Modeling the nitrogen cycling and plankton productivity in the Black Sea using a three-dimensional interdisciplinary model

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[1] A six-compartment ecosystem model defined by a simple nitrogen cycle is coupled with a general circulation model in the Black Sea so as to examine the seasonal variability of the ecohydrodynamics. Model results show that the annual cycle of the biological productivity of the whole basin is characterized by the presence of a winter–early spring bloom. In all the regions this bloom precedes the onset of the seasonal thermocline and occurs as soon as the vertical winter mixing decreases. Phytoplankton development starts in winter in the central basin, while in coastal areas (except in the river discharge area) it begins in early spring. In the Danube’s discharge area and along the western coast, where surface waters are almost continuously enriched in nutrient by river inputs, the phytoplankton development is sustained during the whole year at the surface. The seasonal variability of the northwestern shelf circulation induced by the seasonal variations in the Danube discharge and the wind stress intensity has been found to have a major impact on the primary production repartition of the area. In the central basin the primary production in the surface layer relies essentially on nutrients being entrained in the upper layer from below. Simulated phytoplankton concentrations are compared with satellite and field data. It has been found that the model is able to reproduce the main characteristics of the space-time evolution of the Black Sea’s biological productivity but underestimates the phytoplankton biomass especially in regions extremely rich in nutrients such as the Danube discharge area. INDEX TERMS: 4842 Oceanography: Biological and Chemical: Modeling; 1615 Global Change: Biogeochemical processes (4805); 4815 Oceanography: Biological and Chemical: Ecosystems, structure and dynamics; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; KEYWORDS: mathematical modeling, ecosystem, Black Sea


1. Introduction

[2] The Black Sea is known as one of the best examples of highly stratified marginal seas constituting one of the world’s largest stable anoxic basin. It is by large a land locked basin with only restricted exchanges with the Mediterranean Sea through the Bosphorus Strait (Figure 1). Therefore its overall mass budget and hydrochemical structure critically depend on elements of the hydrological balance. Its hydrographic regime is characterized by low-salinity surface waters of river origin overlying high-salinity deep waters of Mediterranean origin. As a result, a permanent pycnocline (or more precisely a halocline) develops with a depth varying horizontally according to the local hydrodynamics and inhibits the exchanges between the surface and deep waters.

1.1. Biogeochemical Vertical Structure

[3] The Black Sea possesses a distinct vertical biogeochemical structure representing major characteristic features of the oxygen deficient pelagic waters of the world’s oceans (Figure 2). The poor ventilation of the deep waters by the vertical mixing and by lateral influxes conjointly with the degradation of the huge biological production have made the Black Sea almost completely anoxic with oxygen only in the upper 150 m depth (13% of the sea volume) and hydrogen sulfide in the deep waters. The predominant
vertical gradients of biogeochemical properties are confined within the strongly stratified upper 100 m layer, in which the density changes by about 5 kg/m$^3$ from $\sigma_t \sim 11.0$ kg/m$^3$ at the surface to $\sigma_t \sim 16.0$ kg/m$^3$ at 100 m depth.

The water column of the open sea consists of four biogeochemically distinct layers: (1) the surface layer well oxygenated by the seasonal mixing and by active planktonic processes, (2) the oxycline/upper nitraille layer characterized by a steep decrease of the oxygen concentration to about 10 mmol O$_2$ m$^{-3}$ and an increase in the nitrate concentration to about 6–9 mmol N m$^{-3}$ due to the oxidation of regenerated ammonium, (3) the transitional layer, the so-called suboxic zone [e.g., Murray et al., 1995], with a thickness of about 20–40 m where the oxygen and sulphide concentrations are low ($\sim 1–5$ mmol m$^{-3}$) with no overlapping, and (4) the deep anoxic layer of hydrogen sulphide and ammonium pools. In the transitional layer, the oxidation-reduction potential of the water decreases sharply because of oxygen deficiency and the appearance of hydrogen sulphide at its lower boundary. As a result, this layer contains a rich set of bacterially mediated redox reactions involving oxygen, nitrogen, sulphur, carbon, manganese and iron and so, its lower and upper interfaces are characterized by important gradients of biological and chemical variables. These reactions control the downward transport of nitrate and the upward transport of ammonium and sulfide near the interface zone [Oguz et al., 2000]. Also, according to the chemical model developed by Brewer and Murray [1973], the chemiosynthetic bacterial population at the interface between oxic and anoxic waters would seem to act as a fairly effective ‘lid’ for the anoxic basin, trapping much of the upward flux of carbon dioxide, ammonia and phosphate and returning it to the deep water in particulate form, perhaps forming one of the mechanisms whereby the Black Sea basin acts as a ‘nutrient trap’. For instance, it was proposed that the upward fluxes of sulfide and ammonium may be oxidized by Mn(III, IV) and Fe(III), whereas the downward flux of nitrate may be reduced by dissolved manganese and ammonium [e.g., Murray et al., 1995; Oguz et al., 2000]. The oxidation of ammonium by manganese into nitrogen gas, which is lost to the atmosphere, therefore completely decouples the subpycnocline ammonium source from the near surface nitrogen source used for new production. Therefore no new nitrogen would reach the euphotic zone from the deep waters and so, the nitrogen cycle of the surface layer is independent of the chemical processes occurring in the deep waters [e.g., Sorokin, 1983; Yakushev and Neretin, 1997].
Furthermore, this structure implies that the organic matter sedimenting to the deep waters of the open sea is definitely lost for the system and should therefore be compensated by lateral nitrate fluxes, mostly originating from the Danube River discharges and also from the atmosphere.

The recycling of detritus in the oxygenated layer of the Black Sea water column is a rapid and efficient process. Sediment trap observations and model results [e.g., Karl and Knauer, 1991; Oguz et al., 1996; Grégoire and Lacroix, 2001] have indeed shown that more than 75% of the particulate organic nitrogen produced in the euphotic zone is recycled in the upper 100 m of the water column and only 5–25% reaches the anoxic zone and is definitely lost for the upper layer ecosystem [e.g., Karl and Knauer, 1991; Lein and Ivanov, 1991].

1.2. Bathymetry

The geometry of the basin is simple, yet the wide continental shelf regions (depth <100 m) and the flat abyssal plain (maximum depth 2,200 m) represent two vastly different environments interacting via transport processes (Figure 1). The northwestern shelf forms a shallow receptacle for the most important Black Sea rivers (i.e., the Danube River, with a mean annual discharge of about 212 km³) and is well known, as shown by CZCS and SeaWiFS images, as a region of enhanced biological production fuelled by the nutrients brought by the river discharges.

1.3. Existing Models

In the last decade, hydrodynamical, biological and chemical models at different levels of complexity have been developed in order to gain new insights into the basic physical and biogeochemical functioning of the Black Sea basin. These models are often limited to interaction box models applied in a hypothetic homogeneous environment [e.g., Özsoy et al., 1998; Cokacar and Özsoy, 1998] or to one-dimensional (vertical) coupled physical biogeochemical models describing usually nitrogen cycles [e.g., Lebedeva and Shushkina, 1994; Oguz et al., 1996, 1999; Oguz et al., 2000; Oguz et al., 1998, 1999; Staneva et al., 1998; Lancelot et al., 2002]. Models applied in the suboxic zone and describing the nitrogen and sulfur cycles coupled with oxygen dynamics and sometimes, to the manganese cycle as a catalyst for the redox reactions have also been developed [e.g., Yakshev and Neretin, 1997; Yakshev, 1998; Oguz et al., 1998, 2000]. Three-dimensional models of the upper layer ecosystem describing simple nitrogen cycles have been developed by Grégoire [1998], Grégoire et al. [1998], Staneva et al. [1998], and Grégoire and Lacroix [2001]. The ecosystem model developed by Grégoire et al. [1998] considers several size classes of phytoplankton and zooplankton as well as several potential limiting nutrients of...
the phytoplankton development. This model was used to simulate the succession of blooms of the different phytoplankton groups during the first six months of the year (i.e., the winter-early spring bloom and the end of spring bloom occurring at depth feeding on regenerated nutrients) and to test the limitation of the phytoplankton development by the availability of phosphorus and silicate (for diatoms). The competition between the different phytoplankton groups is analyzed in connection with the variability of the hydrodynamics. Grégoire and Lacroix [2001] refine a classic NAPZD ecosystem model (defined by nitrate, ammonium, phytoplankton, zooplankton and detritus) to describe explicitly the oxygen dynamics in order to assess the ventilation process of the Black Sea’s intermediate layer. Staneva et al. [1998] described and analyzed a few simulations performed with a NAPZD ecosystem model in connection with the 3D variability of the physical environment.

