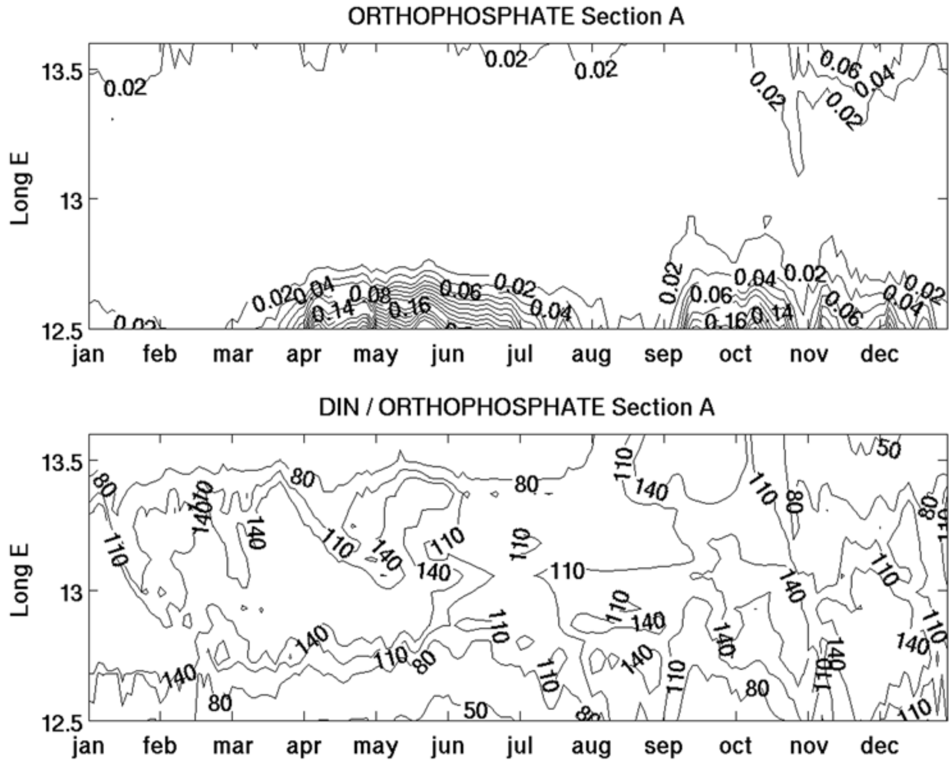

Figure 8. Annual time series of simulated PO_4 concentrations (μmol L^{-1}) and DIN/PO_4 ratio along section A. Values are averaged over the water column.

to stations A3, A7 and C in Figure 1) sub-sampled from the model domain (Figure 4) suggesting that this fraction of DOC contributes to the background DOC level.

[36] Even if DOC climatological data for an adequate validation of the model are not present in literature, a direct comparison was possible using the MAT project data. This comparison (Figures 6 and 7) shows a general good agreement between data and simulations and makes it possible to think that the model proposed is based on correct assumptions.

[37] The analysis of the simulated DOC values along the section A and the comparison with the observational data referred to the same section allows us to speculate about the DOC dynamics in the northern area of the Adriatic sea. The model reproduces (at least qualitatively) the summer maximum values of the observed DOC time series (Figures 6 and 7), both near the Po river delta area and in the central part of the section A. In order to further stress the capacity of the model to reproduce the relatively high DOC concentrations in the centre of the northern Adriatic basin, a comparison between simulated DOC concentrations, along section A at the end of June, and the observational data collected on June 29 2000 in the same section, is offered in Figure 9. Observations were interpolated using the objective analysis technique [*Carter and Robinson*, 1987]. The observed maximum located in the centre of the section is well reproduced by the model even if with a consistent underestimation (120 μmol L^{-1} simulated against 150 μmol L^{-1} observed).

[38] The fact that in the coastal area the model simulates high orthophosphate concentrations, while, in the central part of the basin the simulation highlights a condition of orthophosphate depletion (orthophosphate concentration less than 0.02 μmol L^{-1} and DIN/PO4 more than 100) suggests that the DOC pool present in the centre of the section with relatively high concentration (more than 100 μmol L^{-1}) is not only locally and recently produced because the very low concentration of the limiting nutrient (phosphorus) does not allow to support a high local primary production. As detailed in the next section, the presence of the west-east trophic gradients depicted by the DOC distributions of Figure 3 and already pointed out by the remote sensing chlorophyll estimates [*Barale et al.*, 2005] and previous modelling studies [*Polimene et al.*, 2006b], could determine the accumulation of DOC in the northern Adriatic basin.

