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North-eastern Aegean sea: an effort to estimate steady-state
N & P budgets during September 1998

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Abstract

The north-eastern Aegean sea, characterised by a complex topographical structure, is the area where highly saline waters of Levantine and South-Central Aegean origin are diluted by the outflowing through the Dardanelles of less saline waters of Black Sea origin and by river runoff from the Greek and Turkish mainland. Salinity and nutrient data collected during the INTERREG-I project are used to develop budget calculations and empirical models according to the LOICZ biogeochemical modelling guidelines. The results of the study indicate that the dissolved inorganic nitrogen and phosphorus fluxes imported into the NE Aegean through the Dardanelles are less important than it was believed in the past. Overall, the system acts as a net sink of DIN and DIP, as well as being a net producer of organic matter, as primary production exceeds respiration. Moreover, the system appears to fix more nitrogen than is lost through denitrification.

Keywords: Nutrient budgets; Stoichiometric calculations; North Aegean Sea.

Introduction

The North Aegean Sea constitutes one of the northern extremities of the Mediterranean Sea. The bottom topography of the N. Aegean is characterised by a series of three SW-NE oriented depressions (down to a depth of 1500m), separated by shallow sills and shelves. One of its major characteristics is that it is a region where highly saline waters of Levantine and South-Central Aegean origin are diluted by the inflow of less saline Black Sea waters and river runoff from the Greek and Turkish mainland. The N. Aegean water column consists essentially of three layers: low salinity waters with a high percentage of Black Sea Water (BSW) outflowing through the Dardanelles Strait, within the surface layer; highly saline and warm waters of Levantine origin (LIW) between 100 and 400 m depth; and very dense N. Aegean Deep Water (NADW), within the deep layer of each of the sub-basins. The N. Aegean Sea is characterized by a generally cyclonic circulation. The most characteristic circulation feature of the N. Aegean is the shallow thermohaline front, less

than 40 m thick, formed by the BSW discharged from the Dardanelles. Another mesoscale structure that appears to be a permanent feature of the region is a large anticyclone around the islands of Samothraki and Imvros (ZERVAKIS & GEORGOPOULOS, 2002). Combined analysis of historical and recently gathered data suggests that the NADW is formed locally, at larger than annual intervals (THEOCHARIS & GEORGOPOULOS, 1993). The dense water formation process in the N. Aegean is controlled not only by air–sea interaction, but also by the volume rate of Black Sea water outflowing into the Mediterranean. Two such incidents were identified in the late 1980s/early 1990s, suggesting that the N. Aegean Sea could be the region where events like the Eastern Mediterranean Transient could be triggered (ZERVAKIS *et al.,* 2000).

For years it was considered that the higher phytoplankton and zooplankton assemblages observed in the area close to Dardanelles were associated with the influence of the nutrient-rich BSW outflowing through the Dardanelles (PAGOU & GOTSIS-SKRETAS, 1989; SIOKOU-FRANGOU *et al.,* 1999). Although recent chemical observations in the area did not show any persistent nutrient signal of Black Sea Water in the surface waters (SOU-VERMEZOGLOU & KRASAKOPOU-LOU, 1999), it is interesting to estimate the importance of the advective import of nutrients through the Dardanelles in relation to their inputs from the atmosphere and the rivers and their possible internal sources and sinks.

The present work represents a first attempt to establish the nonconservative budgets of dissolved inorganic nitrogen and phosphorus in the NE Aegean following the LOICZ biogeochemical modelling guidelines (GORDON *et al.,* 1996). Furthermore, this work can be compared with similar models from different coastal areas produced using the same methodology and so contribute to our knowledge of the role of the coastal zone in carbon, nitrogen and phosphorus cycling.

Materials and Methods

The North Aegean Sea ($\sim 39\degree00$ to $41\degree00$ N, $24\degree00$ to $26\degree00$ E) was sampled seasonally in the framework of the 'Interregional Pollution in the North Aegean - INTERREG-I' project (Fig. 1). Salinity and nutrient data collected during the September 1998 cruise are used to develop budget calculations and empirical models according to the LOICZ biogeochemical modelling guidelines (GORDON *et al.,* 1996).