In this paper, an ecosystem model has been coupled with a hydrodynamical model in a 3D frame to understand the macroscale (i.e., timescale of a few weeks to months) ecohydrodynamics over the year. The model has been run for a few years until it reaches more or less established seasonal cycles which, at the scales of our study, do not show a substantial interannual variability. The results illustrate a highly complex spatial variability in the phytoplankton annual cycle imparted by the horizontal and vertical variations of the physical and chemical properties of the water column. Physical structures associated with the vertical stratification (e.g., permanent pycnocline, thermocline), the horizontal frontal boundaries between river waters and open sea haline waters, and the formation of secondary flows are shown to be of the uppermost importance for the dynamics and structures of biological populations. The comparison of the phytoplankton biomass computed by the model with satellite-derived estimates and field observations of chlorophyll concentrations suggests that the model reproduces quite well the seasonal plankton productivity cycle in the different areas of the basin but underestimates the phytoplankton biomass in the Danube’s discharge area.

This paper is organized as follows. Section 2 describes the mathematical tool with the assumptions and idealizations made. The convergence of the model solution to an established seasonal cycle is discussed. Section 3 describes the results of the numerical experiments and their consistency with observed data. The main findings of the hydrodynamic model are summarized, stressing the aspects of the current and hydrological fields that affect the ecosystem. The seasonal variations of the circulation and thermohaline fields are described as well as the space-time evolution of the mixed and mixing layer depths. The seasonal cycle of the phytoplankton bloom is analyzed emphasizing its regional variations induced by the variations of the local hydrodynamics. The model results are compared with field and satellite observations. A discussion on the ability of model results to reproduce the observations is given in section 4. Finally, the main conclusions are given in section 5.

2. Mathematical Tool: Description of the Three-Dimensional Model

The three-dimensional model results from the on-line coupling between a general circulation model and an ecosystem model. Its equations are formulated in the so-called σ coordinate system to follow the bathymetry as closely as possible. To simulate the general circulation and associated synoptic structures, the domain is covered with a 15 km * 15 km horizontal numerical grid and 25 vertical σ layers. The spacing of the vertical layers is adjusted to offer a finer resolution in the vicinity of the surface and in the region of the thermocline (the thickness of the vertical layers is about 5 m in the upper 30 m and 10 m down to 100 m). The influence of biogeochemical processes on the hydrodynamics is not taken into account. The velocity vector, the vertical diffusion coefficients and the temperature are computed in the hydrodynamic model and are introduced at each time step in the ecosystem model.

2.1. Hydrodynamical Model

The GHER general circulation model which has been used in this study of the Black Sea seasonal ecohydrodynamics is three-dimensional, nonlinear and baroclinic. It uses a refined turbulent closure scheme and solves the motions of the free surface. It is well known that the vertical turbulent diffusivity coefficients can be expressed in terms of the kinetic energy of the turbulence k and its dissipation rate ε. In the GHER model, the equation for ε (which, at the general circulation scale contains too many unknown parameters) is dropped and replaced by an algebraic mixing length closure taking into account the intensity of both the stratification and the surface wind mixing. The GHER general circulation model has been successfully applied to explore the general circulation of the Bering Sea [e.g., Deleersnijder and Nihoul, 1988], the North Sea [e.g., Delhez, 1996], the Mediterranean Sea [e.g., Beckers, 1991] and, more recently, the Black Sea [e.g., Grégoire et al., 1998; Grégoire, 1998; Stanev and Beckers, 1999; Grégoire and Lacroix, 2001, 2003].

2.2. Ecosystem Model

The ecosystem model is defined by a simple nitrogen cycle based on the functional role played in the trophic dynamics by planktonic populations. It is described by 6 aggregated variables: the phytoplankton and zooplankton biomasses without reference to species, total detritus (lumping together dissolved and particulate dead organic matter), nitrate, ammonium and benthic detritus. The phytoplankton (ϕ) represents all the primary producers. All the heterotrophs with a size ranging between 2 μm and 2 mm are described by the zooplankton compartment (z). Since the microbial loop of the Black Sea’s oxygenated waters is particularly efficient [e.g., Sorokin, 1983; Karl and Kauer, 1991], the bacterioplankton has been eliminated from the model assuming quasi-equilibrium, prey-predator relationships within the microbial loop. Nitrogen is the most limiting nutrient of the phytoplankton growth to the intense denitrification process occurring in the suboxic layer. In this model, nitrogen is the only limiting nutrient and is divided into ammonium (n1) and nitrate (n2). Nitrate concentrations are not represented because, on the one hand, in the euphotic layer data indicate that they are always smaller than the concentration of other forms of nitrogen [e.g., Codispoti et al., 1991; Basturk et al., 1994] and their contribution to the phytoplankton growth is expected to be small. On
the other hand, data reveal that nitrite oxidation rates are always faster than ammonium oxidation rates (5–10 times faster) [Ward and Kilpatrick, 1991]. Besides, following the model of Oguz et al. [1999], the introduction of nitrite production as an intermediate step of the nitrification process has no distinguishable contribution to the euphotic zone nitrogen budget. Finally, the dead organic matter (particulate and dissolved) is described by the detritus compartment (ω), and the sediments are described by the benthic nitrogen pool $\beta_n$. A schematic representation of the ecosystem model with all the interaction terms written on the arrows is given in Figure 3. The evolution equations of the biogeochemical state variables and the mathematical formulation of the biogeochemical interactions are described in the Appendix A. The estimation of biogeochemical parameters is based on available observations and modeling studies realized in the Black Sea [e.g., Oguz et al., 1996, 1998; Ozsoy et al., 1998] or in other...
similar environments such as the Baltic Sea and the North Sea. The initial and boundary conditions used to force the hydrodynamical and biogeochemical models are described in the Appendix B.

2.3. Transient Adjustment

After ten years of integration of the physical model, the amplitude of the seasonal cycle is more or less established in response to the imposed external forcings and to the internal processes in the system. During the 10-year spin-up, the annual mean vertical stratification does not show substantial trends and remains close to the initial data. After this spin-up time, the hydrodynamical model is in balance and the basin inventory of water and salt remain constant over the annual cycle [Stanev and Beckers, 1999]. This does not mean that trends are totally absent but, at the scale of our study (i.e., the seasonal cycle), the small trends, which may be potentially important for paleoceanography, could not significantly affect the results of the model. Using the results of the tenth year of integration of the physical model, the biological model of the upper layer ecosystem is then integrated to obtain almost repetitive yearly cycles of the biological variables (this is the case after three years of integration).

3. Results

3.1. Hydrodynamics

3.1.1. Circulation and Thermohaline Fields

A basin-scale, coherent, cyclonic boundary current that follows approximately the continental slope is the main feature of the Black Sea general circulation (Figure 4) [e.g., Stanov, 1990; Oguz et al., 1992, 1993; Stanev and Beckers, 1999]. Referred to as the Rim Current by Oguz et al. [1992, 1993], this cyclonic circulation results essentially of the cyclonic wind pattern (positive curl of wind stress) but is also driven by the large-scale hydrothermodynamic forcing (surface and lateral buoyancy) and is controlled by the topography [e.g., Stanov, 1990]. As a result, the sea surface elevation reaches its maximum value in the coastal zone and decreases with increasing distance from the coast. Along the Anatolian and Caucasian coasts, where changes in bottom slope and coastline orientation are particularly important, the Rim Current accomplishes large meanders and unstable features are generated on a wide range of space and timescales [e.g., Blatov et al., 1984; Stanov, 1990; Oguz et al., 1993; Sur et al., 1994].

The coastal areas and the central region enclosed by the Rim Current are occupied by physical structures of different length scales: a number of cyclonic gyres, interacting with the main boundary current and associated with length scales ranging from a few tenths to a few hundreds of kilometers, characterizes the circulation of the central basin during the whole year with seasonal modifications in their number, form and position whereas, a series of semipermanent anticyclonic eddies exists on the periphery between the Rim Current and the undulations of the coast [e.g., Ginzburg et al., 2000, 2001].

In spring and summer, the weakening of the wind stress leads to a decrease of the sea level which tends to promote a cyclonic circulation. Consequently, as shown in Figure 4 and in agreement with previous studies [Stanev, 1990], the intensity of the main current decreases in summer. As a result, the oscillations of the main current observed along the Anatolian and Caucasian coasts intensify and large meanders with length scales of ≈100–200 km are generated. Besides, a weakening of the quasi-permanent cyclonic gyre located in the extreme east of the basin is simulated in agreement with satellite observations which have revealed an intensification of the anticyclonic character of the circulation in the area in summer. In fall, the river discharges reach their minimal values and the circulation is disorganized.

The shallow northwestern shelf constitutes the coldest part of the Black Sea throughout the year [e.g., Özsoy and Ünlüata, 1997; Ginzburg et al., 2001] and receives the fresh water inputs of the Danube, Dnestr and Dnepr Rivers. This leads to the formation of a strong haline front which can be observed during the whole year with seasonal modifications in its intensity and structure resulting mainly from the pronounced seasonal variability of the northwestern shelf circulation (Figure 6). From the end of fall until the middle of spring, the fresh waters from the Dnepr and Dnestr are transported southward by the cyclonic current that occupies the surface northwestern shelf waters at this period and mix with the Danube waters for reaching the Anatolian coast in May. The strong haline front confines river waters along the western coast and prevents the mixing between the coastal waters and the more saline open seawaters characterized by a salinity of ≈18–18.2 (Figure 6).

