2. COASTAL SYSTEMS OF GREECE

<u>The northern Aegean Sea and Thermaikos Gulf</u>

Situated on the southernmost portion of the Balkan Peninsula, Greece is nearly surrounded by seas. The Aegean lies to the east, the Mediterranean to the south, and the Ionian to the west. Continental Greece is mountainous and rugged and the coast is highly indented - as the ancient Greek geographer Strabo (64? BC-24 AD) wrote, "the sea presses in upon the country with a thousand arms". The coastal waters of Greece are shallow, and penetrate far inland by means of the often narrow bays and gulfs.

The Aegean Sea constitutes the north-eastern part of the eastern Mediterranean Sea; it is bounded to the east by the Turkish coastline, to the north and west by the Greek mainland and to the south by the island of Crete and the other Cretan Arc islands. It communicates with the Sea of Marmara through the Dardanelles Strait and with the Mediterranean through the straits of the Cretan Arc. The Thermaikos Gulf is on the north-western continental margin of the Aegean Sea.

The Thermaikos coastal system includes rivers and ephemeral streams (Axios, Aliakmon, Gallikos and Pinios). The sub-aerial part of the coastal zone includes mostly the deltaic plains of the aforementioned rivers, some low-relief late Quaternary coastal plains and cliffs. The coastal zone climate is semi-arid Mediterranean, with rather cold winters. Annual air temperatures range between 0 and 38°C, while the mean annual precipitation is 480 mm (in the city of Thessaloniki). Northerly winds blow throughout the year, more strongly during winter; these are Balkan cold air masses (locally named *Vardaris* wind) originating from the north/north-west following the valley of the Axios River. During summer the wind is dominated by the *Etesians* which blow from the north/north-east and are relatively strong (>6m/s).

[*from: S. E. Poulos, G. Th. Chronis, M. B. Collins and V. Lykousis (2000) Thermaikos Gulf Coastal System, NW Aegean Sea: an overview of water/sediment fluxes in relation to air-land-ocean interactions and human activities. Journal of Marine Systems 25:47-76.*]

2.1 Inner Thermaikos Gulf (NW Aegean Sea, E. Mediterranean): a preliminary approach

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<u>Study area description</u>

The Thermaikos Gulf (40.3-40.6°N, 22.3-22.9°E; Figure 2.1) forms the north-west Aegean continental shelf and it is a typical deltaic platform. Four rivers (Axios, Loudias, Aliakmon, Pinios) constitute the major sources of material input into the marine system of the Thermaikos Gulf. The drainage basin covers an area of ~72,000 km^2. Measurements carried out during the METRO-MED project showed a mean annual water discharge of the river system of about 207 $m^3\ sec^{-1}$ or $18 x 10^6\ m^3\ d^{-1}$ (Karamanos *et al.* 2000).

Thessaloniki Bay, the northern part of the Inner Thermaikos Gulf, receives domestic, agricultural and industrial effluents not only through the rivers but also in sewage from the city of Thessaloniki. Fishing activities and extensive aquaculture farming also occurs, along with water recreational activities. This northern part of the study area is characterized by eutrophic conditions due mostly to the intense nutrient supply through the sewage. The western coast of the Inner Thermaikos Gulf (depth: 0-50 m) is influenced by the three major river estuaries (Axios, Loudias, Aliakmon) and the prevailing eutrophic conditions are also related to this freshwater inflow, whereas the eastern coast is influenced by the oligotrophic Aegean Sea. However, depending to the seasonal variability, eutrophic conditions due to the rivers can be recorded in the whole Inner Gulf area.

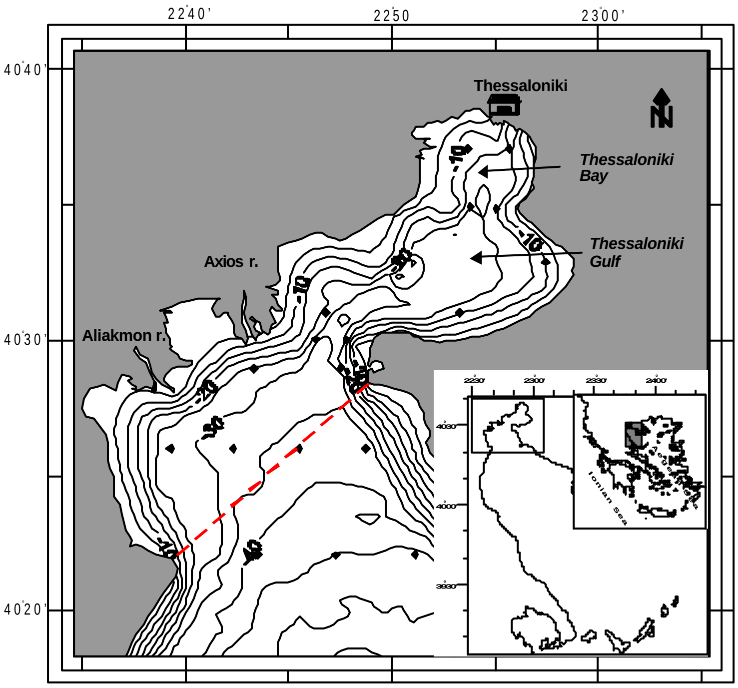

Figure 2.1. Bathymetry (depth contours in m) and network of sampling stations used to build the budgets at Inner Thermaikos Gulf (*from Karageorgis et al. 2000*). The dotted line defines the boundary of the box.

Two different water masses have been detected seasonally: the freshwater from the rivers in the surface layer and the saline Aegean waters in greater depths. Dissolved oxygen and nutrient concentrations are dependent not only on the water masses circulation and stratification, but also on the freshwater discharge, especially during the rainy period, when there are high levels of dissolved nutrients and oxygen. On the other hand, low oxygen and high nutrient concentrations were recorded in Thessaloniki Bay, especially during summer, due to anthropogenic inputs combined with minimal water exchange. The phytoplankton biomass distribution is also affected by water flow and exchange: Thessaloniki Bay is extremely eutrophic, with very high concentrations of chlorophyll á throughout the year, whereas the area around the estuary mouths have high to intermediate values of biomass related to the season and the amount of freshwater entering the sea (Pagou *et al.* 2000a).

Thermaikos Gulf (~39.8°-40.8°N, 22.9°-23.5°E) was sampled seasonally in the framework of the METRO-MED project. Nutrient data derived during this project were used for the budget estimation presented hereafter for two seasons, one wet (February 1998) and one dry (September 1998). The budgetary calculations are focused in the northern inner part of the Gulf (Figure 2.1). Salinity and nutrient data used are the depth-averaged values of each station which then were separately averaged per box. The budgetary analysis was performed according to the LOICZ Biogeochemical Budgeting Guidelines (Gordon *et al.* 1996) and it was also tested using the CABARET software. It was assumed that the water column was homogeneous during both seasons and the 'single box single layer' approach was followed.

The system has an approximate area of 336 km^2 and a volume of $7{,}235x10^6$ m^3 (mean depth of about 21.5 m) and it receives sewage discharges from the city of Thessaloniki (1,000,000 residents), freshwater inputs discharged mainly from the Axios and Aliakmon rivers. Through its southern open boundary it communicates with the more saline southern part of Thermaikos Gulf.

Riverine freshwater discharges were intensively monitored during the METRO-MED project and exhibit strong seasonality, being much larger in February than in September (Karamanos and Polyzonis 2000). However, concentrations of dissolved inorganic nutrients do not follow this pattern and in particular DIP concentrations are almost twice as high in September as in February.

In addition to the riverine supply, a substantial 'freshwater' input is contributed by the sewage outfall of Thessaloniki (1,000,000 residents). Although the water volume of the sewage is small relative to the other freshwater, inputs of dissolved N and P are highly concentrated in the effluent. Sewage discharges to the sea are evaluated assuming a wastewater production of 250 liters per person per day and the discharge coefficients proposed by Sogreah (1974), Padilla *et al.* (1997) and World Bank (1993).

At this stage of the study, due to the absence of any original data from local meteorological stations, the mean annual values referred for the Aegean Sea by Poulos *et al.* (1997) will be used for both seasons (precipitation: 500 mm yr^{-1}; evaporation: 1,280 mm yr^{-1}). These precipitation and evaporation rates are converted to volume fluxes by multiplying by the area of the system. However since rainfall is minimal (or does not occur) throughout the summer months, the precipitation value is probably overestimated at least for September.

Although transport via the atmosphere is recognised as an important route by which nutrients and particles are delivered to the sea surface, unfortunately there are no data available on atmospheric inputs for the study area. Most of the available data on atmospheric inputs of nutrients refer to the western Mediterranean basin and the only published information on the eastern basin concerns measurements on the Israeli coasts (Herut and Krom, 1996; Herut *et al.* 1999). The atmospheric inputs of inorganic nitrogen and phosphorus were estimated using the calculated values of the fluxes for the SE Mediterranean (Herut *et al.* 1999) extrapolated to the surface area of the system. The estimated wet flux of inorganic phosphorus and nitrogen over the SE Mediterranean is about 0.018 g P $m^{-2} yr^{-1}$ or 0.002 mmol P $m^{-2} d^{-1}$ and about 0.24 g N $m^{-2} yr^{-1}$ or 0.05 mmol N $m^{-2} d^{-1}$, respectively. 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 phosphate that is bioavailable in the surface waters.

Water and salt balance

Figure 2.2 summarises the steady-state water and salt budgets for the Inner Thermaikos Gulf. During February the net total freshwater input that drives the whole system is about $22.0x10^6$ m^3 d^{-1}, while in September it is about $6.0x10^6$ m^3 d^{-1}. During both seasons freshwater inflows exceed evaporation and there is seawater outflow to balance this gain of water (V_R =-$21.6x10^6$ m^3d^{-1} and -$5.6x10^6$ m^3d^{-1} for February and September respectively). Due to the uniform values used for the precipitation-evaporation and the sewage discharge (V_O), this residual water flow exhibits seasonally different values attributed to the existing difference in the freshwater loads of the two rivers, being much lower in September.

The salt that is exported through the residual flow must be replaced through the mixing volume with the adjacent 'ocean'. For February, the higher V_R yields to an estimated V_X of about $2,010x10^6$ m^3d^{-1} resulting to the total exchange time: about 4 days. During September, the mixing volume V_X is about $287x10^6$ m^3d^{-1} and the corresponding total exchange time is about 25 days.

Budgets of nonconservative materials

DIP and DIN balance

Nonconservative dissolved inorganic phosphorus (DIP) and nitrogen (DIN) fluxes were calculated using the estimated volume transports (Figures 2.3 and 2.4). Table 2.1 presents the nonconservative fluxes and the stoichiometrically-derived rates scaled per unit area for ease of comparison. During February 1998 *ÄDIP* is positive, indicating that there is a net release of DIP probably related to organic matter regeneration processes. In contrast, the negative *ÄDIP* during September 1998 indicates that there is a net uptake of DIP in order to produce organic matter. For DIN the same pattern was seen during both seasons as for DIP.

Table 2.1. Summary of DIP and DIN fluxes and stoichiometric calculations for Inner Thermaikos Gulf in February and September 1998.

	February '98	**September '98**
	System	System
Area (10^6 m^2)	336	336
Volume (10^6 m^3)	7,300	7,300
t (days)	4	25
ÄDIP (10^6 mol d^{-1})	+108	-134
ÄDIP (mmol m^{-2} d^{-1})	+0.3	-0.4
ÄDIN (10^6 mol d^{-1})	+112	-751
ÄDIN (mmol m^{-2} d^{-1})	+0.3	-2.2
(*p-r*) (mmol C m^{-2} d^{-1})	-32	+42
(*nfix-denit*) (mmol N m^{-2} d^{-1})	-4.5	+4.2

Stoichiometric calculations of aspects of net ecosystem metabolism

The nonconservative *ÄDIP* flux of each season is then used to calculate the rate of net ecosystem metabolism (*p-r*). These calculations are based on the assumption that the decomposed organic material is dominated by plankton having a Redfield composition ([*p-r*]=-106 *ÄDIP*). For February the results suggest that in the Inner Thermaikos Gulf respiration exceeds primary production, whereas during September the ecosystem is a net producer of organic matter.

The nonconservative *ÄDIP* and *ÄDIN* fluxes are used to calculate the difference between nitrogen fixation and denitrification assuming that the nonconservative DOP and DON fluxes are minor [(*nfix-denit*) = *ÄDIN* – (N/P) *ÄDIP*]. The estimation of (*nfix-denit)* was performed using the Redfield N/P ratio (16). The results obtained for both seasons using the Redfield ratio probably mean that the system is changing from net detrification during February to net nitrogen fixing during September.

These results must be regarded as a preliminary approach for the N and P budgets in the Inner Thermaikos Gulf. Other models or approaches should also be applied, such as division of the area into more compartments, since the 'one box' selection can hardly explain the complexity of the Thermaikos ecosystem as it is known from research projects to date.

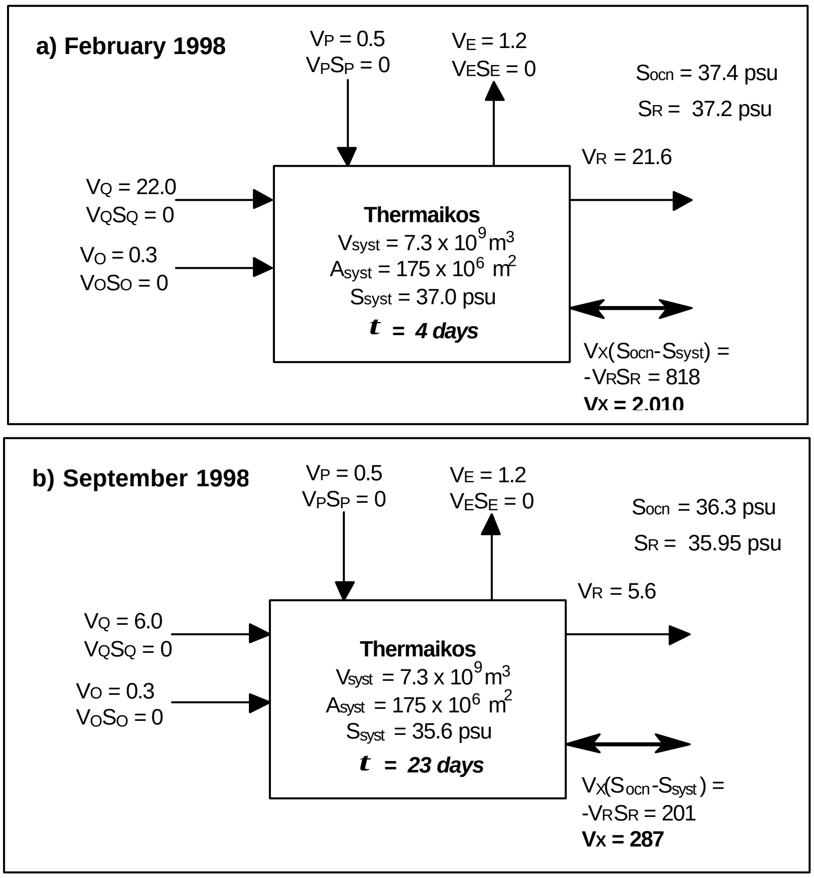

Figure 2.2. Water and salt budgets for Inner Thermaikos Gulf in February (a) and September (b) 1998. Water fluxes in 10^6 m^3 d^{-1} and salt fluxes in 10^6 psu-m^3 d^{-1}.

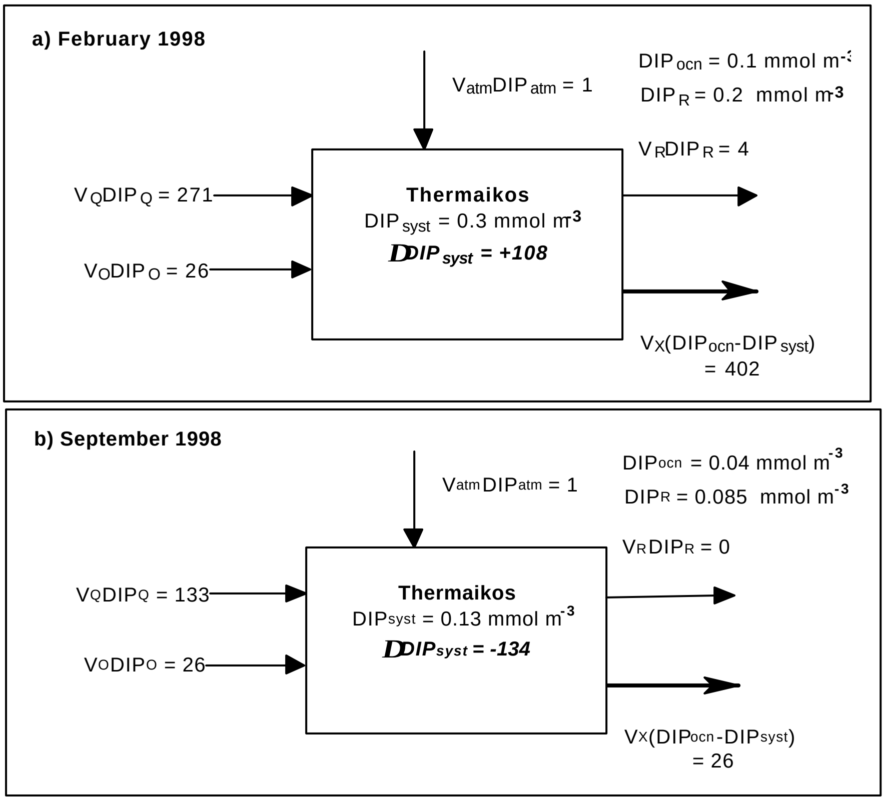

Figure 2.3. DIP budget for Inner Thermaikos Gulf in February (a) and September (b) 1998. Fluxes in 10^3 mol d^{-1}.

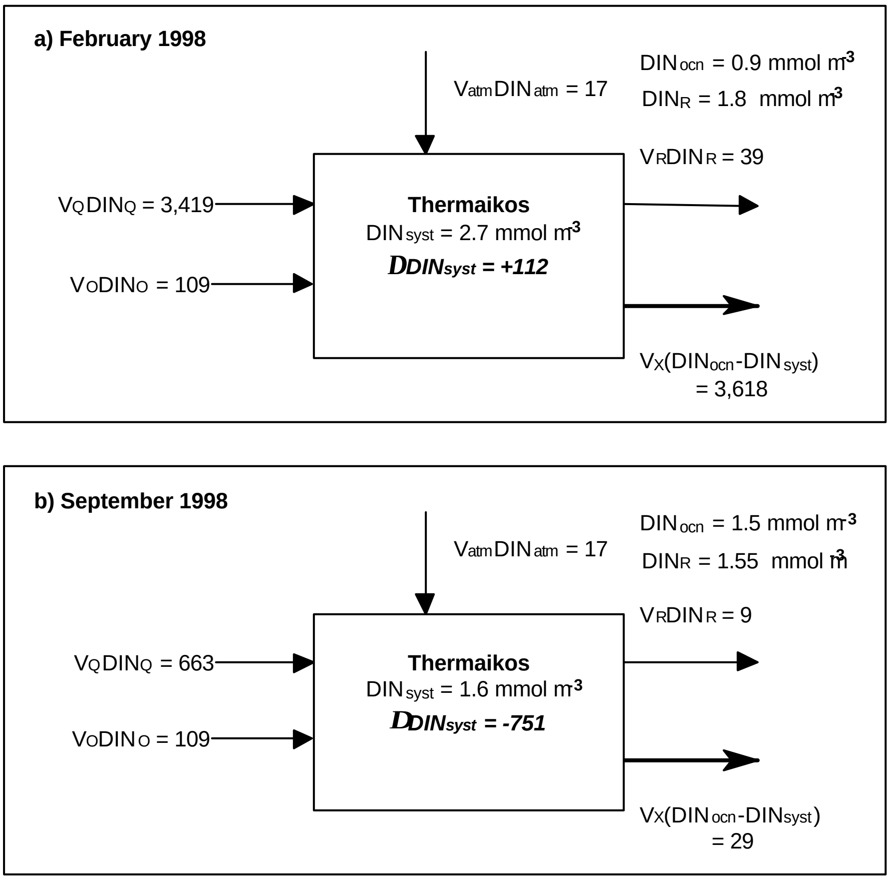

Figure 2.4. DIN budget for Inner Thermaikos Gulf in February (a) and September (b) 1998. Fluxes in 10^3 mol d^{-1}.

2.2 North-eastern Aegean Sea

E. Krasakopoulou, V. Zervakis, E. Souvermezoglou and D. Georgopoulos

<u>*Study area description*</u>

The north-eastern (NE) Aegean Sea (~39.83°-41.00°N, 24.00°-26.00°E; Figure 2.5) covers an area of 19,500 km^2, has a mean depth of 230m and a total volume of 4.5×10^{12} m^3. It presents complex bottom topography and it is characterised by alternating deep trenches and shallow shelves and sills.

The NE Aegean Sea is a region where the 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. For years it was considered that the higher phytoplankton and zooplankton assemblages observed in the area close to Dardanelles were associated to the influence of the nutrient-rich Black Sea Water outflowing through the Dardanelles (Pagou and Gotsis-Skretas 1989; Siokou-Frangou *et al.* 1994). Although recent chemical observations in the area did not show any persistent nutrient signal of Black Sea water in the surface (Souvermezoglou and Krasakopoulou 1999), it is interesting to estimate the importance of the advective import of nutrients through the Dardanelles in relation to inputs from the atmosphere and rivers and possible internal sources and sinks.

Figure 2.5. Bathymetry and network of sampling stations used to build the budgets at NE Aegean Sea. Dotted line defines the boundary of the budgeted system.

The present work comprises a first attempt to establish the nonconservative fluxes of dissolved inorganic nitrogen and phosphorus in the NE Aegean Sea 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 on the role of the coastal zone in carbon, nitrogen and phosphorus cycling.The NE Aegean Sea was sampled seasonally in the framework of the INTERREG-I project. Salinity and nutrient data collected during the September 1998 cruise were used to develop budget calculations.

Water and salt balance

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 σ_Φ, which define the interfaces separating the modified Black Sea, Levantine and North Aegean Deep water masses (Zervakis *et al.* 1998). Due to the irregular bathymetry of the area that exceeds 1,500m depth and to the presence of a sill ~500m deep which limits the lateral communication between the deep layers of the basins (Figure 2.5), it is assumed that the study system is 'sealed' below the 29.3 σ_Φ isopycnal horizon and the budget calculations are performed considering only the two upper layers. During September 1998 the mean thickness of the top layer (σ_Φ<28.8) is about 50m, and the thickness of the intermediate layer (28.8<σ_Φ<29.3) is about 155m. The intermediate layer has an area of about 14,800 km^2. The top layer receives freshwater inputs discharged from Evros, Strimon and Nestos rivers (V_Q) and brackish waters of Black Sea origin inflowing from the Dardanelles Strait (V_{Dar-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 North Aegean (V_D) and at the same time it is assumed that the intermediate layer exports water towards the top layer ($V_{D'}$) and the Dardanelles (V_{Dar-d}). Between the two layers of the NE Aegean Sea exists an additional flow, the vertical mixing flow (V_Z) that exchanges surface and deeper waters within the system. A horizontal mixing ($V_{X-s'}$) in the surface layer between NE Aegean Sea and the Dardanelles Strait is needed to balance out the salt flux of the surface inflow and intermediate counter-flow from and to the Dardanelles Strait. Horizontal mixing in the intermediate layers ($V_{X-d'}$) is zero since the layers have almost the same salinity. This means that there is no net horizontal transport of conservative materials (e.g. salt, nutrients) due to mixing between the intermediate layer of the system and lower layer of the Dardanelles Strait.

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 (Figure 2.5). The same approach was followed in order to define the hydrochemical properties of the adjacent ocean, using the data of the stations that are close to the western boundary of the system. Data for the inner eastern side of the system were not collected as shown by the absence of sampling stations in the area (Figure 2.5).

The annual brackish surface current outflowing from the Dardanelles into the Aegean carries between 274 and 2,740x10^6 m^3 d^{-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 822x10^6 m^3 d^{-1} (Unluata *et al.* 1990; Polat and Turgul, 1996), so for the budgeting calculations it was assumed that some 2,192x10^6 m^3 d^{-1} of Black Sea water flows into the top layer and that 1,370x10^6 m^3 d^{-1} is exported from the intermediate layer towards the Dardanelles (Polat and Turgul 1996). Additionally, the sensitivity of the calculations was tested using a range of flows between 548 and 3,288x10^6 m^3 d^{-1}.

The riverine supply in the area is 20-100 times less than the Dardanelles inflow. The annual riverine freshwater discharges and the corresponding concentrations of dissolved inorganic nutrients used for the budget calculations are based on the values cited in 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 (500 mm yr^{-1} and 1,280 mm yr^{-1}, respectively). These rates are converted to volume fluxes by multiplying with the area of the system. However, since the rainfall is limited (or does not occur) throughout the summer months, the precipitation value is probably overestimated. However, since the water budget is largely driven by the water flow from the Dardanelles Strait, precipitation is not important.

The equations describing the steady state water and salt balance for the two upper layers of the NE Aegean were then constructed and solved in order to estimate the unknown water flows. The results arising through this simple approach are illustrated in Figure 2.6.

