Chapter 7

Marginal Seas

7.1 An Overview of the Marginal Seas[1]

Chen-Tung Arthur Chen

7.1.1 Introduction

Their moderately-sized surface areas notwithstanding, continental margins are essential components in the biogeochemical cycles of carbon and nutrients (Liu et al., 2000) and, as such, have been of considerable interest to the JGOFS and LOICZ (Chen et al., 1994). This chapter is devoted entirely to address marginal seas, defined as semi-enclosed seas adjacent to a continent. It provides a detailed discussion of the C/N/P fluxes for the Baltic, Black, East (Sea of Japan), Mediterranean, North, and Okhotsk Seas, as well as the Mississippi River plume and the adjacent margin in the Gulf of Mexico.

7.1.2 The Baltic Sea

Almost entirely enclosed, the Baltic Sea has been one of the most extensively studied marginal seas in the world and the following summarizes the contribution of Thomas et al. (Sect. 7.2). Particularly as a consequence of its shallow depth, and hence small volume, annual freshwater input makes up almost 4% of the Baltic Sea's total water volume. While the fresher surface water flows out of the sea via the narrow, shallow Kattegat and Skagerrak Straits, the more saline North Sea water enters near the bottom, and thus, a permanent halocline separates the surface waters from the deeper domains. The carbon budget of the Baltic Sea is primarily governed by the fluxes of dissolved inorganic carbon (DIC), and this is definitively greater than it is by dissolved organic carbon (DOC); particulate organic carbon (POC) and fish catch play only minor roles. Rivers and precipitation (in the case of N) transport copious amounts of nutrients into the Baltic Sea, and in fact, in the case of N, the inflow from the North Sea accounts for a mere 7% of the total nutrient input from rivers and precipitation. This is different from that of many marginal seas where rivers only supply a small percentage of nutrients (Chen, Chap. 13). Compared to the inflow from the North Sea to the Baltic Sea, rivers also transport 5 and 23 times as much P and Si, respectively. Clearly, the Baltic Sea is a river-dominated marginal sea, and such large riverine inputs of nutrients make it autotrophic. But, regardless of its high sedimentation and denitrification rates, the Baltic Sea still exports N, P, and Si to the North Sea.

Because of the large freshwater input, total riverine input of carbon (6.8×10^{10} mol/yr or 79% DIC, 1.7×10^{10} mol/yr or 19% DOC, 2% POC) is more than twice the influx from the North Sea (3.3×10^{10} mol/yr or 93% DIC, 2.4×10^{9} mol/yr or 6.6% DOC, 1.6×10^{8} mol/yr or 0.4% POC). Sedimentation removes POC, but the Baltic Sea still exports more carbon (1×10^{11} mol/yr or 82% DIC, 2×10^{10} mol/yr or 16% DOC, and 1.6×10^{9} mol/yr or

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1% POC) to the North Sea than the total amount it receives with the inflow from the rivers and North Sea combined. This difference is compensated for by the air-to-sea flux of CO_2 at a rate of about 0.9 mol/m^2/yr. It should be noted that the outflow of carbon from the Baltic Sea contains 16% DOC compared to 6.6% DOC it receives in the inflow from the North Sea, and there is a net export of 1.7×10^{10} mol/yr of DOC.

7.1.3 The Black Sea

Albeit even more closed than the Baltic Sea, the Black Sea is similar in the sense that it also receives large amounts of nutrient-laden river water. As a result, the fresher surface water leaves the Black Sea through the Bosporus Strait, while saline water from the Mediterranean Sea enters as a bottom flow. Between the 1970s and the late 1980s, land-based nutrient input in the form of nitrate and phosphate to the Black Sea drastically increased three-fold and seven-fold, respectively. Although it now receives 6×10^5 tons/yr of dissolved inorganic nitrogen (DIN) from external sources, the Black Sea still loses 10% nitrogen in the deep in the form of particulate organic nitrogen (PON) and about 13% through denitrification. On the one hand, the Black Sea is different from the Baltic Sea, which exports nutrients to the North Sea, because it receives DIN from the Mediterranean Sea; on the other hand, it is similar to the Baltic Sea as it too exports organic carbon (1.2×10^6 tons/yr) to the Mediterranean Sea (Oguz and Tugrul, Sect. 7.4), but it seems to release CO_2 to the atmosphere (Goyet et al., 1991).

7.1.4 The East Sea (Sea of Japan)

The East Sea or Sea of Japan, referred to as EJS, is unlike the Baltic and Black Seas for, besides being better connected to the outside via four – albeit shallow – straits, it receives small amounts of riverine inputs of nutrients and carbon (Yanagi, 2002). At the same time, nevertheless, the EJS exports carbon (0.055 Gt C) and is a sink for atmospheric CO_2. Kang et al. (Sect. 7.6) have estimated the air-to-sea flux to be 0.045 Gt C/yr, or 3.8 mol/m^2/yr. Earlier Chen et al. (1995) estimated that the EJS contains 0.31 ± 0.05 Gt C of anthropogenic CO_2. These two values are not consistent because with such a high flux, the EJS would contain substantially more anthropogenic CO_2. Kang et al.'s flux of 3.8 mol/m^2/yr is indeed very high when compared to that in most marginal seas in the world, for example, Chen's (2004 and Chap. 13) global average of only 1.1 mol/m^2/yr for continental shelves. Further, the oligotrophic EJS might be expected to have a lower, not higher flux. Worth noting too, for the nutrient-rich Baltic Sea, Thomas et al. (Sect. 7.2) have given an estimated flux of a low 0.9 mol/m^2/yr.

It is also highly interesting that Yanagi (2002) has provided a somewhat comprehensive recent P and N budget for the EJS. This includes for P and N, a riverine flux of 1.3×10^8 g/day and 1×10^9 g/day, respectively; a loss of 8×10^6 g/day P and 1.4×10^8 g/day N due to fish catch; an input of 7.4×10^8 g/day P and 1.23×10^{10} g/day N through the Tsushima Strait; and an outflow of 1.7×10^9 g/day P and 1.36×10^{10} g/day N through the Tsugaru and Soyo Straits. True that the N budget is nearly in equilibrium, but a cloud surrounds the exact reason for the EJS to export so much P.