One of the most important characteristics of the seasonal variability of the northwestern shelf circulation on an ecological point of view is the reversal of the surface current at the middle of spring until the end of fall and the generation, at the Danube’s mouth, of an anticyclonic eddy with a length scale of some tens of km (Figure 4). This reversal of the flow has also been simulated by Blatov et al. [1984] and Oguz et al. [1995]. It cannot be explained by the presence of southerly winds entraining northward the surface waters because the climatological monthly mean wind stress used to force the model is from the north from the middle of spring until the end of fall except in June and July where southerly winds prevail. This eddy appears when the river discharges intensify and reach their peak. The existence of a cyclonic circulation in the northwestern shelf surface waters from the end of fall until the middle of spring can be explained by the presence of strong
Figure 4. Horizontal distribution of the general circulation simulated at 10 m (top) in January and (bottom) in July (currents in m s$^{-1}$).
The northly winds entraining the surface mixing layer (i.e., the zone being actively mixed from the surface) southward. At the beginning of spring, when the mixing layer depth is reduced, only the surface waters are entrained southward by the northly winds. At the middle of spring, the river discharges reach their peak and the wind stress is not strong enough to induce a cyclonic current in the surface layer and the circulation becomes anticyclonic. Below the mixing layer, the circulation remains anticyclonic during the whole year. Besides, some studies have shown that the anticyclonic eddy generated at the Danube’s mouth is better represented with a hydrodynamic model using a higher horizontal resolution [e.g., Grégoire, 1998]. This confirms, in agreement with the previous results of Oguz et al. [1995], that this eddy results more from a nonlinear effect associated to the intrusion of river fresh waters than from a wind effect as suggested by Blatov et al. [1984].

The northeast extension of the haline front in summer has also been revealed by salinity measurements (S. Konovalov and L. I. Ivanov, personal communication).

3.1.2. Mixed and Mixing Layers

The seasonal variations of the mixing layer (i.e., the zone being actively mixed from the surface) depth and the mixed layer depth (i.e., the zone of relatively homogeneous water formed by the history of mixing) simulated by the model and obtained from available hydrographic data [Cokacar and Özsoy, 1998] are compared in different areas of the basin which have been chosen according to their peculiar dynamical and biogeochemical properties (Figure 7).

The mixed layer depth corresponds to the zone above the top of the pycnocline. The peculiar vertical stratification of the Black Seawaters characterized by the presence of a permanent halocline makes impossible to use criteria based
only on the temperature gradient to determine the mixed layer depth. The analyses of mixed layer depths from hydrographic data made by Cokacar and Özsoy [1998] suggested that the detection of the mixed layer depth in the Black Sea required two separate definitions. The first one, used essentially in summer months (i.e., profiles having a surface temperature greater than 12°C are considered to belong to summer months), defines the mixed layer depth as the depth at which a temperature decrease of 1.5°C takes place relative to the surface value. The second criterion, used in the remaining period, is based on the vertical density gradient, defining the mixed layer depth as the depth where the density gradient exceeds a value of 0.03. The same definitions have been used to determine the mixed layer depth in the model.

Since the mixing layer depth generally corresponds to the depth zone in which there is strong turbulence directly driven by surface forcing, it can be best determined from values of overturning length scales, which are perhaps the most direct measure of active mixing processes [Brainerd and Gregg, 1995]. Indeed, overturning length scales within a convecting layer are dominated by static instabilities resulting from cold water in the surface layer and give a good indication of the maximum depth to which the convection can penetrate. Also, criteria based on the value of the overturning length scale and on the vertical diffusivity coefficient have been used in this study to identify the mixing layer depth.

Figure 6 shows that the mixing layer is obviously always included in the mixed layer and, at the beginning of spring and in fall, when the level of turbulence is not very important but is high enough to prevent the presence of a thermocline, the mixed layer is limited by the upper boundary of the main halocline and can be deeper than the mixing layer by more than 60 m. This important difference between the mixed and mixing layer depths has to be taken into account to determine the onset of the phytoplankton winter-early spring bloom as it will be discussed below. In summer, the mixed and mixing layer depths are almost the same and coincide approximately with the upper boundary of the seasonal thermocline. The mixing layer depth varies essentially with the wind speed and the intensity of the cooling of the sea surface temperatures, deepening where and when the winds and cooling are strong, and shallowing in summer when winds are weak. In all the studied areas, the mixing layer depth reaches its peak in February with important regional gradients in its distribution. Figure 8 shows, indeed, that it is on the northwestern shelf, outside the river discharge area, and along the western coast, where the cooling and the winds are the strongest, that the mixing layer is the deepest with values of about 75 m. Besides, as the upper 90 m of the open seawaters are more stratified than the coastal areas, mixing layer depths are shallower in the central basin than along the coast for a given wind speed; that is, the high stratification of the
surface layer of the open sea retards mixing layer depth deepening. For instance, in the center of the cyclonic gyres of the central basin, the winter mixing layer does not extend further than 45 m.

[26] The summer mixing layer depth does not exceed 5 m in all the regions. The autumn season is known to be characterized by weekly storms which are expected to enhance temporarily upward flux of nitrate into the surface layer [Oguz et al., 1996]. However, since the model is forced at the air-sea interface by the mean wind stress at macroscale produced by a monthly mean wind and not, as it should have been, by the mean wind stress including a quite significant component due to nonlinear interactions of mesoscale winds, small-scale events, such as storms, are not well represented. This leads to an underestimation of the production of turbulent kinetic energy at the surface and therefore also of the mixing layer depth. On the other hand, at the surface, temperature values are relaxed toward climatological monthly mean values and this leads to an overestimation of surface temperatures. Therefore the vertical mixing by convection is also underestimated. For instance, in November, the surface temperatures of the central basin are relaxed toward about 14°C during the whole month. However, field observations give a surface temperature of about 11°C at the mid-November [Oguz et al., 1996]. Besides, it should be noted that using a nudging scheme for the temperature to force the model at the surface instead of the heat fluxes underestimates the vertical penetration of the seasonal atmospheric signal. For instance, in spring, only the first upper 15 m are affected by the seasonal heating of the water column. As a result, in summer, the vertical extension of the thermocline is estimated to about 13 m while field observations give a vertical extension of about 30 m.

[27] The mixed layer depth is limited by the upper boundary of the main halocline in winter and by the top of the thermocline in summer. In winter, the upward motion of the main halocline in the central basin reduces the mixed layer depth to about 40–70 m. In particular, in the eastern part of the sea (at longitude 37°E), where the cyclonic current is the most intense and the main pycnocline the shallowest, the mixed layer does not extend further than 45 m in winter as confirmed by the observations of Ovchinnikov and Popov [1987]. On the other hand, along the western coast, south of the Romanian coast, and along the Anatolian coast, the downward motion of the main pycnocline allows the extension of the mixed layer to 70–100 m. On the northwestern shelf, outside the river plume, the water column is almost not stratified. As a result, the Rim Current often appears as a boundary between regions of different mixed layer depths.

[28] In the Danube’s discharge area, the intrusion of the fresh river waters creates a strong vertical stratification and the mixed layer does not extend further than 30 m. This restriction will create optimal conditions for the development of the primary production throughout the year. Besides, in agreement with observations, the seasonal thermocline develops earlier (in March) and maintains longer

**Figure 7.** Seasonal variations of the averaged mixed layer depth in the different regions illustrated in Figure 1, (left) obtained from databases (Reprinted from Cokacar and Özsoy [1998] with permission from Kluwer Academic Publisher; the 95% confidence limits are marked by error bars, solid bars denote values obtained from the recent database (1986–1995), while dashed bars denote values obtained from the Mamayev (1923–1992) database), (right) simulated by the model (in bold). In the model the mixing layer depth has also been represented. The depth of this layer has been defined as the depth to which a daily average vertical diffusivity coefficient of 10 cm² s⁻¹ is simulated (in continuous normal line) or a daily average mixing length of 1 m is simulated (in dashed line) (both criteria approximately lead to the same value of the mixing layer depth).

**Figure 8.** Horizontal distribution of the winter mixing layer depth (in meters).
(until October/November) in the eastern part of the basin than in the western and northwestern basin (where the thermocline starts in April until August/September) because of the presence of higher atmospheric temperatures and weaker winds in this area at the beginning of spring and fall.

[29] The analysis of the seasonal cycle of the mixed and mixing layer depths confirms that the winter meteorological conditions are not severe enough to generate a vertical mixing which is able to erode the main pycnocline which is therefore permanent and remains throughout the year.