Freshwater inflow (V_P+V_Q) is almost equal to evaporative losses; the net total freshwater loss is estimated about $13x10^6$ m^3d^{-1}. The surface inflow (V_{Dar-s} = $2,192x10^6$ m^3d^{-1}) from the Dardanelles minus the net freshwater flow drives the water and salt budgets for the whole system. The total water flow from the surface layer (V_{surf}) of the system to the adjacent NW Aegean is $8,764x10^6$ m^3 d^{-1}. The required counter flow to the deeper layer of the system from the deep layer of adjacent sea to replace the salt loss due to V_{surf} is $7,955x10^6$ m^3 d^{-1} (V_D) which then is exported towards the upper layer ($V_{D'}$) and the Dardanelles (V_{Dar-d} = $1,370x10^6$ m^3d^{-1}). The bottom water upward flow ($V_{D'}$) is $6,585x10^6$ m^3 d^{-1}. Vertical mixing (V_Z) is $227x10^6$ m^3d^{-1}. V_Z is very much smaller than $V_{D'}$. It is likely that the vertical mixing of this intermediate water with water below the 29.3 σ_Φ isopycnal horizon is even smaller, which supports the approximation that the bottom layer is sealed.

The salt flux imported through the Dardanelles Strait surface flow to the NE Aegean ($61,376x10^6$ psu-m^3d^{-1}) is greater than the salt exported from the Aegean back to the Dardanelles via the subsurface counter flow ($53,293x10^6$ psu-m^3d^{-1}). The mixing volume ($V_{X-s'}$) required to balance this excess salt is estimated as $1,092x10^6$ m^3d^{-1}.

Water exchange time in the upper 50 m layer was about 100 days and for the upper 200 m layer about a year in September 1998.

<u>*Budgets of nonconservative materials*</u>

DIP and DIN balance

The annual means of DIP and DIN (nitrate+nitrite) concentrations in the surface flow of the Dardanelles (reported by Polat and Turgul 1996) were used to evaluate the DIP and DIN budget. Ammonium ($NH4^+$) data were not available and were assumed to be insignificant relative to (nitrate+nitrite).

Although transport via the atmosphere is recognised as an important route by which nutrients and particles are delivered to the sea surface, there are no data available on atmospheric inputs for the study area. The atmospheric inputs of inorganic nitrogen and phosphorus were calculated using the estimated wet fluxes of 0.018 g P m^{-2} yr^{-1} or 0.6 mmol P m^{-2} yr^{-1} and 0.24 g N m^{-2} yr^{-1} or 17 mmol N 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 they probably represent the amount of phosphate that is bioavailable in the surface waters.

The nonconservative dissolved inorganic phosphorus (DIP) and nitrogen (DIN) fluxes were calculated using the estimated volume transports multiplied by the appropriate nutrient concentration (Figures 2.7 and 2.8). In order to obtain reliable estimates of the nutrient fluxes it is important that the volume transports estimated through the 'hydrogaphic' budget are accurate. Actually, the calculated vertical mixing volume V_Z ($227x10^6$ m^3 d^{-1}) appears rather higher than similar estimates from open sea budgets and roughly corresponds to a vertical velocity of about ~10.0 mm d^{-1} (Gargett 1984).

Table 2.2 presents the nonconservative fluxes for NE Aegean Sea in September 1998. In the top layer *DDIN* and *DDIP* are negative indicating that DIN and DIP are taken up. It is also interesting to note that the DIN flux imported in NE Aegean via the Dardanelles surface flow is evenly important to the DIN atmospheric input, while the respective DIP flux imported to the system through the Dardanelles is comparable to the DIP flux transported by the rivers (Figures 2.7 and 2.8). It is also noteworthy that the mixing volume ($V_{X-s'}$) in the upper layer adds $66x10^3$ mol d^{-1} of DIP and at the same time removes

328×10^3 mol d^{-1} of DIN, as a result of the existing differences in the nutrient concentrations between the system and the Dardanelles.

Table 2.2. Nonconservative DIP and DIN fluxes and stoichiometric calculations for NE Aegean Sea in September 1998. w/o V_X and w/ V_X mean without and with V_X, respectively.

NE Aegean Sea	Surface ($ó_è$<28.8) w/o V_X; w/ V_X	Intermediate (28.8<$ó_è$<29.3) w/o V_X; w/ V_X	Whole System w/o V_X; w/ V_X
ÄDIP (10^3 mol d^{-1})	-687; -753	+89; +89	-598; -664
ÄDIP (mmol m^{-2} d^{-1})	-0.04; -0.04	+0.006; +0.006	-0.03; -0.03
ÄDIN (10^3 mol d^{-1})	-9,120; -8,792	-1,409; -1,409	-10,529; 10,201
ÄDIN (mmol m^{-2} d^{-1})	-0.5; -0.5	-0.1; -0.1	-0.5; -0.5
(*p-r*) (mmol C m^{-2} d^{-1})	+4; +4	-0.6; -0.6	+3; +3
(*nfix-denit*) (mmol N m^{-2} d^{-1})	+0.1; +0.1	-0.2; -0.2	0.0; 0.0

Moreover it becomes clear that the intermediate layer of the adjacent ocean feeds with nutrients the layer with 28.8<σ_Φ<29.3 (intermediate layer) and due to the vertical 'loop circulation' the major part of this supply flows upward and enriches the with σ_Φ<28.8 (surface layer) of the system.

Stoichiometric calculations of aspects of net ecosystem metabolism

Without further interpretation the nutrient budgets do not provide information on the processes which account for the summed sources minus sinks. The nonconservative DIP flux (*DDIP*) of each layer is then used to calculate the rates of net ecosystem metabolism (*p-r*). These calculations are based on the assumption that the decomposed organic mater is dominated by plankton having a Redfield composition [(*p-r*) = -106 *DDIP*]. The surface layer with σ_Φ<28.8 is a net producer of organic matter, as primary production exceeds respiration, while in the deeper layer with 28.8<σ_Φ<29.3 it seems that organic oxidation processes predominate. Data on pelagic primary production measured in the study area during September 1997 (Siokou *et al.* 2001) suggest that gross *p* is about 19.2 mmol C m^{-2} d^{-1} and therefore about 84% of gross production is consumed through respiration; (*p-r*) = +0.16*p*. Although (*p-r*) is usually about ±0.1*p*, our estimate seems to be reasonable for this system because a major part of the system is shallow enough to support benthic primary production, so that gross *p* for the whole system is expected to be higher than 19.2 mmol C m^{-2} d^{-1} and consequently (*p-r*) approaches +0.1*p*.

The difference between nitrogen fixation and denitrification was also calculated, assuming that the nonconservative DOP and DON fluxes are minor [(*nfix-denit*) = *DDIN* – 16*DDIP*]. In the surface layer with σ_Φ<28.8, which includes the great part of the shallow coastal area, it seems that an important portion of DIN could originate from biological fixation of atmospheric nitrogen by seagrasses (*Posidonia oceanica*) and by bacterioplankton species (*Trichodesmium, Synechococcus*) (Bethoux *et al.* 1992). In contrast, in the layer with 28.8<σ_Φ<29.3 the 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 and Cohen, 1987). Overall, the whole system appears to balance nitrogen fixing and denitrification [(*nfix-denit*) = 0].

The budgetary calculations were also performed using a range of Dardanelles inflow (V_{Dar-s}) in the top layer; the corresponding exported flow (V_{Dar-d}) was defined as the net annual flow through the Dardanelles Strait, 822×10^6 m^3 d^{-1} (Unluata *et al.* 1990; Polat and Turgul 1996). The nonconservative fluxes of DIN and DIP as well as the stoichiometric calculations for three selected V_{Dar-s} flows (1,370; 2,192 and 3,288 x10^6 m^3 d^{-1}) are presented in Table 2.3. The different (V_{Dar-s}) used affect the exchanged flows between the two layers and the ocean and consequently the nonconservative fluxes. However, it is obvious from Table 2.3 that the fluxes obtained vary slightly as a function of the used V_{Dar-s} flows and remain within the same range. Therefore it could be considered that the nonconservative 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. Furthermore, horizontal mixing ($V_{X'}$) between the system and the Dardanelles Strait does not significantly affect the nutrient budgets (Table 2.2).

Table 2.3. Nonconservative DIP and DIN fluxes and stoichiometric calculations for different Dardanelles inflow and outflow to the NE Aegean Sea in September 1998.

V_{Dar-s} V_{Dar-d} *(10^6 m^3 d^{-1})*	1,370 548	2,192 1,370	3,288 2,466
D***DIP*** (10^3 mol d^{-1})	-720	-598	-651
D***DIP*** (mmol m^{-2} d^{-1})	-0.04	-0.03	-0.03
D***DIN*** (10^3 mol d^{-1})	-10,742	-10,529	-9,166
D***DIN*** (mmol m^{-2} d^{-1})	-0.6	-0.5	-0.5
(*p-r*) (mmol C m^{-2} d^{-1})	+4	+3	+3
(*nfix-denit*) (mmol N m^{-2} d^{-1})	0.0	0.0	0.0

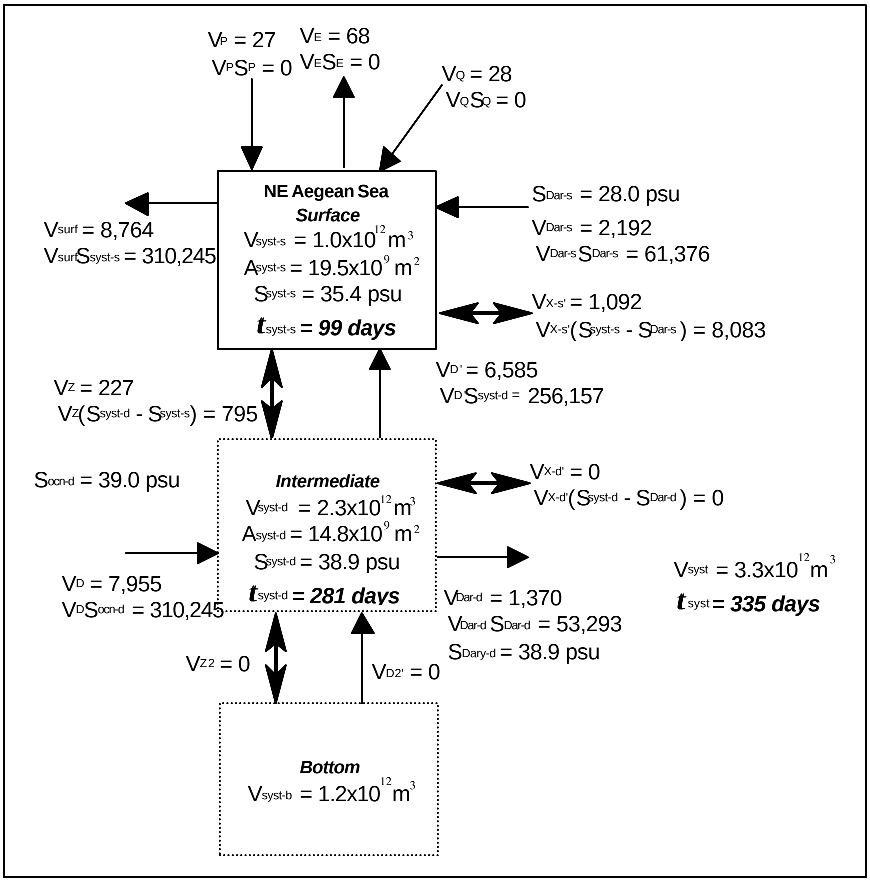

Figure 2.6. Steady state, two-layer model water and salt budgets for NE Aegean Sea in September 1998. Water fluxes in 10^6 m^3 d^{-1} and salt fluxes in 10^6 psu-m^3 d^{-1}.

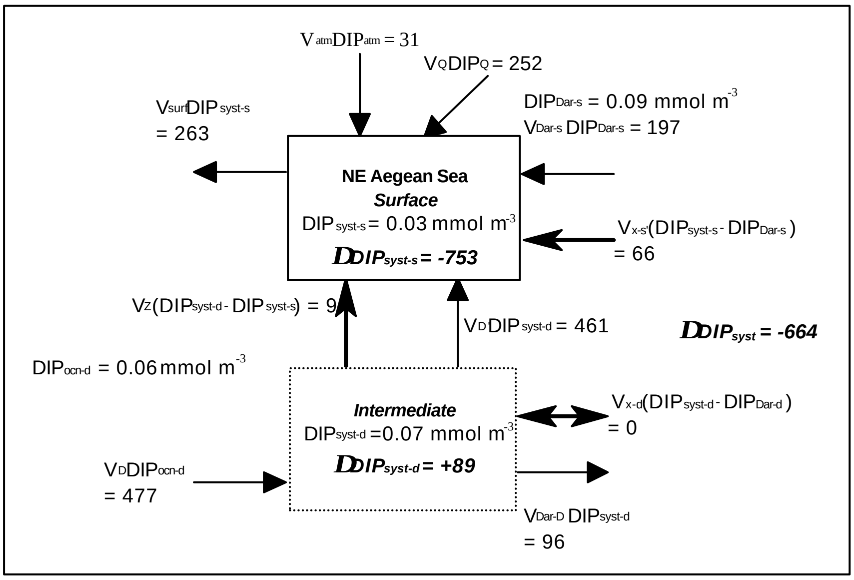

Figure 2.7. Steady state, two-layer DIP budget for NE Aegean Sea in September 1998. Fluxes in 10^3 mol d^{-1}.

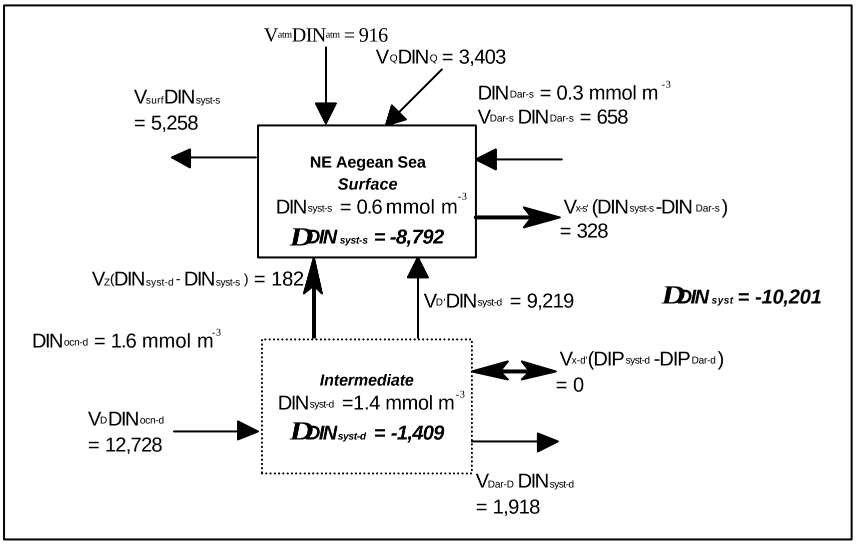

Figure 2.8. Steady-state, two-layer DIN budget for NE Aegean Sea in September 1998. Fluxes in 10^3 mol d^{-1}.

3. ESTUARIES OF UKRAINE

The north-western shelf of the Black Sea

The Black Sea and the Sea of Azov form the southern border of Ukraine, which consists of vast flat plains generally lower than 300 m high. Most rivers flow into the Black Sea, including the Dniester into the central part, the Southern Bug and Dnieper into the north-west, and the Danube into the far south. The major rivers discharge annually about 266 km^3 from a watershed of 1,462, 820 km^2. This freshwater volume is about 80% of the total annual run-off to the Black Sea. The rivers have marked seasonal variations with a pronounced spring flood peak and low discharge during autumn.

The north-western shelf (NWS) of the Black Sea comprises the embayment north of the 45ºN, with an area of 48,000 km^2 and a volume of 1,150 km^3. The coastlines of the Black Sea Lowland ("Prichernomorskaya nizmennost") and Crimean Peninsula make up its north-western and eastern boundaries. The western coast is relatively straight; the eastern one irregular, with several sandy islands, bays and lagoons deeply entrenching inland. The bottom gently slopes down toward the open sea. The maximum depth does not exceed 50 m and the mean depth is about 24 m. The dynamically important feature is a north-south depression in the center of the region. Cold and saline water from the open sea penetrates far north along this depression. The shallow east-west Odessa bank (shoal) in the north has local dynamic effect in vicinity of the Dnieper-Bug estuary mouth (Tolmazin, 1987).

All rivers except the Danube drain into the sea via shallow estuaries called "limans". The word "liman" (meaning harbor in Greek) is an echo of the colonization of the Black Sea region by Greeks in ancient times (beginning in VI-V centuries B.C.). Some 20 "limans" (water bodies with or without connection to the sea) are located along the coast of the NWS. The largest are the Dnieper–Bug and Dniester estuaries with surface areas of 800 km^2 and 360 km^2 and catchments areas of 577,610 km^3 and 75, 200 km^3 respectively. The estuaries lie in the middle and southern zones of the Black Sea Lowland, with a flat steppe landscape. The land slopes from the north to the south (west coast of the NWS), to the south-east (north coast) and to the south-west (east coast). The shores of the estuaries are formed from loess, red clay, sand and camstone. The bottom is covered by silt and sand. All estuaries have a long and narrow bar (barrier) of sand and gravel that protects them from the open sea. The estuarine systems are highly productive, especially in comparison with spare steppe landscape around them. About 200 species of estuarine fauna have been found there (Swebs 1988).

The climate of Ukraine is temperate and continental, with a subtropical mediterranean climate in the southern Crimea. Temperatures range from -8 to 2°C in winter, and 17-25 °C in summer. Rainfall averages 400 mm annually, decreasing from the north-west to the south-east. Evaporation everywhere exceeds precipitation and is about 760 mm per year (Terziev 1986). The NWS lies in the moderate-continental climate, with short, relatively mild winters and hot, dry summers. The region experiences influence of polar (continental and marine), tropical and arctic air masses. In winter, spurs of the Siberian anticyclone create a strong current of cold air, and the NWS cools down, with regular ice formation in the shallow coastal areas and estuaries. The invasion of polar continental air (average 185 days annually) brings strong north-easterly winds, rapid temperature drops, and frequent precipitation. The annual air temperature in the region, averaged on the observations of the coastal meteorological stations, is 10.5º C. Average temperatures range from -1.3º C in winter to 22.3º C in summer.

The majority of people live in large towns as Odessa (1,122,000 inhabitants), Mykolajiv (518,700), Kherson (370,500) and surrounding suburban areas.

The coastal zone has been intensively used for urban development, industry, agriculture, fishing, recreation, and marine supply activities. The agricultural sector of the economy is focused on crops of corn, vegetables, fruits, grape and livestock products - cattle, pigs, poultry, milk, meat, and eggs. The soil consists of high fertile humus (north-west) and dark maroon humus (south-east). The arable land-includes 70-75% of total land.

Industry is mainly represented by ship-building and -repainting, fish processing, fishing; chemical and gas industries, cotton, cosmetics, sugar and textiles, tea-packing and food-processing. Marine activities include port operations, transportation and reloading of sea cargoes, crude oil and oil products (ports of Odessa, Iljichevsk and Mykolajiv). Fishing, at present, is mostly oriented on fish catch in the Atlantic and Pacific oceans. Recreational resources are used for local fishing, swimming, and bathing.

High concentration of industrial enterprises along the coast, intensive use of land for agricultural purposes, location of several large ports in the estuaries and bays, increasing urbanization with old systems of sewage treatment and input of large European rivers have created serious threats to the marine and coastal environment of the NWS. In 1999, the level of pollution of the NWS was assessed as super high (west coast, at the Danube delta and the Dniester estuary mouth), very high (north coast), high (south-east coast) and average (Cap Tarchankut, western tip of the Crimean Peninsula). The main polluting components of the sea are petroleum products.

However, the environmental situation in the region is improving. Nutrient concentrations in the water during the last few years have stabilized at a point below the permissible levels for nitrates, nitrites and phosphates (MEPNSU, 1999). Romanian scientists have reported decreases in nutrient loads from the Danube River to the shelf and Romanian coastal waters (Cosiasu et. al. 1999). This is closely related to a reduced application of mineral fertilizers and pesticides to the arable land, that has led to decrease of the nutrients and polluting matters washing out from the rivers catchment basins, and is a consequence of the economic collapse in central and eastern European countries in the past decade.

Inna Yurkova

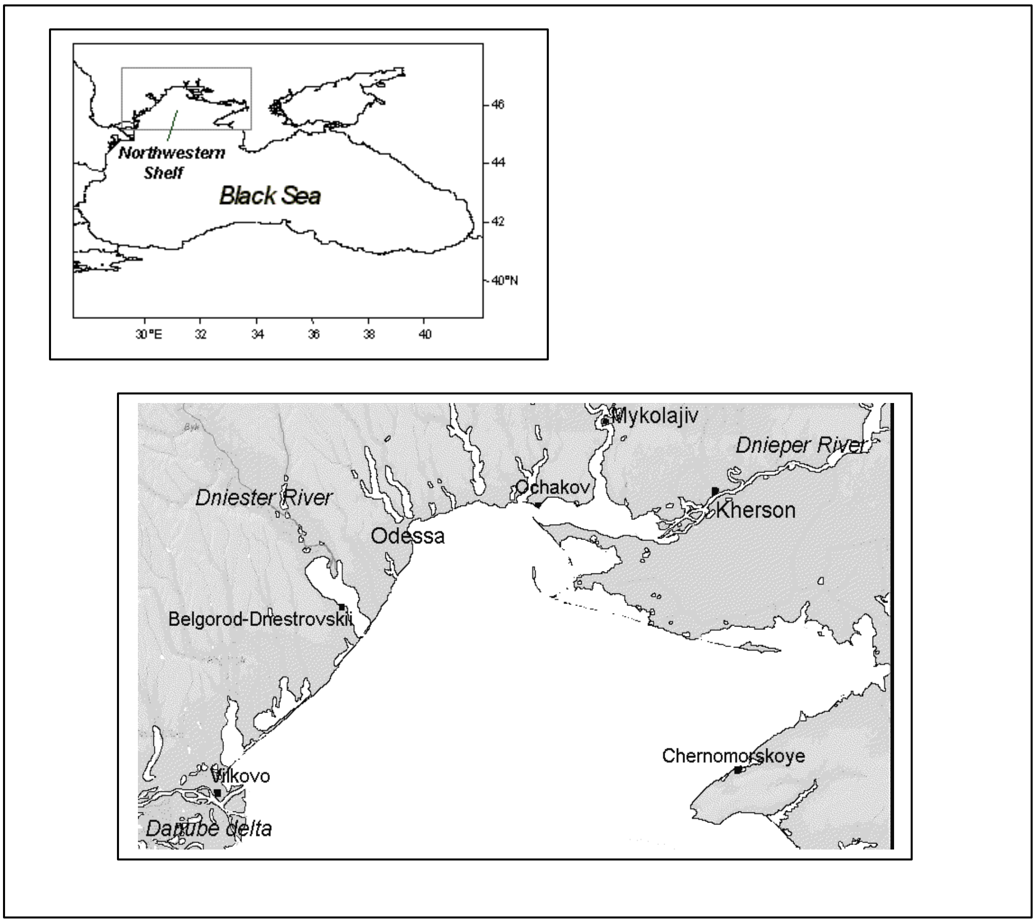

Figure 3.1. Location of the northwestern shelf of the Black Sea.

3.1 Dnieper-Bug estuary system

Inna Yurkova

Study area description

The Dnieper-Bug estuary system is the largest estuary system in the north-western part of the Black Sea (46.60°N, 31.50°E). It consists of two arms: the Dnieper estuary and the Bug estuary (Figure 3.1). The Dnieper estuary has a length of 60 km (east-west) and a surface area of 750 km^2, with a mean depth of 4 m and a volume of $3x10^9$ m^3. Communication with the sea is through the Kinburn channel (4 km wide, 11 m deep). The Bug estuary is located on the northern coast of the Dnieper estuary and has a length of 30 km, a surface area of 50 km^2 and an average depth of 6 m.

The Dnieper and South Bug rivers drain into the estuaries with annual flow of $47x10^9$ m^3 $yr^{-1}$and $3x10^9$ m^3 yr^{-1} respectively, delivering 19% of the total annual runoff to the north-western part of the Black Sea (Dziganshin and Yurkova 2001). 60% of the annual river discharge enters the system between March and June, whereas during the rest of the year riverine outflow is relatively low.

The river water is of great importance to hydrological conditions in the Dnieper-Bug estuary. In the flood period the Dnieper water fills the estuary. Average flushing time is about 9 days. Intrusions of seawater are implemented by wind-induced surges (tides are negligibly small) and longitudinal pressure gradients due to density differences which are most pronounced in the bottom layer. A noticeable salt wedge with salinity 3-7 psu above average is formed under low wind (less than 5 m sec^{-1}) or ice conditions. During north-easterly and easterly winds the water column is fairly homogeneous, and the longitudinal salinity differences do not exceed 4-5 psu.