The system covers an area of 1.43×10^4 km^2 and has a total volume of 3.90×10^{12} m^3. For budgeting purposes the system is considered as a three layer system; the layers are separated by the isopycnal horizons of 28.8 and 29.3 kg m^{-3}, which define the interfaces separating the modified Black Sea, Levantine and North Aegean Deep water masses (ZERVAKIS & GEORGOPOULOS, 2002). During September 1998 the mean thickness of the top layer ($\sigma_\theta < 28.8$) is about 50m, and the thickness of the intermediate layer ($28.8 < \sigma_\theta < 29.3$) is about 300m. The top layer receives freshwater inputs discharged from the Evros, Strimon and Nestos rivers (V_Q) and brackish waters of Black Sea origin outflowing through the Dardanelles Strait ($V_{D\text{-}s}$); additionally through its western open boundary it communicates with the more saline western part of the North Aegean Sea (V_{surf}). The intermediate layer receives water from the adjacent intermediate layer of the western part of the N. Aegean (V_d) and exports water towards the Dardanelles ($V_{D\text{-}d}$). The bottom layer exchanges water with the rest of the North Aegean Trough (V_b). V_{up1} and V_{up2} represent the vertical mass fluxes through the 28.8 and the 29.3 kg m^{-3} isopycnals respectively. Vertical mixing flows (V_{mix1} and V_{mix2}) also exist across the interfaces. A horizontal mixing (V_x) is needed to balance out the salt flux of the surface inflow and bottom counter flow from and to the Dardanelles Strait. The horizontal mixing in the layer $28.8 < \sigma_\theta < 29.3$ is considered zero, since the lower layer of the Dardanelles has almost the same salinity. This means that
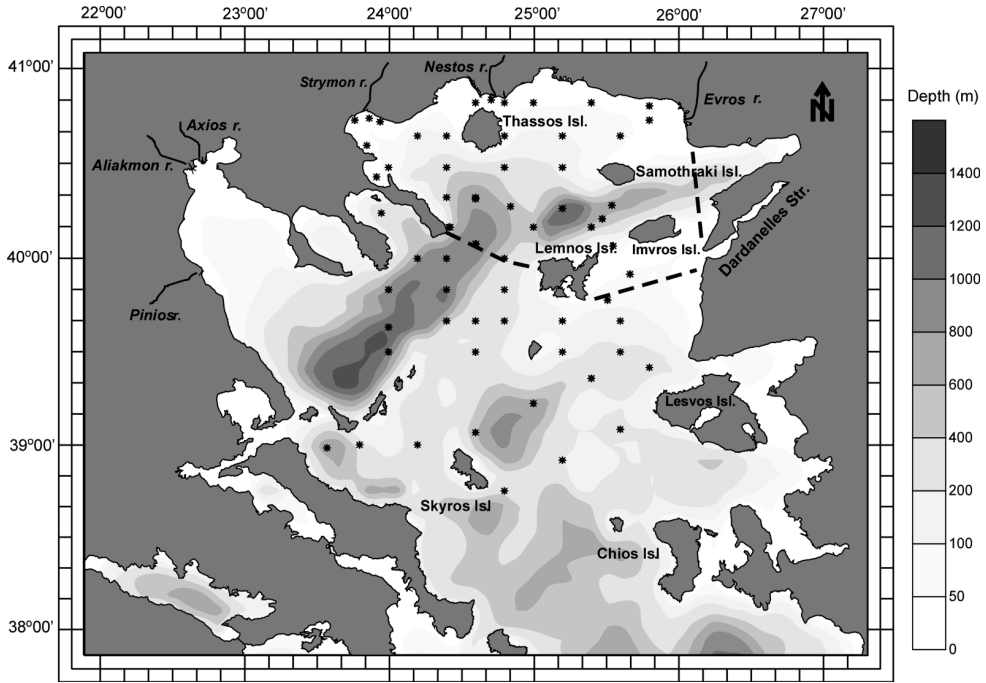
44

Medit. Mar. Sci., 3/1, 2002, 43-53

Fig. 1: Bathymetry and network of sampling stations used to build the budgets in the NE Aegean Sea. – – – – = line defining the boundary of the system.

there is no horizontal transport of salt and nutrients due to mixing between the intermediate layer of the system and the lower layer of the Dardanelles.

The equations describing the steady state water and salt balance for the three layers of the NE Aegean were then constructed (Eqs. 1-7) and solved in order to estimate the unknown water flows.

(1) Water mass balance for the layer with $\sigma_\theta < 28.8$
$$V_Q + V_P + V_E - V_{surf} + V_{up1} + V_{D-s} = 0$$

(2) Salt mass balance for the layer with $\sigma_\theta < 28.8$
$$- V_{surf} S_{syst-s} + V_{up1} S_{syst-d} + V_{D-s} S_{D-s} +$$
$$+ V_{mix1}(S_{syst-s} - S_{syst-d}) = 0$$

(3) Water mass balance for the layer with $28.8 < \sigma_\theta < 29.3$
$$V_d - V_{up1} + V_{up2} - V_{D-d} = 0$$

(4) Salt mass balance for the layer with $28.8 < \sigma_\theta < 29.3$
$$V_d S_{ocn-d} - V_{up1} S_{syst-d} + V_{up2} S_{syst-b} -$$
$$- V_{D-d} S_{syst-d} - V_{mix1}(S_{syst-s} - S_{syst-d}) +$$
$$+ V_{mix2}(S_{syst-d} - S_{syst-b}) = 0$$

(5) Water mass balance for the layer with $\sigma_\theta > 29.3$
$$V_b - V_{up2} = 0$$

(6) Salt mass balance for the layer with $\sigma_\theta > 29.3$
$$V_b S_{ocn-b} - V_{up2} S_{syst-b} -$$
$$- V_{mix2}(S_{syst-d} - S_{syst-b}) = 0$$

(7) Salt mass balance between the system and the Dardanelles
$$V_{D-s} S_{D-s} - V_{D-d} S_{syst-d} = V_x(S_{syst-s} - S_{D-s})$$

As presented above, the problem constitutes an underdetermined linear system of 8 variables (V_{surf}, V_d, V_b, V_{up1}, V_{up2}, V_{mix1},

V_{mix2} and V_x) and 7 equations. In order to obtain a solution, we need to reduce the number of variables. For that purpose, we can exploit recent estimates of eddy diffusion coefficient (K_v) for the deep layers of the North Aegean (ZERVAKIS *et al.,* 2002) to assess the vertical mixing term V_{mix2}. The vertical diffusion of salt, can be approximated as

$$\frac{\partial}{\partial Z}\left(K_v \frac{\partial S}{\partial Z}\right) \approx K_v \frac{\Delta S}{(\Delta D)^2}$$

where $\Delta S = S_{syst-d} - S_{syst-b}$, the salinity difference between the two lower layers, and ΔD the depth interval over which the salinity difference develops. For the vertical diffusion described as above, the salinity flux across the 29.3 kg m^{-3} interface is given by $K_v A \Delta S (\Delta D)^{-2}$, and thus the equivalent V_{mix2} will be given by $V_{mix2} = K_v A (\Delta D)^{-1}$. Using $K_v = 2 \times 10^{-4}$ m^2 s^{-1} (ZERVAKIS *et al.,* 2002), A = 3.9x10^9 m^2 and $\Delta D = 50$m, we estimate a $V_{mix2} = 15600$ m^3 s^{-1}. Having parameterized V_{mix2}, the linear system becomes well-determined and can be solved exactly for the remaining variables.

In order to determine the fluxes, the known and/or assumed values of water volume fluxes and the relevant salinity values have been introduced into the mass balance equations. The salinity and nutrient data of each layer used for the calculations are the depth-averaged values of each station which then were averaged per layer for the area included in the dashed lines (Fig. 1). The same approach was followed in order to define the hydro-chemical properties of the adjacent ocean, using the data of the stations that are close to the western boundary of the system.