3.2. Ecodynamics

3.2.1. Phytoplankton

[30] The seasonal evolution of the surface phytoplankton spatial pattern simulated by the model is illustrated in Figure 9. Figure 10 shows the SeaWiFS estimates of the sea surface chlorophyll a concentration. Figure 11 compares the surface phytoplankton annual cycle obtained from model results and observations (satellite and field measurements) in different parts of the basin characterized by particular dynamical conditions. For comparison of phytoplankton biomass with chlorophyll a observations, one uses a conversion factor of 1 mmol N ~ 1 mg chl. This conversion factor considers an algal carbon to chlorophyll ratio of 100 and carbon to nitrogen ratio of 8.5, even though these numbers are subject to seasonal and regional variabilities over the Black Sea [e.g., Karl and Knauer, 1991; Oguz et al., 1999]. Both model results and observations illustrate a highly complex spatial variability of the phytoplankton annual cycle imparted by the horizontal and vertical variations of the physical and chemical properties of the water column.

[31] In all the regions, the phytoplankton annual cycle is characterized by the presence of a winter-early spring bloom. In the Danube’s discharge area and along the western coast, where surface waters are almost continuously enriched in river nutrient, the phytoplankton development is sustained during the whole year at the surface with seasonal modifications in its intensity. Conversely, in the central basin, the primary production in the surface layer relies essentially on nutrients being entrained in the upper layer from below and a winter-early spring bloom is simulated in agreement with field observations (Figure 11). Along the Caucasian coast, satellite observations show the presence of high chlorophyll concentrations throughout the year. This bloom seems to be enhanced by local inputs of nutrients along the coast, and thus it cannot be represented by the model.

[32] At the end of spring and in summer, the maximum development of the phytoplankton is observed at depth, below the thermocline, except at the Danube’s mouth where it occurs at the surface all over the year. At the beginning of fall, the observations reveal the presence of a new bloom in the surface layer of the central basin. However, this bloom is strongly underestimated in the model because of the underestimation of the vertical mixing at this period. The bloom is delayed and only occurs in November–December (Figure 11). Here below, the seasonal evolution of the phytoplankton bloom is described in details on the base of the analysis of model results.

3.2.1.1. Winter

[33] In winter, the enrichment of surface waters in nutrient depends on the intensity of the vertical mixing and on its ability to erode substantially the nitracline which coincides approximately with the main halocline. Therefore it is necessary that during a lapse of time, the winter mixing and mixed layers coincide approximately. Figure 7 shows that this is the case in almost all the regions in February. However, if the vertical mixing is usually beneficial for the biological production because it deepens the mixing layer and enriches surface waters in nutrient, an intensive mixing may have a negative effect if it expands the mixing layer so deep that the phytoplankton spends too much time in low light conditions. Indeed, it is usually considered that, when primary production relies on nutrients being entrained in the upper layer from below, the most favorable situation might be when the critical depth (i.e., the depth at which the integral net production is zero) equals the depth of the mixing layer [Sverdrup, 1953]. Therefore the cyclonic gyres of the central basin are regions particularly favorable to the development of a winter bloom of the phytoplankton because on the one hand, this is in these regions that the nitracline is the shallowest and, on the other hand, the soft meteorological conditions and the shallow pycnocline reduce the mixing layer depth to about 30–50 m. This bloom reaches its peak in winter in the eastern cyclonic gyre where the main pycnocline is the shallowest and in early spring in the western basin (Figure 11). In the Danube’s discharge area, the continual input of nutrients and the reduction of the mixing layer depth by the presence of a strong vertical stratification allow the development of phytoplankton in the surface layer throughout the year. All these considerations explain why, in January, the maximum development of phytoplankton is simulated in the surface waters of the eastern main cyclonic gyre of the central basin and also in the Danube’s discharge area with maximum concentrations of respectively 1.5 and 3 mmol N m⁻³ (Figures 9 and 11). In the coastal areas (along the western and Anatolian coasts) and on the northwestern shelf outside the river plume, the phytoplankton concentrations do not exceed 1 mmol N m⁻³ in January because of the light limitation of its growth. In these regions, model results show that the phytoplankton development intensifies in March and reaches concentrations of about 3 mmol N m⁻³ as soon as the mixing layer depth decreases and becomes comparable to the euphotic layer.

[34] It should be noted that everywhere the model shows that the bloom precedes the onset of the seasonal thermocline (Figure 12). This confirms that the formation of a thermocline is not always necessary to allow the occurrence of a phytoplankton bloom as already observed by Oguz et al. [1996]. This emphasizes that the key parameter in the onset of a phytoplankton bloom is more the depth of the mixing layer rather than the depth of the mixed layer.

[35] In agreement with field observations [Vedernikov and Demidov, 1993; Mikaelyan, 1995], in the main part of the central basin, where the permanent pycnocline moves to the sea surface and inhibits the penetration at depth of the vertical mixing (Figure 13), the vertical extension of the bloom does not exceed 35–40 m (Figure 14) because of the light limitation of the phytoplankton development below the pycnocline. Conversely, in coastal areas and on the shelf, phytoplankton populations extend vertically until 70–80 m.

3.2.1.2. Spring

[36] At the end of April, the horizontal extension of the high productivity surface waters is reduced (Figure 9).
Phytoplankton populations occupy the northwestern shelf and the coastal areas along the western and Anatolian coasts and remain confined close to the coast by the main haline front. Model results and satellite observations reveal, however, some large extensions of the bloom toward the open sea along the Anatolian coast where the interactions of the main boundary current with the abrupt modifications of the coastline orientation and of the topography lead to frontal

Figure 9. Model-simulated sea surface phytoplankton distribution (in mmol N m$^{-3}$): (a) in January, (b) in March, (c) in May, (d) in June, (e) in August, and (f) in December.
instabilities (Figures 9 and 10). In the central basin, the nutrient content of surface waters decreases progressively and the phytoplankton populations migrate to greater depths feeding on regenerated nutrient. Simulated concentrations are of about 0.5 mmol N m\(^{-3}\) and are in good agreement with field and satellite chlorophyll \(\alpha\) observations that are between 0.2 and 0.5 mg m\(^{-3}\) [Vedernikov and Demidov, 1993; Nezlin et al., 1999].

Figure 9. (continued)
At the middle of spring, the reversal of the flow on the northwestern shelf transports the phytoplankton populations in the northeastern part of the shelf. Model results, in agreement with satellite observations (Figures 9 and 10), show the presence of high productivity waters on the whole northwestern shelf and along the western and Anatolian coasts with large intrusions toward the open sea at the shelf break. According to Sur et al. [1994], coccolithophorids dominate the early summer primary production except at the Danube’s mouth where species rich in chlorophyll $a$ develop.

### 3.2.1.3. Summer

In summer, in a general way, the phytoplankton feeds mainly on regenerated nutrient and reaches its maximum development at depth just at the seasonal thermocline, except at the Danube’s mouth where maximum concentrations are still observed in the surface layer. For instance, in the central basin, phytoplankton develops between 15 and 35 m with maximal concentrations of 0.6 mmol N m$^{-3}$. This value is slightly lower than field observations which are between 0.75 and 1.2 mmol N m$^{-3}$ at 40 m [Vedernikov and Demidov, 1993]. Along the Anatolian and western coasts, phytoplankton reaches its maximum development between 15 and 40 m with concentrations between 0.5 (along the eastern Anatolian coast) and 1.4 mmol N m$^{-3}$ (along the western coast).

At the end of September, the bloom initiated on the northwestern shelf in the Danube area continues its propagation offshore. This is at this period that the western basin is enriched in the nutrients brought by the rivers on the northwestern shelf. However, this enrichment occurs mainly at depth (about 70–80 m) and therefore does not considerably enhance the phytoplankton development. Also, a small bloom with concentrations of only 0.1–0.2 mmol N m$^{-3}$ occupies the surface layer of the region at this time (Figure 11). In front of the Caucasian coast, intense upwel-
Figure 11

Western open regions

- in situ data
- model results (region 6)
- CZCS (25%)
- CZCS (75%)

Eastern open regions

- in situ data
- model results (region 7)
- model results (region 8)
- CZCS (25%)
- CZCS (75%)

Eastern Anatolian coast

- in situ data
- model results (region 5)
- CZCS (25%)
- CZCS (75%)

Figure 11
lings bring to the surface cold nutrient rich waters and enhance the phytoplankton development.

### 3.2.1.4. Autumn

The autumn period corresponds to the preconditioning and initial cooling phase. The seasonal thermocline weakens and the deepening of the mixing layer begins by the end of October. The thermocline collapses almost completely on the northwestern shelf while in the central basin the simulated mixed layer extends to about 30 m (Figure 7). A secondary bloom is simulated along the western coast while in the central basin, the underestimation of the vertical mixing at this period, delays the occurrence of a new phytoplankton bloom (Figure 11).

In November–December, the intensification of the wind stress destroys the seasonal thermocline of the central basin. Surface waters are enriched with nutrient entrained from below and a new phytoplankton bloom occurs in the surface layer of the area (Figure 11).

Taking 1 mmol N approximately equivalent to 0.1 g C, the euphotic layer vertically integrated phytoplankton biomasses obtained from model results and field observations for the open sea are compared (Figure 15). The integrated biomass has its maximum peak in early spring with lower values in the centre of the eastern gyre where the main pycnocline is the shallowest and limits the vertical extension of the phytoplankton bloom to the upper 30–35 m. Values of about 5.5 gC m$^{-2}$ are simulated in this region while values of about 8 gC m$^{-2}$ are simulated in the western basin. These values reflect the typical measured biomasses in different parts of the central basin at the same period which are between 5 and 8 gC m$^{-2}$.