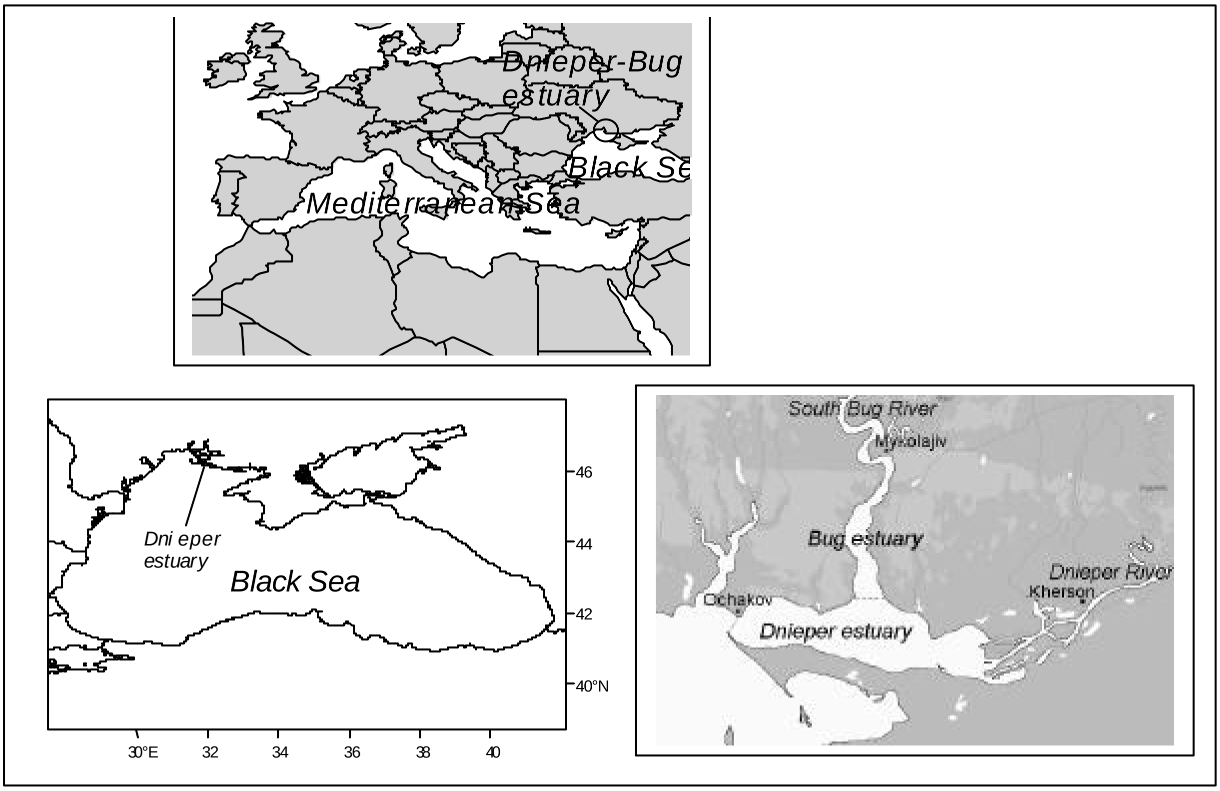

Figure 3.2. Location and map of Dnieper-Bug estuarine system, with boundaries marked.

The climate is determined by atmospheric processes over the European part of the former USSR. There are four seasons: winter (December-February), spring (March-May), summer (July-August), and autumn (September-November). The climate of the eastern part of the estuary is more continental than in the west. The mean annual temperature of the air is 10.0ºC at the meteorological station in Kherson, 9.7ºC in Mykolajiv, and 9.8ºC in Ochakov (see Figure 3.2 for location of these stations). The warmest months of the year are July and August, while the coldest months are January and February. The average annual precipitation is 435 mm yr^{-1}. Precipitation in autumn and winter is less than in summer. As summer evaporation exceeds precipitation there is drought in summer. Evaporation from the water surface reaches 660 mm yr^{-1} (Kherson) and 860 mm yr^{-1} (Ochakov) being highest in July and lowest in January/February. Evaporation from land is about 350 mm yr^{-1} (Mykolajiv), 340 mm yr^{-1} (Kherson), 302 mm yr^{-1} (Ochakov). It snows from October to April, with 21-23 snow days at Kherson and Ochakov and 29 days at Mykolajiv. The maximum number of days with snow are recorded in January: (8 days at Mykolajiv, 6 days at Ochakov and 5 days at Kherson) (Kostianitsyn 1964).

The Dnieper-Bug estuarine system has been impacted from port, industrial, urban, and agricultural development in the region. Starting in the early 1950s, six large storage reservoirs and several smaller ones (with a combined storage capacity of 44 km^3) were built on the Dnieper River for producing hydroelectric power. When the hydroenergy complexes and water withdrawal and disposal systems became fully operational in the early 1970's, seasonal river flow patterns had been artificially modified and the annual river discharge from the Dnieper River had noticeably decreased. New flow conditions changed the concentration of organic materials and nutrients, which determine the biological productivity of the receiving basin. Following reservoir construction (1956-1969) the transport of the nitrogen in the lower Dnieper River and the estuary increased by 53% (Tolmazin 1985). In 1980-1990 the discharge of total nitrogen from the Dnieper River increased by 1.6 times and the total phosphorus discharge from the Dnieper River increased by 5 times compared to the discharges of 1951-1960 (Zaitsev 1993).

The rivers and the port and metropolitan areas of Mykolajiv and Kherson remain the main sources of pollutant fluxes to the estuary. There are >33 million people living in the Dnieper River basin, with populations of Mykolajiv and Kherson about 503,000 and 355,000. Annually, Mykolajiv contributes about 49% of the total waste load of the Dnieper–Bug estuary and Kherson about 32%. About 63% of wastewater discharges into the Bug estuary and 37% into the Dnieper estuary. In 1999 about $114x10^6$ m^3 of wastewater (including $7.2x10^6$ m^3 without purification, $62.5x10^6$ m^3 with insufficient purification, 800 t of nitrogen and 289 t of phosphates) were discharged into the estuary (Ryabinin 2000). This amount was 1.7 times less than in 1995.

The budget calculations were based on the following data: the nutrient concentrations for the rivers and the estuaries were taken from Gubanov *et al.* (1995) as averages for 1987-1991 years; salinity and nutrient concentrations for the adjacent coastal waters were taken from Garkavaya, et al. 2000; and salinity for the estuaries were from Ryabinin (1999).

Water and salt balance

As the Dnieper-Bug estuary includes two estuaries, a two-box in series model was used for budget calculations.

Two rivers provide most of the freshwater input into the systems: the Dnieper River into the Dnieper estuary and the South Bug River into the Bug estuary. The river discharge is $128x10^6$ m^3 d^{-1} for the Dnieper river and $8x10^6$ m^3 d^{-1} for the South Bug river. The groundwater discharge is about $0.2x10^6$ m^3 d^{-1} (Timchenko 1990). The precipitation in the region is about 420 mm yr^{-1} for the Dnieper estuary and 470 mm yr^{-1} (meteorological station Mykolajiv) for the Bug estuary. Evaporation is 760 mm yr^{-1} and 764 mm yr^{-1} accordingly. As groundwater discharge, net precipitation and evaporation rates are small compared with riverine inputs, they are assumed equal to 0.

The salinity of the system increases from east (delta of the Dnieper) to west (Kinburn canal) with vertical and horizontal gradients of salinity, except of flooding time when the waters of the Dnieper fill the estuary. Samples were usually taken at the surface (0-0.5m) and near the bottom (1m from the bottom). As the depth of the Dnieper estuary is variable, to a maximum of 12m, it was difficult to determine a depth for surface and bottom layers to use a two-layer model, so a one-layer model was used. The mean salinity of the Dnieper estuary is taken to be 6.6 psu and of the Bug estuary is 5.1 psu. The mean salinity of the adjacent sea area is 11.1 psu. Mean annual characteristics of each estuary are summarized in Table 3.1.

Table 3.1. Salinity and nutrient concentrations in the river, estuaries and adjacent sea for the Dnieper-Bug estuary system.

Parameter		**Salinity** (psu)	**DIP** (mmol m^{-3})	**DIN** (mmol m^{-3})
Bug	River	0	6.4	23.4
	System	5.1	6.1	19.5
	Sea	6.6	3.0	6.2
Dnieper	River	0	3.7	24.3
	System	6.6	3.0	6.2
	Sea	11.1	1.5	1.5

The water and salt budgets were calculated using these data (Figure 3.3). The two estuaries have the same water exchange time of about 7 days. The exchange time for the whole Dnieper–Bug system is 8 days.

<u>*Budgets of nonconservative materials*</u>

Figures 3.4 and 3.5 illustrate DIP and DIN balance calculations for the Dnieper–Bug estuary. The DIN and DIP carried by the waste load to the system are taken to be 800 t yr^{-1} and 289 t yr^{-1}, respectively, that is equivalent to 157×10^3 mol d^{-1} and 26×10^3 mol d^{-1}. Assuming that 63% of total waste load discharges into the Bug estuary and 37% into the Dnieper estuary, the DIP and DIN load into the Bug estuary is 16×10^3 mol d^{-1} and 99×10^3 mol d^{-1} accordingly, the DIP and DIN load into the Dnieper estuary is 10×10^3 mol d^{-1} and 58×10^3 mol d^{-1}.

DIP balance

Nonconservative flux of dissolved inorganic phosphorus (*DIP*) for the Bug estuary is $+65 \times 10^3$ mol d^{-1} or +1.3 mmol m^{-2} d^{-1}. The *DIP* for the Dnieper estuary is $+92 \times 10^3$ mol d^{-1} or +0.1 mmol m^{-2} d^{-1}. The total *DIP* for the Dnieper-Bug estuarine system is $+157 \times 10^3$ mol d^{-1} or +0.2 mmol m^{-2} d^{-1}. Therefore, averaged over the year, the Bug and the Dnieper estuaries are net DIP sources. The whole system is a net DIP source (Table 3.2 and Figure 3.4).

DIN balance

Nonconservative flux of dissolved inorganic nitrogen (*DIN*) for the Bug estuary is approximately $+229 \times 10^3$ mol d^{-1} or +4.6 mmol m^{-2} d^{-1}. The *DIN* of the Dnieper estuary is $-1{,}899 \times 10^3$ mol d^{-1} or -2.5 mmol m^{-2} d^{-1}. The *DIN* for the Dnieper-Bug estuarine system is $-1{,}670 \times 10^3$ mol d^{-1} or -2.1 mmol m^{-2} d^{-1}. Averaged over the year, the Bug estuary is a net DIN source, the Dnieper estuary is a net DIN sink and the whole estuarine system is a net nitrogen sink (Table 3.2 and Figure 3.5).

Stoichiometric calculations of aspects of net system metabolism

Net nitrogen fixation minus denitrification (*nfix-denit*) is calculated as DIN_{obs} minus DIN_{exp}, where DIN_{exp} is *DIP* multiplied by the N: P ratio of the reacting particulate material (assumed to be 16:1). Thus, for the Bug estuary: (*nfix-denit*) = -16 mmol N m^{-2} d^{-1}. The Bug estuary is denitrifying in excess of nitrogen fixation. The Dnieper estuary is also denitrifying in excess of nitrogen fixation, (*nfix-denit*) = -4 mmol N m^{-2} d^{-1}. For the Dnieper-Bug estuary system, (*nfix-denit*) = -5 mmol N m^{-2} d^{-1}. The whole system is net denitrifying in excess of nitrogen fixation (Table 3.2).

Table 3.2. Summary of nonconservative nutrient fluxes, apparent net metabolism (*p-r*) and nitrogen fixation minus denitrification (*nfix-denit*) for the Dnieper-Bug estuary.

Parameters	Bug	Dnieper	Whole System
DDIP (10^3 mol d^{-1})	+65	+92	+157
DDIP(mmol m^{-2} d^{-1})	+1.3	+0.1	+0.2
DDIN (10^3 mol d^{-1})	+229	-1,899	-1,670
DDIN(mmol m^{-2} d^{-1})	+4.6	-2.5	-2.1
(*p-r*)(mmol m^{-2} d^{-1})	-138	-11	-21
(*nfix-denit*) (mmol m^{-2} d^{-1})	-16	-4	-5

Net ecosystem metabolism, the difference between primary production and respiration (*p-r*) is estimated as *DIP* multiplied by the C:P ratio of the reacting organic material (assumed to be 106:1). Therefore, for the Bug estuary (*p-r*) is estimated to be -138 mmol C m^{-2} d^{-1}. Bug estuary appears to be net heterotrophic. For the Dnieper estuary, (*p-r*) = -11 mmol C m^{-2} d^{-1}) thus appears to be net heterotrophic. For Dnieper-Bug estuary system, (*p-r*) = -21 mmol C m^{-2} d^{-1}. The whole system appears to be net heterotrophic (Table 3.2).

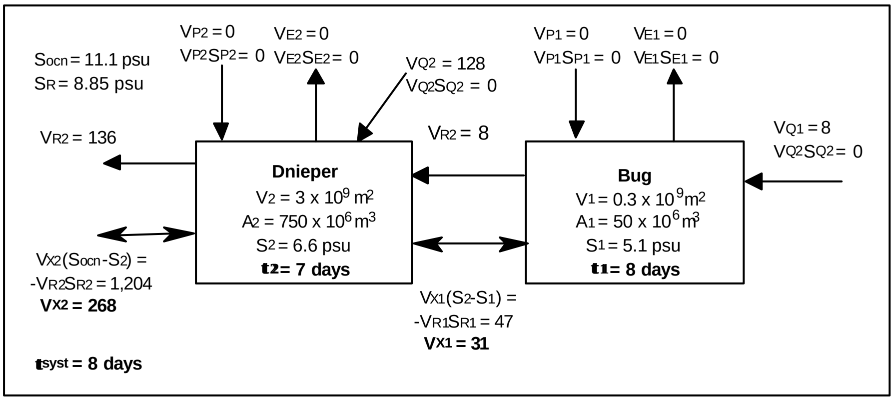

Figure 3.3. Water and salt budgets for the Dnieper-Bug estuary. Water flux in 10^6 m^3 d^{-1} and salt flux in 10^6 psu-m^3 d^{-1}.

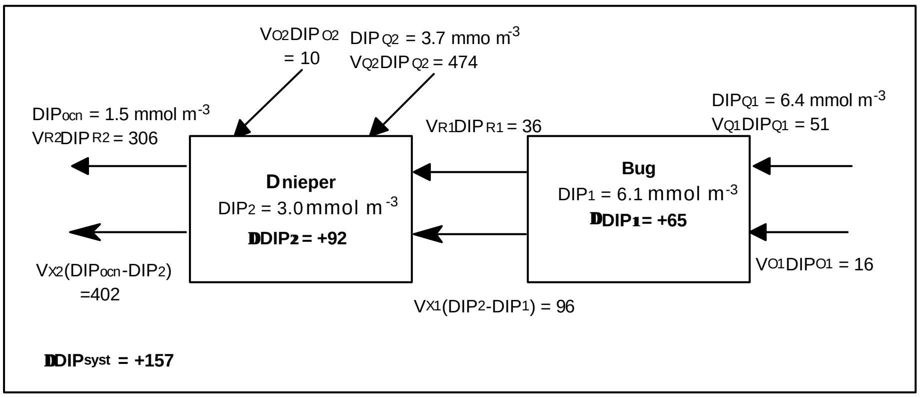

Figure 3.4. DIP budget for the Dnieper-Bug estuary. Flux in 10^3 mol d^{-1}.

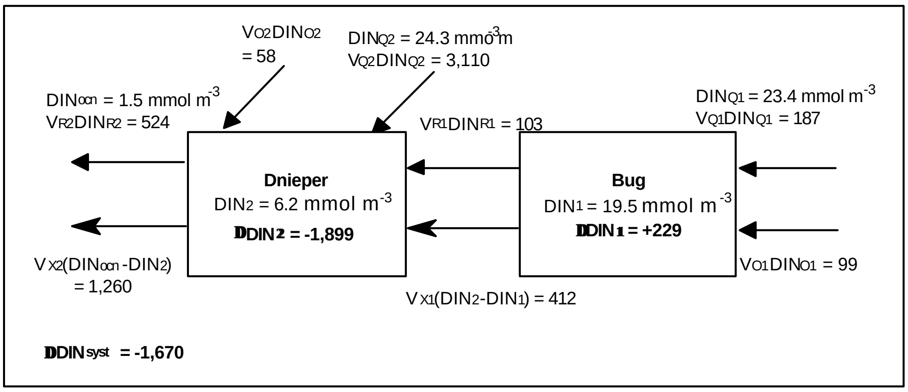

Figure 3.5. DIN budget for the Dnieper-Bug estuary. Flux in 10^3 mol d^{-1}.

3.2 Dniester River Estuary

Inna Yurkova

<u>*Study area description*</u>

Located on the western coast of the north-western shelf of the Black Sea, the Dniester estuary (46.08°N, 30.48°E, Figure 3.6) is a shallow water body of relatively simple shape and smooth bottom morphology with surface area of 360 km^2, average depth of 1.5 m and volume of 540×10^6 m^3. The Dniester River enters the estuary via two straits: the arm of the Dniester River and the short (3 km) and narrow (65 m) Turunchuk Channel. The river delivers an annual average of $9{,}900 \times 10^6$ m^3 yr^{-1} or 27×10^6 m^3 d^{-1} of freshwater to the estuary i.e., 4% of riverine water supply to the north-western shelf of the Black Sea (Dziganshin and Yurkova 2001). The Dniester River runoff shows significant seasonal variations with maximum discharge in the spring and minimum in the autumn-winter period. Water exchange between Dniester estuary and the Black Sea is established through the Tsaregrad Channel (depth *ca* 4.5 m, width *ca* 300 m). The amount of seawater entering the estuary depends on a combination of three major factors: the head of freshwater flow, wind forcing and longitudinal density gradient. Wind-driven exchange is less pronounced in the Dniester estuary because wind-induced surges along the straight western coast are relatively small, and the narrow estuarine orifice presents a considerable hindrance to free influx. Only exceptional southern and south-eastern winds can cause an overflow into the estuary of short duration with intense mixing of seawater and freshwater inside. The southern winds are more frequent in summer, while the north-western winds dominate in winter (Tolmazin 1985).

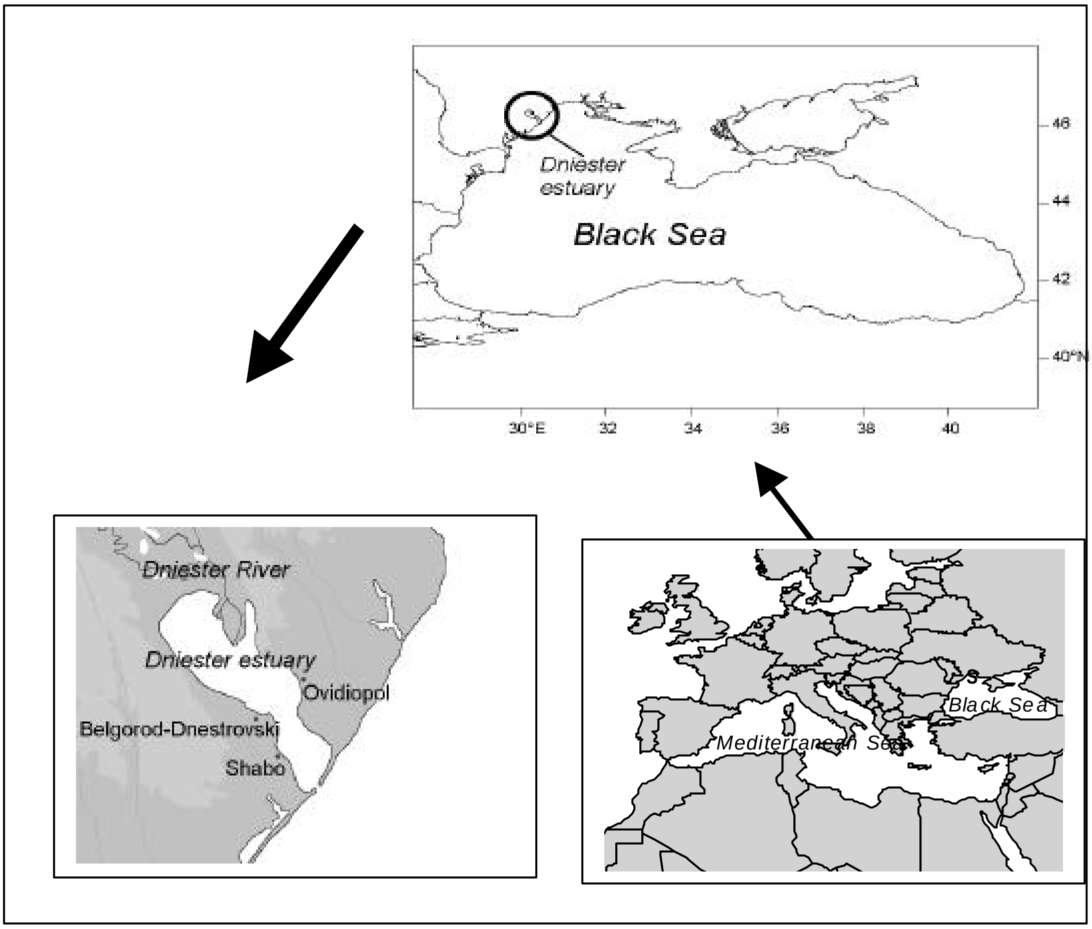

Figure 3.6. Location and map of the Dniester estuary.

The salinity of the estuary changes from 0.0 to 9.0 psu from the delta of the Dniester River to the Tsaregrad Channel. The temporal variability of average salinity can reach 2.0-3.5 psu during a low-flow year and 0.1-0.8 psu during full flow years.

The estuary is located in the region with four pronounced seasons: winter, spring, summer and autumn. The mean annual temperature of the air is 10.4-10.5 ^{0}C. Mean annual precipitation is 2 mm d^{-1} and evaporation is 3 mm d^{-1}. Maximum evaporation occurs between June and August (Braginskii 1992).

The Dniester River basin and the estuary area are the regions of high agricultural, hydrotechnical and port economical activities. Chemical, wood, structural and engineering enterprises are located in the watershed of the estuary. Agriculture is based on production of corn, vegetables, wine and stock raising. The population in the coastal zone is about 750,000 people (Swebs 1988).

Dniester River nutrient concentrations and loading to the Dniester estuary has changed dramatically last decades. The mean annual concentration of the nitrogen in 1980-1990 comparison to the 1951-1960 increased by 6.5 times, the mean annual concentration of the phosphorus increased by 7 times of the concentration to the 1951-1960 (Zaitsev 1993). The increase of nutrient flux during last decades has lead to broad–scale degradation of the marine environment of the estuary (Braginskii 1992).

Data of nutrient concentrations for the estuary and the Dniester River summarized by Sirenko *et al.* (in Braginskii 1992) and nutrient concentrations for adjacent sea estimated by Garkavaya *et al.* (2000) were used in the budget calculations described here.

Water and salt balance

Figure 3.7 illustrates the annual water and salt budgets for Dniester estuary. The estuary was budgeted following LOICZ approach as well-mixed system (Gordon *et al.*, 1996). Groundwater discharge (V_G) of about 0.1×10^6 m^3 d^{-1} (Timchenko, 1990) is negligible compared to the river discharge and was assumed to be 0 in the budget. The average annual precipitation in the estuary is 0.7×10^6 m^3 d^{-1} and the annual evaporation is 1.2×10^6 m^3 d^{-1}. Precipitation minus evaporation (V_P-V_E) is negligible compared to the river discharge thus also assumed 0. The river discharge (V_Q) is 27×10^6 m^3 d^{-1}. Other freshwater inputs (V_O) were assumed 0. The average salinity of the estuary is about 2.1 psu and the salinity of the adjacent sea is taken about 12.4 psu (Table 3.3). Residual flow (V_R) is therefore equal to the river discharge. Volume mixing (V_X) calculated from the salt balance is 19×10^6 m^3 d^{-1}. The water exchange time (τ) calculated as $V_{syst}/(V_X + |V_R|)$ is about 12 days. The water exchange time is consistent with that estimated by Tolmazin 1985 which is about 11 days.

Table 3.3. Salinity and nutrient concentrations in the river, system and adjacent sea for the Dniester estuary.

Parameter	**Dniester estuary**	
Salinity (psu)	River	0
	System	2.1
	Sea	12.4
DIP (mmol m^{-3})	River	2.9
	System	1.7
	Sea	1.1
DIN (mmol m^{-3})	River	135
	System	116
	Sea	7

Budgets of nonconservative materials

Due to lack of necessary data, it was difficult to estimate the contribution of all human activities to the nutrient input into the Dniester estuary, thus only estimated waste load from household activities (i.e., solid waste, domestic sewage, detergent) was considered in the budget calculations. $V_O DIP_O$ and $V_O DIN_O$ were estimated for the coastal population of 750,000 people using San Diego-McGlone *et al.* (2000). It was assumed that 25% of the waste water enters the estuary.

DIP balance

Figure 3.8 illustrates the dissolved inorganic phosphorus (DIP) budget, assuming that nutrient loads are largely delivered through the river. The nonconservative DIP flux (*DIP*) was estimated from the total inputs (river and waste loads) and total outputs (residual and exchange fluxes); *DIP* of the system is -49×10^6 mmol d^{-1} (or -0.1 mmol m^{-2} d^{-1}). The estuary appears to be a net sink of DIP.

DIN balance

Figure 3.9 shows the dissolved inorganic nitrogen (DIN) budget. The nonconservative DIN (*DIN*) of the system is approximately $+5 \times 10^6$ mmol d^{-1} (or +0.01 mmol m^{-2} d^{-1}). The system seems to be a net source of DIN.