The brackish surface current outflowing from the Dardanelles into the Aegean carries between 100 and 1000 km^{3}yr^{-1} and has a salinity ranging between 24-28 psu (UNLUATA *et al.,* 1990). The flow regime exhibits significant seasonal variations depending on the meteorological and hydrological conditions in the adjacent seas and the total fresh water input to Black Sea. In general the net annual flow through the Dardanelles is about 300 km^{3}yr^{-1}

(UNLUATA *et al.,* 1990; POLAT & TUGRUL, 1996), so for the budgeting calculations it was adopted that some 800 km^{3}yr^{-1} of BSW flow into the top layer (V_{D-s}) and that 500 km^{3}yr^{-1} are exported from the intermediate layer towards the Dardanelles (V_{D-d}) (POLAT & TUGRUL, 1996). Additionally, the sensitivity of the calculations of the DIN and DIP fluxes was tested using a range of flows between 200 and 1200 km^{3}yr^{-1}. The annual means of DIP and DIN (nitrite+nitrate) concentrations in the surface flow of the Dardanelles reported by POLAT & TUGRUL (1996) are used in order to evaluate the DIP and DIN budget.

The riverine supply in the area is 20-100 times less than the Dardanelles inflow. The annual riverine freshwater discharges (V_Q) and the corresponding concentrations of dissolved inorganic nutrients used for the budget calculations are based on the values referred to the report of EEA (1999).

In order to complete the freshwater budget of the system the mean annual precipitation and evaporation values referred for the Aegean Sea by POULOS *et al.,* (1997) are used (P: 500 mm yr^{-1}; E: 1280 mm yr^{-1}). These rates are converted to volume fluxes (V_P; V_E) by multiplying by the area of the system. However, it is well known that rainfall is limited (or does not occur) throughout the summer months and probably the precipitation value is over-estimated.

Although transport via the atmosphere is recognised as an important route by which nutrients and particles are delivered to the sea surface, unfortunately data on atmospheric inputs for the study area are not available. The atmospheric inputs of inorganic nitrogen and phosphorus were calculated using the estimated wet fluxes of 0.24 g N m^{-2}yr^{-1} and 0.018 g P m^{-2}yr^{-1} over the SE Mediterranean (HERUT *et al.,* 1999) extrapolated to the surface area of the system. In the case of phosphorus, the aforementioned value is the sum of wet and leachable fluxes because it is suggested that they represent the amount of

46

Medit. Mar. Sci., 3/1, 2002, 43-53

phosphate that is bioavailable in the surface waters.

Results and Discussion

Preliminary calculations using the three-box model have revealed a major disadvantage of this configuration: the model is very sensitive to the salinity difference between the waters of the lowest box (S_{syst-b} = 39.023 psu) and the external bottom waters (S_{ocn-b} = 39.049 psu). Small changes in these quantities lead to vastly different solutions of the model regarding the direction of the deep and bottom flows and the sign of the entrainment between the deep and bottom boxes. Despite the small estimated difference, which could be attributed to sampling bias, scale analysis suggests that the salinity of the bottom waters should become horizontally homogeneous over time-scales of the order of several months. Several hydrographic observations within the deep North Aegean Trough support such an assumption.

Furthermore, observations suggest that the assumption of steady state for the bottom box of our model is not valid: observations ranging from 1993 to 2000 reveal that during stagnation periods, the deeper than 400 m layers of the North Aegean lose salt and gain buoyancy as a result of vertical mixing with the overlying intermediate waters (ZERVAKIS *et al.*, 2002). Thus, a steady-state bottom box is unjustified and introduces unrealistically high entrainment terms into our system.

Thus, the three-box system was replaced by a two-box system, where the lower box is sealed from the bottom waters. For that purpose, equations (5) and (6), as well as the terms representing the interaction with the bottom waters, were omitted from our system. Furthermore, a two-and-a-half box system was developed, where two boxes (surface and deep waters) describe the system. However, the vertical mixing term between deep and bottom waters (V_{mix2}) was included as a source of salt

for the deep layer. The vertical diffusive salinity flux is not constant (as S_{syst-b} is a function of time), but represents the flux in September 1998. Comparative runs of the three models are represented in the following Table 1. The third solution, representing the 2.5-box model, is selected as best representing the budget and the results arising through this approach are illustrated in Fig. 2.

Table 1
Comparative results obtained by running the three different models (volume fluxes in 10^{10} m^3 yr^{-1}).

	3-box model	2-box model	2.5-box model
V_{surf}	241.1	244.6	243.6
V_d	70.2	214.7	213.6
V_b	140.9	-	-
V_{up1}	161.1	164.7	163.6
V_{up2}	140.9	-	-
V_{mix1}	4.2	0.6	1.7

Freshwater inflow (V_P+V_Q) is almost equal to evaporative losses; the net total freshwater loss is estimated about 0.7×10^{10} m^{3}yr^{-1}. The surface inflow from the Dardanelles (80×10^{10} m^{3}yr^{-1}) minus the net freshwater flow drives the water and salt budget for the whole system.

The total water flow from the upper layer of the system (V_{surf}) to the adjacent NW Aegean is 243.6×10^{10} m^{3}yr^{-1}. The required counter flow to the deeper layer of the system from the deep layer of the adjacent sea to replace the salt loss due to V_{surf} is 213.6×10^{10} m^{3}yr^{-1} (V_d), which then is exported towards the upper layer (V_{up1} = 163.6×10^{10} m^{3}yr^{-1}) and the Dardanelles (V_{D-d} = 50×10^{10} m^{3}yr^{-1}). Vertical mixing (V_{mix1}) is 1.7×10^{10} m^{3}yr^{-1} and it is very much smaller than V_{up1} as well as V_{mix2}. The fact that mixing is less intense in the upper part of the water column ($V_{mix2} >> V_{mix1}$) is consistent with the strong stratification observed in the area in particular during summer (reaching 30 cph against 10 cph the common value for the open ocean). The salt flux imported through the Dardanelles Strait surface flow to the NE Aegean (2240×10^{10} psu-m^{3}yr^{-1}) is greater than the salt exported from