7.1.5 The North Sea

The North Sea is one of the most thoroughly studied marginal seas in the world. As for its connection with the Atlantic Ocean, unlike the Baltic, Black and the East Seas, the North Sea has an open northern boundary; on the other hand, it has a less open boundary with the English Channel to the south. It is also connected to the Baltic Sea near its northeast corner. Given the nature of the physical boundaries, carbon exchanges across the northern North Sea boundary dominate the budget. About 90% of the carbon inflow is from the north, 8% via the English Channel, 7% from rivers, 1% from the Baltic Sea, and 0.6% from the atmosphere. Thomas et al. (Sect. 7.3) reports that less than 1% of the carbon is deposited in the sediments, and the major export to the Atlantic Ocean is in the form of DIC (97%) and DOC (<3%). The air-to-sea flux of 1.4 mol/m^2/yr is close to the global shelf average.

The N, P, and Si budgets, just like carbon, are dominated by exchanges with the Atlantic Ocean: approximately 80% of N is imported from across the northern

From the nutrient budgets it is evident that the contributions of inorganic and organic species to input and output are in a similar order of magnitude for all nutrients. However, the North Sea gets a net excess amount of organic material from the external sources, i.e. the open boundaries with the Atlantic Ocean and the Baltic, the atmosphere and the continents (due to river runoff). This material is converted into inorganic material and exported into the open North Atlantic Ocean. This feature is mainly caused by the input of near-surface organic material from the northwest and the export of deep inorganic material through the Norwegian Trench (Pätsch and Kühn, 2008). According to the simulation with ERSEM which neglects benthic denitrification the North Sea is a source of total nitrogen for the North Atlantic (74 Gmol N a^{-1}).

Concerning nitrogen, 30.5 Gmol N a^{-1} are imported into the North Sea in the form of organic matter, of which 50% are converted into dissolved inorganic nitrogen and exported into the North Atlantic, the other 50% are stored in the different biological compartments.

With phosphorus the situation is somewhat different: approximately 82% of the net import of organic phosphorus (2.2 Gmol P a^{-1}) is converted into dissolved inorganic phosphorus and exported, whereas only 18% are stored and/or buried as particulate organic phosphorus.

All budgets given and especially the direct comparison between the carbon and the nutrient budgets should be interpreted carefully. The main critical items are

- For the carbon budget the underlying water budget stems from climatological estimates, it does not correspond directly with the values used for the nutrient budgets.
- The nitrogen budget suffers from the lack of simulated benthic denitrification.
- The budgets are mean budgets, and the variability of the atmospheric, hydrodynamic and riverine forcing is not considered.

The variability of the driving forces is large and so is the variability of the resulting budgets (Pätsch and Radach, 1997; Radach and Pätsch, 2007). Therefore a 3D physical – biogeochemical coupled model including the carbon chemistry, the biological interactions of carbon, nitrogen, phosphorus and silicon, and the benthic denitrification will be established. In combination with observations this tool will allow to calculate simultaneously time-dependent budget for the relevant elements of the marine ecosystem.

7.4 The Black Sea and the Turkish Straits System

Temel Oguz and Suleyman Tugrul

7.4.1 Introduction

The Black Sea, located between latitudes of 41° to 46°N and longitudes of 28° to 41.5°E, is an elongated, elliptic, nearly enclosed basin with a narrow opening to the Aegean basin of the Eastern Mediterranean through the Bosphorus and Dardanelles Straits and the Sea of Marmara (Fig. 7.4.1). Together with the Sea of Marmara, it is characterized by eutrophication-induced strong and extended phytoplankton blooms and complex ecosystem structure as compared to the mesotrophic Aegean Sea and the oligotrophic Mediterranean Sea. The surface chlorophyll concentration distribution, depicted in Fig. 7.4.1, increases by an order of magnitude from the saltier Eastern Mediterranean to the brackish Black Sea, which receives large nutrient input from rivers discharging into the northwestern shelf (hereinafter referred to as NWS) of the basin. The underflow through the Bosphorus also introduces some nutrients available in the salty waters of Mediterranean into the Black Sea. The presence of a permanent pycnocline between the brackish upper layer and the saltier deep waters prevents ventilation of deep layer below 100–150 m depth. Within the last ∼7000 years, the Black Sea therefore developed distinctly different chemical features in the water column, the most significant of which were the oxic/anoxic transition zone between the upper oxygenated layer and sulfide-bearing deep layer and a series of complicated oxidation–reduction processes mediated by bacterial activities. Long-term observations have shown that the Black Sea ecosystem has been drastically modified

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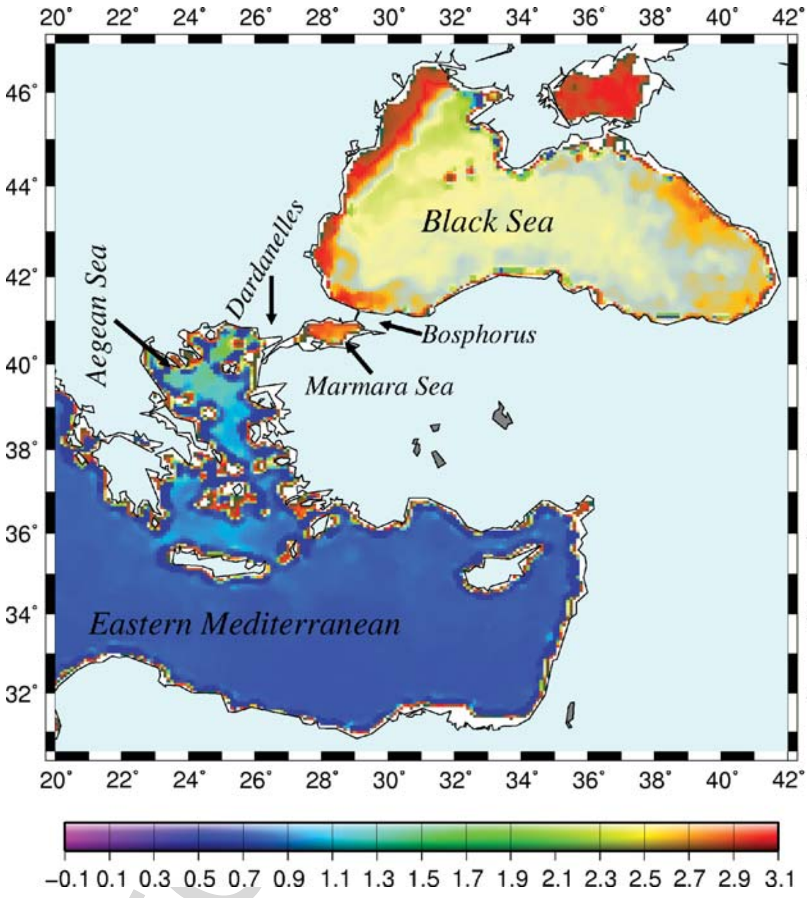