In April, a secondary peak of biomass is simulated in the eastern gyre and corresponds to the development of a subsurface bloom. The summer biomass values of about 0.5–0.8 g C m$^{-2}$ are also in the range of measured values (0.5–1.5 g C m$^{-2}$). However, at the beginning of fall, the simulated values are below the observations because the model does not simulate the early autumn bloom in the surface layer.

### 3.2.2. Nitrate

In the deep basin where waters below 100–150 m are anoxic, the vertical nitrate profile is characterized by the presence of a nitracline throughout the year (Figures 2 and 12). Indeed, the oxidation of the ammonium produced in the regeneration of detritus leads to the formation of a nitrate peak and below, nitrate decreases with depth likely because of heterotrophic denitrification. Therefore this nitrate maximum corresponds to the transition between the nitrification and denitrification processes in the water column. Its position varies horizontally according to the local physical and biogeochemical properties of the water column. For instance, in the central basin, the maximum is observed at 60–80 m while, along the Anatolian coast, maximum concentrations are reached at about 100 m (Figure 12).

In winter, the vertical mixing erodes partially the nitracline and the nitrate concentration in the mixing layer reaches about 2 mmol N m$^{-3}$ in the central basin, 3.7 mmol N m$^{-3}$ and 1.4 mmol N m$^{-3}$ along respectively the western and eastern Anatolian coast, 5 mmol N m$^{-3}$ along the western coast and 15 mmol N m$^{-3}$ in the Danube’s discharge area. In summer, nitrate is below detection limit in the euphotic zone of the central basin and increases below this depth region because of the oxidation of regenerated ammonium. Conversely, the surface waters of the northwestern shelf and along the western coast are continuously fed in the nutrient brought by the rivers on the northwestern shelf. However, this is only at the end of the year that the rich nutrient river waters reach the central basin and enrich the region in nutrient (in September, for the western basin and in December, for the eastern basin).

### 3.2.3. Ammonium

During the whole year, the ammonium content is minimal in the surface layer with a typical concentration that does not exceed 0.1–0.2 mmol N m$^{-3}$ (Figure 12). At the base of the euphotic layer, the ammonium concentration increases after the winter-early spring bloom and reaches a maximum of about 0.5 mmol N m$^{-3}$ because of the recycling of detritus. In summer, this regenerated ammonium is oxidized into nitrate. In the upper part of the anoxic layer, where the nitrification process ceases because of the lack of oxygen, the ammonium concentration increases.

### 3.2.4. Zooplankton

In the central basin, the zooplankton reaches its peak of development in April, about one month after the winter-early spring bloom. The use of a threshold feeding concentration in the mathematical expression of the zooplankton grazing rate leads to the absence of zooplankton development when the prey biomass is below the threshold feeding concentration. This explains why, in the central basin, the zooplankton reaches very small concentrations in summer. While along the western coast and on the northwestern shelf, where the phytoplankton is abundant and where waters are enriched in detritus by river discharges, the zooplankton reaches very small concentrations in summer. While along the western coast and on the northwestern shelf, where the phytoplankton is abundant and where waters are enriched in detritus by river discharges, the zooplankton reaches very small concentrations in summer. 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While along the western coast and on the northwestern shelf, where the phytoplankton is abundant and where waters are enriched in detritus by river discharges, the zooplankton reaches very small concentrations in summer.
maximum and detritus accumulates below the surface water until about 150 m. Concentrations gradually decrease at the end of spring because of remineralization into ammonium. In summer, detritus accumulates below the seasonal thermocline to 100 m along the western coast, and 60–70 m in the open sea, with concentrations of about 0.1–0.2 mmol N m\(^{-3}\) in July/August. Almost all the organic matter produced in the euphotic layer is remineralized in the oxygenated layer. The model estimates to about \(40 \times 10^3\) tons the annual loss of particulate organic nitrogen toward the anoxic waters.

4. Discussion and Conclusions

A 3D coupled biogeochemical-hydrodynamical model has been used to analyze and explain the spatial and temporal variability of the seasonal cycle of the biological productivity in connection with the variability of the hydrodynamical and chemical properties of the water column. The hydrodynamical model is able to reproduce the main features of the Black Sea hydrodynamics. In particular, the cyclonic circulation and interior upwellings induced by the wind field are simulated as well as the frontal system on the northwestern shelf. The biogeochemical model is defined by a simple nitrogen cycle based on the functional role played in the trophic dynamics by planktonic populations. It is described by six compartments: the phytoplankton and zooplankton biomasses, nitrate, ammonium, pelagic, and benthic detritus. After 3 years of spin-up run, the amplitude of the simulated seasonal cycle is more or less established and the results of an additional annual simulation are compared with satellite images and field observations collected in the area. The biogeochemical results illustrate a highly complex spatial variability in the phytoplankton annual cycle imparted by the horizontal and vertical variations of the physical and chemical properties of the water column. The annual cycle of the biological productivity of the whole basin is characterized by the presence of a winter-early spring bloom. In all the regions, this bloom precedes the onset of the seasonal thermocline. It occurs as soon as the mixing layer depth reduces and becomes comparable or shallower than the euphotic layer depth. In the Danube’s discharge area and along the western coast, where surface waters are almost continuously enriched in nutrient by river inputs, the phytoplankton development is sustained during the whole year at the surface with seasonal modifications in its intensity. The seasonal variability of the northwestern shelf circulation induced by the seasonal variations in the Danube discharge and the wind stress intensity has been found to have a major impact on the primary production repartition of the area.

At the end of spring and in summer, the maximum development of the phytoplankton is observed at depth below the thermocline almost everywhere, except at the Danube’s mouth where it occurs at the surface all over the year. The early autumn bloom revealed by field and satellite observations in the central basin is postponed to the end of fall in the model. This delay is essentially caused by the underestimation, in the model, of the vertical mixing at the beginning of fall because this period is characterized by weekly storms which are expected to enhance temporarily the upward flux of nitrate into the surface layer [Oguz et al., 1996] but are not adequately represented in the model.

The qualitative comparison of model results with SeaWiFS satellite data shows that the model reproduces reasonably well the space-time evolution of the phytoplankton distribution. On a quantitative point of view, it seems, however, that in the Danube’s discharge area, the bloom intensity is underestimated by the model. Indeed, the simulated concentrations are of about 1 mmol N m\(^{-3}\) and are far below field and satellite observations which give values for the chlorophyll a concentration of about 4 mg m\(^{-3}\) and even more. Nevertheless, it should be noted that, according to Longhurst et al. [1995], satellite data may overestimate, chlorophyll concentrations of marginal seas and coastal areas, especially because of the presence of high concentrations of yellow substances in suspension. In the Danube’s discharge area and along the western coast, where nutrients are abundant in the surface layer throughout the year allowing the growth of phytoplankton at saturation conditions, model results have shown that the most limiting factor of the phytoplankton development is the grazing pressure (except in winter when, in coastal areas, the light availability is the most limiting factor). In these regions, the phytoplankton reaches its peak of development in March with concentrations of 4.5 mmol N m\(^{-3}\) on the northwestern shelf and 3.5 mmol N m\(^{-3}\) along the western coast. However, as soon as the phytoplankton biomass reaches a threshold value, its development is rapidly controlled by the zooplankton that maintains a strong pressure throughout the year and prevents the explosion of the phytoplankton. Also, although the nutrient content of surface waters in these regions is extremely high and could sustain huge blooms, the phytoplankton biomass does not exceed 1 mmol N m\(^{-3}\). This particularity seems to be typical of simple ecosystem models considering only one phytoplankton compartment and one zooplankton compartment. Similar conclusions have been found earlier by Sarmiento et al. [1993] in their North Atlantic model and by Oguz et al. [1999] in their Black Sea model. As a result, the totality of the huge amount of nitrate discharged every year by the rivers on the shelf cannot be consumed and does not participate to the upper layer nitrogen cycling.

Some sensitivity studies of the model solution to the value of biogeochemical parameters have shown that the simulation of more intense phytoplankton blooms with such a simple model requires an unrealistic 10-fold decrease of the zooplankton grazing rate. Conversely, an unrealistic 10-fold increase of the phytoplankton maximum growth rate does not lead to an increase of the bloom intensity but to an increase of the zooplankton biomass stressing the strong control played by the zooplankton on the phytoplankton development. On the other hand, Armstrong [1994] pointed out that multiple prepredator models can

Figure 12. Seasonal variations of the vertical profiles of the biogeochemical state variables and of the temperature field in three typical areas of the basin characterized by peculiar hydrodynamical and biogeochemical properties: (a) the central basin (region 6), (b) the western coast (region 3), and (c) the Anatolian coast (region 4).
Figure 12
Figure 12. (continued)
Figure 12. (continued)
alleviate the limitations imposed by 1P1Z model and, as in the North Atlantic case, may generate increased chlorophyll concentrations comparable with observations [Oguz et al., 1999].