Medit. Mar. Sci., 3/1, 2002, 43-53

47

$V_E = 1.83$
$V_E S_E = 0$

$V_P = 0.72$
$V_P S_P = 0$

$V_Q = 1.04$
$V_Q S_Q = 0$

$S_{D-s} = 28.0$ psu
$V_{D-s} = 80$
$V_{D-s} S_{D-s} = 2240$

$V_{surf} = 243.6$
$V_{surf} S_{syst-s} = 8620$

$\sigma_\theta < 28.8$
$V_{syst-s} = 0.71 \times 10^{12}$ m^3
$S_{syst-s} = 35.389$ psu

$V_x = 39.6$
$V_x(S_{syst-s} - S_{D-s}) = 292.6$

$V_{up1} = 163.6$
$V_{up1} S_{syst-d} = 6372$

$V_{mix1} = 1.7$
$V_{mix1}(S_{syst-s} - S_{syst-d}) = 6.1$

$S_{ocn-d} = 38.96$ psu

$V_d = 213.6$
$V_d S_{ocn-d} = 8322$

$28.8 < \sigma_\theta < 29.3$
$V_{syst-d} = 1.97 \times 10^{12}$ m^3
$S_{syst-d} = 38.949$ psu

$V_{D-d} = 50$
$V_{D-d} S_{syst-d} = 1947.4$

$V_{mix2} = 49.5$
$V_{mix2}(S_{syst-d} - S_{syst-b}) = 3.66$

$S_{ocn-b} = 39.049$ psu

$\sigma_\theta > 29.3$
$V_{syst-b} = 1.22 \times 10^{12}$ m^3
$S_{syst-b} = 39.023$ psu

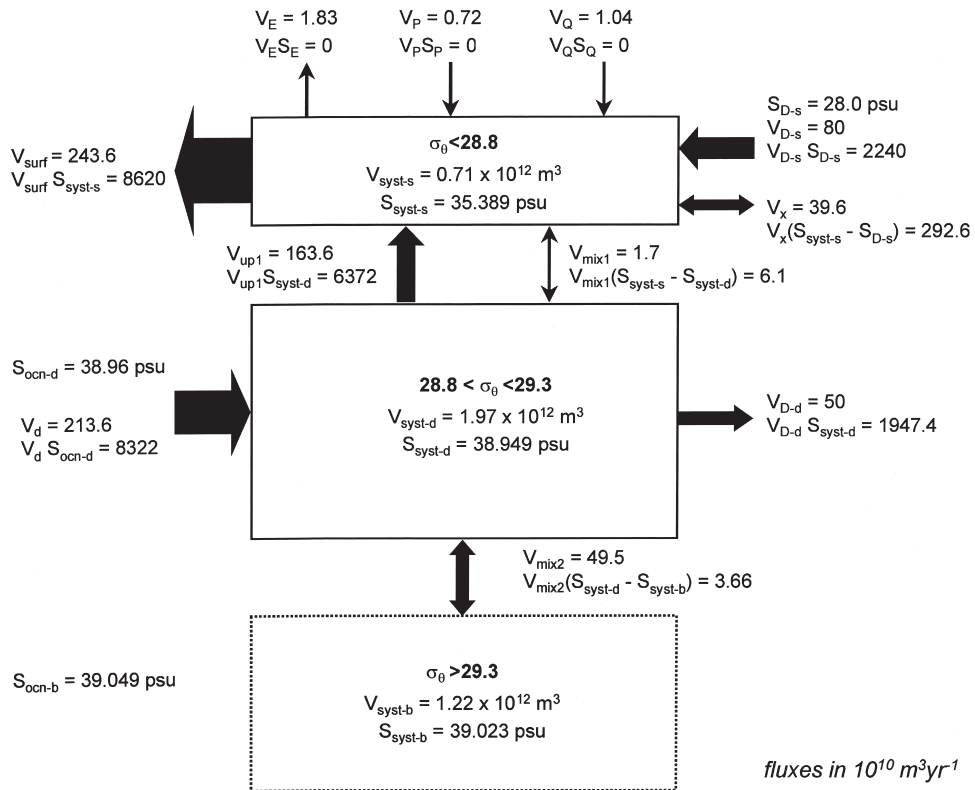*fluxes in 10^{10} m^{3}yr^{-1}*

Fig. 2: Steady state two-and-a-half box model for water and salt budgets in NE Aegean Sea during September 1998.

the Aegean back to the Dardanelles via the subsurface counter flow (1947x10^{10} psu-m^{3}yr^{-1}). The mixing volume (V_x) required to balance this excess salt is estimated as 39.6x10^{10} m^{3}yr^{-1}.

The non-conservative dissolved inorganic phosphorus (DIP) and nitrogen (DIN) fluxes were calculated using the estimated volume transports based on the 2.5-box model and multiplied by the appropriate nutrient concentration (Figs 3 & 4).

Table 2 presents the non-conservative fluxes and the stoichiometrically derived rates scaled per unit area for ease of comparison. In the top layer ΔDIN and ΔDIP are negative, indicating that DIN and DIP are taken up in order to produce organic matter. Overall about 60% of the DIN and about 75% of the DIP fluxes entering this layer are assimilated. It is also interesting to note that the DIN flux

imported into the NE Aegean through the Dardanelles is evenly important to the DIN atmospheric input, whereas the respective DIP flux is comparable to the DIP flux transported by the rivers (Figs 3 & 4).