[39] In Figure 10 are shown the total DOC concentration, the Bacterial Growth Efficiency (BGE), the DOC "utilization time" (defined below) and the ratio between the semilabile and the semi-refractory DOC. In all the pictures the velocity field is overlaid on the biochemical field. The figure is referred to a surface snapshot of the first day of July, that is the month in which, usually, there is the highest increase of DOC concentration and when mucilage phenomena are frequently observed.

[40] The simulated value of the BGE ranges from 0.4 near the Po river delta to 0.1 in the central part of the basin; these values are in agreement with the BGE values reported by *del Giorgio and Cole* [1998] for estuarine coastal areas and oligotrophic open water areas, respectively.

[41] In the central part of the northern Adriatic basin it is evident that the cyclonic circulation structure, noted already in Figure 4 for July, carries high values of DOC from the coastal runoff dominated strip toward the more oligotrophic

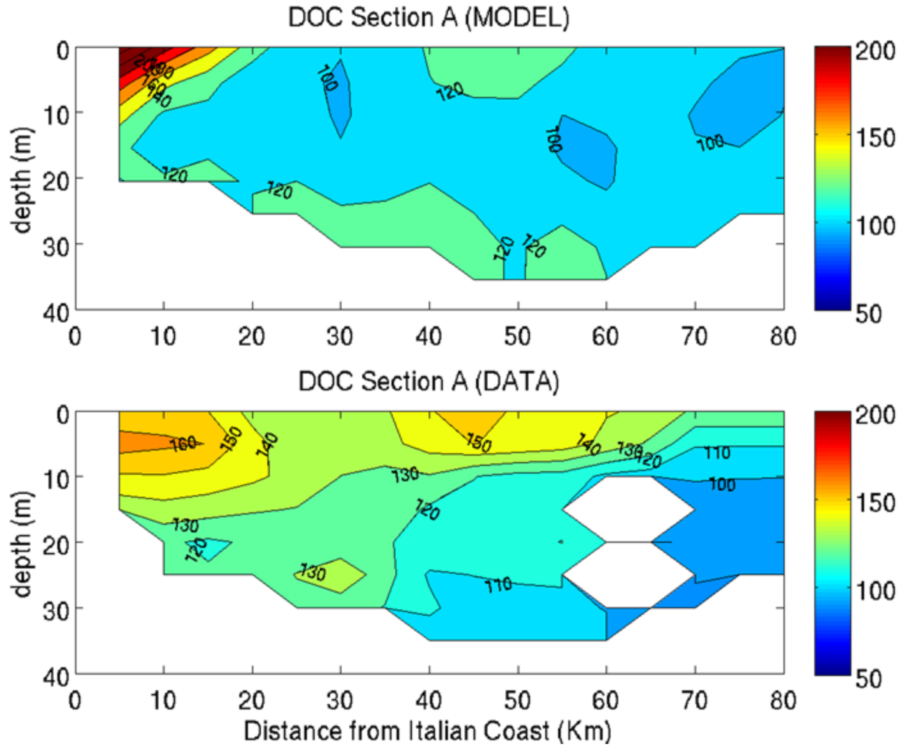

Figure 9. Simulated and observed total DOC concentrations (μmol L^{-1}) along section A. Model simulations are referred to the last day on June, while data are those sampled on June 29, 2000 during the MAT project. Data plot was obtained by interpolating observations with the objective analysis technique.