Model results in agreement with previous studies [e.g., Yakushev and Neretin, 1997; Konovalov et al., 2000] have shown that the denitrification process occurring in the suboxic layer constitutes the main process of nitrogen elimination in the Black Sea providing its ability to resist to the dramatic eutrophication process. 67% (i.e., $4.5 \times 10^5$ tons N yr$^{-1}$) of the total annual load of nitrogen brought into the Black Sea shelf by the rivers is irreversibly lost by denitrification. For comparison, on the base of in situ measurements performed during the EROS-21 expeditions on the

Figure 13. Horizontal distribution of the turbulent kinetic energy at 40 m in February (in $10^{-3}$ m$^2$ s$^{-2}$).

Figure 14. Horizontal distribution of the phytoplankton field at 40 m in February (in mmol N m$^{-3}$).
Black Sea northwestern shelf, Grégoire and Friedrich [2004] have estimated that the process of burial in the shelf sediments is responsible for a nitrogen loss of $57/10^3$ tons PON yr$^{-1}$.

The analysis of model results highlights the unavoidable limitations imposed by such a simple ecosystem model. However, this type of models is very helpful to obtain a first understanding of the system and, in particular, of the influence of physical processes on the ecosystem. The model described in this paper has been used for performing diagnostic computations in the 3D frame, and notably, for computing the exchange fluxes of nutrient, water and organic matter between the shelf and the deep sea and between the continental slope and the deep sea. Results of this study are presented by Grégoire and Lacroix [2003].

Nevertheless, the model will have to be refined to remedy to its above mentioned main deficiency. This will be made by notably considering several size classes of phytoplankton and zooplankton, a description of gelatinous carnivores (which are important in the present-day Black Sea eutrophicated ecosystem) and an explicit representation of the microbial loop. However, the complexity of the model should not be increased beyond the unavoidable limit of reliability imposed by the restricted set of data to initiate, calibrate and validate the model.

Appendix A

The evolution in space and time of the 3D biogeochemical state variables (except $b_h$) is described by equations of the general following form:

$$\frac{\partial y}{\partial t} + \nabla_y \cdot (u_y \, y) + \frac{\partial y}{\partial z} + \frac{\partial (w_y \, y)}{\partial z} = Q^y + \frac{\partial}{\partial z} \left( \lambda^z \frac{\partial y}{\partial z} \right) + \lambda_H \nabla^2_y y$$

Notation:
- $y$: any 3D biogeochemical state variable.
- $t$: the time.

$z$: the vertical coordinate.
$\partial$: partial differentiation.
$\nabla_H$: the horizontal differential operator.
$u$: the horizontal velocity.
$w$: the vertical velocity.
$\lambda^z$: the vertical turbulent diffusivity coefficient.
$\lambda_H$: the horizontal diffusion coefficient.
$Q^y$: the local production-destruction term resulting from biogeochemical interactions
$w_s$: the sedimentation velocity (only for detritus).

The mathematical expression of $Q^y$ is given in Figure 3. The mathematical formulation of the biogeochemical processes is given in Table A1 and the parameters used are listed in Table A2.

A1. Phytoplankton

The major biogeochemical fluxes governing the phytoplankton evolution (see the different terms of $Q^y$ in Figure 3) are nutrient uptake (see equation (A4) in Table A1), lysis (see equation (A10) in Table A1) and grazing by heterotrophs (see equation (A14) in Table A1). The total primary production, $F_{\text{tot}}$, (see equation (A1) in Table A1) is expressed as the product between the photosynthetic rate $L(I)$ (see equation (A5) in Table A1), described by the mathematical formulation of Platt and Jassby [1976], and the nutrient uptake function, $N_j(n_1, n_2)$, represented by the classical Michaelis-Menten-Monod kinetics (see equation (A4) in Table A1). A $Q_{10}$ law is used to model the temperature influence on the phytoplankton development (see equation (A3) in Table A1).

A2. Zooplankton

For the zooplankton compartment, the fluxes involved are the grazing (see equation (A11) in Table A1), excretion (see equation (A18) in Table A1) and mortality (see equation (A17) in Table A1) (see the different terms of $Q^z$ in Figure 3). The zooplankton is assumed to feed on phytoplankton and detritus with different but constant...
Ingestion rate, capture efficiencies (see equation (A13) in Table A1). The ingestion rate, $F_{0}$, as a function of the food concentration is assumed to follow a Michaelis-Menten type relationship considering that when the prey concentration is under a given threshold the zooplankton ceases its feeding activity [e.g., Mullin, 1963; Andersen and Nival, 1988].

### A3. Pelagic Detritus

The zooplankton fecal pellets (see equation (A16) in Table A1), constituting the unassimilated part of the ingested food, as well as the phytoplankton and zooplankton lysis (see equations (A10) and (A17) in Table A1) are the source of detritus. Detritus are recycled in the water column as a result of ingestion by zooplankton (see equation (A15) in Table A1) and remineralization into ammonium (see equation (A19) in Table A1) (see the different terms of $Q_d$ in Figure 3). They are also submitted to sedimentation. The detritus migration velocity, $w_{det}$, is expressed as a function of the detritus concentration to take into account that at high concentrations, detritus can form aggregate and this aggregation speeds up the sedimentation [e.g., Totterdell et al., 1993; Oguz et al., 1998].

### A4. Benthic Detritus

Benthic detritus are formed by the sedimenting particulate organic nitrogen which is deposited on the bottom (see the different terms of $Q_{bent}$ in Figure 3). They are recycled via benthic remineralization according to a first-order law proposed by Billen and Lancelot [1988] (see equations (B1) and (B2) in Appendix B). As a result, ammonium is injected from the benthic compartment into the bottom layer of the water column.

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Mathematical Expression of the Biological Processes</th>
<th>Equation Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{0}$</td>
<td>Flux of nitrogen consumed by phytoplankton</td>
<td>(A1)</td>
</tr>
<tr>
<td>$F_{0}$</td>
<td>$F_{0} = \nu_{0}(T, \psi, n_{1}, n_{2})\phi$</td>
<td></td>
</tr>
<tr>
<td>$\nu_{0}(T, \psi, n_{1}, n_{2}) = \nu_{0}(T = 20^\circ C)\phi(T)N_{0}(n_{1}, n_{2})L_{0}(I)$</td>
<td>(A2)</td>
<td></td>
</tr>
<tr>
<td>$\phi(T) = \frac{Q_{10}^{\phi}}{1 + e^{(T-10)/\alpha_{\phi}}}$</td>
<td>(A3)</td>
<td></td>
</tr>
<tr>
<td>$N_{0}(n_{1}, n_{2}) = \frac{n_{1}}{c_{1} + n_{1}} + \frac{n_{2}}{c_{2} + n_{2}}$</td>
<td>(A4)</td>
<td></td>
</tr>
<tr>
<td>$L_{0}(I) = \frac{1}{1 + e^{tanh(I - \delta(I))}}$</td>
<td>(A5)</td>
<td></td>
</tr>
<tr>
<td>$I(z) = I(z = 0) \exp[-\int_{0}^{z} k(z)dz]$</td>
<td>(A6)</td>
<td></td>
</tr>
<tr>
<td>$k = k_{w} + k_{d}$</td>
<td>(A7)</td>
<td></td>
</tr>
<tr>
<td>$F_{n}$</td>
<td>Flux of ammonium consumed by phytoplankton</td>
<td>(A8)</td>
</tr>
<tr>
<td>$F_{n} = \nu_{0}(T = 20^\circ C)\phi_{n}(T)\phi(T)N_{0}(n_{1}, n_{2})L_{0}(I) \frac{n_{1}}{c_{n} + n_{1}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_{n}$</td>
<td>Flux of nitrate consumed by phytoplankton</td>
<td>(A9)</td>
</tr>
<tr>
<td>$F_{n} = \nu_{0}(T = 20^\circ C)\phi_{n}(T)\phi(T)N_{0}(n_{1}, n_{2})L_{0}(I) \frac{n_{2}}{c_{n} + n_{2}}$</td>
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<tr>
<td>$F_{z}$</td>
<td>Flux of phytoplankton mortality</td>
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<td></td>
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<tr>
<td>$F_{z}$</td>
<td>Flux of zooplankton ingestion</td>
<td>(A11)</td>
</tr>
<tr>
<td>$F_{z} = \xi_{z}(\omega)(b_{z}z) = \left[\xi_{z}(\omega)\right]_{\max} \frac{\omega}{\max} U(z)$</td>
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<tr>
<td>$U(z)$ is the Heaviside function</td>
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<tr>
<td>$F_{z}$</td>
<td>Flux of zooplankton ingestion by zooplankton</td>
<td>(A12)</td>
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<tr>
<td>$F_{z} = \xi_{z}(\omega) = \frac{\nu_{0}(b_{z}z)}{\max} \omega$</td>
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<tr>
<td>$F_{z}$</td>
<td>Flux of detritus ingestion by zooplankton</td>
<td>(A13)</td>
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<tr>
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<tr>
<td>$pF_{z}$</td>
<td>Flux of zooplankton egestion</td>
<td>(A14)</td>
</tr>
<tr>
<td>$pF_{z} = (1 - p)F_{z}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(1 - p)F_{z}$</td>
<td>Flux of zooplankton mortality</td>
<td>(A15)</td>
</tr>
<tr>
<td>$F_{z}$</td>
<td>Flux of zooplankton excretion</td>
<td>(A16)</td>
</tr>
<tr>
<td>$F_{e} = b_{e}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_{z}$</td>
<td>Flux of detritus remineralisation</td>
<td>(A17)</td>
</tr>
<tr>
<td>$F_{r} = b_{r}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_{n}$</td>
<td>Flux of nitrification</td>
<td>(A18)</td>
</tr>
<tr>
<td>$F_{n} = b_{n}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_{n}$</td>
<td>Flux of denitrification</td>
<td>(A19)</td>
</tr>
<tr>
<td>$F_{n} = b_{n}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_{n}$</td>
<td>Flux of ammonium consumed by phytoplankton</td>
<td>(A20)</td>
</tr>
<tr>
<td>$f_{n}(\sigma) = f_{n}(\sigma)U(\sigma_{1} - \sigma) + \frac{g_{n}(\sigma)}{R_{n} + g_{n}(\sigma)}U(\sigma_{2} - \sigma)U(\sigma_{1} - \sigma)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$U(z)$ is the Heaviside function</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_{n}$</td>
<td>Flux of denitrification</td>
<td>(A21)</td>
</tr>
<tr>
<td>$f_{n}(\sigma) = f_{n}(\sigma)U(\sigma - \sigma_{2})$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A5. Ammonium