Fig. 7.4.1 The location map of the Black Sea–Turkish Straits System and its connection to the rest of the Mediterranean Sea. The SeaWIFS surface chlorophyll concentration (mg m^{-3}) distribution for March 2001 is also included in order to show the range of its variation from oligotrophic Mediterranean to the eutrophic Black Sea during the most productive period of the year

within the last three decades by a combination of natural and anthropogenic pressures. In particular, large amounts of nutrients and pollutants discharged from major rivers have adversely changed the ecosystem and the biogeochemical structures in the transition layer (Konovalov and Murray, 2001).

The counter flows within the Turkish Strait System (TSS) constitute a part of a two-layer system, where a sharp halocline of a thickness of 10–20 m separates brackish waters (22–26 psu) in the thin upper layer of the Marmara Sea (15–20 m) from the saltier waters (38.5–38.6 psu) in the lower layer throughout the year. The brackish Black Sea flow spends 4–5 months (on average) in the productive upper layer of the Marmara Sea during its transit to the Aegean Sea. The underflow spends about 6–7 years in the deeper layers of the Marmara basin (Unluata et al., 1989; Beşiktepe et al., 1994). The exchange flows in TSS therefore reach the adjacent seas with considerable modifications in their biochemical properties (Polat and Tugrul, 1995, 1996; Polat et al., 1998).

Riverine discharges introduce nitrogen and phosphorus ions into the Black Sea coastal waters with high molar ratios. Algal production in the northwestern shelf (NWS) is limited by phosphate due to selective removal of reactive phosphorus. On the other hand, dissolved inorganic nitrogen species limit primary productivity within the rest of the Black Sea due to low N/P ratio (4–8) in the oxycline and very limited ammonia input into the surface layer from the anoxic zone (Sorokin, 2002; Tugrul et al., 1992; Murray et al., 2005). In the open Black Sea, production rate of biogenic particles is sensitive to influxes of biologically available nitrogen species both vertically and laterally. The overall system is therefore primarily controlled by the nitrogen fluxes, and the phosphorus budget is of a secondary importance. The present work first describes the water budget of the Black Sea and the TSS in Sect. 7.4.2. It is then followed by the dissolved inorganic nitrogen budget in Sect. 7.4.3 and the total organic carbon budget in Sect. 7.4.4.

7.4.2 Water Balance

The Black Sea is a dilution basin with a positive water balance in which the sum of precipitation $Q_p \sim 300\,km^3\,yr^{-1}$ and runoff $Q_r \sim 350\,km^3\,yr^{-1}$ exceeds evaporation $Q_e \sim 350\,km^3\,yr^{-1}$ (Unluata et al., 1989). The Danube itself contributes about $210\,km^3\,yr^{-1}$ of water discharge which is more than entire freshwater supply to the North Sea. Dniepr and Dniestr deliver about a total of $60\,km^3\,yr^{-1}$ into the same region, while the rest is distributed around the basin. The excess of net freshwater input into the sea is compensated by the net freshwater loss through the Bosphorus Strait.

The water and salt budgets of the Black Sea considered here consists of five boxes (Fig. 7.4.2) whose water fluxes are computed using the steady-state analysis on the basis of long-term salinity measurements. The main elements of the Black Sea upper layer flow incorporated into these budgets are the cyclonic basin-wide peripheral circulation and the freshwater-induced current system along the western coast. These current systems partially enter into the Bosphorus Strait, undergo lateral exchanges with each other as well as with the lower layer. Two of the boxes represent the interior basin and the western shelf of the upper layer flow system with typical salinities of 18.0 and 16.5 psu, respectively. In the lower layer, the Mediterranean underflow is assumed to enter into the Black Sea with a salinity of 35.5 psu at the Bosphorus exit. It is then subject to considerable vertical mixing with the less saline ambient waters during its transit across ∼40–50 km long Bosphorus–Black Sea junction region (Latif et al., 1991), and ultimately fills the entire deep basin below the permanent halocline/pycnocline at depths of 100–150 m. The lower layer system is therefore represented by two boxes signifying the junction region and the interior basin having salinities of 25.5 and 22.5 psu, respectively. The cyclonic upper layer circulation system is maintained by a continuous supply of water transport from the lower layer, except around the periphery of the basin. The fifth box allows exchanges of these boxes with the Bosphorus and then rest of the TSS.

As presented in Fig. 7.4.2, the lower layer budget of the Black Sea involves an inflow of $\sim 304\,km^3\,yr^{-1}$ Mediterranean water into the Bosphorus–Black Sea junction region. There, it mixes with $426\,km^3\,yr^{-1}$ upper layer flow to generate a lower layer transport of $730\,km^3\,yr^{-1}$ into the basin interior. This input is balanced by a difference of $487\,km^3\,yr^{-1}$ downward flux and $1217\,km^3\,yr^{-1}$ upward flux across the interface between the upper and the lower layers. In the upper layer $350\,km^3\,yr^{-1}$ freshwater input primarily maintains the coastal current system of the western inner shelf. Of this coastal flow, $54\,km^3\,yr^{-1}$ enters into the Bosphorus, whereas the rest ($296\,km^3\,yr^{-1}$) provides a net supply into the basin circulation. An additional flux of $550\,km^3\,yr^{-1}$ water enters into the Bosphorus from the interior to maintain the water balance of the upper layer flow system.