It is also noteworthy that the mixing volume (V_x) adds into the upper layer 62x10^3 mol d^{-1} of DIP, while at the same time removes 305x10^3 mol d^{-1} of DIN, as a result of the existing differences in the nutrient concentrations between the system and the Dardanelles. Moreover, from the same figure it becomes clear that the intermediate layer of the adjacent ocean feeds the layer with $28.8 < \sigma_\theta < 29.3$ with nutrients and due to the vertical 'loop circulation', the major part of this supply flows upward and enriches the layer with $\sigma_\theta < 28.8$ of the system. Finally the intermediate layer
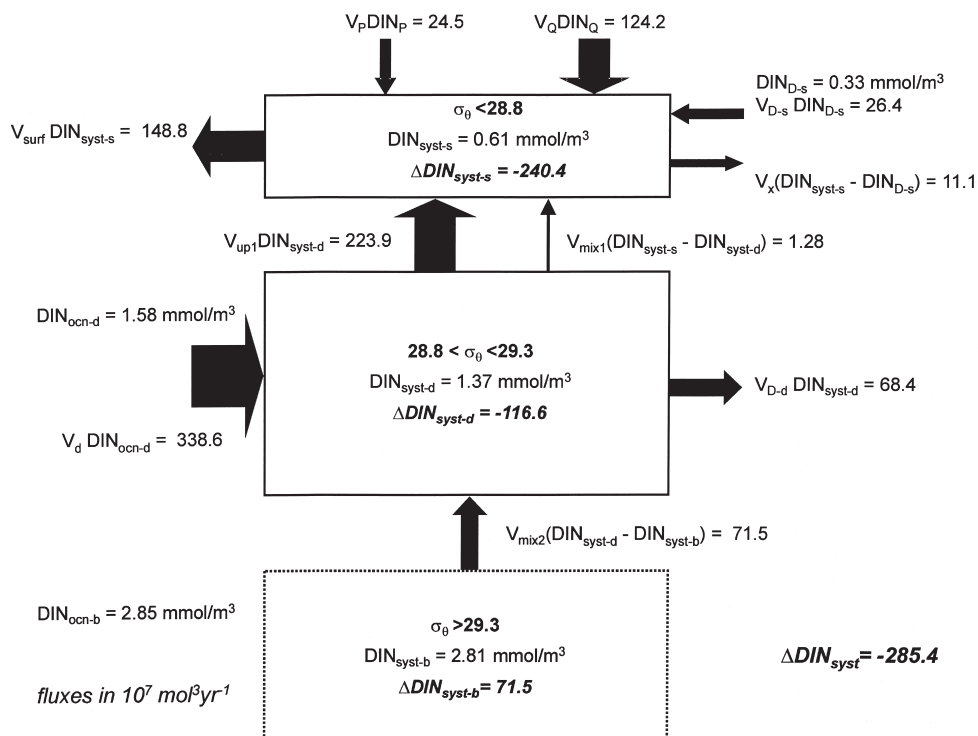
48

Medit. Mar. Sci., 3/1, 2002, 43-53

$V_P DIN_P = 24.5$ $V_Q DIN_Q = 124.2$

$DIN_{D-s} = 0.33\ mmol/m^3$
$V_{D-s}\ DIN_{D-s} = 26.4$

$V_{surf}\ DIN_{syst-s} = 148.8$

$\sigma_\theta < 28.8$
$DIN_{syst-s} = 0.61\ mmol/m^3$
$\Delta DIN_{syst-s} = -240.4$

$V_x(DIN_{syst-s} - DIN_{D-s}) = 11.1$

$V_{up1} DIN_{syst-d} = 223.9$ $V_{mix1}(DIN_{syst-s} - DIN_{syst-d}) = 1.28$

$DIN_{ocn-d} = 1.58\ mmol/m^3$

$28.8 < \sigma_\theta < 29.3$
$DIN_{syst-d} = 1.37\ mmol/m^3$
$\Delta DIN_{syst-d} = -116.6$

$V_{D-d}\ DIN_{syst-d} = 68.4$

$V_d\ DIN_{ocn-d} = 338.6$

$V_{mix2}(DIN_{syst-d} - DIN_{syst-b}) = 71.5$

$DIN_{ocn-b} = 2.85\ mmol/m^3$

$\sigma_\theta > 29.3$
$DIN_{syst-b} = 2.81\ mmol/m^3$
$\Delta DIN_{syst-b} = 71.5$

$\Delta DIN_{syst} = -285.4$

fluxes in $10^7\ mol^3yr^{-1}$

Fig.3: Steady state two-and-a-half box model for DIN budget in the NE Aegean Sea during September 1998.

acts as a sink of DIP and DIN (ΔDIP and ΔDIN are negative).

Without further interpretation, the nutrient budgets do not provide information on the processes which account for the summed sources minus sinks. The non-conservative ΔDIP flux of each layer is then used to calculate the rates of net ecosystem metabolism, that is the difference between primary production (p) and respiration (r) and is roughly estimated as (p-r) = -ΔDIP (C/P)$_{part}$ (GORDON *et al.,* 1996). The calculations are based on the assumption that the decomposed organic mater is dominated by plankton having a Redfield composition (C:N:P = 106:16:1). In the two upper layers with $\sigma_\theta < 28.8$ and $28.8 < \sigma_\theta < 29.3$ primary production exceeds respiration (Table 2) and they appear to be net producers of organic matter. Data on pelagic primary production measured in the study area

during September 1997 (SIOKOU-FRANGOU *et al.,* 2002), suggest that *p* is about 19.2 mmol C m^{-2} d^{-1} and therefore the estimated total net ecosystem metabolism for the two upper layers apparently accounts for about 28% of the corresponding p. Although usually the quantity (*p-r*) is about ±0.1*p*, this latter estimation seems to be reasonable, as a major part of the study system is shallow enough to support benthic primary production.