Stoichiometric calculations of aspects of net system metabolism.

The rate of nitrogen fixation minus denitrification (*nfix-denit*) can be calculated as DIN_{obs} minus $DIN_{exp,}$ where DIN_{exp} is *DIP* multiplied by the N:P ratio of the particulate material in the system (assumed to be 16:1 as the Redfield N:P molar ratio for phytoplankton).Thus, (*nfix-denit*) = +2 mmol m^{-2} d^{-1} (Table 3.4). The estuary appears to be fixing nitrogen in excess of denitrification.

Table 3.4. Summary of nonconservative nutrient fluxes, apparent net metabolism (*p-r*) and nitrogen fixation minus denitrification (*nfix-denit*) for Dniester estuary.

Parameters	**Dniester estuary**
DDIP (10^3 mol d^{-1})	-49
DDIP(mmol m^{-2} d^{-1})	-0.1
DDIN (10^3 mol d^{-1})	+5
DDIN(mmol m^{-2} d^{-1})	+01
(*p-r*)(mmol m^{-2} d^{-1})	+11
(*nfix-denit*) (mmol m^{-2} d^{-1})	+2

Net ecosystem metabolism, the difference between primary production and respiration (*p-r*) is estimated as *DIP* multiplied by the C: P ratio of the reacting organic material (assumed to be 106:1). Therefore, (*p-r*) = +11 mmol m^{-2} d^{-1}. The estuary appears to be net autotrophic.

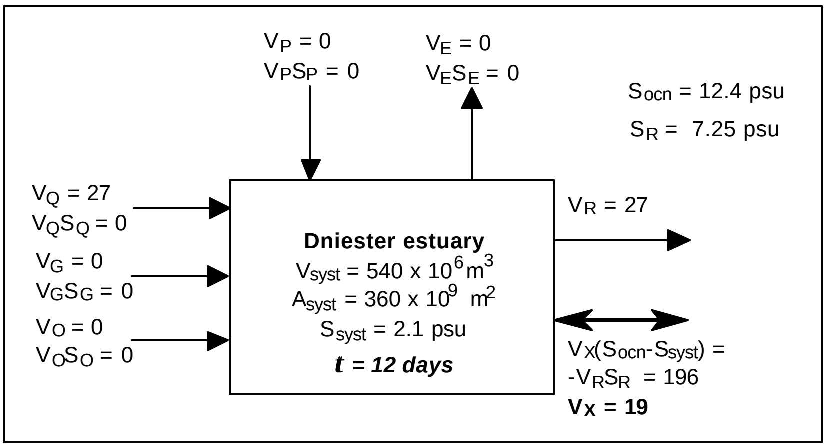

Figure 3.7. Water and salt budgets for the Dniester estuary. Water flux in 10^6 m^3 d^{-1} and salt flux in 10^6 psu-m^3 d^{-1}.

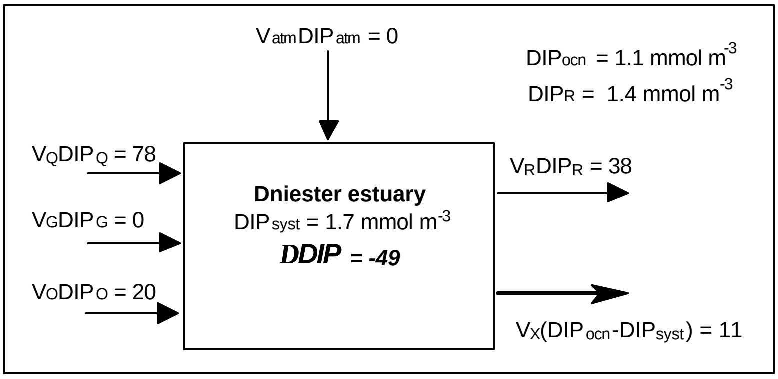

Figure 3.8. DIP budget for the Dniester estuary. Flux in 10^3 mol d^{-1}.

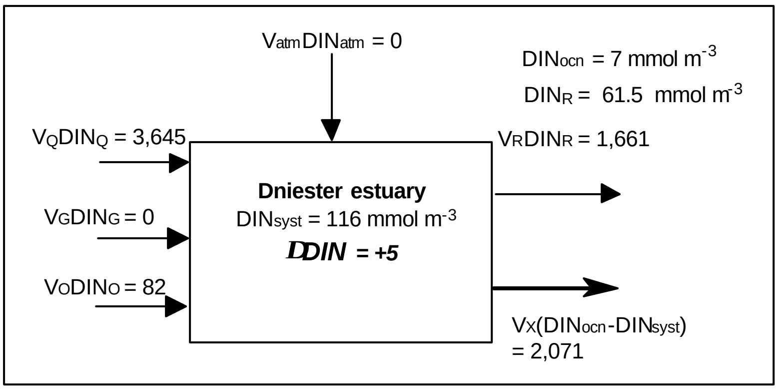

Figure 3.9. DIN budget for the Dniester estuary. Flux in 10^3 mol d^{-1}.

3.3 Donuzlav Estuary

Inna Yurkova

Study area description.

The Donuzlav estuary (45.5°N, 33.0°E; Figure 3.10) is located on the north-west coast of the Crimean Peninsula in Ukraine. The estuary occupies an area of 48 km^2 with a length of about 30 km oriented from north-east to south-west. The estuary is shallow (1-3 m), although the depths in the central rough reach 20-25 m.

Until the 1960s the Donuzlav estuary was isolated from the sea by a sand barrier and was the second largest salt lake in the Crimea. In 1961, the lake was connected to the sea by navigable canal (400 m wide, 12m deep). The salinity of the estuary equalised to the salinity of the adjacent coastal waters in the 1970s, and now varies from 17.5 to 18.2 psu. The dynamics of the estuary are determined by its morphology and by wind conditions. Wind is the main force driving water exchange with the adjacent sea. The process of water mixing affects shallow waters from surface to bottom; water exchange in the deeper part of the estuary occurs through anti-currents, cyclonic and anti-cyclonic circles. In some deep trenches there is restricted water exchange leading to stagnation phenomena (Kovrigina. and Nemirovsky 1999). There is no significant river discharge into the estuary.

The climate of the region is moderate-continental with a warm winter and a hot summer. The average annual temperature of the air is 11.0°C, the mean temperature of the warmest month is 23.2°C, and the mean temperature of the coldest one (January) is -0.1°C (Bazov 1983). Annual precipitation is about 358 mm yr^{-1} and evaporation is about 785 mm yr^{-1}.

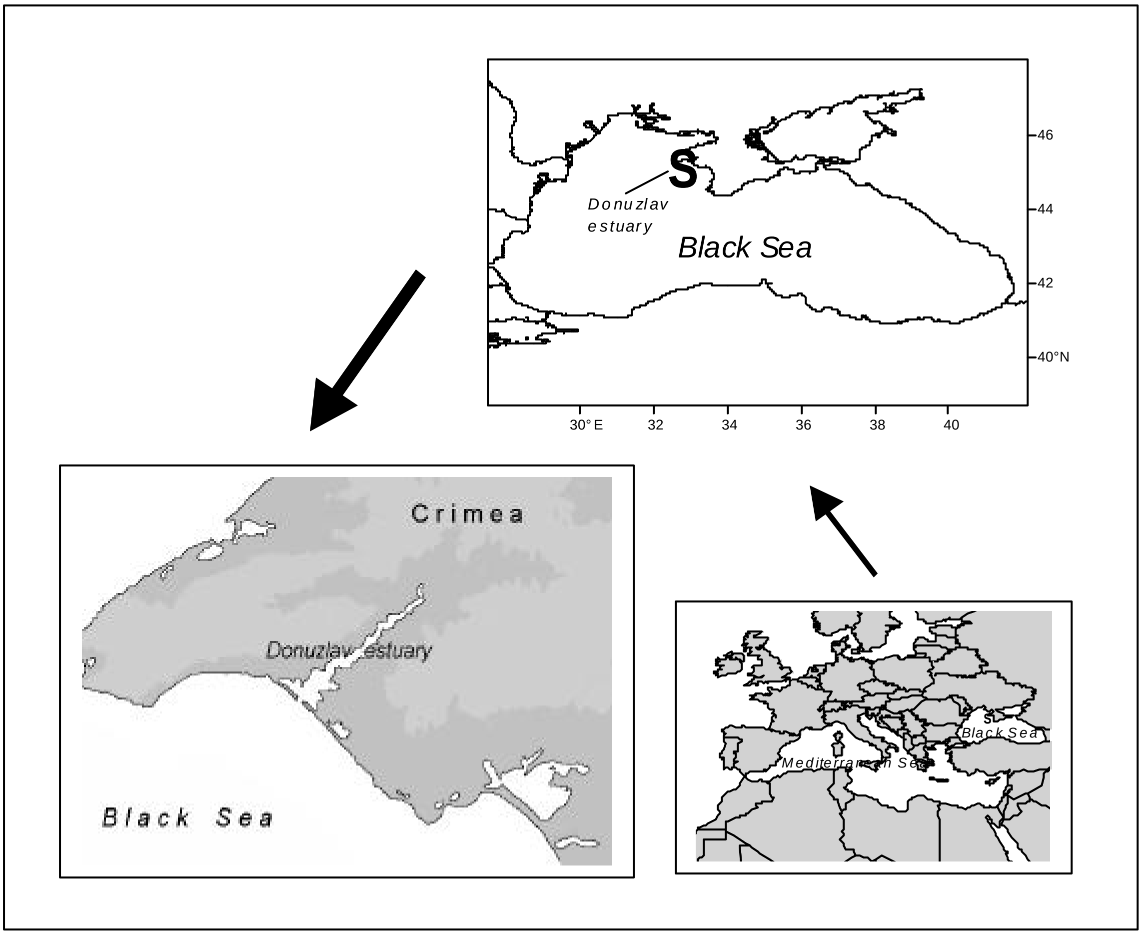

Figure 3.10. Location and map of the Donuzlav estuary.

The Donuzlav estuary is an area of reproduction and nursery for many valuable fish species, such as mullet, flatfish and sturgeon. It is also the location of one of the largest Ukrainian underwater sand quarrying operations, which occupies about 7.5 % of the shallow estuarine area. Approximately $200x10^3$ m^3 to $300x10^3$ m^3 of sand are removed annually (1994 data). Investigations showed that the sand withdrawal did not negatively affect pelagic fish (Zuev and Boltachev 1999). The estuary also contains a naval base and several small towns with a total population of about 6,000 (as of 1992).

The hydro-chemical regime of the Donuzlav estuary is relatively poorly known. The first studies of the estuary (1963 to 1964) are reported in Shulgina (1966). Further studies were made 30 years later (Kovrigina and Kuftarkova 1997). The estuarine salinity and nutrient data used for the budget calculations were means of measurements collected in May-October 1990 and June-August 1997 (Kovrigina and Nemirovsky 1999). The nutrient concentrations of the adjacent sea were taken from Garkavaya *et al.* (2000).

Water and salt budgets.

Figure 3.11 shows the water and salt budgets for Donuzlav estuary. The estuary was treated as single box, single layer model due to developed mixing processes in the system. The mean salinity of the estuary is about 18.2 psu higher than salinity of the adjacent sea which is 18.0 psu (Kovrigina and Nemirovsky 1999). As there is no significant river input to the estuary and data on the groundwater discharges are not available, they are assumed to be zero. The annual precipitation is $50x10^3$ m^3 d^{-1} and evaporation is $100x10^3$ m^3 d^{-1}. The calculated residual flow is $50x10^3$ m^3 d^{-1} (V_R). Mixing exchange is about $4{,}500x10^3$ m^3 d^{-1} (V_X). Estimated V_X using an alternative equation without relying on the salinity difference but vertical shear diffusion (Yanagi 2000) is about $4{,}600x10^3$ m^3 d^{-1} which agrees well with the V_X estimated through water and salt balance approach. Residual flow velocity (U) used in the shear diffusion equation was 10^4 m d^{-1} or 0.1 m sec^{-1}. Water exchange time for the Donuzlav estuary is estimated to be about a month (31 days).

Budgets of nonconservative materials

There are no data on waste load into the estuary, so the DIN and DIP export from the 6,000 people living near the coast were calculated using LOICZ approach. It was assumed that because the sewage-disposal systems are old, 40% of the wastewater is discharged to the estuary. The calculated DIN and DIP fluxes ($V_O DIP_O$ and $V_O DIN_O$) from the population are 200 mol d^{-1} and 1,000 mol d^{-1}, respectively.

DIP balance

Figure 3.12 summarizes the dissolved inorganic phosphorus (DIP) budget. The estuary is a net sink for the dissolved inorganic phosphorus; *DDIP* = -210 mol d^{-1} (-0.004 mmol m^{-2} d^{-1}).

DIN balance

Figure 3.13 summarizes the dissolved inorganic nitrogen (DIN) budget. The estuary is a net source for the dissolved inorganic nitrogen; *DDIN* = $+2.1x10^3$ mol d^{-1} (+0.04 mmol m^{-2} d^{-1}).

Table 3.5. Salinity and nutrient concentrations in the Donuzlav estuary system and adjacent sea.

Parameter	**Donuzlav estuary**	
Salinity (psu)	System	18.2
	Sea	18.0
DIP (mmol m^{-3})	System	0.2
	Sea	0.2
DIN (mmol m^{-3})	System	1.2
	Sea	0.5

Stoichiometric calculations of aspects of net system metabolism
Stoichiometric estimates can be based on the molar C:N:P ratio of reacting material in the system. It is assumed that this material is plankton, with a Redfield C:N:P molar ratio of 106:16:1.

Stoichiometric analysis of the nonconservative fluxes indicated that the estuary is net nitrogen-fixing: (*nfix-denit*) = +0.1 mmol m^{-2} d^{-1} and net autotrophic: (*p-r*) = +0.4 mmol m^{-2} d^{-1} (see Table 3.6).

Table 3.6. Summary of nonconservative nutrient fluxes, apparent net metabolism (*p-r*) and nitrogen fixation minus denitrification (*nfix-denit*) for the Donuzlav estuary.

Parameters	Donuzlav estuary
DDIP (mol d^{-1})	-210
DDIP(mmol m^{-2} d^{-1})	-0.004
DDIN (10^3 mol d^{-1})	+2,125
DDIN(mmol m^{-2} d^{-1})	+0.04
(*p-r*)(mmol m^{-2} d^{-1})	+0.4
(*nfix-denit*) (mmol m^{-2} d^{-1})	+0.1

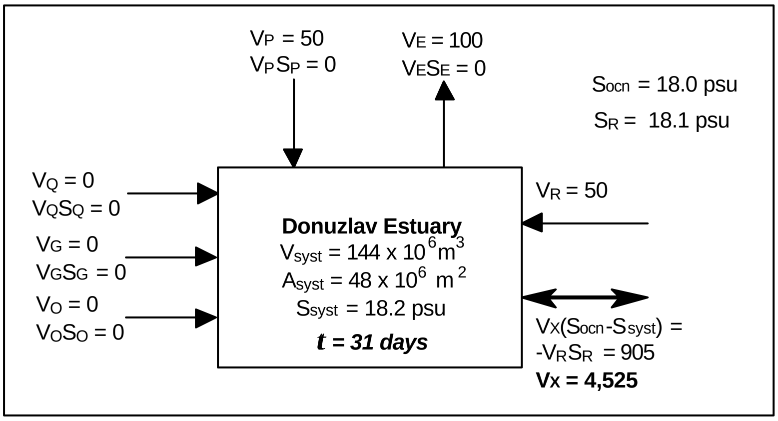

Figure 3.11. Water and salt budgets for the Donuzlav estuary. Water flux in 10^3 m^3 d^{-1} and salt flux in 10^3 psu-m^3 d^{-1}.

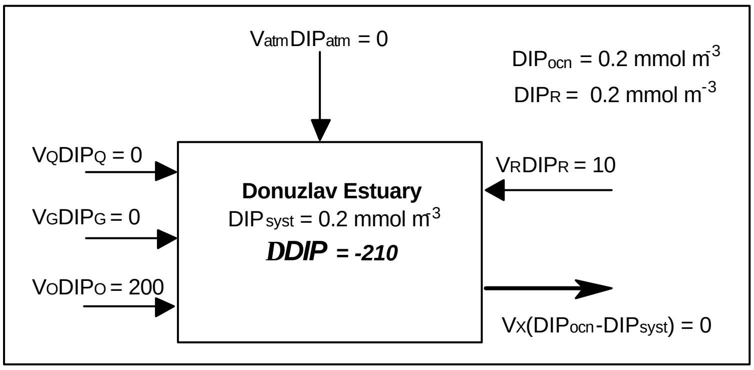

Figure 3.12. DIP budget for the Donuzlav estuary. Flux in mol d^{-1}.

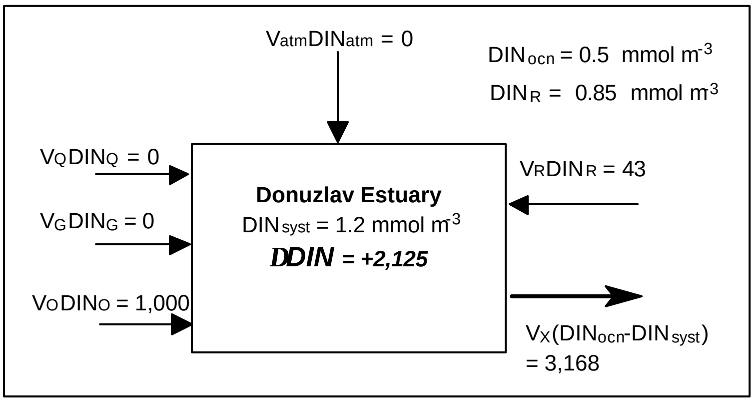

Figure 3.13. DIN budget for the Donuzlav estuary. Flux in mol d^{-1}.

3.4 Malii Adzalik Estuary

Inna Yurkova

<u>*Study area description*</u>

The Malii Adzalik estuary (46.59°N, 32.02°E) is situated on the north coast of the north-western part of the Black Sea in Ukraine (Figure 3.14). The catchments area of the estuary is about 260 km^2. The estuary has a water surface area of 8 km^2, width of 1 km, length of 11 km and mean depth of about 2 m. After construction of the navigation canal (width of 180 m, depth of 14 m, length of 3.3 km) in 1978, the Malii Adzalik estuary became permanently artificially open. The connection with the sea is through a channel about 500 m wide.

The climate of the area is continental with a relatively mild winter and a dry summer. The average temperature of January is -4°C and the average temperature of July is 22°C (Marinich 1993). Rainfall averages about 440 mm yr^{-1} and evaporation is assumed to be similar to the Tiligul Liman, about 820 mm yr^{-1} (Swebs 1988). The Malii Adzalik River discharge is low and in summer it is often equal to zero.

The estuary is an area of port activities (the port of Yuznii). The population of Yuznii is about 50,000.

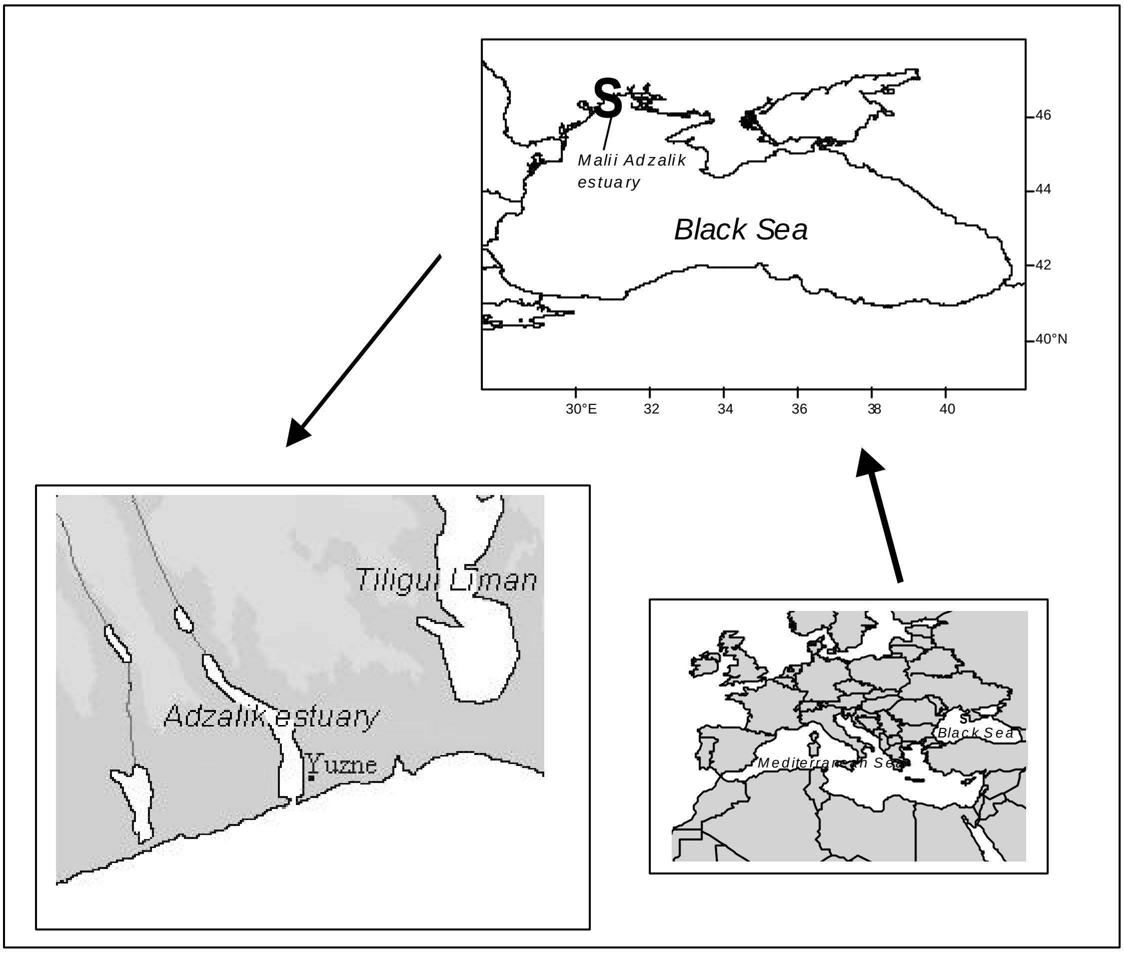

Figure 3.14. Location of the Malii Adzalik estuary.

Salinity and nutrient concentrations for the Malii Adzalik estuary used for the budget calculations were taken from Ryasinceva *et al.* (2000) as averages of data of 12 studies made from 1992 to 1996 in the estuary. Nutrient concentrations for the adjacent coastal waters were taken from Garkavaya *et al*. (2000); salinity of the sea was taken from Terziev (1986). The estuary was considered as a one-box model.

Water and salt balance

Precipitation (V_P) and evaporation (V_E) are $10x10^3$ m^3d^{-1} and $20x10^3$ m^3d^{-1}, respectively. The river discharge in the water budget can apparently be ignored due to its insignificance and is assumed to be zero. The salinity of the system is 14.8 psu and the adjacent sea is 13.5 psu.

Figure 3.15 summarizes the water and salt budget calculations for the Malii Adzalik estuary. The calculated water exchange time is 126 days.

Budgets of nonconservative materials

Wasteload to the estuary was calculated using the LOICZ approach for the 50,000 residents of Yuznii. Assuming that only 25 % of the wastewater enters the estuary, the DIP and DIN fluxes are 1,400 mol d^{-1} and 5,400 mol d^{-1}, respectively.

Table 3.7. Salinity and nutrient concentrations in the system and adjacent sea for Malii Adzalik estuary.

Parameter	Malii Adzalik estuary	
Salinity (psu)	System	14.8
	Sea	13.5
DIP (mmol m^{-3})	System	0.8
	Sea	0.9
DIN (mmol m^{-3})	System	1.6
	Sea	1.0

DIP balance.
The *DIP* of the system is -1,420 mol d^{-1} (-0.2 mmol m^{-2} d^{-1}). The estuary is a net sink of phosphorus (Figure 3.16).

N balance
The *DIN* of the system is -5,348 mol d^{-1} (-0.7 mmol m^{-2} d^{-1}). The estuary is a net sink of nitrogen (Figure 3.17).

Stoichiometric calculations of aspects of net system metabolism
It was assumed that reacting material in the system is plankton, with a Redfield C:N:P molar ratio of 106:16:1. Net nitrogen fixation minus denitrification (*nfix-denit*) for the estuary is +2 mmol m^{-2} d^{-1}. The estuary appears to be fixing nitrogen in excess of denitrification. Net ecosystem metabolism, the difference between primary production and respiration (*p-r*) is +19 mmol m^{-2} d^{-1}. The estuary appears to be a net autotrophic (see Table 3.8).

Table 3.8. Summary of nonconservative nutrient fluxes, apparent net metabolism (*p-r*) and nitrogen fixation minus denitrification (*nfix-denit*) for the Malii Adzalik estuary.