[61] The excretion of zooplankton (see equation (A18) in Table A1) as well as the remineralization of detritus (see equation (A19) in Table A1) constitute the ammonium sources. The consumption of ammonium results from its uptake by phytoplankton (see equation (A8) in Table A1) and its oxidation into nitrate in the nitrification process occurring in aerobic waters (see equation (A20) in Table A1) (see the different terms of $Q^{\text{nitrification}}$ in Figure 3). The depth distribution of nitrification is tied to the supply of ammonium from decomposition of organic matter and is restricted to very low light or aphotic regions because of light inhibition of nitrifying bacteria. Indeed, according to several authors [e.g., Olson, 1981; Wada and Hattori, 1991], nitrification is photo-inhibited and limited to depths of 1–0.1% light penetration for the oxidation of ammonium into nitrite, depths of less than 0.1% light penetration for the oxidation of nitrite into nitrate. One should expect then that the nitrification process affects the lower layers of the euphotic zone until the lower boundary of the oxycline below which the oxygen content of the water becomes insufficient to allow the oxidation of ammonium. The nitrification is particularly active at the base of the euphotic layer where the ammonium produced by the regeneration of the dead organic matter accumulates.

[62] In this paper, the nitrification process is not light-dependent because the ammonium produced by the regeneration of detritus accumulates mainly below the euphotic zone. It has been short-circuited and modeled as a direct conversion of ammonium into nitrate without the intermediate level of nitrite formation. In the Black Sea, its timescale ranges between 17 and 60 days [Ward and Kilpatrick, 1991], and thus this process belongs to the spectral window of the modeled processes. In the central basin, it plays a key role by preventing a progressive exhaustion of the nitrate consumed by the primary producers and an accumulation of the ammonium produced by heterotrophic excretion and organic matter regeneration. On the shelf, the nitrification process amplifies the input of

## Table A2. Signification, Values and Units of the Parameters Used in the Formulation of the Biological Interaction Terms

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Signification</th>
<th>Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_n$ (T = 20°C)</td>
<td>growth rate at 20°C</td>
<td>d⁻¹</td>
<td>3</td>
</tr>
<tr>
<td>$Q^{10}$</td>
<td>Q₁₀ factor</td>
<td>-</td>
<td>1.88</td>
</tr>
<tr>
<td>$c_{n1}$</td>
<td>half-saturation constant for ammonium uptake</td>
<td>mmol N m⁻³</td>
<td>0.2</td>
</tr>
<tr>
<td>$c_{n2}$</td>
<td>half-saturation constant for nitrate uptake</td>
<td>mmol N m⁻³</td>
<td>0.5</td>
</tr>
<tr>
<td>$\psi$</td>
<td>constant of inhibition of nitrate uptake by the presence of ammonium</td>
<td>(mmol N m⁻³)⁻¹</td>
<td>1.46</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>photosynthetic efficiency</td>
<td>(W m⁻²)⁻¹ d⁻¹</td>
<td>0.015</td>
</tr>
<tr>
<td>$k_p$</td>
<td>pure water diffusive attenuation coefficient</td>
<td>m⁻¹</td>
<td>0.08</td>
</tr>
<tr>
<td>$k_p$</td>
<td>phytoplankton attenuation coefficient</td>
<td>m⁻¹(mmol N m⁻³)⁻¹</td>
<td>0.07</td>
</tr>
<tr>
<td>$\mu_z$</td>
<td>mortality rate</td>
<td>d⁻¹</td>
<td>0.05</td>
</tr>
<tr>
<td>$(h_{z,\infty})_{\text{max}}$</td>
<td>maximum grazing rate</td>
<td>d⁻¹</td>
<td>0.9</td>
</tr>
<tr>
<td>$a_\alpha$</td>
<td>assimilation efficiency</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>$c_\alpha$</td>
<td>Half-saturation constant for ingestion</td>
<td>mmol N m⁻³</td>
<td>0.5</td>
</tr>
<tr>
<td>$b_\alpha$</td>
<td>threshold concentration</td>
<td>mmol N m⁻³</td>
<td>0.6</td>
</tr>
<tr>
<td>$e_{wz}$</td>
<td>capture efficiency of phytoplankton</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>$e_{cz}$</td>
<td>capture efficiency of detritus</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>$k_x^d$</td>
<td>excretion rate</td>
<td>d⁻¹</td>
<td>0.1</td>
</tr>
<tr>
<td>$m_z$</td>
<td>mortality rate</td>
<td>d⁻¹</td>
<td>0.05</td>
</tr>
<tr>
<td>$R^{n1}_n$</td>
<td>maximum nitrification rate</td>
<td>d⁻¹</td>
<td>0.1</td>
</tr>
<tr>
<td>$R^{n1}_n$</td>
<td>half-saturation constant for the limitation function of the nitrification process by the availability of oxygen</td>
<td>mmol O₂ m⁻³</td>
<td>10</td>
</tr>
<tr>
<td>$r_\alpha$</td>
<td>density of the oxycline upper boundary</td>
<td>kg m⁻³</td>
<td>14.8</td>
</tr>
<tr>
<td>$r_\alpha$</td>
<td>density above which the nitrification process ceases</td>
<td>kg m⁻³</td>
<td>15.6</td>
</tr>
<tr>
<td>$s_{\text{O}}$</td>
<td>density of the oxygen concentration</td>
<td>-</td>
<td>0.87</td>
</tr>
<tr>
<td>$s_{\text{O}}$</td>
<td>density above which the nitrification process stops</td>
<td>-</td>
<td>0.87</td>
</tr>
<tr>
<td>$s_{\text{O}}$</td>
<td>density of the oxygen concentration</td>
<td>-</td>
<td>0.87</td>
</tr>
<tr>
<td>$N_{\infty}^d$</td>
<td>maximum denitrification rate</td>
<td>d⁻¹</td>
<td>0.015</td>
</tr>
<tr>
<td>$R_d$</td>
<td>constant used in the inhibition function of the denitrification rate by the presence of oxygen</td>
<td>mmol O₂ m⁻³</td>
<td>2.5</td>
</tr>
<tr>
<td>$R^{d1}_d$</td>
<td>remineralization rate</td>
<td>d⁻¹</td>
<td>0.07</td>
</tr>
<tr>
<td>$(w_{\infty})_{\text{max}}$</td>
<td>maximum detrital sinking velocity</td>
<td>m d⁻¹</td>
<td>8</td>
</tr>
<tr>
<td>$c_w$</td>
<td>half-saturation constant used in the expression of the detritus sinking rate</td>
<td>mmol N m⁻³</td>
<td>0.2</td>
</tr>
<tr>
<td>$k_{\text{sed}}$</td>
<td>benthic detritus remineralization rate</td>
<td>d⁻¹</td>
<td>0.03</td>
</tr>
</tbody>
</table>
nitrates by the rivers by oxidizing the ammonium formed by the remineralization of the huge amount of dissolved organic nitrogen discharged by the Danube.