In contrast to the upper and intermediate layers, in the bottom layer with $\sigma_\theta > 29.3$, as to be expected, organic matter oxidation processes predominate. It is useful to mention the very high oxygen consumption rates observed in the deep layers (depth>500m) of the North Aegean Sea during a two-year stagnation period (SOUVERMEZOGLOU & KRASAKOPOULOU, 2002). The mean oxygen consumption rate obtained from the pre-
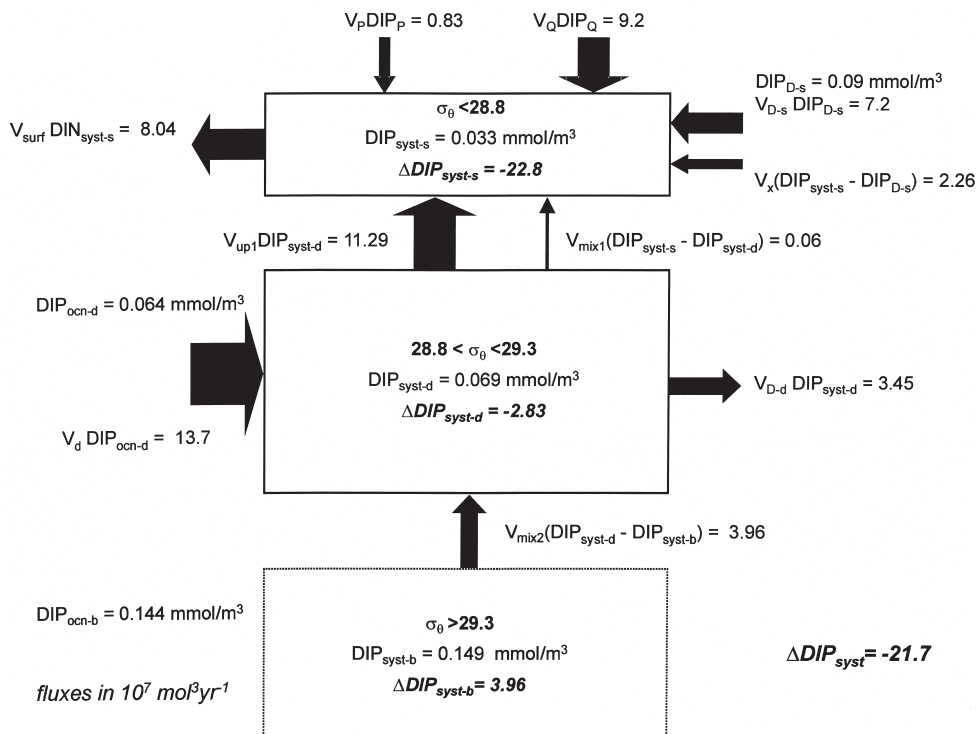
$V_P DIP_P = 0.83$ $V_Q DIP_Q = 9.2$

$DIP_{D-s} = 0.09$ mmol/m³
$V_{D-s} DIP_{D-s} = 7.2$

$\sigma_\theta < 28.8$
$DIP_{syst-s} = 0.033$ mmol/m³
$\Delta DIP_{syst-s} = -22.8$

$V_{surf} DIN_{syst-s} = 8.04$

$V_x(DIP_{syst-s} - DIP_{D-s}) = 2.26$

$V_{up1} DIP_{syst-d} = 11.29$ $V_{mix1}(DIP_{syst-s} - DIP_{syst-d}) = 0.06$

$DIP_{ocn-d} = 0.064$ mmol/m³

$28.8 < \sigma_\theta < 29.3$
$DIP_{syst-d} = 0.069$ mmol/m³
$\Delta DIP_{syst-d} = -2.83$

$V_d DIP_{ocn-d} = 13.7$

$V_{D-d} DIP_{syst-d} = 3.45$

$V_{mix2}(DIP_{syst-d} - DIP_{syst-b}) = 3.96$

$DIP_{ocn-b} = 0.144$ mmol/m³

fluxes in 10⁷ mol³yr⁻¹

$\sigma_\theta > 29.3$
$DIP_{syst-b} = 0.149$ mmol/m³
$\Delta DIP_{syst-b} = 3.96$

$\Delta DIP_{syst} = -21.7$

Fig.4: Steady state two-and-a-half box model for DIP budget in the NE Aegean Sea during September 1998.

vious work, integrated over the volume and averaged over the surface area of the deep layer of the system, is about 5.6 mmolO₂ m⁻²d⁻¹ and corresponds to the regeneration of about 4.3 mmolC m⁻²d⁻¹. This value is 31% higher than the (*p-r*) rate obtained through the stoichiometric calculations (2.95 mmolC m⁻²d⁻¹); the difference between these two estimates strengthens the assumption that dissolved organic matter is the major constituent responsible for the high oxygen consumption in the deep layers of the North Aegean Sea (SOUVERMEZOGLOU & KRASAKO-POULOU, 2002). Another plausible alternative explanation includes the possibility that organic material remineralised at depth has a substantially higher C/P ratio than assumed here. In general, the choice of elemental ratios is particularly complicated in eastern Mediterranean waters where a relative phosphate deficit is reported by many investigators

(KRESS & HERUT, 2001 and references therein). Overall, the production of organic matter seems to be more efficient than its oxidation and the NE Aegean Sea can be considered as an autotrophic system.

The difference between nitrogen fixation and denitrification was also calculated, assuming that the non-conservative DOP and DON fluxes are minor, and is calculated as (nfix-denit) = ΔDIN_obs - ΔDIN_exp. ΔDIN_obs is the observed non-conservative flux of DIN, and ΔDIN_exp is the flux that would be expected if the only flux pathway was the production or consumption of organic matter with a Redfield N:P ratio and thus (nfix-denit) = ΔDIN_obs - (N/P) ΔDIP (GORDON *et al.,* 1996). In the layer with σθ<28.8, where the greater part of the shallow coastal area is included, it seems that an important portion of DIN could originate from biological fixation of atmospheric nitrogen by seagrasses (*Posidonia*

Table 2
Non-conservative DIN and DIP fluxes and stoichiometric calculations for the NE Aegean Sea during September 1998.