Parameters	Malii Adzalik estuary
DDIP (mol d^{-1})	-1,420
DDIP(mmol m^{-2} d^{-1})	-0.18
DDIN (mol d^{-1})	-5,348
DDIN(mmol m^{-2} d^{-1})	-0.7
(*p-r*)(mmol m^{-2} d^{-1})	+19
(*nfix-denit*) (mmol m^{-2} d^{-1})	+2

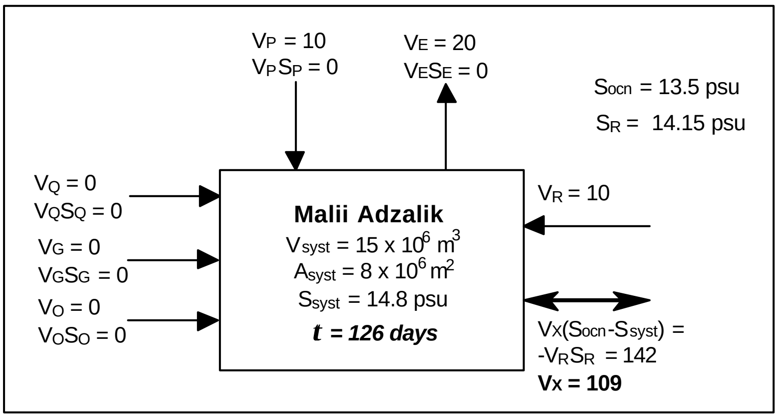

Figure 3.15. Water and salt budgets for Malii Adzalik estuary. Water flux in 10^3 m^3 d^{-1} and salt flux in 10^3 psu-m^3 d^{-1}.

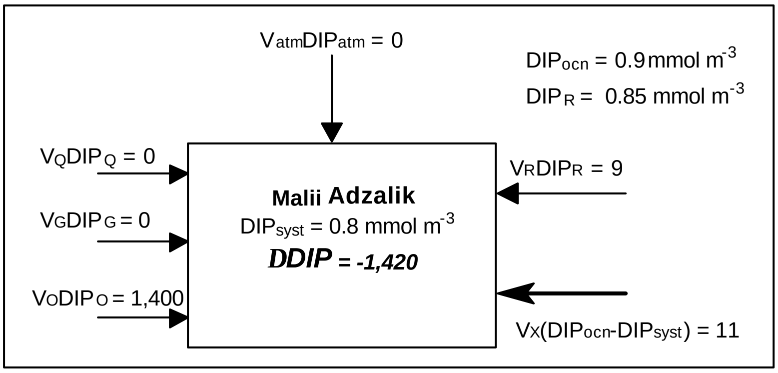

Figure 3.16. DIP budget for Malii Adzalik estuary. Flux in mol d^{-1}.

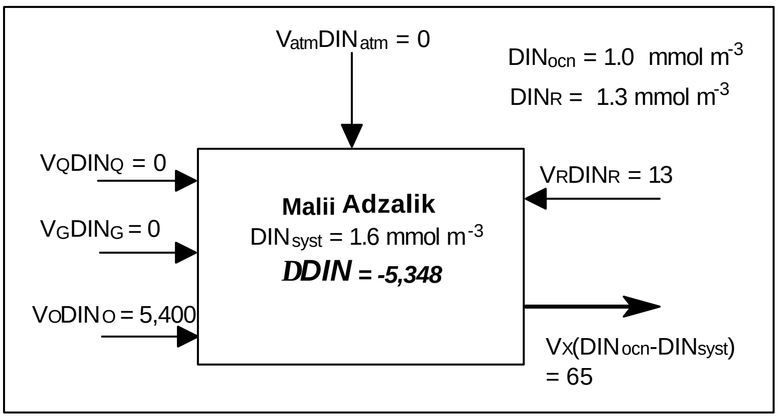

Figure 3.17. DIN budget for Malii Adzalik estuary. Flux in mol d^{-1}.

ESTUARINE SYSTEMS OF ITALY

<u>Northern Adriatic Sea region</u>

The Northern Adriatic Sea is a sheltered marine system bounded to the east and north by the coastline of Italy and to the west by the coastlines of Slovenia and Croatia. It covers an area of approximately 40,000 km^2 between 43°00'N and 45°45'N latitude and 12°15'E and 15°00'E longitude. It is very shallow (average depth 30-40 m) with a bottom gently that slopes southward down to 100 m; thereafter a steeper slope separates the northern from the central basin of the Adriatic Sea. Although located in the Mediterranean region, the climate is not typically "mediterranean" due to the high precipitation (up to 1000 mm) and low winter air temperatures (below 0^oC). The climate is usually classified as continental and temperate with cold, foggy winters and hot, sultry summers. In winter, a strong, dry, cold wind called the "Bora" blows from the north with peak velocities of more than 100 km/h.

The circulation and distribution of the water masses along the Italian coast are strongly influenced by riverine inflow, temperature variations and Coriolis forcing. In winter, cold water diluted by the western river inflow remains confined within the coastal belt and flows southward along the coastline. In summer, this part of the Adriatic Sea is highly stratified with strong salinity and temperature gradients and a wider area is affected by river discharge due to the lateral spreading of the low salinity water. The Italian coastline from Trieste south to Ravenna is characterised by the presence of numerous coastal lagoon and salt marsh systems which cover about 1000 km^2: these include very large systems such as Grado Marano and Venice lagoons, the Po River delta bays, the sheltered Valli di Comacchio and the Piallasse of Ravenna. These environments at the land-sea interface receive high nutrients loads.

The major freshwater inputs to the sea are from the Po and Adige rivers, plus a series of minor contributors. The Po River drains a large part of northern Italy (67,000 km^2) where about 15.5 million people live and intense industrial and agricultural activity takes place. For this catchment, a total load equivalent to 120 million inhabitants was used when industrial and agricultural inputs were estimated. The Adige River drains an area of 11,900 km^2 with an estimated load equivalent to 8 million inhabitants. Annual nutrient loads are estimated to be 190,000 and 14,900 tons of nitrogen and 13,200 and 1,000 tons of phosphorus for the Po and Adige Rivers respectively. Due to these large nutrient inputs, the Italian coast of the Northern Adriatic Sea is highly eutrophic; in some areas large blooms of phytoplankton occur and often induce summer anoxia causing widespread benthic mortality. Recently there have also been sporadic problems due to the formation of banks of mucillagenous material thought to be derived from the phytoplankton blooms.

Gianmarco Giordani

4.1 Sacca di Goro Lagoon

***P. Viaroli, G. Giordani, E. Cattaneo, J.M. Zaldívar and C.N. Murray*[2]**

<u>Summary</u>

The Sacca di Goro is an eutrophic lagoon located along the North Adriatic Coast of Italy. It is the estuary of the southernmost branch of the Po River delta. This lagoon was investigated at two levels: water budgets were estimated for the decade 1991-2000 and seasonal water and nutrients budgets were calculated for 1997. For both levels, a single box–single layer model was applied. Figure 4.3 shows the water exchange flows calculated following the two different procedures utilised (see text). For 1997, a mean water exchange time of 3 days was estimated. Both annual mean *DDIP* and *DDIN* were positive indicating that the system is a net source of both DIP and DIN. On a seasonal basis, the system can be divided in two parts. The first semester with negative *DDIP* was characterised by high organic matter production. The second semester with positive *DDIP* was characterised by high organic matter mineralisation. These *DDIP* variations conformed to the seasonal trends of macroalgal biomass growth and decomposition. Stoichiometric calculations were performed considering both the Redfield ratio (C:N:P=101:16:1) and the ratio for macroalgae (C:N:P=335:35:1) reported by Atkinson and Smith (1983).

The latter seems more suitable for the Sacca di Goro, which is affected by large blooms of macroalgae. On an annual basis, the lagoon can be considered as heterotrophic, with a net ecosystem metabolism $(p\text{-}r)_{macroalgae}$ of about -50 mmol C m^{-2} d^{-1}. The DIN budgets also indicated two periods, which conformed to the macroalgal patterns. The first semester had a positive $(nfix\text{-}denit)_{macroalgae}$, whilst the second one was negative confirming the summer dystrophic event as the boundary between an autotrophic and the following heterotrophic phase.

Study area description

The Sacca di Goro (Figure 4.1) is a shallow-water embayment of the Po River Delta (44.78-44.83°N, 12.25-12.33°E). The surface area is 26 km^2 and the total water volume is approximately 26×10^6 m^3. Numerical models have demonstrated a clear zonation of the lagoon with the low energy eastern area separated from two higher energy zones, the western area influenced by freshwater inflow from the Po di Volano and the central area influenced by the sea. The eastern zone is very shallow (maximum depth 1 m) and accounts for one half of the total surface area and one quarter of the water volume.

The lagoon is surrounded by embankments. The main freshwater inputs are the Po di Volano River (approximately 350×10^6 m^3 yr^{-1}), the Canal Bianco (about 20×10^6 m^3 yr^{-1}) and Giralda (30×10^6 m^3 yr^{-1}). Freshwater inlets are also located along the Po di Goro River and are regulated by sluices. There are no direct estimates of the freshwater input from the Po di Goro, which is usually assumed to be equivalent to that of the Po di Volano. The freshwater system is mostly located in a subsident area and is regulated by a system of pumping stations (scooping plants).

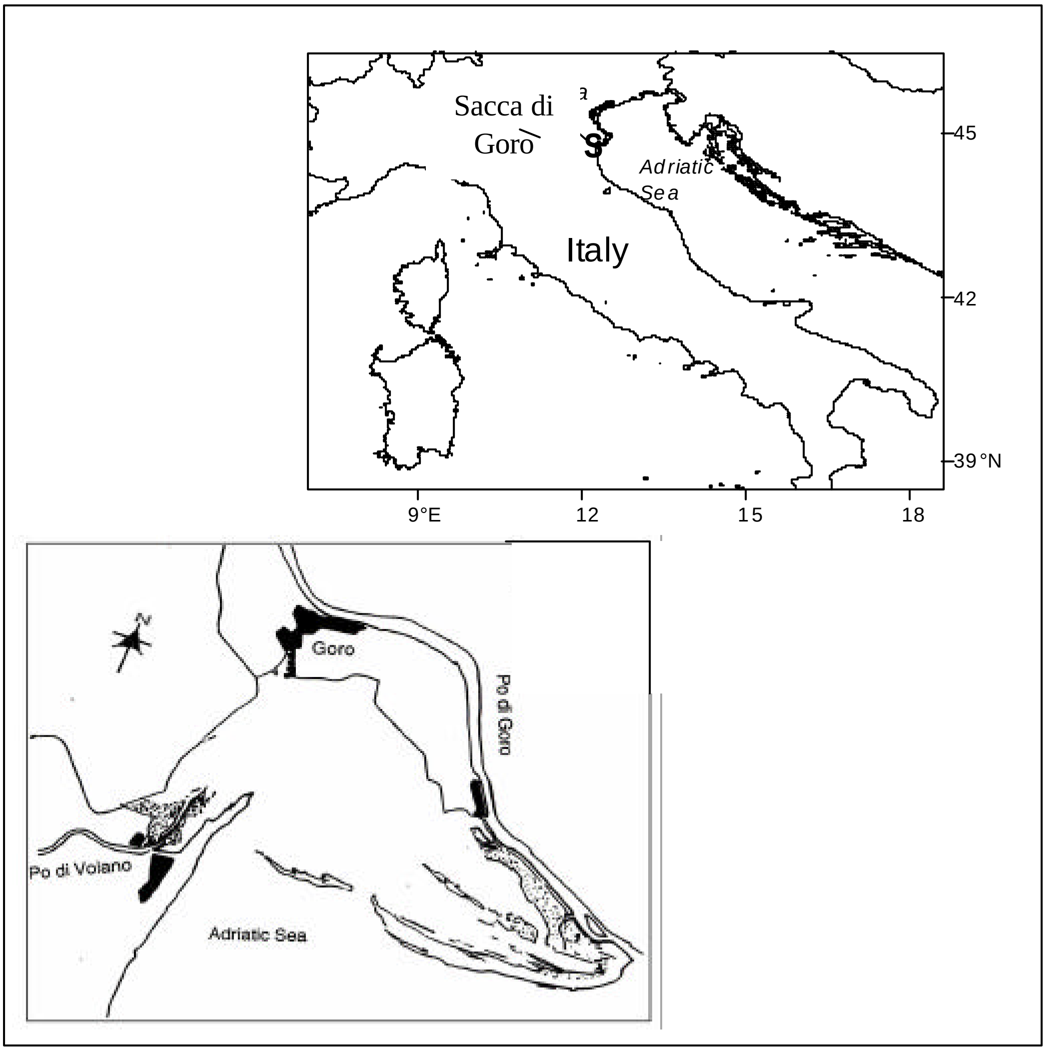

Figure 4.1. Map and location of the Sacca di Goro Lagoon.

The bottom of the lagoon is flat and the sediment is alluvial mud with high clay and silt content in the northern and central zones. Sand is more abundant near the southern shoreline, whilst sandy mud occurs in the eastern area.

The climate of the region is mediterranean with some continental influence (wet mediterranean). Precipitation is approximately 600 mm yr^{-1}, with late spring and autumn peaks. However, this pattern is undergoing significant changes with an increase of short-term intense events.

The catchment is heavily exploited for agriculture, whilst the lagoon is one of the most important aquacultural systems in Italy. About 10 km^2 of the aquatic surface are exploited for farming of the Manila clam (*Tapes philippinarum*), with an annual production of about 15,000 tons. The annual revenue has been oscillating during the last few years around 100 million Euros.

In the last decade the nitrogen loading has been persistently high (about 2,000 t yr^{-1}), whilst the phosphorus loading has decreased from *ca* 200 to *ca* 60 t yr^{-1}. The lagoon is subjected to anthropogenic eutrophication, which causes extensive growth of seaweeds, especially the chlorophyceans (*Ulva* sp. and *Cladophora* sp.) in the sheltered eastern area and phytoplankton in the deeper central zone. Macroalgal growth is responsible for summer anoxia and dystrophy, which usually take place in the eastern area (for an updated review see Viaroli *et al.* 2001). Recent studies have also demonstrated that the clam stock can contribute to the oxygen depletion and internal loading (Bartoli *et al.* in press).

For Sacca di Goro water budgets were estimated for the decade 1991-2000 and seasonal water and nutrients budgets for 1997, when the lagoon was studied with the financial support of two EU-ELOISE projects.

Meteorological data from the Volano station for the period 1987-2000 were supplied by the Regional Agency for Environmental Protection (ARPA, Regione Emilia-Romagna, Bologna). Temperature and salinity of coastal waters for the period 1984-1998 were provided by ARPA-DAPHNE Cesenatico. We used mainly data from Station 2 (44º47'07", 12º15'45"; depth 3 m; distance from coast 500 m), in front of Sacca di Goro. Data concerning temperature and salinity for Sacca di Goro were obtained from Colombo *et al.* (1994) and Milan (1999). Data concerning freshwater loadings were obtained from Dimensione Ambiente (1991-1997) and Consorzi di Bonifica Ferraresi (1991-1999).

For 1997, four periods were identified: January-March, April-June, July-September, and October-December. Data were obtained from the ELOISE Projects "NICE: nitrogen cycling in estuaries" and "ROBUST: the role of buffering capacities in stabilising coastal lagoon ecosystems". From January to December 1997, water samples were collected in the central part of the lagoon and analysed for nitrate, nitrite, ammonium and dissolved reactive phosphorus using standard analytical procedures (Dalsgaard *et al.* 2000). Macrophyte biomasses, primary production, benthic fluxes of oxygen and nutrients, denitrification rates and sulphur, phosphorus, iron and nitrogen were also investigated (Bartoli *et al.*, 2001, Viaroli *et al.* 2001). Air temperature and wet deposition data were obtained from the meteorological network of the Province of Ferrara. The meteorological stations considered are located close to the lagoon. Hydrochemical data for the Adriatic Sea stations are reported by ARPA-DAPHNE (1998). Freshwater discharge in the lagoon and additional hydrochemical data have also been obtained from Bencivelli (1998).

Water and salt balance

Because the Sacca di Goro Lagoon is so shallow, the water and salt budgets were calculated using a single box–single layer model.

The LOICZ water budget can be written as:

$$dV_{SGt}/dt = V_Q + V_P + V_G + V_O + V_E + V_R \qquad (1)$$

where V_{SG} refers to the Sacca di Goro volume, V_Q include the inflows from stream runoff, V_P is the flow due to direct precipitation, V_G refers to groundwater, V_O refers to other inflows such as sewage, V_E refers to evaporation and V_R refers to residual flow. For LOICZ conventions, each of the fluxes may have negative or positive value depending on the direction of the flow (negative value for outflow from the system and positive for inflow to the system). Note that, by this convention, the numerical value for V_E is negative.

It is useful to consider that V_R is the difference between V_{in} and V_{out} which driven by the water budget ($V_R = V_{in} - V_{out}$). In fact, V_R can be obtained assuming $dV_{SG}/dt = 0$ as:

$$V_R = V_{in} - V_{out} = -V_Q - V_P - V_G - V_O - V_E \qquad (2)$$

For the Sacca di Goro water budget, as we used monthly evaluations of the fluxes, the term dV_{SG}/dt in Eq. (1) will tend towards zero (this term should be considered in case of time periods similar to a single tide cycle). V_Q was evaluated using data from 1980 to 1997 from Dimensione Ambiente (1991-1997) and Consorzi di Bonifica Ferraresi (1991-1999). An exact estimation of the V_Q entering into Sacca di Goro is difficult since we have not found data on the amount entering from Po di Goro due to the continually changing connections between the river and the lagoon. This flow is considered of the same order of magnitude of Po di Volano.

V_P has been obtained from meteorological data from Po di Volano station, whereas V_E has been evaluated using an equation based on the rate of heat loss by evaporation (H_E):

$$V_E = \frac{H_E \cdot A_{SG} \cdot 10^{-2}}{\rho_W \cdot \lambda_W} \qquad (3)$$

where ρ_W is the water density in g cm^{-3}, λ_W is the latent heat of vaporisation in cal g^{-1}, A_{SG} is the Sacca di Goro surface in m^2, and H_E can be evaluated using Thomann and Mueller, 1987:

$$H_E = (19.0 + 0.95\ ws^2)(Pv_s - Pv_a) \qquad (4)$$

where ws is the wind speed in m s^{-1} and Pv_s and Pv_a are the saturated vapour pressure of water (mm Hg) at surface temperature and the saturated vapour pressure of water at air temperature multiplied by the relative air humidity.

As can be seen from the calculations (Figure 4.2), the contributions from direct precipitation and evaporation could be neglected, as a first approximation, in comparison with the stream runoff from Po di Volano and Canal Bianco. This is due to the fact that both terms are, generally, one order of magnitude lower than V_Q and with opposite signs. V_G and V_O were also considered negligible. In the subsequent calculations, we have used V_R whenever possible, otherwise we have replaced V_R by $-V_Q$.

The salt budget can be written as:

$$V_{SG}\frac{dS_{SG}}{dt} = V_{in} \cdot (S_2 - S_{SG}) - V_{out} \cdot (S_{SG} + S_2)/2 \qquad (5)$$

where S_{SG} refers to the Sacca di Goro salinity and S_2 is the salinity in the sea just outside the lagoon. It has been assumed that other salinity values (runoff, groundwater, etc.) are likely to be small and can be considered to be zero. In this equation, the mixing terms V_{in} and V_{out} remain as the unknowns. By combining equations (2) and (5), it is possible to obtain:

$$V_{in} = \frac{1}{(S_2 - S_{SG})}\left(V_{SG}\frac{dS_{SG}}{dt} - V_R(S_{SG} + S_2)/2\right) \qquad (6)$$

This flow is called the water mixing flow and, using LOICZ notation, is called V_X.

There is an alternative to estimate the mixing flow (V_X) without relying on a salinity difference between the system and the ocean (Yanagi 2000). In this method the value of the horizontal dispersion coefficient D_H ($m^2 s^{-1}$) is estimated from the current shear and the diffusivity normal to the current shear by the following equations (Taylor 1953):

a) In case of dominant vertical shear (narrow and deep estuarine system)

$$D_H = \frac{1}{120}\left(\frac{H^4}{K_V}\right)\left(\frac{U}{H}\right)^2 \quad (7)$$

b) In the case of dominant horizontal shear (wide and shallow estuarine system)

$$D_H = \frac{1}{120}\left(\frac{W^4}{K_h}\right)\left(\frac{U}{W}\right)^2 \quad (8)$$

where H (m) is the average depth of the open boundary system; W (m) is the length of the open boundary, that is the width of the open system mouth; U ($m\ s^{-1}$) is the residual flow velocity at the surface layer of the open boundary; K_V is the vertical diffusivity (typically 10^{-4} m^2 s^{-1} in the case of stratification or 10^{-3} m^2 s^{-1} in the case of vertically well-mixed system); and K_h is the horizontal diffusivity (m^2 s^{-1}), which may be estimated using Okubo's (1971) relationship:

$$K_h = 18W^{1.15} \quad (9)$$

where K_h is given in m^2 d^{-1} (for LOICZ notation).

In order to decide which type of equation one should employ for a particular system, i.e., narrow and deep or wide and shallow, Yanagi (2000) established the following criteria:

-narrow and deep: L/W > 2 and W/H<500
-wide and shallow: L/W<2 and W/H>500

where L (m) is the distance from the centre of the system to its mouth.

Once D_H is calculated then Vx can be evaluated using the following equation:

$$V_x = D_H\left(\frac{A}{F}\right) \quad (10)$$

where A denotes the cross-sectional area of the open boundary of the system (m^2) and F is the distance (m) between the geographic center of the system and the observation point for oceanic salinity.

V_{in} (or Vx) has been calculated using Eq. (6) and salinity data from Colombo *et al.* (1991, 1994) and Milan (1999). In parallel, the method developed by Yanagi (2000) has been applied. For this reason, we have evaluated the variation of W (width of the Sacca di Goro mouth) during the last 20 years (Table 4.1) using data from Simeoni *et al.* (2000).

Table 4.1. Width evolution of the Sacca di Goro mouth(s) from 1980 to 2000 (Simeoni *et al.* 2000).

Year	**1980**	**1981**	**1982**	**1983**	**1984**	**1985**	**1986**	**1987**	**1988**	**1989**	**1990**
W(m)	2,580	2,580	2,580	2,480	2,383	2,286	2,189	2,092	1,995	1,900	1,700
Year	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	
W(m)	1,500	1,350	1,200	1,284	1,368	1,452	1,536	1,626	1,716	1,790	

The principal mouth of Sacca di Goro has suffered a progressive decrease over the last 20 years. In order to compensate for this decrease a channel was opened in 1993. This channel has evolved in a second mouth (~860 m) while the main mouth has continued to decrease (~930 m). Table 4.2 shows the relative parameters used for the calculation. The Sacca di Goro may be considered as a wide and shallow lagoon and, hence, Eq. (8) must be employed to calculate D_H.

Table 4.2. Data for the calculation of V_X for the Sacca di Goro Lagoon.

Variable/System	Sacca di Goro
L(m)	2,270
W_{min} (m)	1,200
W_{max} (m)	2,580
H (m)	1.5
A_{min} (m^2)	1,800
A_{max} (m^2)	3,870
L/ W_{min}	1.89
L/W_{max}	0.88
W_{min}/H	800
W_{max} /H	1,720
Classification	wide & shallow
F (m)	4,760
U (m/d)	11,490*

*From Ciavola *et al*. (2000): mean 0.133 m/s; min. 6.0 10^{-3} m/s; max. 0.42 m/s; standard deviation 0.125 m/s.

Figure 4.3 represents the exchange flows calculated following both procedures, i.e. Eq. (6) and Eq. (10). Points represent the calculation based on the salinity budget Eq. (6), lines represent the calculation based on Eq. (10) taking into account the mean value of the current measurement and the standard deviation points. These experimental measurements were performed during a few days in May, so their validity for representing a whole year is not guaranteed. However, both procedures gave similar values and probably incorporated all the uncertainties. The calculations based on the mean salinity showed a high variability, which was mainly due to the wide salinity ranges in both the Sacca di Goro (15-35 psu) and the adjacent sea (15-35 psu). Considerable differences also occurred among stations in the lagoon, since several stations are dominated by freshwater inputs whereas others are mainly influenced by the Adriatic Sea. Furthermore, the marine Station 2 is affected by freshwater of the Po River plume. Therefore the coastal environment of the Sacca di Goro should be considered as a transient dynamic system. Intra-station salinity changes up to 20 psu may also occur in the short term (e.g. daily), mostly during extreme events, namely riverine floods and spring tides. Considering the above-mentioned features of the coastal system, the salt balance should be estimated at a time-scale as short as possible, probably from days to weeks. Unfortunately, there are not data enough to carry out such calculations, since the sampling frequency is from weekly to monthly. However, the short-term variability can be evaluated based on the data recorded by an oceanographic buoy which is deployed in the central part of the lagoon (see for example Viaroli *et al.* 1996a).

This first generation budget does not consider the above constraints. Salt budgets were calculated following Eq. (6). The annual and four seasonal budgets for the 1997 are summarised in Table 4.3. On an annual basis, freshwater inputs were dominated by riverine discharges which were about 5 times lower than the sea-lagoon exchange flow. Freshwater inputs peaked in spring and summer (Table 4.3), V_R was negative for all seasons indicating a continuous net export of lagoonal water to the sea and V_X ranged from 6 to 11×10^6 m^3 d^{-1}. Water exchange time ranged from 2 to 4 days depending on water fluxes.

Table 4.3. Seasonal water and salt budgets for Sacca di Goro lagoon in 1997. Water fluxes in 10^3 m^3 d^{-1}, water exchange time (τ) in days and salinity in psu.