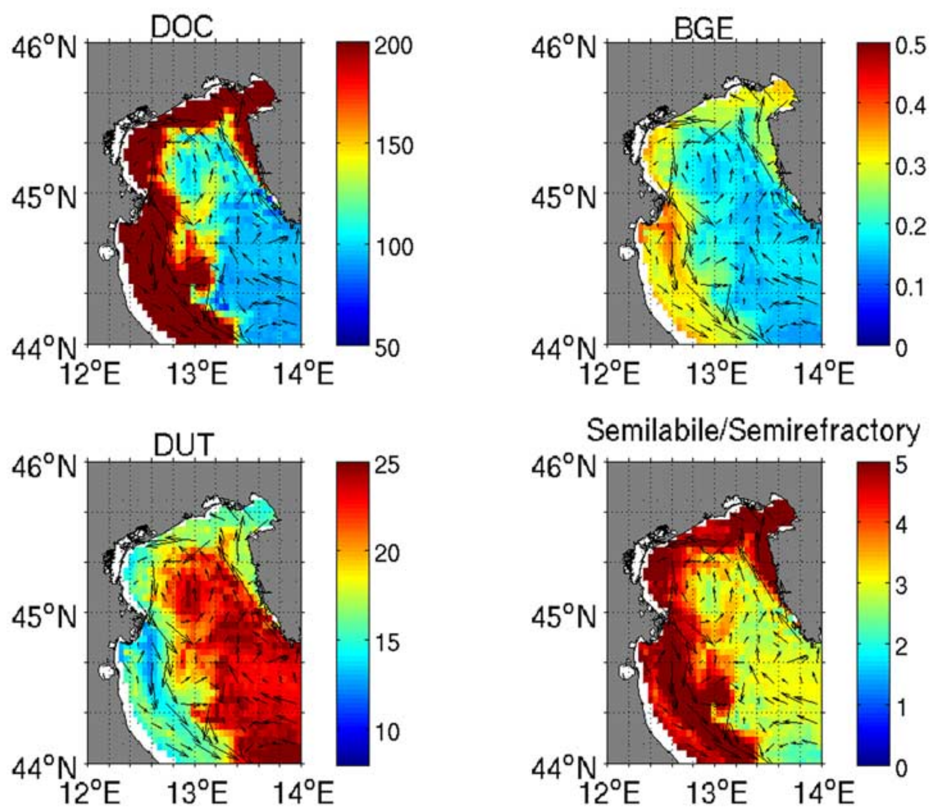

Figure 10. Snapshot (July first) of simulated total DOC (μmol L^{-1}), BGE, DOC utilization time (days) and semi-labile to semi-refractory DOC ratio in the northern Adriatic Sea. Velocity field (vectors) is superimposed to the distribution of the biogeochemical properties.

central basin areas. This advective process, by transporting DOC in areas with remarkably different trophic characteristic, might play a crucial role in triggering the DOC accumulation process. The presence of high values of both DOC and BGE in the Po river delta area, indicates that the high nutrients discharge allows the phytoplankton growth and, consequently, the DOM production, but, at the same time, enhances the bacterial capacity to convert dissolved matter in biomass; thus, the DOC present in this area, can be produced and used rapidly because the system is highly energetic. The DOM dynamics in this zone is then characterized by high production (and consumption) but not accumulation. In order to clarify this concept we define the theoretical DOC Utilization Time (DUT) by dividing the total DOC amount for the bacterial carbon demand (BCD) that is the bacterial production plus the bacterial respiration:

$$DUT = DOC/BCD$$

The high values of DOC near the coasts are located in an area characterized by low DUT (less than 10 days) (Figure 10) and high BGE, while the relatively high DOC concentrations (more than 100 μmol L^{-1}), transported by the cyclonic recirculation in the central part of the basin, are in a zone where the DUT strongly increases and the BGE is low (less than 0.2). In this context the transfer of organic carbon to the high trophic levels is low and the DOC may accumulate. Furthermore, the reduced production of fresh DOC implies an increase in its semi-refractory component, as indicated by the semi-labile/semi-refractory DOC ratio (Figure 10).

[42] Following this idea it is evident that in order to accumulate DOC it is necessary to have two different (contrasting) conditions in the proximity of each other: the first is a region with high primary production, such as the western Adriatic coastal area, and the second is an area characterized by an ecological regime of very low BGE that normally is connected to the open ocean. We have shown that, when these two different systems exists and can exchange properties through physical circulation structures, an ‘‘anomalous’’ DOC accumulation may occur.

[43] In the northern Adriatic Sea, during summer, seasonal sub basin scale circulation structures (Figures 4 and 10) link the eutrophic western part with the more oligotrophic central part of the basin. The cyclonic re-circulation produces offshore currents that transport DOC produced in the coastal areas toward the off-shore regions where the system has low BGE and long DUT. The WACC detachment and the cyclonic gyre, allowing the lateral transport of biochemical properties described in Figure 10, is a major component of the complex process that allows DOC to accumulate at the centre of the basin.

[44] A recent study [*Engel et al.*, 2004] demonstrated that polysaccharide aggregation is one of the main mechanisms causing sinking of dissolved organic carbon in the ocean; we can speculate that the aggregation processes are a function of the amount of carbon present in the water column and its residence time. Thus the DOC residence time, here given as DUT, could be a key point in order to understand the aggregation mechanisms leading to phenomena such as marine snow and mucilage.

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