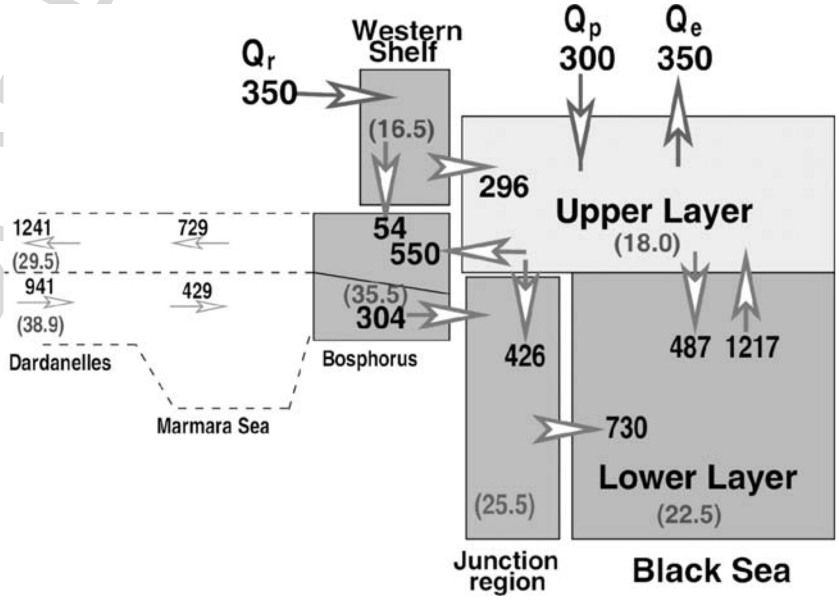

Fig. 7.4.2 The lateral and vertical exchanges of water fluxes (in $km^3\,yr^{-1}$) within the Black Sea and the Turkish Straits System. The average salinities used in the computations are shown in brackets. Q_r, Q_p, Q_e denote the fluxes due to river discharge, precipitation, and evaporative loss. (A colored version of this figure is available on-line. See Appendix C.)

Table 7.4.1 The long-term average measured salinities of the upper layer (S_1) and the lower layer (S_2) and the corresponding water fluxes (Q_1, Q_2) estimated at various sections along the TSS as well as across the interface in the upward (Q_u) and downward (Q_d) directions

	Upper layer S_1 (psu)	Upper layer Q_1, Q_u ($km^3\ yr^{-1}$)	Lower layer S_2 (psu)	Lower layer Q_2, Q_d ($km^3\ yr^{-1}$)
Bosphorus–Black Sea Junc.	18.0	604	35.5	304
Bosphorus Interior	18.6	*56*	36.4	*42*
Bosphorus–Marmara Junc.	19.2	618	37.3	318
Marmara Interior	22.0	*254*	38.0	*33*
Dardanelles–Marmara Junc.	24.8	839	38.6	539
Dardanelles Interior	27.1	*423*	38.7	*21*
Dardanelles–Aegean Junction	29.5	1241	38.9	941

The estimates of water fluxes, together with the prescribed values of the upper and lower layer salinities, within the Bosphorus–Marmara Sea–Dardanelles system are presented in Table 7.4.1. The upper layer salinity of 18 psu at the northern end of the Bosphorus increases by about 5 psu both in the Marmara Sea and in the Dardanelles Strait and attains the value of 29.5 psu at the Aegean Sea junction. On the contrary, the lower layer water mass, entering from the Aegean Sea with the salinity of 38.9 psu, reduces to about 37 psu at the southern end and to 35.5 psu at the northern end of the Bosphorus. These changes in the layer salinities are associated with considerable upward transport of water from the lower layer. Accordingly, the upper layer flow increases by an almost 100% during its transit along the Turkish Straits System. The upper layer flow of 604 $km^3\ yr^{-1}$ leaving the Black Sea traverses the Bosphorus without much change, but increases to 839 $km^3\ yr^{-1}$ on the western side of the Marmara Sea and ultimately to 1241 $km^3\ yr^{-1}$ at the Aegean exit of the Dardanelles. In the lower layer, the Mediterranean underflow entering the Dardanelles with 941 $km^3\ yr^{-1}$ leaves the strait as 539 $km^3\ yr^{-1}$. It further decreases by more than 200 $km^3\ yr^{-1}$ in the Sea of Marmara. The lower layer transport reduces to the value of 304 $km^3\ yr^{-1}$ when it finally arrives at the Black Sea (see Table 7.4.1).

7.4.3 *Dissolved Inorganic Nitrogen Budget*

The strongly stratified shallow upper layer (~100 m) is accompanied by four biochemically distinct layers. The uppermost part from the free surface to the 1% light depth is defined as the euphotic zone of about 40–50 m thick in the open sea. This is the layer of active planktonic processes (e.g. uptake, grazing, mortality, microbial loop, etc.). Most of the sinking biogenic particles are remineralized there as well as in the subsequent 20–30 m part of the aphotic zone. The latter region of active particulate organic material degradation is also characterized by intense oxygen consumption and efficient nitrogen cycling, as suggested by rapid variations in oxygen and nitrate concentrations. At the base of this so-called oxycline/upper nitracline zone, oxygen concentration reduces to suboxic levels of 10–20 μM, whilst the nitrate concentration increases to its peak values of around 6–9 μM (Tugrul et al., 1992). Organic matter decomposition proceeds via denitrification at slightly deeper and oxygen deficient part of the water column and forms the "lower nitracline" with steady and sharp decreases in nitrate concentrations to undetectable levels (<0.1 μM) in a zone of about 20–40 m below the nitrate peak. This oxygen and sulfide deficient zone, known as the "Suboxic Layer (SOL)" (Murray et al., 1989), is followed by the deep anoxic layer of hydrogen sulfide and ammonium pools. The water column from the surface to the anoxic interface involves a series of different bacterially mediated redox processes, which give rise to distinctly different nitrogen cycling in the Black Sea as compared to oxygenated basins in other parts of the world oceans.