Season	V_Q	V_P	V_E	V_R	S_{sea}	S_{syst}	V_X	*t*
Jan-Feb-Mar	1,500	0	0	-1,500	27.0	23.3	10,300	2
Apr-May-Jun	2,300	100	-100	-2,300	32.0	23.8	7,800	3
Jul-Aug-Sep	2,500	0	-100	-2,400	24.0	19.3	11,100	2
Oct-Nov-Dec	1,100	100	0	-1,200	30.0	24.2	5,700	4
Annual	1,900	0	-100	-1,800	28.3	22.7	8,200	3

Budgets of nonconservative materials

The equation for a mass balance for compound(s) which undergo chemical transformations within the coastal lagoon is:

$$V_{SG}\frac{dY_{SG}}{dt} = V_Q Y_Q + V_{atm} Y_{atm} + V_R Y_R + V_X\,(Y_2 - Y_{SG}) + \Delta Y_{SG} \qquad (11)$$

where Y refers to the concentration of the chemical species (Table 4.4), and *DY* is the net nonconservative flux. The last term (*DY*) of Eq. (11) represents the tendency of the system to be sink or source for Y.

Table 4.4. Seasonal nutrient concentrations for the river, Sacca di Goro lagoon and adjacent Adriatic Sea.

Season	DIP_Q	DIP_{syst}	DIP_{sea}	DIN_Q	DIN_{syst}	DIN_{sea}
	(mmol m^{-3})					
Jan-Feb-Mar 97	1.1	0.3	0.2	154	73	40
Apr-May-Jun 97	1.3	0.1	0.3	67	54	18
Jul-Aug-Sep 97	0.7	1.5	0.1	35	50	9
Oct-Nov-Dec 97	1.3	1.2	0.3	164	71	27
Annual	1.0	0.7	0.2	87	61	24

The nonconservative flux (*DY*) can be written as RV_{SG}, where R is the sum of all the processes (physical, chemical or biological) taking place within the system:

$$R = \sum_{i=1}^{n} \nu_i \cdot r_i \qquad (12)$$

where ν_i is the stoichiometric coefficient for the i-th transformation.

DIP balance

The annual and seasonal DIP budgets for 1997 are summarised in Table 4.5. A net annual export of about $5x10^3$ moles P d^{-1} from the lagoon was estimated, whilst the net input of freshwater DIP was about $2x10^3$ moles P d^{-1}. The highest seasonal DIP input was estimated in spring with value of about $3x10^3$ moles P d^{-1}. Therefore, assuming steady state conditions, a net annual internal source of $+3x10^3$ moles P d^{-1} was estimated. Thus, on an annual basis, the lagoons acted as a DIP source with a *DDIP* mean of +0.12 mmol m^{-2} d^{-1}. Since data on dry deposition are not available, we assumed atmospheric DIP inputs to be zero. However, atmospheric loads may account for some of the DIP input to the lagoon. *DDIP* was negative in winter and spring and positive in summer and autumn. These *DDIP* variations conformed to the seasonal trends of macroalgal biomass growth and decomposition (Viaroli *et al.* 2001). Spring was characterised by high macroalgal growth rates and high DIP uptake was expected. Macroalgal biomasses reached maximal values early in summer. Afterwards, rapid decomposition processes took place with high rates of organic matter mineralisation and DIP release. Due to the relatively high temperature (up to 20°C) a residual net DIP mineralisation was estimated also early autumn, while in winter a moderate DIP uptake was recorded due to a new *Ulva* growth cycle.

Table 4.5. Seasonal DIP budgets for Sacca di Goro lagoon in 1997.

Season	$V_Q\,DIP_Q$	$V_R\,DIP_R$	$V_X\,DIP_X$	*DDIP*	
	(10^3 mol d^{-1})			(10^3mol d^{-1})	(mmol m^{-2} d^{-1})
Jan-Feb-Mar 97	1.7	-0.4	-1.0	-0.3	-0.01
Apr-May-Jun 97	3.0	-0.5	1.6	-4.1	-0.16
Jul-Aug-Sep 97	1.8	-1.9	-15.5	+15.6	+0.60
Oct-Nov-Dec 97	1.4	-0.9	-5.1	+4.6	+0.18
Annual	1.9	-0.8	-4.1	+3.0	+0.12

DIN balance

The annual and seasonal DIN budget for 1997 are shown in Table 4.6. The annual DIN input was 163×10^3 moles N d^{-1}, with peaks in winter. On the annual basis, ammonium and nitrate loads were similar. In the lagoon, DIN concentrations were highest in winter and consisted mainly of nitrate (60-70%) and were lowest in summer when the main form was ammonium (70-75%). The net export of 380×10^3 moles N d^{1} from the lagoon accounted for a net mobilisation of 215×10^3 moles N d^{-1}. Therefore, the lagoon was expected to act as a source of DIN with a mean *DDIN* of +8.3 mmol m^{-2} d^{-1}. The seasonal *DDIN* were always positive indicating a dominance of DIN release processes over assimilation. However, the remobilisation within the lagoon was supported by the high riverine loads of organic nitrogen. For example, in the Po di Volano channel dissolved and particulate organic nitrogen accounted for 70% of the annual load in 1997 (Viaroli unpublished data).

Table 4.6. Seasonal DIN budgets for Sacca di Goro lagoon in 1997.

Season	$V_Q DIN_Q$	$V_{atm} DIN_{atm}$	$V_R DIN_R$	$V_X DIN_X$	***DDIN***	
	(10^3 mol d^{-1})				(10^3 mol d^{-1})	(mmol m^{-2} d^{-1})
Jan-Feb-Mar 97	231	0	-85	-340	+194	+7.5
Apr-May-Jun 97	154	10	-83	-281	+200	+7.7
Jul-Aug-Sep 97	88	0	-71	-455	+438	+16.8
Oct-Nov-Dec 97	180	10	-59	-251	+120	+4.6
Annual	165	0	-77	-303	+215	+8.3

Stoichiometric calculations of aspects of net system metabolism

The LOICZ biogeochemical model makes the assumption that net organic matter production or mineralisation in the system can be directly estimated by *DDIP*. In Sacca di Goro, the differences between DIP input and output are related to the balance of all the processes occurring in the system, therefore the net balance inherently includes inorganic nutrient fluxes at the water-sediment interface. The negative values of *DDIP* in the first half of the 1997 were consistent with the macroalgal blooms occurring in the same period with density peaks of up to 1,200 g DW m^{-2} (Figure 4.4). In this period, DIP and DIN were intensively assimilated above macroalgal need (luxury uptake, Viaroli *et al.* 1996b). The surficial sediment was oxidised due to high oxygen concentration in the water column (up to 200%) and DIP was actively adsorbed (Giordani *et al.* 1997). In the subsequent period the decomposition of *Ulva* biomasses supported high mineralisation rates with net release of DIP and DIN. The surficial sediment was also reduced due to the anoxic conditions, with a further release of DIP.

Since the lagoon was colonised by dense beds of floating macroalgae for most of the investigated period and by intense blooms of phytoplankton, two different C:N:P ratios were used in the stoichiometric calculations. The Redfield ratio (C:N:P=101:16:1) was used for phytoplankton and the C:N:P=335:35:1 (Atkinson and Smith 1983) was applied for macroalgae.

Results of the seasonal budgets are summarised in Table 4.7. $DDIN_{exp}$ is the DIN variation expected on the basis of organic matter production and mineralisation and was calculated by multiplying the *DDIP* by the N:P ratio of the dominant primary producer. Net nitrogen fixation minus the denitrification (*nfix-denit*) was calculated by the difference between the observed and expected *DDIN's*. Using the Redfield ratio, $(nfix\text{-}denit)_{plankton}$ was positive over the whole investigated period, indicating that net DIN inputs such as nitrogen fixation appeared to dominate over losses via denitrification. Using the Atkinson and Smith ratio, which seems more suitable for the Sacca di Goro, the year can be divided in two parts, one with positive $(nfix\text{-}denit)_{macroalgae}$ and the other with negative $(nfix\text{-}denit)_{macroalgae}$. Even if the values are really high and the explanations for that trend are mainly speculative, the presence of a "switch" after the peak of macroalgal biomass can be confirmed.

Table 4.7. Seasonal variation of *DDIN*$_{exp}$, *(nfix-denit)* and net ecosystem metabolism (*p-r*) for Sacca di Goro lagoon in 1997.

Season	***DDIN***$_{exp}$	**(*nfix-denit*)**	**(*p-r*)**	***DDIN***$_{exp}$	**(*nfix-denit*)**	**(*p-r*)**
	Plankton (C:N:P = 106:16:1) (mmol m^{-2} d^{-1})			Macroalgae (C:N:P = 335:35:1) (mmol m^{-2} d^{-1})		
Jan-Feb-Mar 97	-0.2	+7.7	+1	-0.4	+7.9	+3
Apr-May-Jun 97	-2.6	+10.3	+17	-5.6	+13.3	+54
Jul-Aug-Sep 97	+9.6	+7.2	-64	21.0	-4.2	-201
Oct-Nov-Dec 97	+2.9	+1.7	-19	6.3	-1.7	-60
Annual	+2.4	+6.7	-16	+5.3	+3.8	-51

The net ecosystem metabolism NEM or (*p-r*) was positive for the first semester of the investigated period with values of 1 to 50 mmol m^{-2} d^{-1} depending on the C:P ratio considered, whilst in the second part, (*p-r*) was negative (-20 to -200 mmol m^{-2} d^{-1}). The high negative *DDIP* which relates to (*p-r*) in the first phase was probably due to combination of organic matter assimilation of DIP and abiotic processes (i.e., phosphate adsorption). The high positive *DDIP* in the second phase was probably due to organic matter mineralisation and surficial sediment release of DIP in the reduced environment. The system is apparently highly autotrophic in the first semester and highly heterotrophic in the remaining part of the year. For 1997, on the annual basis, the Sacca di Goro can be considered as an heterotrophic system, since organic matter mineralisation exceeded production of 15 or 40 mmol C m^{-2} d^{-1} depending of the C:P considered.

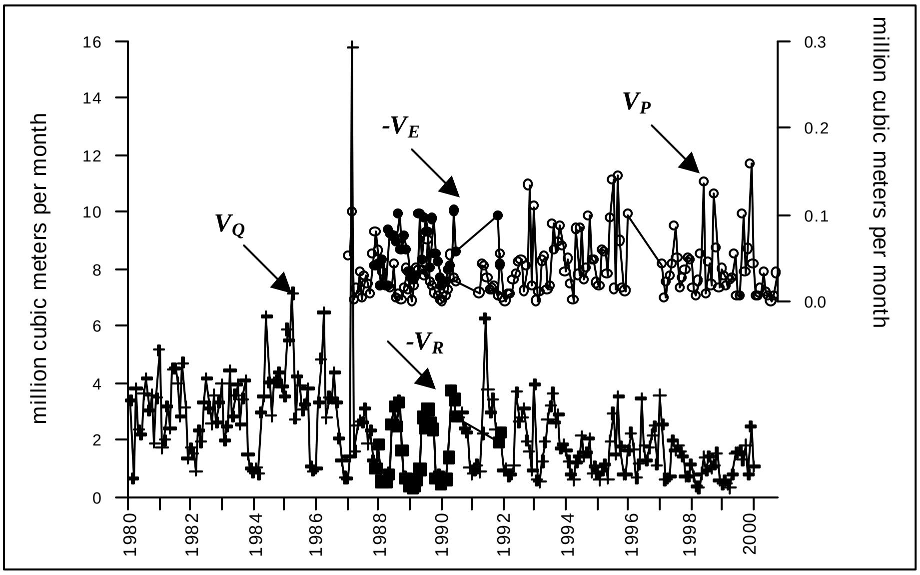

Figure 4.2. Estimated freshwater monthly contribution of Burana-Volano watershed (V_Q) in Sacca di Goro from 1980 to 2000 in comparison with V_P, $-V_E$ and $-V_R$. Note the offset scale for V_P and $-V_E$.

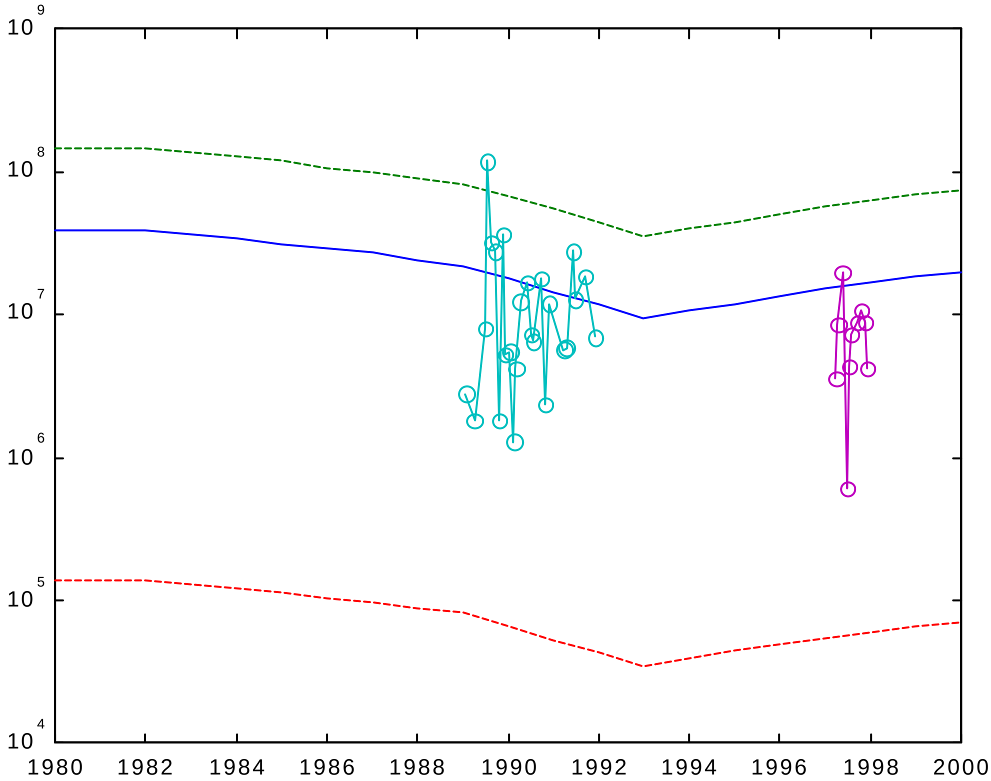

Figure 4.3. Exchange fluxes calculated using Eq. (6) (hollow points) and Eq. (10) (lines). Continuous line: V_X calculated using the U_{mean} value from Ciavola *et al.* (2000), and discontinuous lines calculated considering standard deviation, i.e. $U = U_{mean} \pm DU$.

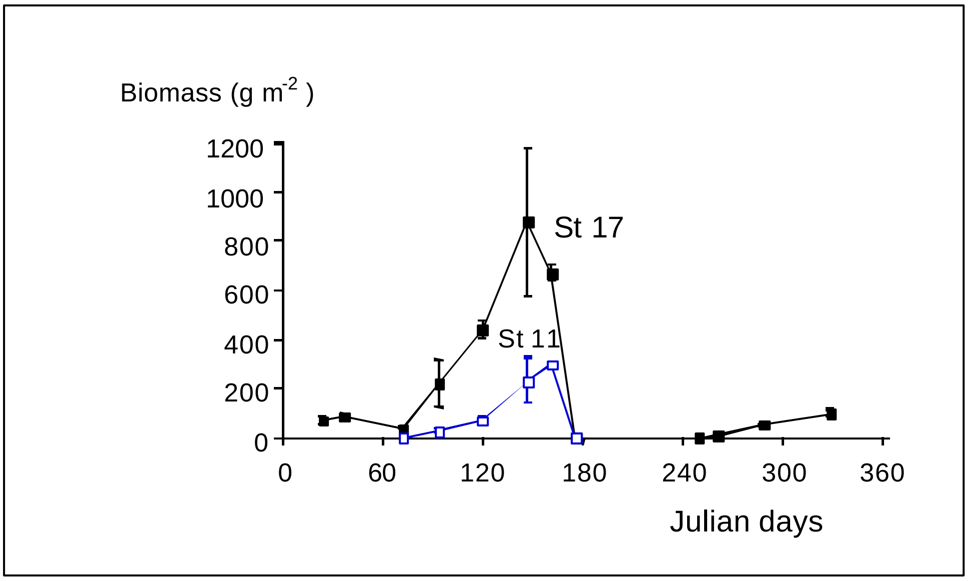

Figure 4.4. Representation of the seasonal trends of macroalgal biomass of *Ulva* in Sacca di Goro in the 1997 in 2 stations (St. 17 in the eastern part and in St. 11 in the central part of the lagoon).

4.2 Valli di Comacchio

P. Viaroli and G. Giordani

Summary

The Valli di Comacchio is a wide hyper-eutrophic lagoon system situated on the Adriatic coast of the Emilia Romagna region of Italy. It was studied in 1997 applying a single box–single layer model. The water exchanges were low since freshwater inputs were absent and the connection with the sea was limited to three channels. As expected, a long water exchange time was calculated (about 247 days). The main inputs of DIP were from the sea, while DIN inputs were dominated by precipitation. The lagoon acts as a source for DIP and a sink for DIN even if ΔDIP and ΔDIN are very low considered on a surface area basis (+1 and -27 µmol m^{-2} d^{-1}, respectively). Denitrification appears to dominate over nitrogen fixation, with an estimated net N loss equivalent to 0.04 mmol m^{-2} d^{-1}. In this system organic matter mineralisation seems slightly dominant over production since (*p-r*) was estimated to be -0.1 mmol C m^{-2} d^{-1}. Thus, the Valli di Comacchio can be considered as a net heterotrophic system.

Study area description

The Valli di Comacchio lagoon system is located on the coast of the Adriatic Sea, 20 km south of the Po River delta (44.63°N, 12.28°E; Figure 4.5). It consists of three main lagoons (Magnavacca, Fossa and Campo) plus a series of smaller ponds, with a total surface area of 115 km^2 and a mean depth of 0.8 m. It is separated from the sea by a 2.5 km wide spit and exchanges with the marine area are via 3 narrow man-regulated channels.

The Valli di Comacchio can only be considered to some extent as a natural system as it has been subjected to intensive modifications and controls by aquaculture activities. In fact, for centuries, the Valli di Comacchio was among the most valuable fishing grounds in Italy, being rich in eels, mullet, clams, shrimp and other animals.

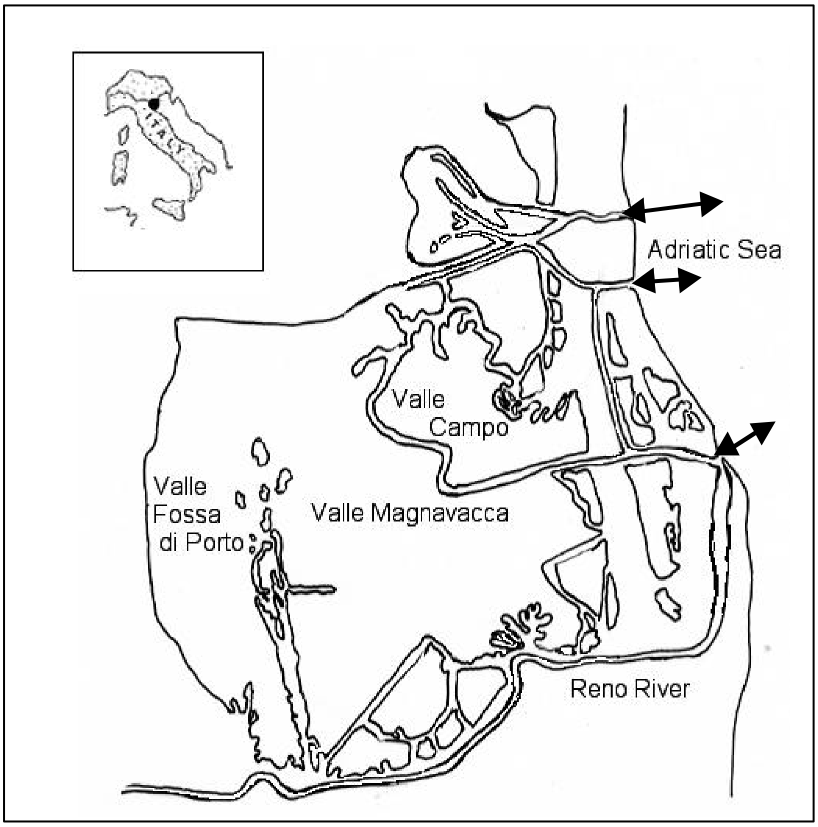

Figure 4.5. Location and map of Valli di Comacchio Lagoon. The three connection canals to the Adriatic Sea are indicated with double-headed arrows.

However, during recent decades it has suffered what Sorokin *et al.* (1996) described as "an ecological catastrophe" due to the occurrence of extremely dense blooms of picocyanobacteria. Recent results (Andreoli *et al.* 1998) disagree with this description but confirm the hyper-eutrophic conditions of the lagoons.

Water exchange with the Adriatic Sea via the three regulated communication channels occurs only in spring and autumn. In spring, water mainly enters into the lagoon to allow the entrance of juvenile fishes while in autumn the flow is mainly towards the sea. Thus, water exchanges are limited and their evaluation is difficult since they are dependent upon the timing of the channel openings. Limited water exchanges are also observed with the southern Reno River which is nutrient-rich and heavily polluted. The water inputs from the Adriatic Sea are also nutrient-rich since the Po River delta is nearby and the river plume affects the area in front of the lagoon. The main water exchanges are with the atmosphere but these do not significantly affect nutrient availability. Salinity ranges between 30 and 38 psu with peaks in the summer months.

The climate is mediterranean, with some continental influence. Precipitation is approximately 600 mm yr^{-1}, with late spring and autumn peaks.

An annual single box–single layer model was applied to the 1997 data, because the Valli di Comacchio system is characterised by a complicated net of water and nutrients fluxes between the individual incompletely defined shallow lagoons. Temperature and wet deposition data were obtained from the meteorological network of the Province of Ferrara, while hydrochemical data for Adriatic Sea and Valli di Comacchio stations are reported in ARPA-DAPHNE (1998) and Dallocchio *et al.* (1998) respectively.

Water and salt balance

The water and salt budgets of Valli di Comacchio are shown in Figure 4.6.

Freshwater inputs to the lagoon are considered negligible in comparison to the volume of the system. Losses of lagoonal water via ground filtration have been calculated by Vincenzi (1995) and were taken into consideration. Precipitation data (V_P) were obtained from the Meteorological Station of Ferrara and evaporation losses (V_E) were calculated according to the Hargreaves' equation.

To balance the water losses via infiltration and evaporation, a net water input of $50x10^3$ m^3 d^{-1} from the sea were evaluated (V_R). While, considering the salinity gradient between the lagoon system and the sea, the exchange flux (V_X) was calculated at $321x10^3$ m^3 d^{-1}. Salinity of the seawater in front of the lagoon is low due to the Po River influence. The estimated water residence time was 247 days.

These calculated water fluxes are somewhat larger but of in the same order of magnitude as those previously reported for the lagoon (Vincenzi 1995) from direct measurements carried out in 1991-1992 with current-meters positioned in the three channels which connect the lagoons to the sea. Vincenzi evaluated the water output from the system at $202x10^3$ m^3 d^{-1} and the water inputs at $162x10^3$ m^3 d^{-1}.

Budgets of nonconservative materials

DIP balance

The annual DIP budget for the year 1997 is shown in Figure 4.7. Atmospheric DIP inputs were assumed to be zero since no data on dry deposition were available.

The input of DIP to the lagoon was from the net water inputs from the sea ($V_R DIP_R$) while bigger DIP outputs were calculated from the water exchanges between the sea and the system ($V_X(DIP_{ocn}$-$DIP_{syst})$ and for groundwater losses ($V_G DIP_{syst}$). To balance for these outputs (138 mol d^{-1}) and residual input from the sea (20 mol d^{-1}), a release of DIP of 116 mol d^{-1} would be required to maintain the steady state conditions.

Thus, for the investigated period, the Valli di Comacchio lagoons acted as a net source of DIP (*DDIP* = 116 mol d^{-1}) although this value is low (1 µmol $m^{-2}d^{-1}$) when referred to the surface area of the system.

DIN balance

The annual DIN budget for 1997 is shown in Figure 4.8. DIN concentrations in the lagoon were low for the whole investigated period with winter peaks of 34.7 µM. Ammonium was the dominant form accounting for 47-95 % of DIN. Higher DIN concentrations were measured in both the seawater and rainwater inputs. Quantitatively, the main load of DIN to the lagoons was due to precipitation ($18x10^3$ mol d^{-1}) because of the high surface area of the lagoon system and the high average DIN concentration in the rainwater (97 µM). The DIN input from the sea was also significant, since the exchanges of water account for a net input of DIN estimated at $3x10^3$ mol d^{-1}. The sum of the estimated DIN inputs quantitatively dominate the DIN outputs which mainly occur via groundwater, indicating an internal net removal of DIN.

During 1997, the lagoon acted as a net sink for DIN since *DDIN* was negative ($-3x10^3$ mol d^{-1}) even if the *DDIN* calculated on areal basis is very low (-0.03 mmol m^{-2} d^{-1}).

Stoichiometric calculations of aspects of net system metabolism

In accordance with the assumptions of the model, positive *DDIP* values can be considered as an indication of net organic matter mineralisation and can be directly estimated from the coupled DIP release.