NE Aegean Sea September '98	layer 1 ($\sigma_\theta < 28.8$)	layer 2 ($28.8 < \sigma_\theta < 29.3$)	layer 3 ($\sigma_\theta > 29.3$)	Total (layers 1 + 2 + 3)
Surface area (10^{10} m^2)	1.43	1.13	0.39	
ΔDIP (10^7 mol yr^{-1})	-22.8	-2.83	3.96	-21.7
ΔDIP (mmol m^{-2} d^{-1})	-0.044	-0.007	0.028	-0.023
ΔDIN (10^7 mol yr^{-1})	-240.4	-116.6	71.5	-285.4
ΔDIN (mmol m^{-2} d^{-1})	-0.46	-0.28	0.50	-0.24
(p-r) (mmol C m^{-2} d^{-1})	4.63	0.73	-2.95	2.41
(nfix-denit) (mmol N m^{-2} d^{-1})	0.24	-0.17	0.06	0.12

oceanica) and by free-living bacterioplancton species (*Trichodesmiun, Synechococcus*) (BETHOUX *et al.,* 1992; BETHOUX *et al.,* 1998) as well as by epi- and endosymbionts cyanobacteria (*Richelia*) on diverse marine diatoms (ZEHR *et al.,* 2000). In several studies *Trichodesmiun* is reported as the most common diazotrophic cyanobacteria (CAPONE *et al.,* 1997; CAPONE, 2001), however it is not a common species in the Mediterranean in contrast to *Synechococcus*, which is essentially abundant in Mediterranean waters but whose population consists of very small-sized cells (BETHOUX *et al.,* 1998 and references therein). Although direct measurements of the fixation rates of atmospheric nitrogen by the different bacterioplanktonic populations in the eastern Mediterranean are not available, several results support the hypothesis that nitrogen-fixing cyanobacteria might be responsible for a large part of the nitrogen budget. Recent isotopic analyses of carbon and nitrogen in settling organic matter reveal the potential importance of N$_2$ fixation through cyanobacteria and suggest that biological fixation would constitute a major source of nitrogen in the Mediterranean (KERHERVE *et al.,* 2001).

However, in the layer with $28.8 < \sigma_\theta < 29.3$ denitrification obviously represents a large sink of DIN. Although denitrification in the water column occurs under low oxygen conditions, in subsurface waters where rates of organic matter degradation are large enough to deplete the existing oxygen content, it is possible that denitrification occurs in microenvironments such as the interior of sinking particulate organic matter and may account for the relatively high denitrification rate (CHRISTENSEN, 1994; ALLDREDGE & COHEN, 1987). The stoichiometric calculation of (nfix-denit) does not seem to work well for the layer with $\sigma_\theta > 29.3$, because in the deep layer of the ocean would not nitrogen fixation be expected to occur. We suspect that this discrepancy is mainly due to the low N/P ratio used for the calculations; the high N/P ratio, higher than the Redfield ratio of 16 usually found in the ocean, constitutes one of the most exceptional characteristics of the deep waters in the eastern Mediterranean and it is attributed to the oxidation of particulate organic matter deficient in P. Several hypotheses have been proposed to explain the depletion in P relative to N of the Mediterranean waters (KRESS & HERUT, 2001 and references therein; MOUTIN & RAIMBAULT, 2002 and references therein). Overall, the system appears to fix more nitrogen than is lost through denitrification. This conclusion remains qualitatively the same even without taking into account the layer with $\sigma_\theta > 29.3$. It is evident (Table 2) that the nitrogen fixation processes that take place in the layer with $\sigma_\theta < 28.8$ overwhelm the denitrification that occurs in the deeper layer with $28.8 < \sigma_\theta < 29.3$.

The budgetary calculations were also performed using a range of Dardanelles inflow

Table 3
Nonconservative DIP and DIN fluxes and stoichiometric calculations for different Dardanelles inflow and outflow to the NE Aegean Sea in September 1998.

V_{D-s}	500	800	1200
V_{D-d}	200	500	900
(km^3 yr^{-1})			
ΔDIP (10^7 mol yr^{-1})	-20.7	-21.7	-25.2
ΔDIP (mmol m^{-2} d^{-1})	-0.021	-0.023	-0.029
ΔDIN (10^7 mol yr^{-1})	-214.5	-285.4	-369.0
ΔDIN (mmol m^{-2} d^{-1})	-0.095	-0.241	-0.414
(p-r) (mmol C m^{-2} d^{-1})	2.2	2.4	3.1
(nfix-denit) (mmol N m^{-2} d^{-1})	0.24	0.12	0.05

(V_{D-s}) in the top layer; the corresponding exported flow (V_{D-d}) was defined in a manner that the net annual flow through the Dardanelles strait is always 300 km^{3}yr^{-1} (UNLUATA *et al.,* 1990; POLAT & TUGRUL, 1996). The non-conservative fluxes of DIN and DIP as well as the stoichiometric calculations for three selected V_{D-s} flows (500; 800 and 1200 km^{3}yr^{-1}) are presented in Table 3. The different (V_{D-s}) used affect the exchanged flows between the two layers and the ocean and consequently the non-conservative fluxes. However, it is obvious from Table 3 that the obtained fluxes vary slightly as a function of the used V_{D-s} flows and remain within the same range. It is also noteworthy that the system remains autotrophic and the nitrogen fixation processes dominate over the denitrification losses, independently of the V_{D-s} flow used. Therefore, it could be considered that the non-conservative fluxes and the stoichiometric calculations are not particularly sensitive to the Dardanelles inflow, probably due to the low inorganic nutrient levels of the inflowing waters.

Although the uncertainty about the estimates of the DIN and DIP budgets was not determined, this work, based on the LOICZ biogeochemical modelling guidelines, enabled for the first time ever, the quantification of the non-conservative fluxes of dissolved inorganic nitrogen and phosphorus in NE Aegean and the assessment of the dominant processes affecting the nutrient fluxes in the system.

References

ALLDREDGE, A.L. & COHEN, Y., 1987. Can microscale chemical patches persist in the sea? Microelectrode study of marine snow, fecal pellets. *Science,* 235, 689-691.

BETHOUX, J.P., MORIN, P., CHAUMERY, C., CONNAN, O., GENTILI, B. & RUIZ-PINO, D., 1998. Nutrients in the Mediterranean Sea, mass balance and statistical analysis of concentrations with respect to environmental change. *Marine Chemistry,* 63, 155-169.