A6. Nitrate

[63] The nitrification process constitutes the only internal source of nitrate associated to biogeochemical processes (see equation (A20) in Table A1). The consumption of nitrate results from its uptake by phytoplankton (see equation (A9) in Table A1) and its reduction into nitrogen gas (i.e., the denitrification) (see equation (A22) in Table A1) (see the different terms of \( Q^v \) in Figure 3). Heterotrophic denitrification occurring in waters deficient in oxygen constitutes the main process leading to nitrate exhaustion in the transitional layer. Nitrate reduction results in the formation of nitrite and, in the final stage, of nitrogen gas that can escape to the atmosphere. Thus this process represents a loss of nitrogen for the Black Sea. Ward and Kilpatrick [1991] measured the nitrate reduction rate by 15N tracer addition during the 1988 Knorr expedition. In the suboxic zone characterized by nitrate concentrations between 2 and 8 mmol N m⁻³ this rate ranged from 0.6 \times 10⁻⁶ to 60 \times 10⁻⁶ mmol N m⁻³ d⁻¹ [Oguz et al., 2000]. If all the nitrate reduction can be attributed to heterotrophic denitrification, then the denitrification rate can roughly be estimated to 0.001–0.002 d⁻¹. This value is thus at least one order of magnitude lower than the typical rate of the biogeochemical processes modeled in this paper. However, to reach a steady state solution in the model, the denitrification process has absolutely to be taken into account to prevent the progressive accumulation of the huge nitrate stock discharged by the rivers.

[64] According to Murray et al. [1995] and Oguz et al. [1998], nitrate is also used to oxidize NH₄ and H₂S at the lower part of the transitional layer. These processes lead to the formation of nitrogen gas and are particularly important because they prevent the NH₄ and H₂S diffusing from the anoxic waters to reach the euphotic layer. However, their contribution to the consumption of the nitrate of the transitional layer is negligible compared to the denitrification process [e.g., Yakushev and Neretin, 1997], and thus they have not been represented in this model.

[65] The occurrence of the nitrification/denitrification process is conditioned by the presence/absence of oxygen in the water column. According to Yakushev and Neretin [1997] and Oguz et al. [1998], the nitrification and denitrification rates can be expressed by the following mathematical expression:

\[
F^v = \frac{\delta^v}{\sigma} f(O_2) a
\]

where, \( \delta^v \) is the maximum nitrification/denitrification rate, \( f(O_2) \) is a non-dimensional function of the dissolved oxygen concentration modeling the positive/inhibiting influence of oxygen on nitrification/denitrification, \( a \) and \( b \), are respectively \( n_1 \), \( n_2 \) in the nitrification process and \( n_2 \), \( N_2 \) in the denitrification process.

[66] Figure 2 shows that the surface oxygen profile on a density scale reveals a rather simple structure throughout the basin without possessing any seasonal variability [e.g., Buesseler et al., 1994; Saydam et al., 1993]. This makes possible to use it diagnostically in the biogeochemical model. This characteristic has been confirmed by the modeling studies of Oguz et al. [1998], and therefore the nitrification/denitrification process can be represented by an equation of the following type:

\[
F^v = \frac{\delta^v}{\sigma} g(\sigma) a
\]

where, \( g(\sigma) \), is an adimensional function of the density. Equations (A20)–(A21) and (A22)–(A23) in Table A1 give the mathematical expression of the nitrification and denitrification processes, respectively, used in this paper.

Appendix B

B1. Initial Conditions

[67] The hydrodynamic model is initialized with horizontally homogeneous temperature and salinity fields presenting a vertical stratification typical of the mean climatological Black Sea state. The most important characteristics of the vertical stratification are the sharp halocline from the sea surface down to 200 m and the cold intermediate layer (CIL), analogous to the 18°C water layer in the Atlantic Ocean [Stan and Beckers, 1999]. The initial vertical profiles of inorganic nutrients are computed as a function of the density rather than depth so as to exclude variability resulting from dynamical effects. Spatial and temporal mean vertical profiles on a density scale reconstructed from in situ data collected during the 1988 Knorr and 1991 Bilim research cruises throughout the Black Sea are used (profiles taken from Tugrul et al. [1992] and Saydam et al. [1993]). The NH₄ concentration in the deep waters is set initially to zero because, on the one hand, this ammonium does not take part in the nitrogen cycle of the oxygenated layer [e.g., Brewer and Murray, 1973; Murray et al., 1995; Yakushev and Neretin, 1997; Oguz et al., 2000] and, on the other hand, the model does not represent some important chemical reactions involving, notably, the manganese and iron cycles which prevent the ammonium of the deep basin reaching the euphotic layer. For the organic matter (living and dead), initial constant values are imposed.

B2. Boundary Conditions

[68] The hydrodynamic model is forced by monthly mean climatological forcing functions. In particular, this includes the large-scale free surface gradients along the Bosphorus Strait, the wind stress at the air-sea interface and the outflow of the Danube, the Dnepr and the Dnestr Rivers on the northwestern shelf. Since the contribution to the water budget of the basin of the Bulgarian and Turkish rivers discharge is small, their water inputs are regularly distributed in the above mentioned model rivers. The wind stress curl is cyclonic during the whole year with a maximum in January and a minimum in April–May. Contrary to the wind stress curl, which has a single maximum, the wind stress magnitude reaches two maxima (in winter and summer) and two minima (in spring and fall) [Staneva and Stan, 1999]. The wind stress data are based on ship observations. Temperature and salinity values are relaxed toward climatological monthly mean values at the surface. Monthly mean data of Altman and Kumish [1986] are used to compute the river fresh water discharges.

[69] The compensation of the fresh water flow at the surface takes place in the Bosphorus Strait. In this strait, the exchanges with the Mediterranean Sea are organized as a two-layer flow. Increased river discharges in spring and early
summer tend to increase the sea surface elevation, which amplifies the Bosphorus surface current. The magnitude of the undercurrent decreases correspondingly. In this way, the Black Sea exports water in excess to the Marmara Sea. The sea surface elevation then constantly drops in fall, which results in increasing magnitude of the inflowing undercurrent. The model calculates the baroclinic velocities in the strait. The Bosphorus undercurrent is maintained by the higher salinity values prescribed below 50 m in the strait. The corresponding salinity value was chosen after carrying out several sensitivity experiments, aiming to simulate reasonable magnitudes of the two-layer exchange. The barotropic current is computed from a simple linear formula based on the results of Oguz et al. [1990] and on the model-simulated sea surface elevation computed in the strait:

\[ Q = \alpha \eta_b + Q_b \]

where \( Q \) is the flux in the Bosphorus Strait which is self-adapting to the interior evolution, \( \eta_b \) is the sea surface elevation at the Bosphorus Strait and \( Q_b \) is the barotropic transport when \( \eta_b = 0 \). The constants \( \alpha \) and \( Q_b \) are estimated from the study of Oguz et al. [1990]. Since the net precipitation-evaporation flux, the river runoff and the flux in the Bosphorus Strait are all of the same order of magnitude, the precipitation and evaporation over the basin must be added or subtracted from the sea surface elevation; otherwise, the Bosphorus flux would simply tend toward the value of the river discharges, which is, of course, not the case in reality. It should be noted that a delay between changes in river discharges and fluxes through the Bosphorus Strait is to be expected [Stanev and Beckers, 1999].

[70] All the forcing functions used to force the hydrodynamic model are described in extenso by Stanev and Beckers [1999] and Staneva and Stanev [1999]. Since the model is forced by climatological monthly mean fields, the results are representative of a situation typical of the mean Black Sea’s climatological state.

[71] The role of atmospheric sources of nutrient appears to be marginal compared to river input (total atmospheric \( NO_3 + NO_2 \) input estimated to be 13% of the Danube input [Kubilay et al., 1995]). Also, the vertical fluxes of all biogeochemical state variables are set to zero at the surface. The bottom boundary of the water column is assumed to be impermeable except for sedimenting substances. Also, when they reach the bottom, the detritus enrich the sediments compartment \( \beta_h \). This flux is compensated by an upward flux of ammonium produced by benthic remineralization with a timescale of \( \frac{1}{k_{sed}} \)

\[ \frac{\partial n_1}{\partial z} = -k_{sed} \beta_h \]  

The input of nutrient and detritus by the rivers (i.e., the Danube, the Dnepr and the Dnestor) is computed from monthly mean values obtained in the literature [e.g., Cociasu et al., 1997]. The ratio of inorganic nitrogen river discharges into the shelf (6–8 \( \times \) \( 10^5 \) tons N yr\(^{-1} \)) on the shelf surface (~50,000 km\(^2\)) is by about 10 times higher than what is usually observed in the Global Ocean (surface of the global shelf: 26 \( \times \) \( 10^6 \) km\(^2\), total river flux of dissolved nitrogen = \( 35 \times \) \( 10^6 \) tons N yr\(^{-1} \)) [Wollast, 1998]. In comparison, the total annual input of inorganic nitrogen by major Turkish rivers has been estimated to 25 \( \times \) \( 10^3 \) tons [Sur et al., 1994]. Also, the inputs of nutrient from these rivers and from the continent have been neglected although they can lead to coastal phytoplankton blooms as revealed by satellite observations. At the Bosphorus Strait, monthly mean vertical profiles of inorganic nutrients and detritus are imposed [Polat and Tugrul, 1995].

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