In 1997, the lagoons were affected by persistent blooms of phytoplankton of *Nannochloropsis* and *Synechococcus* genera (Andreoli *et al.* 1998), while the rooted phanerogam community had almost disappeared (Piccoli 1998). The Redfield C:N:P ratio (106:16:1) was used for the stoichiometric calculations.

During 1997, an expected *DDIN* of 0.02 mmol m^{-2} d^{-1} was calculated for the Valli di Comacchio lagoons by multiplying the observed *DDIP* by the N:P ratio of the organic matter mineralised. The difference between the observed and expected *DDIN* was considered as the net ecosystem nitrogen fixation minus denitrification (*nfix-denit*). In the Valli di Comacchio lagoons, (*nfix-denit*) was -0.2 mmol m^{-2} d^{-1}, indicating that denitrification losses dominate over nitrogen fixation inputs.

These results indicate that denitrification dominates despite the relatively high densities of N_2-fixing cyanobacteria (up to 300 cells ml^{-1} of *Synechococcus* sp.) in the lagoon. High denitrification rates can occur in these lagoons as indicated by low concentrations of DIN in the water column although no estimations of denitrification rates are available for this system.

The net ecosystem metabolism NEM or (*p-r*) was calculated from *DDIP* values considering the C:P ratio of the mineralised organic matter. During the investigated period (*p-r*) was negative indicating a net mineralisation of organic matter even if the value estimated was very low (-0.1 mmol m^{-2} d^{-1}). Thus, the Valli di Comacchio lagoons can be considered as slightly heterotrophic in terms of total net metabolism.

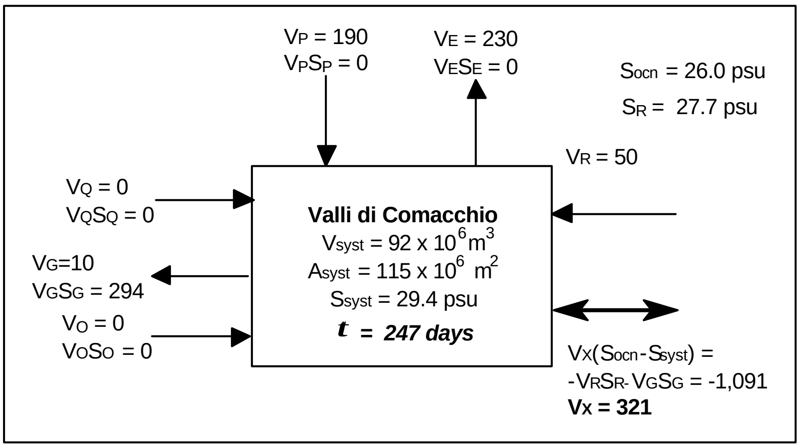

Figure 4.6. Water and salt budgets for Valli di Comacchio Lagoon for 1997. Water fluxes in 10^3 m^3 d^{-1} and salt fluxes in 10^3 psu m^3 d^{-1}.

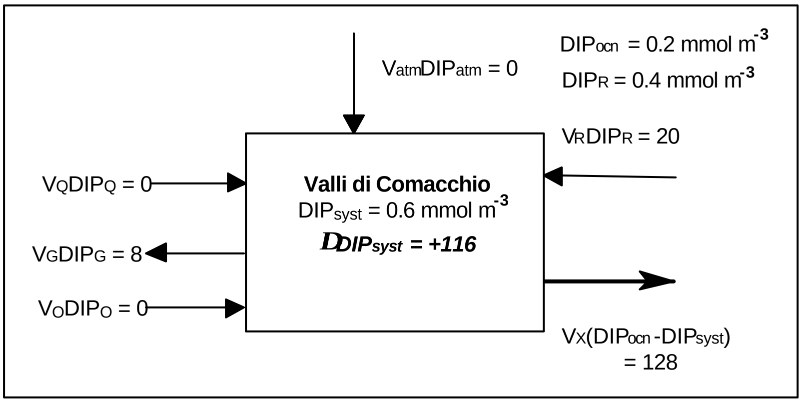

Figure 4.6. DIP budget for Valli di Comacchio Lagoon for 1997. Fluxes in mol d^{-1}.

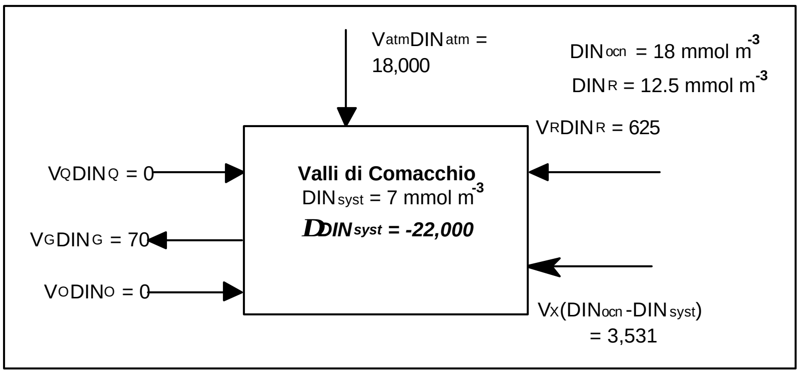

Figure 4.7. DIN budget for Valli di Comacchio lagoon for 1997. Fluxes in mol d^{-1}.

4.3 Valle Smarlacca Lagoon (sub system of the Valli di Comacchio lagoons)

G. Giordani and P. Viaroli

Summary

Water and nutrient budgets were calculated for Valle Smarlacca, a small and shallow Italian lagoon, using a single box–single layer model. This lagoon is used for aquaculture and water fluxes are artificially regulated with two replacements per year of approximately half the water volume, in October and February. In spring and summer the lagoon is completely isolated except for small water inputs to compensate for evaporation. In 1997, DIP inputs were largely dominated by groundwater inputs from a well, which was used to warm the intensive fish breeding ponds. DIN input from brackish water pumped from the Reno River was slightly higher than DIN input from groundwater. Due to the peculiar hydrology, the mean water exchange time estimated for the 1997 approximates to a year and water exchange time is particularly long in spring and summer (1,060 and 430 days, respectively). In 1997 the Valle Smarlacca acted as a sink for both DIN and DIP since the output was lower than the total input, so the system can be considered autotrophic with a net production of organic matter of about 2 mmol C m^{-2} d^{-1} in autumn and winter. For the spring and summer months, the system seems to be regulated by a rapid turnover and internal nutrient sources; net ecosystem metabolism was close to zero. Denitrification dominated over nitrogen fixation since (*nfix-denit*) was negative for the whole of the investigated period (-0.3 to -0.8 mmol N m^{-2} d^{-1}, average of -0.5 mmol N m^{-2} d^{-1}). Independent measurement for gross denitrification rates in the system (0.05 to 0.25 mmol N m^{-2} d^{-1}) is within the same magnitude of the net denitrification estimated by the LOICZ approach.

Study area description

The Valle Smarlacca Lagoon is located on the north-western Adriatic coast of Italy, in the Emilia-Romagna region (Figure 4.8).

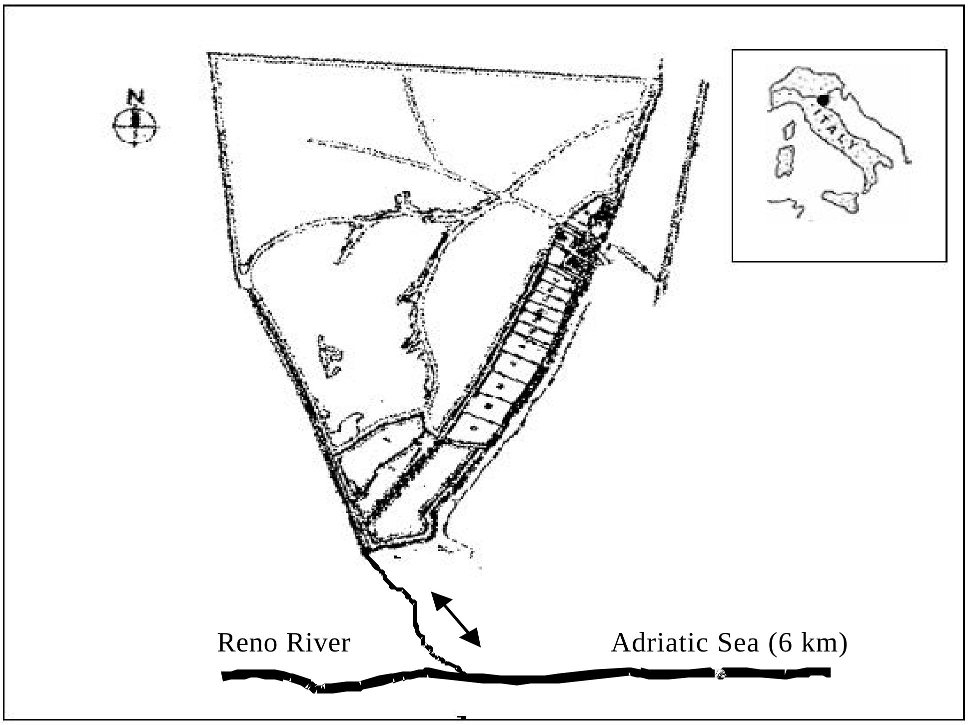

Figure 4.8. Map and location of the Valle Smarlacca Lagoon.

The lagoon is part of the Valli di Comacchio lagoonal system (44.58°N, 12.23°E), a wide complex of shallow water impoundments covering 115 km^2 (see the Valli di Comacchio, this report). The Valle Smarlacca Lagoon is located in the south-east corner of Valli di Comacchio, close to the Reno River. It has surface area of 2 km^2 and a mean water depth of 0.8 m. The surficial sediment is mainly composed of organic-rich silts. This organic layer is 10-20 cm thick and overlies a deeper clay layer. The salinity is relatively stable (22 to 24 psu) but can rise to 25-30 psu in summer due to evaporation. The lagoon is surrounded by embankments and is completely separated from the other lagoons of the Valli di Comacchio system. The Valle Smarlacca receives freshwater and nutrient inputs from the adjacent Reno River through artificially-regulated sluices and from a well by which groundwater is pumped into the lagoon.

The lagoon is exploited for fish farming of european seabass (*Dicentrarchus labrus)* and gilthead seabream (*Sparus auratus)*. The aquatic phanerogam *Ruppia cirrhosa* forms patchy meadow, alternating between areas of dense canopy and areas devoid of plants.

The lagoon is regularly subjected to dystrophic crises during summer, a phenomenon widely described in other European shallow water lagoons. During the warmest summer months, the emerging *Ruppia* fronds become covered by dense tufts of epiphytic algae, whose decomposition leads to a significant oxygen uptake as well as sulphide accumulation in the water column.

The climate is mediterranean with some continental influence. Precipitation is approximately 600 mm per year, with late spring and autumn peaks. However, this pattern is undergoing significant changes with an increase of short-term intense events.

The data set used is from the year 1997 and was obtained during the ELOISE Projects "NICE-nitrogen cycling in estuaries" and "ROBUST: the role of buffering capacities in stabilising coastal lagoon ecosystems".

From January to December 1997, water samples were collected in the central part of the lagoon and analysed for nitrate, nitrite, ammonium, dissolved reactive phosphorus by standard procedures (Dalsgaard *et al*. 2000). Macrophyte biomasses, primary production, benthic fluxes of oxygen and nutrients, denitrification rates and sulphur, phosphorus, iron and nitrogen were also investigated (Hejis *et al.* 2000; Azzoni *et al.* 2001; Bartoli *et al.* 2001).

Air temperature and wet deposition data were obtained from the meteorological network of the Province of Ferrara. Hydrochemical data for the Reno River were directly measured and for Adriatic Sea stations are reported in ARPA-DAPHNE (1998).

Water and salt balance

The water budget of the Valle Smarlacca Lagoon was calculated on a seasonal basis, using a single box–single layer model since this lagoon is small and shallow.

The lagoon exchanges water with the Reno River through a pumping station, which is artificially regulated depending on aquaculture requirements. Every February the water level of the lagoon is lowered by 50-60 cm to force the fish to move to the deepest point of the lagoon for harvesting. Following fish collection, the pumping station is activated and water is pumped from the Reno River into the lagoon to restore the water level. The pumping station is activated mainly at high tide when the salt wedge in the Reno River reaches the canal which connects the river to the lagoon. The water collected by the pumping station is normally brackish since the salinity of the water moving from the sea is higher than the freshwater of the Reno River, which is heavily polluted. From spring to summer the lagoon is isolated from the Reno River, with only occasional inputs from the pumping station to compensate for evaporation losses. In October the water level is lowered again for the second annual fish harvest and subsequently the normal water level is restored by pumping brackish water from the

Reno River in the lagoon. Due to these constraints, it is not possible to calculate a water budget based on salinity variations in the lagoon water.

The bottom of the lagoon is composed of a thick layer of clay which is not permeable to groundwater, but in late autumn and in winter when the temperature is lowest, "warm" groundwater (14°C) is pumped from a well into the intensive fish farming ponds and it then flows into the lagoon. This groundwater is rich in dissolved inorganic P (54 µM) and ammonium (1,250 µM) of fossil origin and is an important source of nutrient input, inducing intense blooms of phytoplankton in the following spring (chlorophyll-a up to 330 µg L^{-1}).

Precipitation data (V_P) for 1997 were obtained from the Meteorological Station and evaporation (V_E) was calculated by the Hargreaves equation. V_E and V_P were similar on an annual basis even evaporation exceed precipitation in spring and summer while precipitation dominated in autumn.

Since all the water fluxes except evaporation and precipitation are completely artificially regulated some assumptions were made. Firstly, the water volume input and output of the lagoon in the fishing periods were calculated by multiplying the water level changes by the lagoonal surface area. Secondly, since the water inputs and the water outputs are temporally separated and no exchanges of water occurs between the River and the lagoon, the mixing volume (V_X) was considered to be zero. In the budgets, V_Q indicates the brackish water input from the Reno River, V_G the groundwater input from the well and V_R the water export from the lagoon via the pumping station. For these reasons the salt budget was not calculated.

The seasonal water budgets are summarised in Table 4.8. Mean daily water inputs and outputs were extremely small, compared to the volume of the lagoon and consequently the estimated water exchange time (t) was very long, more than a year. On a seasonal basis, t is very long in spring when the pump does not operate. A lower water exchange time was estimated for summer due to higher evaporation rates and the water pumped in from the river to compensate for evaporation losses. In winter and autumn water exchange time was approximated 4 months.

Table 4.8. Seasonal water budgets of the Valle Smarlacca lagoon in 1997. Mixing volume (Vx) was considered zero.

Season	V_Q	V_G	V_P	V_E	V_R	t
	(10^3 m^3 d^{-1})					(days)
Jan-Feb-Mar	11.6	0.6	1.9	-1.9	-12.2	130
Apr-May-Jun	1.5	0.0	3.8	-5.3	0.0	1,060
Jul-Aug-Sep	3.7	0.0	2.7	-6.4	0.0	430
Oct-Nov-Dec	11.4	0.6	3.9	-1.9	-14.0	114
Annual	7.1	0.3	3.1	-3.9	-6.6	434

Budgets of nonconservative materials

DIP balance

Since no data on dry deposition was available, atmospheric DIP inputs were assumed to be zero. On an annual basis, the DIP exchanges were very low and nonconservative flux of DIP (*DDIP*) averaged -0.01 mmol m^{-2} d^{-1}. The main DIP sources were the groundwater inputs pumped from the well, which were about 7 times higher than the surficial inputs. In spring and in summer, DIP concentrations in the water column were below the detection limit of the method (0.1 µM) for most of the time (Table 4.9). This is in agreement with the low inputs reported for these periods and with the high metabolic activity of the biotic community composed mainly of rooted phanerogams, epiphytes, macroalgae and phytoplankton which need P for growth. *DDIP* was very low, close to zero in spring and summer, and reached values of -0.02 mmol m^{-2} d^{-1} in winter and autumn when DIP inputs were close to 40 mol d^{-1}. *DDIP* was negative for the whole period investigated, indicating that the lagoon acts as a net sink of DIP. The seasonal dissolved inorganic phosphorus (DIP) budgets are reported in Table 4.10.

Table 4.9. Nutrient concentrations for the Reno River, groundwater and lagoon.

SEASON	DIP_Q	DIP_G	DIP_{sst}	DIN_Q	DIN_G	DIN_{atm}	DIN_{syst}
	(mmol m^{-3})						
Jan-Feb-Mar	0.9	54	1.1	100	1,250	97	45
Apr-May-Jun	0.9	54	0.1	100	1,250	97	9
Jul-Aug-Sep	0.9	54	0.1	100	1,250	97	17
Oct-Nov-Dec	0.9	54	0.3	100	1,250	97	19
Annual	0.9	54	0.4	100	1250	97	23

Table 4.10. Seasonal DIP budgets of the Valle Smarlacca Lagoon.

Season	V_QDIP_Q	V_GDIP_G	V_RDIP_R	*ΔDIP*	
	(mol d^{-1})			(mol d^{-1})	(mmol m^{-2} d^{-1})
Jan-Feb-Mar	10	32	-13	-29	-0.02
Apr-May-Jun	1	0	0	-1	0.00
Jul-Aug-Sep	3	0	0	-3	0.00
Oct-Nov-Dec	10	32	-4	-38	-0.02
Annual	5	16	-2	-19	-0.01

DIN balance

The seasonal dissolved inorganic nitrogen (DIN) budgets are reported in Table 4.11. The main DIN inputs to the lagoon were the brackish water inputs from the Reno River, groundwater from the well and precipitation. In contrast to the DIP budget, surficial DIN inputs dominated over groundwater inputs on an annual basis even if they were of the same order of magnitude. DIN inputs were dominated by ammonium in both the surficial and ground water sources. Ammonium was also the dominant nitrogen species in the water column of the lagoon (60-90%) during the investigated period. DIN peaks (up to 67 µM) were measured in winter and autumn when DIN inputs were approximately $2x10^3$ mol d^{-1}. As with DIP, DIN concentrations in the water column of the lagoon decreased in spring and summer attaining values of 3 and 6 µM for nitrate and ammonium, respectively. *ΔDIN* was negative for the whole period investigated, especially in autumn and winter, indicating that the lagoon acted as a net sink for DIN.

Table 4.11. Seasonal DIN budgets of the Valle Smarlacca Lagoon.

Season	V_QDIN_Q	V_GDIN_G	$V_{atm}DIN_{atm}$	V_RDIN_R	*ΔDIN*	
	(mol d^{-1})				(mol d^{-1})	(mmol m^{-2} d^{-1})
Jan-Feb-Mar	1,160	750	184	-275	-1,819	-1.0
Apr-May-Jun	150	0	369	0	-519	-0.3
Jul-Aug-Sep	370	0	262	0	-632	-0.3
Oct-Nov-Dec	1,140	750	378	-133	-2,135	-1.1
Annual	570	375	301	-68	-1,178	-0.6

Stoichiometric calculations of aspects of net system metabolism

On an annual basis, the lagoon can be considered a net autotrophic system since the negative *DDIP* values calculated can be considered as an estimate of net DIP assimilation for organic matter production, as indicated in the LOICZ procedure. The annual average of the net ecosystem metabolism (NEM) taken as the difference between ecosystem production and respiration (*p-r*), was +1 mmol C m^{-2} d^{-1} in 1997, assuming production of organic matter with a Redfield C:N:P ratio. Results of the seasonal budgets are summarised in Table 4.12. NEM values of +2 mmol C m^{-2} d^{-1} were estimated for the autumn and winter months when nutrient inputs were high, while negligible values were estimated for the spring and summer periods. In the spring and summer months, the lagoon is almost completely isolated, water column DIP and DIN concentrations are very low and biological activity is driven by the rapid recycling of nutrients and internal nutrient sources. Thus, whilst imports and exports of material are practically zero, there is an extremely high level of biological activity within the lagoon and large movements of nutrients between the ecosystem compartments. The low observed NEM values indicated good balance between production and respiration in the system which would agree with the high coupling between P-regeneration and primary production.

Table 4.12. Seasonal variation of $DDIN_{exp}$, (*nfix-denit*) and net ecosystem metabolism (*p-r*) in the Valle Smarlacca in the 1997.

Season	$DDIN_{exp}$	(*nfix-denit*)	(*p-r*)
	(mmol m^{-2} d^{-1})		
Jan-Feb-Mar	-0.3	-0.7	+2
Apr-May-Jun	0.0	-0.3	0.0
Jul-Aug-Sep	0.0	-0.3	0.0
Oct-Nov-Dec	-0.3	-0.8	+2
Annual	-0.2	-0.4	+1.1

In these months, the net production of organic matter, which was dependent on internal nutrient sources and the primary producers' internal nutrient reserves, if calculated using the LOICZ model was below +0.1 mmol C m^{-2} d^{-1}. However, estimates based on DIP concentrations in the water column can hardly be considered significant for budgeting, as these concentrations were below the detection limits of the method for much of this period. This is due to the strong coupling between P-regeneration rates and primary production, as sediment to water column fluxes of phosphate can be significant (Heijs *et al.* 2000).

The $DDIN_{exp}$ values indicated in Table 4.12 were calculated by multiplying the *DDIP* by the Redfield N:P ratio and (*nfix-denit*) was calculated from the difference between observed and expected *DDIN*. In the Valle Smarlacca lagoon, losses via denitrification appear to be dominant since (*nfix-denit*) was always negative (Table 4.12). Nitrogen fixation was not a quantitatively important process in the N-budget of this lagoon since (*nfix-denit*) is in relatively good agreement with denitrification rates measured in the same year at a single station in the lagoon, which ranged between 0.05 and 0.25 mmol m^{-2} d^{-1} (Bartoli *et al.* 2001). The latter result is somewhat unexpected since the rooted phanerogam meadows generally exhibit high nitrogen fixation rates and net N-inputs (Welsh 2000). However, this result should be considered with caution, particularly in spring and in summer, since it is based on low DIP inputs, on a Redfield N:P ratio which can not be representative of the heterogeneous organic matter produced and decomposed in the lagoon (phanerogams, epiphytes, macroalgae, plankton, fish food) and on denitrification rates measured at a single station and extrapolated to the whole lagoon. Moreover the patchy distribution of rooted phanerogam meadows has to be considered.

Salento subregion (Apulia, southern Italy)

Apulia is a region of about 19,000 km^2 in the south-east of Italy. The Salento Peninsula extends from the Otranto Channel (Adriatic Sea) to Taranto Gulf (Ionian Sea). The landscape consists mainly of horizontal lines and gentle contours, which sometime take on the appearance of hills (Murge Salentine). These forms are due to large expanses of limestone rocks in vast horizontal or sub-horizontal strata. As a result there are few surficial runoffs, streams or rivers, and considerable karst phenomena. On the other hand many wetlands occur along the coast. The are covered by wetlands has greatly reduced in the last 50 years; now, Lake Alimini is the largest coastal lake in the region. The Salento Penisula has a Mediterranean climate, with mild wet winters and hot dry and windy summers. The precipitation, falling mainly in winter, is somewhat low, with a mean of only 620 mm $year^{-1}$ over the last 30 years. Average annual temperatures range from 10 ºC in winter to 30 ºC in summer.

Salento is a heavily-populated region and tending to increase. Currently, the population density is about 250 ind./km^2. Agricultural production is remarkable, particularly for grapes and olives, which don't require very fertile land. The industrial sector is highly developed, mainly around the cities of Taranto and Brindisi.

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4.4 Lake Alimini Grande, Lecce

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Summary

Lake Alimini Grande is a brackish lake located on the Adriatic coast of southern Italy, 40 km south of Lecce. Physical and chemical features of the lake studied from September 1998 to September 1999 were used to calculate seasonal and annual budgets using a single box, single layer LOICZ model. Rainfall data were recorded at a field station on the lake shoreline and compared with the long-term time series data collected from two pluviometric stations close to Lake Alimini Grande. Freshwater inputs showed a strong seasonal variability, and the estimated water exchange time varied accordingly. Estimated water exchange time varied from approximately a month (i.e., 40 days) during autumn to more than a year during summer. Summer budgets were calculated applying non-steady state of salt between seasons because the data collected in the summer led to negative *Vx* values when steady state was assumed. As regards to the nutrient balance, the lake was neither a net sink nor source for dissolved inorganic phosphorous (DIP); ΔDIP is effectively 0. The lake was slightly a sink of dissolved inorganic nitrogen (DIN). Net ecosystem metabolism [NEM or (*p-r*)] is 0, suggesting a good balance between production and respiration of organic materials. Denitrification prevailed over nitrogen fixing [(*nfix-denit*)<0].

Study area description

Lake Alimini is located on the Adriatic coast of southern Italy (40.19°-40.22°N, 18.44°-18.46°E; Figure 4.9). It consists of two basins, Lake Alimini Grande and Lake Alimini Piccolo (or "Fontanelle"), connected through a natural canal 1.5 km long, called the "Strittu". The two lakes represent the last residual edges of a long system of wetlands of the Apulian region of Italy. Their importance is internationally recognised because the lakes lie along a principal migratory route of many birds (Tursi 1989).

The two lakes are divided by a dam and have different hydrological characteristics. Alimini Grande is a brackish lake, whereas Alimini Piccolo is a freshwater lake fed by groundwater through many springs called "fonti" (in Italian), hence the nickname "Fontanelle" for the lake.