The land-based nutrient input to the Black Sea has increased by three–four fold in nitrates and seven fold in phosphates from the early 1970s to the late 80s (Mee, 1992). The mean dissolved inorganic nitrogen ($DIN = NO_3 + NH_4$) input from Danube is approximately 340 000 tons yr^{-1} during this period, which constitutes about 60% of the total input of

570 tons yr^{-1} including additional contributions from other rivers as well as domestic and industrial sources. Such a continuous supply of DIN has fueled the euptrophication, resulting in dramatic impacts on the vertical structure of biochemical properties of the whole Black Sea. The most pronounced signatures of the biochemical changes are the formation of hypoxia/anoxia in bottom waters of the NW shelf, the enlargement of SOL toward the surface, an increase of nitrate concentration in the oxic/suboxic interface zone from 2 to 3 µM in the late 1960s to 6–9 µM during the 1980s and 90s. This long-term nitrate increase in the interface has also risen the nitrate/phosphate ratio from 2–4 in the late 60s to 4–8 during the last two decades (Tugrul et al., 1992; Konovalov and Murray, 2001).

The land-based DIN input, which has been mostly concentrated along the northwestern coast, has not been uniformly distributed over the basin, but mostly stored within the western shelf waters and transported to the other parts of the basin only partially through the coastal current system and the cross-shelf transports. The overall nitrogen balance of the Black Sea therefore needs to distinguish the shelf and deep basin budgets, linked by lateral advective fluxes (Fig. 7.4.3). Assuming the shelf compartment constitutes about 25% of the total surface area, the areas of shelf and deep compartments are taken as ~100 000 and ~300 000 km^2, respectively.

According to long-term data presented by Polat and Tugrul (1995), the surface flow to the Marmara Sea contains DIN concentrations of less than 0.5 µM during late spring–autumn period. But, it is enriched up to 5–7 µM in winter when the uptake by photosynthesis ceases and coastal waters are vertically well mixed in the western basin. The annual mean value of DIN in the Bosphorus surface flow is given by 2.10 µM (Table 7.4.2). Due to modifications in the chemical properties of the surface flow within the Marmara basin, its value decreases to 0.96 µM in the Sea of Marmara and 0.48 µM near the Aegean Sea exit of the Dardanelles Strait. Considering the Bosphorus volume fluxes given previously in Table 7.4.1, the

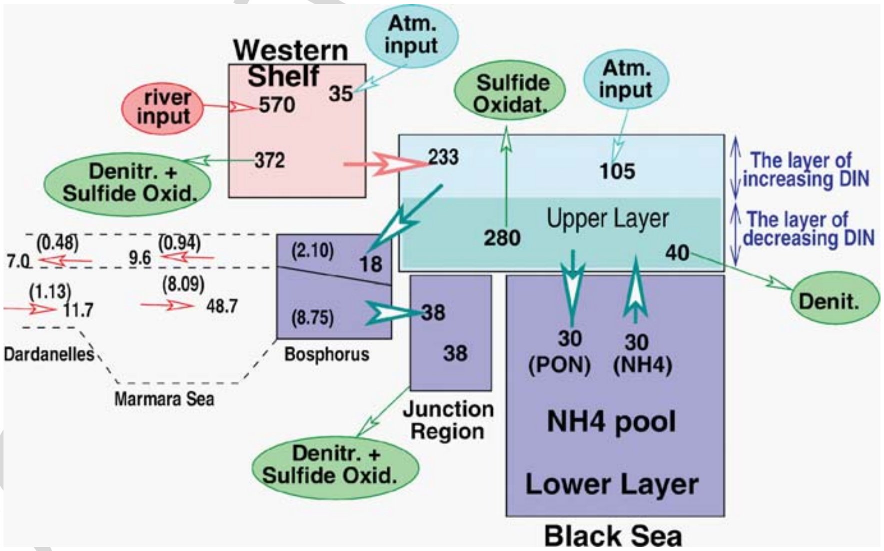

Fig. 7.4.3 The dissolved inorganic nitrogen (DIN) budget of the Black Sea – Turkish Straits System. The average concentrations (in µM) at various sections of the system are given in brackets. The DIN fluxes are given in kilo tons yr^{-1}

Table 7.4.2 The long-term average measured DIN concentration (in µM) in the upper and lower layers (C_1, C_2) of the Bosphorus and Dardanelles Straits and the Sea of Marmara and the corresponding DIN fluxes (F_1, F_2) along the TSS in 10^{+3} tons yr^{-1}

	Upper layer C_1 (µM)	Upper layer F_1 (10^{+3} tons yr^{-1})	Lower layer C_2 (µM)	Lower layer F_2 (10^{+3} tons yr^{-1})
Bosphorus Interior	2.10	18.0	8.75	38.0
Marmara Interior	0.94	9.6	8.09	48.7
Dardanelles Interior	0.48	7.0	1.13	11.7

DIN export from the Black Sea to the Marmara Sea is nearly 18 000 tons yr^{-1}, which then becomes 9600 and 7000 tons yr^{-1} in the Sea of Marmara and the Dardanelles Strait, respectively (see Table 7.4.2 and Fig. 7.4.3). On the other hand, the annual mean DIN content of the salty Mediterranean water at the Aegean Sea–Dardanelles junction region is 1.13 μM as estimated by the long-term data. It increases to 8.09 μM during its 6–7 years residence in the Sea of Marmara lower layer and to 8.75 μM near the Bosphorus entrance of the Black Sea. About 11 700 tons yr^{-1} DIN supply from the Aegean Sea increases up to 38 000 tons yr^{-1} along its transit from the nitrate-enriched Marmara lower layer via the Bosphorus undercurrent. Once entering into the Black Sea, it is lost in the Bosphorus–Black Sea junction region via the denitrification and sulfide oxidation.