BETHOUX, J.P., MORIN, P., MADEC, C., & GENTILI, B., 1992. Phosphorus and nitrogen behaviour in the Mediterranean Sea. *Deep-Sea Res.,* 39(9), 1641-1654.

CAPONE, D.G., 2001. Marine nitrogen fixation: what's the fuss? *Current Opinion in Microbiology,* 4, 341-348.

CAPONE, D.G., ZEHR, J.P., PAERL, H.W., BERGMAN, B. CARPENTER, E.J., 1997. Trichodesmium, a globally significant marine cyanobacterium. *Science,* 276, 1221-1229.

CHRISTENSEN, J.P., 1994. Carbon export from continental shelves, denitrification and atmospheric carbon dioxide. *Continental Shelf Research,* 14 (5), 547-576.

EEA, 1999. Discharges via rivers. In: *State and pressures of the marine and coastal Mediterranean environment.* Environmental assessment series nº 5, 137 p.

GORDON, JR.D.C., BOUDREAU, P.R., MANN, K.H., ONG, J.-E., SILVERT, W.L., SMITH, S.V., WATTAYAKORN, G., WULFF, F. & YANAGI, T., 1996 LOICZ Biogeochemical Modelling Guidelines. LOICZ *Reports & Studies 5,* LOICZ, Texel, The Netherlands, 96 pages.

HERUT, B., KROM, M.D., PAN, G. MORTIMER R. 1999. Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes and possible impact. *Limnol. Oceanogr,* 44 (7), 1683-1692.

KERHERVE, P., MINAGAWA, M., HEUSSNER, S. MONACO, A., 2001. Stable isotopes (^{13}C/^{12}C and ^{15}N/^{14}N) in settling organic matter of the northwestern Mediterranean Sea: biogeochemical implications. *Oceanologica Acta,* 24, S77-S85.

KRESS, N. & HERUT, B., 2001. Spatial and seasonal evolution of dissolved oxygen and nutrients in the Southern Levantine Basin (eastern Mediterranean Sea): chemical characterization of the water masses and inferences on the N:P ratios. *Deep Sea Research I,* 48 , 2347-2372.

MOUTIN T. & RAIMBAULT P., 2002. Primary production, carbon export and nutrients availability in western and eastern Mediterranean Sea in early summer 1996 (MINOS cruise). *Journal of Marine Systems,* 33–34, 273– 288.

PAGOU, K. & GOTSIS-SKRETAS, O., 1989. Phytoplankton. In: *Pollution research and monitoring programme in the Aegean and Ionian Seas,* A. Bousoulengas & A.V. Catsiki (eds). National Centre for Marine Research, Athens, Hellas, Technical Report (1986-87), 128-156.

POLAT, C. & TUGRUL S., 1996. Chemical exchange between the Mediterranean and the Black Sea via the Turkish Straits. *Bulletin de l'Institut oceanographique,* Monaco, nº special 17, CIESM Science Series nº 2, 167-186.

POULOS, S.E., DRAKOPOULOS, P.G. & COLLINS, M.B. 1997. Seasonal variability in sea surface oceanographic conditions in the Aegean Sea (eastern Mediterranean): an overview. *Journal of Marine Systems,* 13, 225-244.

SIOKOU-FRANGOU, I., BIANCHI, M., CHRISTAKI, U., CHRISTOU, E., GIANNAKOUROU, A., GOTSIS, O., IGNATIADES, L., PAGOU, K., PITTA, P., PSARRA, S., SOUVERMEZOGLOU, E., VAN WAMBEKE, F. & ZERVAKIS, V. 2002. Carbon flow in the planktonic food web along a gradient of oligotrophy in the Aegean Sea (Mediterranean Sea). *Journal of Marine Systems,* 33-34, 335-353.

SIOKOU-FRANGOU, I., PANCUCCI-PAPADOPOULOU, M.I. & CHRISTOU, E., 1994. Sur la répartition du plankton superficiel des mers entourant la Gréce (Printemps 1987), *Biologia Gallo-Hellenica,* 21, 313-330.

SOUVERMEZOGLOU E. & KRASAKOPOU-LOU E., 1999. Evolution of oxygen and nutrient concentrations in the deep basins of the northern Aegean Sea. 4th MTP Workshop, 28-30 October 1999, Perpignan, France, pp. 150-151.

SOUVERMEZOGLOU E. & KRASAKOPOU-LOU E., 2002. High oxygen consumption rates in the deep layers of the North Aegean Sea (eastern Mediterranean). *Mediterranean Marine Science,* this issue.

THEOCHARIS A. & GEORGOPOULOS D., 1993. Dense water formation over the Samothraki and Limnos Plateaux in the North Aegean Sea (eastern Mediterranean Sea). *Continental Shelf Research,* 13, No 8/9, 919-939.

UNLUATA, U., OGUZ, T., LATIF, M.A. & OZSOY, E., 1990. On the physical oceanography of the Turkish straits. In: L.J. Pratt (editor), *The Physical Oceanography of Sea Straits.* Kluwer, Dordrecht, pp. 25-60.

ZEHR, J.P., CARPENTER, E.J. & VILLAREAL, T.A., 2000. New perspectives on nitrogen-fixing microorganisms in tropical and subtropical oceans. *Trends in Microbiology,* 8, 68-73.

ZERVAKIS, V. & GEORGOPOULOS, D., 2002. Hydrology and Circulation in the North Aegean (eastern Mediterranean) throughout 1997-1998. *Mediterranean Marine Science,* this issue.

ZERVAKIS, V., D. GEORGOPOULOS & P. G. DRAKOPOULOS, 2000: The role of the North Aegean Sea in triggering the recent eastern Mediterranean climatic changes. *Jour. Geophys. Res.,* 105, C11, 26,103-26,116.

ZERVAKIS, V., KRASAKOPOULOU, E., GEORGOPOULOS, D., & SOUVERME-ZOGLOU, E., 2002. Vertical diffusion during stagnation periods in the deep North Aegean. *Manuscript submitted to Deep Sea Research I.*