Nitrogen influx from atmosphere through precipitation was suggested to constitute about 15–25% of the total load of DIN (Mee, 1992). On the other hand, atmospheric transport modeling products suggest an input of 140 000 tons yr^{-1} as an average of 12 year annual mean fluxes (for 1985–1996) varying in the range of 105 000 and 215 000 tons yr^{-1}. In the present calculations, the atmospheric input is assumed to constitute ~20% of the total DIN load to the whole Black Sea. It is partitioned between the shelf and the deep basin as 35 000 and 105 000 tons yr^{-1}, respectively.

Assuming carbon to nitrogen ratio of ~8.5 (Coban-Yildiz et al., 2000) and using the euphotic layer-integrated mean primary productivity of 0.14 g C m^{-2} day^{-1} (Vedernikov and Demidov, 1993), the total loss of annual mean nitrogen during the phytoplankton uptake is 1.4 mmol N m^{-2} day^{-1}, or ~300 000 tons yr^{-1}. Considering that 90% of DIN made available for primary productivity is supported by recycling within the upper layer water column, and only its 10% is lost to the deep in the form of PON, this loss is estimated to be about 30 000 tons yr^{-1}. It is compensated by a similar influx of ammonium from the anoxic layer into the suboxic zone where it is utilized by chemosynthetic bacteria and also oxidized to nitrate by aerobic bacteria especially in winter when dissolved oxygen is introduced to the interface zone by vertical- and lateral-mixing processes in the rim currents and coastal margins. In the cyclonic open sea, ammonia is probably oxidized to molecular nitrogen by particulate manganese oxides (MnO_2) available at the top of the suboxic–anoxic interface zone.

Denitrification rate within the interior part of the Black Sea has been shown to vary from undetectable levels to a peak value of 1.2×10^{-3} mmol m^{-3} day^{-1} within about 15 m layer near the base of the SOL (Ward and Kilpatrick, 1991). Multiplying this by the surface area of the interior basin, a gross estimate of nitrate loss by denitrification is obtained as ~40 000 tons yr^{-1}. Nitrate ions within the anoxic interface zone is also used to oxidize dissolved Mn (II) ions diffusing into the interface waters; particulate manganese produced by this reaction then oxidizes hydrogen sulfide. The oxidation rate varies from zero to a maximum value of 6 nM hr^{-1} within a water column of about 20 m (Tebo, 1991; Lewis and Landing, 1991), or equivalently, a loss of ~230 000 tons yr^{-1}. The rates of iron and ammonium oxidation by nitrate are approximately an order of magnitude smaller (Lewis and Landing, 1991), and thus provides individually a loss of ~25 000 tons yr^{-1}. The total loss of DIN within the layer between the nitrate maximum and the anoxic interface, together with the loss to the Bosphorus, thus amounts to ~338 000 tons yr^{-1}. The steady state interior basin nitrogen balance therefore requires a lateral advective supply of ~233 000 tons yr^{-1} from the western shelf.

The western shelf zone maintains annually 372 000 tons yr^{-1} net supply of DIN as a difference between inputs of 570 000 and 35 tons yr^{-1} from anthropogenic and atmospheric sources, respectively, and 233 tons yr^{-1} loss into the deep basin. The steady state shelf balance thus implies its consumption by denitrification, some other oxidation processes as well as sedimentation. We note that these losses are comparable with those from the interior basin, even though the shelf covers only one-fourth of its cross-sectional area. This suggests three times more intense organic matter and sulfide oxidation in the shelf. This is in fact expected since the primary productivity within the shelf is 3–4 times higher than in the interior, implying more intense organic matter decomposition, higher rate of oxygen consumption as evident by hypoxia and anoxia events (Zaitsev and Mamaev, 1997). The lack of oxygen promotes more intense utilization of nitrate for organic matter decomposition and sulfide oxidation.

7.4.4 Total Organic Carbon Balance

The total organic carbon (TOC) is defined as the sum of particulate (POC) and dissolved (DOC) organic carbon constituents. Using TOC concentration of 10–12 g m^{-3} being typical for the polluted rivers of the northwestern Black Sea (Meybeck, 1982), the annual carbon influx into the basin is estimated as 3.5–4.2 × 10^{+6} tons yr^{-1}. This value is twice of the estimate given earlier by Deuser (1971) due presumably to increasing TOC loads of river waters since the late 1970s. On the other hand, long-term measurements at the northern end of the Bosphorus (Polat and Tugrul, 1995) indicate that TOC concentration varies between 2 and 3 g m^{-3} in the Black Sea surface waters flowing into the Marmara Sea via Bosphorus; the peak values appeared during the bloom period in the western Black Sea and lowest values in winter when primary productivity being low. The saltier Mediterranean waters are originally poor in TOC (0.8–1.0 g m^{-3}) in the Aegean Sea–Dardanelles junction region before occupying the lower layer of the Marmara Sea, where primary production is limited to the upper layer throughout the year. During its transit the Marmara basin, TOC content of the Mediterranean water remains almost constant due to decomposition of particulate organic matter (POM) sinking from the upper layer.

The annual means of TOC concentrations along the TSS are compiled in Table 7.4.3. Having the mean TOC concentration of 2.55 g m^{-3} in the Strait, the Bosphorus upper layer flow introduces 1.55 × 10^{+6} tons yr^{-1} TOC into the Marmara upper layer, which then increases to 1.72 × 10^{+6} tons yr^{-1} in the Sea of Marmara and 2.32 × 10^{+6} tons yr^{-1} near the Aegean exit of the Dardanelles with the respective TOC concentrations of 2.35 and 2.32 g m^{-3}. The counterflow in the Dardanelles introduces 0.80 × 10^{+6} tons yr^{-1} TOC flux into the Dardanelles with the mean concentration of 0.59 g m^{-3}. The TOC flux then becomes 0.35 × 10^{+6} tons yr^{-1} along the Bosphorus during its transit to the Black Sea at the mean concentration of 0.92 g m^{-3}. Thus, there exists a net loss of 1.2 × 10^{+6} tons TOC yr^{-1} from the Black Sea, which is nearly one-third of the total riverine input (4.0 × 10^{+6} tons yr^{-1}). The net total organic carbon input of 2.5–3.0 × 10^{+6} tons yr^{-1} into the Black Sea is in fact equivalent to an organic carbon synthesis of 0.02 g C m^{-2} d^{-1} in the euphotic zone, which is much smaller than the organic carbon produced annually by surface primary productivity. This implies that, as in the case of the dissolved inorganic nitrogen budget, the Black Sea organic carbon budget is mainly dominated by biogeochemical pump acting within the upper layer water column as discussed below.

Based on long-term data collected within the interior parts of the basin during the last 20 years, Vedernikov and Demidov (1997) estimated the monthly averaged primary productivity in the range of 0.4–0.7 g C m^{-2} day^{-1} during the productive period from November to March and between 0.2–0.4 g C m^{-2} day^{-1} from April to October. The annual mean value of 0.14 g C m^{-2} day^{-1} agrees with the other estimates of 0.12–0.17 g C m^{-2} day^{-1} by Finenko (1993) and 0.10–0.13 g C m^{-2} day^{-1} by Chebotarev et al. (1983). As they represent the conditions for the interior basin, primary productivity acquires much higher values of around 0.5–0.85 g C m^{-2} day^{-1} along the eutrophic western coastal waters and of 2.8 g C m^{-2} day^{-1} in the vicinity of the Danube discharge (Vedernikov and Demidov, 1993). In addition, bacterial production of heterotrophic and chemoautotrophic origins can provide an equally important contribution to the TOC budget of the Black Sea. Its annual mean estimate is around 0.1 g C m^{-2} day^{-1} both within the euphotic zone and near the oxic–anoxic interface of the central waters (Sorokin, 2002; Sorokin et al., 1995).

Table 7.4.3 The long-term average measured TOC concentration (in g m^{-3}) in the upper and lower layers (C_1, C_2) of the Bosphorus and Dardanelles Straits and the Sea of Marmara and the corresponding DIN fluxes (F_1, F_2) along the TSS in 1^{+6} tons yr^{-1}

	Upper layer C_1 (g m^{-3})	Upper layer F_1 (10^{+6} tons yr^{-1})	Lower layer C_2 (g m^{-3})	Lower layer F_2 (10^{+6} tons yr^{-1})
Bosphorus Interior	2.55	1.55	0.92	0.35
Marmara Interior	2.35	1.72	0.83	0.36
Dardanelles Interior	2.23	2.32	0.80	0.59

Karl and Knauer (1991) presented a local carbon budget of the Black Sea based on measurements conducted at two adjacent stations in the western Black Sea interior during May 1988. Their data set included standing stocks of particulate and dissolved carbon, rates of microbial production as well as downward particle flux using sediment traps deployed during 16–20 May 1988 at 7 depths between 60 and 350 m. The near-surface traps were positioned 20 m apart to resolve variations across the base of the euphotic zone, the oxic–anoxic interface and the sulfide-bearing zone. The measurements suggested fairly high rate of algal production of 0.58 g C m^{-2} day^{-1} within the euphotic zone extending from the surface to 55 m depth. Heterotrophic bacterial production in the euphotic zone was also quite high (0.26 g C m^{-2} day^{-1}) and constituted almost half of the contemporaneous photoautrophic production. These values were representative of the conditions of recycled production following an intense early-spring new production season, and therefore were somewhat higher than their annual mean values reported above. On the other hand, the chemoautotrophic and heterotrophic bacterial productions of 0.09 and 0.075 g C m^{-2} day^{-1}, respectively, around the oxic–anoxic interface agree with those reported by Sorokin (2002) and Sorokin et al. (1995).

The sediment trap data reported by Karl and Knauer (1991) indicated that POC flux from the base of the euphotic zone (at 60 m) was 0.14 g C m^{-2} day^{-1}, suggesting that approximately 83% of the biological production was recycled inside the euphotic zone. Similar recycling efficiency has also been suggested by the modeling studies (Oguz et al., 1996, 2000). Beneath 60 m, the POC flux showed a rapid decrease with depth to 0.04 g C m^{-2} day^{-1} at 80 m depth corresponding roughly to the anoxic interface. This corresponds to ∼5% of the total euphotic zone production of 0.86 C m^{-2} day^{-1}. Analysing bi-weekly/monthly data sets obtained at several stations along peripheral waters of the Caucasian coast during 1979, Lebedeva and Vostokov (1986) suggested that nearly 70% of the detritus formed annually in the surface waters by plankton community is consumed by heterotrophic activity in the euphotic zone; about 10% (larger-size fraction) sinks down to subhalocline waters, whilst the rest (20%) is made available for chemical and microbial processes in the permanent pycnocline below the euphotic zone. Their estimates also indicate that the mean POC export from the euphotic zone is in the range of 0.05–0.10 gr C m^{-2} day^{-1}. Finally, based on 1.3 g C m^{-3} total organic carbon (TOC) concentration determined in the subhalocline waters (Tugrul, 1993) and the net upward water transport of ∼300 km^3 yr^{-1}, we can estimate a net upward TOC flux of $\sim 0.4 \times 10^{+6}$ tons yr^{-1} into the upper layer.

The total organic carbon budget of the Black Sea can be established by using the annual water fluxes and chemical concentrations measured in different compartment of the Black Sea and the Bosphorus two-layer flow regimes (see Table 7.4.3). The annual TOC fluxes (in 10^{+6} tons yr^{-1}) were calculated as follows:

(i) the input from river runoff = 4.0
(ii) input via Bosphorus underflow = 0.35
(iii) outflux through the Bosphorus surface flow = 1.55
(iv) autotprohic production in the EZ = 20.4 (corresponding to 0.14 g C m^{-2} day^{-1})
(v) bacterial production in the EZ = 14.6 (corresponding to 0.1 g C m^{-2} day^{-1})
(vi) chemoautotrophic and heterotrophic bacterial production in the oxic–anoxic interface zone = 14.0 (corresponding to 0.1 g C m^{-2} day^{-1})
(vii) net upward TOC flux from the lower layer = 0.4.

As shown in Fig. 7.4.4, the internal and external sources lead to $\sim 38 \times 10^{+6}$ tons yr^{-1} net TOC input to the euthopic zone (EZ) of the Black Sea. Considering that 75% of total input is recycled ($28 \times 10^{+6}$ tons yr^{-1}) in the EZ, the particulate organic carbon export flux into the oxic–anoxic transition (chemocline) zone can be estimated as $\sim 10 \times 10^{+6}$ tons yr^{-1}. This value agrees favorably well with the one estimated as the annual mean value of 0.07 g C m^{-2} day^{-1} by Lebedeva and Vostokov (1986). Considering 10% of the total source ultimately goes into the deep waters, this loss is estimated around $3\text{–}4 \cdot 10^{+6}$ tons yr^{-1}, leaving the rest ($6\text{–}7 \times 10^{+6}$ tons yr^{-1}) for the contribution to the biogeochemical processes within the chemocline region. Including an additional local production of about 14 tons yr^{-1}, a total of ∼20 tons yr^{-1} total organic carbon is made available for consumption during decomposition, redox-depended biochemical processes within the interface zone (e.g. nitrate, manganese, sulphate reductions), as well as deposition to the sediment in coastal and shelf zones. The budget estimates, therefore, indicate participation of

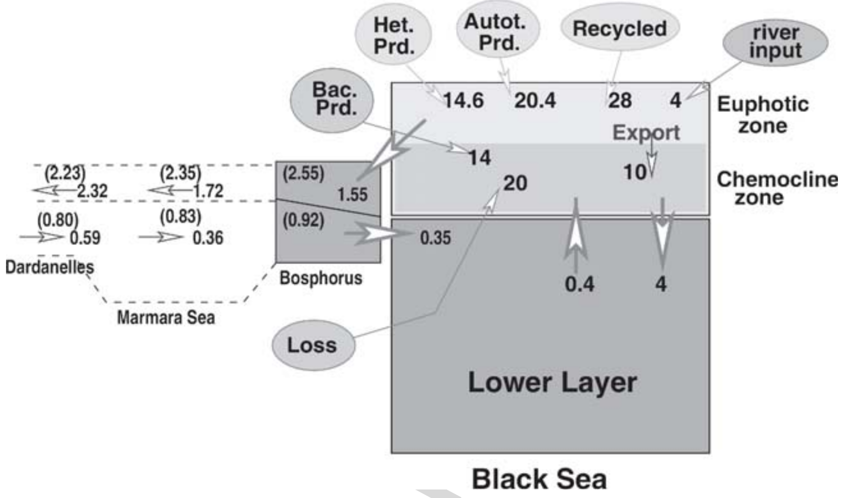

Fig. 7.4.4 The total organic carbon (TOC) budget of the Black Sea – Turkish Straits System. The average concentrations (in g m^{-3}) at various sections of the system are given in brackets. The TOC fluxes are given in mega tons yr^{-1}. (A colored version of this figure is available on-line. See Appendix C.)

the chemocline zone processes to the Black Sea TOC balance as actively as in the euphotic zone. This phenomenon constitutes a major distinguishing feature of the Black Sea biogeochemical pump as compared to typical oxygenated oceanic systems. Approximately 10% of the net loss of TOC into the anoxic deep waters is recovered in the form of dissolved organic matter by the net upward flux of 0.4 tons yr^{-1} into the chemocline zone. The rest ($\sim 3.6 \times 10^{+6}$ tons yr^{-1}) of is ultimately consumed by various anaerobic organisms in the anoxic water column and sediment layer.

7.4.5 Summary

The water, dissolved inorganic nitrogen (DIN) and total organic carbon (TOC) budgets of the Black Sea and the Turkish Straits System (TSS) were obtained using the steady-state assumption, two-layer approximation of the vertical structure and long-term measurements. The volume of more saline Mediterranean waters entering into the Dardanelles from the Aegean Sea amounts to 941 km^3 yr^{-1}. It undergoes considerable changes in transit the TSS and reduces to 304 km^3 yr^{-1} at the northern end of the Bosphorus Strait. The upper layer flow of 604 km^3 yr^{-1} leaving the Black Sea traverses the Bosphorus without much change, but increases to 1241 km^3 yr^{-1} at the exit of the Dardanelles. The Black Sea surface layer receives 605 kilo tons of DIN annually from external sources mainly into the northwestern shelf (NWS). About 60% of it was consumed via denitrification and sulfide oxidation inside the shelf, whereas the rest is transported into the deep basin. Nearly 90% of the total annual DIN input to the interior Black Sea upper layer is utilized in the vicinity of the anoxic interface zone; the rest is exported to the sulfide-bearing lower layer waters and accumulated as dissolved ammonia. Annually 49 $\times 10^{+6}$ tons of TOC are produced biologically in the euphotic and chemosythetic zones, which considerably exceed the external input. The net TOC export to the anoxic layer is nearly $4 \times 10^{+6}$ tons yr^{-1}, which is almost compensated by the river runoff. Comparison of the TOC fluxes in the Bosphorus Strait indicate a net export of $1.2 \times 10^{+6}$ tons yr^{-1} TOC from the organic matter – enriched Black Sea surface layer to the Marmara upper layer and eventually to the Aegean basin of the Mediterranean Sea. On the other hand, the Aegean inflow at the entrance of the Dardanelles Strait Sea is relatively poor in both DIN (1.13 μM) and TOC (0.80 g m^{-3}). It is markedly enriched in DIN (8.75 μM) without significant changes in its TOC values (0.92 g m^{-3}) when it reaches the southern entrance of the Bosphorus Strait. The exchanges of DIN and TOC between the Black Sea and the TSS are found nearly an order of magnitude lower as compared to those inside the Black Sea. Therefore, in terms of the DIN and TOC fluxes, the Black Sea may be regarded as an enclosed basin without contributing much to the budgets of the Mediterranean Sea. Its effect appears to be limited to the northern Aegean Sea ecosystem.