The objective of this paper was to determine the water, salt and nutrient budgets of Lake Alimini Grande by applying the LOICZ budget modelling approach (Gordon *et al.* 1996).

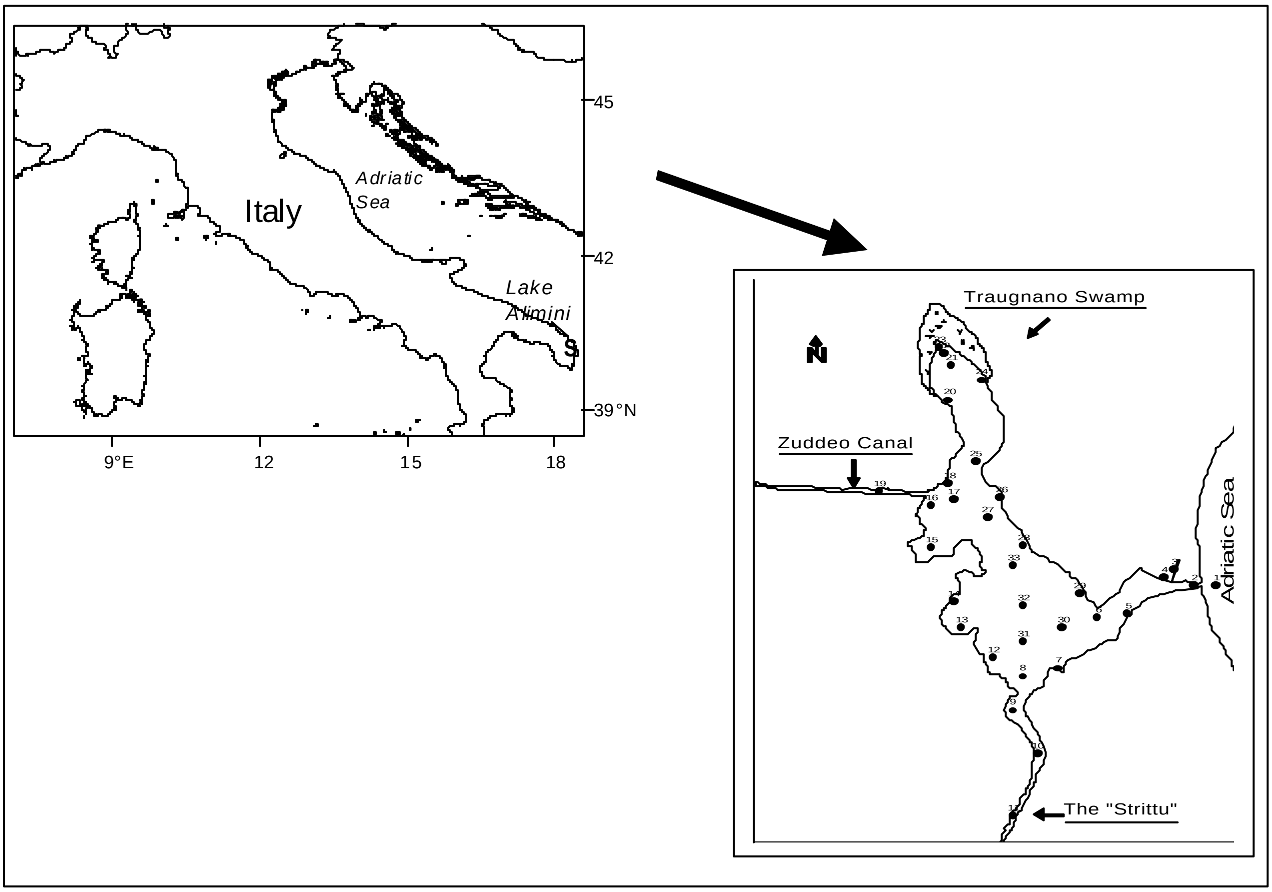

Figure 4.9. Map of Lake Alimini Grande with the sampling stations marked.

The data used in the model were collected from September 1998 to September 1999 at 33 sampling sites distributed throughout the lake and at the connections between the lake and its input and output environments (Strittu Canal, Zuddeo Canal, Traugnana Swamp and Adriatic Sea; Figure 4.9). In this study, the freshwater Lake "Fontanelle" is considered one of the input environments of Lake Alimini Grande through the "Strittu" Canal. Lake Alimini Grande has a surface area of 1.4 km^2, an average depth of 1.5 m and a volume of 2.1×10^6 m^3. The main freshwater inputs enter the lake from the "Strittu" Canal, from the Zuddeo Canal and from the Traugnano Swamp. On average, 64% of the freshwater inputs come from the Zuddeo Canal, 30% from the Strittu and 5% from the Traugnano Swamp. The freshwater fluxes vary seasonally since in the Apulian region is very hot and dry during summer. Consequently, water salinity also changes seasonally in Lake Alimini Grande (33.6 ± 1.1 psu during summer and early fall and 22.0 ± 1.5 psu during winter).

Lake Alimini Grande is connected with the sea through its mouth (Figure 4.9), and is subject to level variations linked to the tidal exchanges. These exchanges are affected by the low tide excursion occurring in the southern Adriatic Sea and by the efficiency of communication with the sea, which is frequently low due to the formation of sand dams.

Primary producers in Lake Alimini Grande are restricted to phytoplankton and littoral macrophyte guilds (submerged macrophytes occur at a very low density and only locally). The littoral macrophyte guilds are dominated by the reed *Phragmites australis.* Data collected during this study suggested the occurrence of a strong phosphorus limitation of primary production in Lake Alimini Grande. Phosphorus limitation was supported by the results from field manipulations (Basset *et al*. 2001) and by the very high N_{TOT}/P_{TOT} ratios (N_{TOT}/P_{TOT} = 134; Basset, Fiocca and Negro, unpublished) both in the lake and in the catchment area (mean value of phosphorus 0.2 µM; mean value of nitrogen 71 µM). However, water and sediment chemistry, phytoplanktonic biomass and water transparency, which are commonly used as trophic state indicators, supplied contrasting evidence. The rate at which nutrients are renewed in the water column (Basset *et al.* 2001) suggested eutrophic conditions for the lake.

From September 1998 to September 1999, water samples were collected from 29 stations within the lake and from 4 stations located in its input or output environments (Strittu, Zuddeo and Traugnano canals and the adjacent sea). Water salinity, nitrate, nitrite, ammonium and phosphorus concentrations were determined using standard procedures. Dissolved reactive phosphorus absorbance was measured with a 10 cm cell in order to increase standard method sensitivity, since phosphorus concentration was very low in the lake. Primary production and phytoplankton, macrophyte and seston biomass were also investigated. Air temperature and rainfall data were obtained from a meteorological station on the lake shoreline. Evaporation data were calculated by the Hargreaves equation.

<u>*Water and salt balance*</u>

In Lake Alimini Grande, the major freshwater inputs are derived from the three canals (Strittu, Zuddeo and Traugnano, V_Q) and from direct precipitation into the system (V_P). Evaporation (V_E) is the only freshwater output from Lake Alimini Grande.

In the study year, direct rainfall to the lake was 542 mm. This value is within the 95% confidence interval of the annual average for the region computed for a 30-year time series (1960-1990). Rainfall showed a strong seasonal pattern, with a very dry summer period. Evaporation largely exceeded precipitation during the dry season (spring and summer, Figure 4.10).

The water and salt budgets for seasonal and annual budgets are shown in Table 4.13. Net export of water from the lake to the sea, indicated by negative residual flow (V_R), was observed in the autumn, winter and spring.

Table 4.13. Seasonal water flux, salinity and water exchange time for Lake Alimini Grande in 1998-99. * indicates data calculation involved non-steady state of salt budget between seasons.

Season	V_Q	V_P	V_E	V_R	**S**			

Season	V_Q	V_P	V_E	V_R	S_{syst}	S_{sea}	V_X	t
	(10^3 m^3 d^{-1})				(psu)		(10^3 m^3 d^{-1})	(days)
Autumn	6.8	4.6	-1.8	-9.6	30.4	38.0	43.2	40
Winter	7.2	2.1	-1.5	-7.8	23.2	38.2	15.9; 13.3*	89
Spring	4.7	1.0	-2.3	-3.4	28.0	37.9	11.3; 11.9*	143
Summer	2.5	0.4	-3.1	+0.2	33.2	38.3	-1.4; 2.7*	656*
Annual*	5.3	2.0	-2.2	-5.2	28.7	38.1	18.4	232

In the summer, a net import from the sea to the lake was observed (V_R was positive). The highest negative residual flow values were observed in winter and autumn during the rainy period. The V_X values, which indicate the mixing volume between the lake and the sea also showed a maximum in the autumn season. During summer the total freshwater input into the lake was lower than evaporation, which requires a net inflow of seawater from the adjacent sea to conserve the water volume of the system. Despite the positive residual flow, the salinity of the system remained lower than the adjacent seawater salinity. In theory, it could depend both on the occurrence of groundwater inputs and on a very low efficiency of water exchange with the sea. The latter seems likely to be the case in Lake Alimini Grande. Groundwater inputs are very unlikely in Lake Alimini Grande, since in Lake Alimini Piccolo, which is certainly fed by groundwater, water levels decreased 30-cm during August; on the other hand, the efficiency of the lake mouth was greatly reduced during that month by artificial sand dams, related to tourist activity in the area. Since it was not possible to develop a steady state salt budget in the summer because salinity remained lower in the system than in the adjacent sea despite the net inflow of seawater from the adjacent sea, a non-steady state salt budget between seasons was applied to derive V_X in the summer. Mixing volumes calculated from non-steady state and other data derived using the non-steady state of salt are indicated in the tables with asterisk (*). V_X* for the winter and spring were also calculated as non-steady state and compared with the Vx calculated as steady state.

Using the salt balance equation:

$$\frac{(V_{syst} dS_{syst})}{dt} = \overline{V}_Q \overline{S}_Q + \overline{V}_X (\overline{S}_{ocn} - \overline{S}_{syst}) + \overline{V}_R \overline{S}_R$$

At non-steady state, $\frac{(V_{syst} dS_{syst})}{dt} \neq 0$ which is the change of salt in the system between two seasons (e.g., season1 and season2) and where the parameters with over-bar are the averages of parameters of season1 and season2.

$\overline{V}_X$ is then calculated as:

$$\overline{V}_X = \frac{(V_{syst} dS_{syst}) / dt - \overline{V}_Q \overline{S}_Q - \overline{V}_R \overline{S}_R}{(\overline{S}_{ocn} - \overline{S}_{syst})}$$

Mixing volume of season2 (V_{X2}*) is then calculated as

$$V_{X2}* = 2\overline{V}_X - V_{X1}$$

where V_{X1} is the mixing volume of season1.

Mixing volume derived from non-steady state in winter and spring did not vary much with that calculated from steady state. V_X* in the summer was relatively low compared to the other seasons.

Expected water exchange time was short in the autumn and winter seasons (40 days in autumn and 89 days in the winter) with respect to spring (143 days). Water exchange time in the summer calculated as non-steady state was more than a year. Annual water exchange time for Lake Alimini Grande was 232 days as the average of the seasonal estimates.

<u>*Budgets of nonconservative materials*</u>

DIP balance

The DIP content of the system and of its input and output environments are reported in Table 4.14 and annual and seasonal budgets for DIP are reported in Table 4.15.

Table 4.14. Seasonal and average annual nutrient concentrations for the river, Lake Alimini Grande lagoon and adjacent sea.

Season	DIP_Q	DIP_{syst}	DIP_{sea}	DIN_Q	DIN_{syst}	DIN_{sea}
	(mmol m^{-3})					
Autumn	0.15	0.03	0.01	172	36	16
Winter	0.12	0.06	0.07	221	90	23
Spring	0.19	0.10	0.01	184	73	20
Summer	0.1	0.04	0.01	36	71	14

Mean values of DIP were not statistically higher in the system than in the sea (0.06 ± 0.03 µM - Lake Alimini Grande; 0.03 ± 0.03 µM – sea- Table 4.14). These values were very low, suggesting an oligotrophic state for both Lake Alimini Grande and the Southern Adriatic Sea, which is in agreement with published data on the water chemistry and trophic state of the southern Adriatic Sea (e.g., Socal *et al.* 1999) but which is not supported by values of other trophic state descriptors observed in Lake Alimini Grande (Basset 2000).

Table 4.15. Seasonal DIP budgets for Lake Alimini Grande lagoon in 1998-99. * indicates data calculation involved non-steady state of salt budget between seasons.

Season	$V_Q DIP_Q$	$V_R DIP_R$	$V_X DIP_X$	*DDIP*	
	(mol d^{-1})			(mol d^{-1})	(mmol m^{-2} d^{-1})
Autumn	1.0	-0.2	-0.9	+0.1	0
Winter	0.9	-0.5	0.2	-0.6	0
Spring	0.9	-0.2	-1.0	+0.3	0
Summer*	0.3	0	-0.1	-0.2	0
Annual*	0.8	-0.2	-0.5	-0.1	0

The input of DIP to Lake Alimini Grande came from the freshwater canals. The largest input was observed in autumn, in correspondence with the highest concentration and major freshwater input from the catchment basin. The contribution to the DIP input by three canals, Zuddeo, Strittu and Traugnano was quite similar even though water discharges were very different.

From the DIP budget, *DDIP* of Lake Alimini Grande is effectively 0 for all seasons.

DIN balance

The DIN annual and seasonal budgets are reported in Table 4.16. The overall DIN input into Lake Alimini Grande is three-orders of magnitude larger than the DIP input, resulting in a strongly unbalanced N_{TOT}/P_{TOT} ratio. Nitrates are the dominant form of dissolved inorganic nitrogen in every season. The lake is a sink for DIN for the three seasons and a source for the summer. Overall, about 5% of the DIN entering the lake from the catchment basin is retained (i.e., *DDIN* is negative). While *DDIN* is small, it is different from zero.

Table 4.16. Seasonal DIN budgets for Lake Alimini Grande in 1998-99. * means calculation involved non-steady state of salt budget between seasons.

Season	$V_Q DIN_Q$	$V_R DIN_R$	$V_X DIN_X$	*DDIN*	
	(mol d^{-1})			(mol d^{-1})	(mmol m^{-2} d^{-1})
Autumn	1,170	-250	-864	-56	-0.04
Winter	1,591	-441	-1,065	-85	-0.06
Spring	865	-158	-599	-108	-0.08
Summer*	90	+9	-171	+72	+0.05
Annual*	929	-210	-675	-44	-0.03

Stoichiometric calculations of aspects of net system metabolism

According to the assumption of the LOICZ biogeochemical model, the *DDIP* values allow a direct estimate of the net energy budget of the system, determining whether the system is a net consumer [*DDIP*>0 and (*p-r*)<0] or a net producer [*DDIP*<0 and (*p-r*)>0] of organic matter. Lake Alimini Grande seems to balance primary production and respiration [*DDIP*=0 and (*p-r*)=0].

Since *DDIP* is 0, nitrogen fixation minus denitrification (*nfix-denit*) is equal to *DDIN*. For the all the seasons except summer in Lake Alimini Grande denitrification prevailed over nitrogen fixation [i.e., (*nfix-denit*) was negative]. Nitrogen fixing minus denitrification (*nfix-denit*) was positive in the summer. Annual (*nfix-denit*) for Lake Alimini Grande was negative, the system is net denitrifying.

Discussion and conclusion

Water and salt balance in Lake Alimini Grande indicated that the lake exports water to the adjacent sea during the autumn, winter and spring and imports water during summer. In the summer, using non-steady state equation for salt budget, water exchange time was very low which confirms the notion of low efficiency of water exchange at the lake mouth, due to ecosystem management related to tourists.

The nutrient budgets indicated that Lake Alimini Grande was a neither a net sink nor source for DIP and a net sink for DIN. On average (*nfix-denit*) was negative suggesting that, denitrification processes prevailed over fixation processes. The NEM equal to 0 suggested a low accretion rate of lake sediments, which represents a positive element, in terms of ecosystem health, of the potentially eutrophic Lake Alimini Grande.

Acknowledgements

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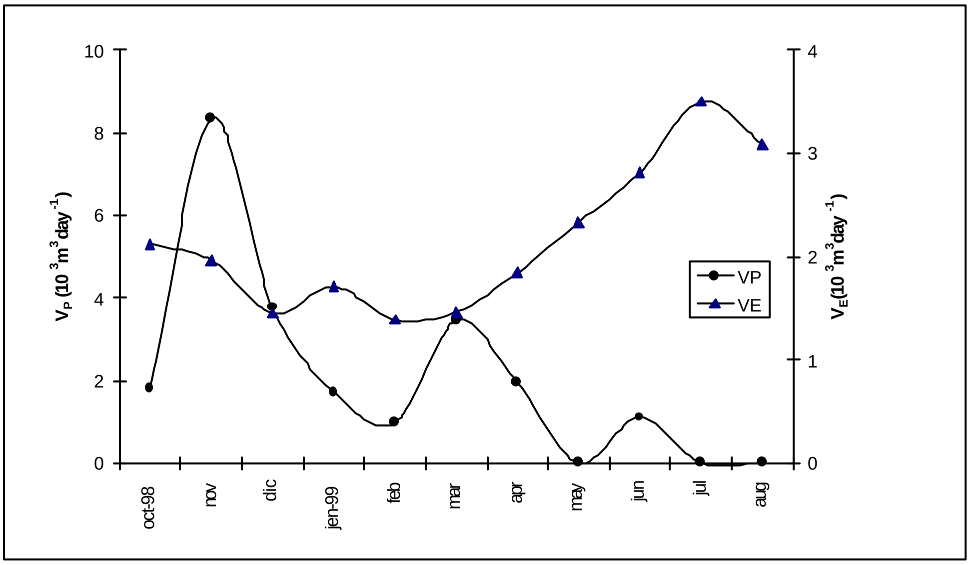

Figure 4.10. Annual trend of V_E and V_P values in Lake Alimini Grande during the study period.

Oristano province, Sardinia (Italy)

Sardinia is the second largest island (23,813 km^2) in the Mediterranean Sea.

The morphology of the island is the result of complex tectonic processes and volcanic activity in the Cenozoic era on a mass of Paleozoic rock upthrust from the sea, later severely affected by late Paleozoic orogenesis. Sardinian waterways (creeks, streams and rivers) are fast-flowing, with a relatively high water discharge in winter, reduced to a trickle in summer.

Many freshwater and saltmarsh ecosystems occur in the area. The River Tirso, which flows into the Gulf of Oristano, is the largest river of Sardinia; 159 km long with a catchment area of 3376 km^2. Cabras, Santa Giusta and S'Ena Arrubbia are the major saltmarsh lakes and coastal basins occurring in the area.

The climate is Mediterranean, with long hot dry breezy summers and short mild rainy winters, except at high altitudes. Average annual temperatures range from 18ºC along the coastal belt to 14ºC inland. Precipitation is largely confined to the winter months and distribution is somewhat irregular, with as much as 1,300 mm $year^{-1}$ in the highlands and 600mm $year^{-1}$ in the lowlands. Population density is of 59 ind. km^{-2}. The primary sector is still of outstanding importance, especially goat and sheep rearing (good production of cheese). The tourist sector is highly developed in Oristano province and is linked to its extraordinarily beautiful coastline. The principal industry consists of sugar refineries.

4.5 S'Ena Arrubia Lagoon, Oristano, western coast of Sardinia

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Summary

S'Ena Arrubia, an eutrophic lagoon situated on the west coast of Sardinia, Italy, was studied in 1994 and 1995. Four seasonal budgets per year were calculated using the single box–single layer model. The 1994 budgets are considered more representative of "normal" conditions for the lagoon since this period was characterized by water fluxes within the annual average values measured during the previous 10 years. Whilst, the 1995 budgets, due to low precipitation and low water exchanges, can be considered representative of particularly dry conditions. Estimated water exchange times averaged at about a month, but range from a few days during the rainy seasons to more than a year in dry periods. The lagoon acts as a sink for both dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN). Nitrogen metabolism appears to be highly nitrogen fixing, with an estimated net metabolism equivalent of +0.3-2.6 mmol m^{-2} d^{-1} (average of +1.1 mmol m^{-2} d^{-1}). In both years the system can be considered net autotrophic, (p-r) = 3-42 mmol C m^{-2} d^{-1}(average of +14 mmol m^{-2} d^{-1}).

Study area description

S'Ena Arrubia Lagoon is a shallow water body located on the coast of central west Sardinia (39.83° N, 8.67°E; Figure 4.11). The surface area is 2 km^2, the mean depth 0.4 m and the corresponding total volume is $8x10^5$ m^3. The lagoon is naturally affected by eutrophication, but in the last few years the trophic status has deteriorated, mainly due to large nutrient inputs leading to massive macroalgal and phytoplankton blooms. Freshwater flows into the lagoon from a pumping station (Idrovora Sassu) and two minor canals, and is conveyed through an internal artificial channel that connects the lagoon with the sea. Nutrient inputs are mainly due to domestic sewage and agriculture. The catchment area (90 km^2) coincides with a former wetland, which was reclaimed in the early 20th century. Nowadays, this area is exploited mostly for agriculture (maize and grasses) and dairy farming. This agricultural activity causes two principal problems. Firstly, there is a conflict for water use as the Sardinian climate is generally very dry. This gives rise to excessive use of water for irrigation (both ground- and surface water) and a drastic cut in freshwater flow in the summer months. As a consequence of this and the high summer temperatures there are frequent increases of salinity in the lagoon. Secondly, when the pumping station is working, the water flowing into the lagoon is very rich in nutrients, with peaks of 100 mmol m^{-3} of total phosphorus and 350 mmol m^{-3} of total nitrogen. Seaweeds cover almost 100% of the lagoon surface area with a pronounced monotony and a clear dominance of chlorophyceans. The lagoon is exploited for aquaculture, mostly mussels and European seabream.

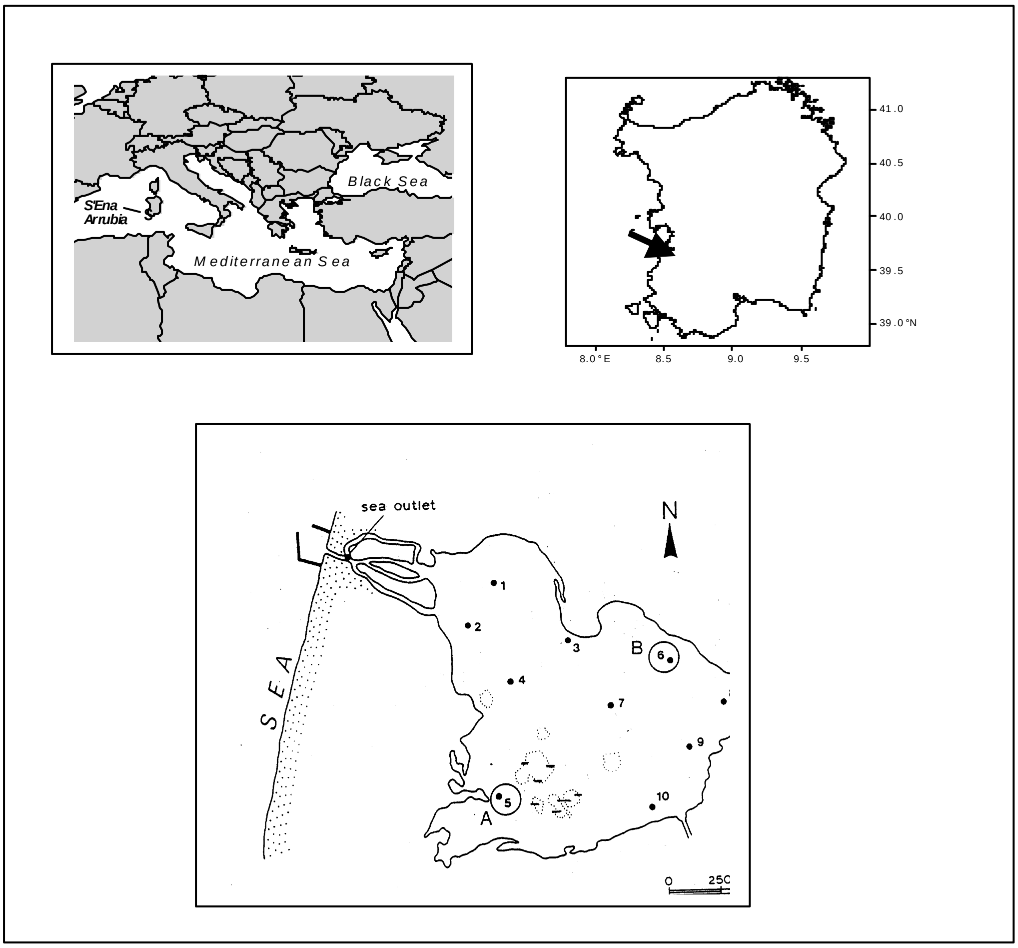

Figure 4.11. Location and map of the S'Ena Arrubia lagoon. Sampling sites are indicated.

The climate is mediterranean, with an average rainfall of about 500 mm per year. The main tributaries of the lagoon are the Idrovora Sassu channel and two minor canals: Santa Anna and Acque Medie. The first two drain a heavily exploited farming area (Piana di Arborea), the latter receives freshwater from the Tirso River during the flooding events.

From January 1994 to December 1995, water samples were collected in a grid of 10 stations within the lagoon, plus a station located just upstream of the pumping station and analysed for salinity, nitrate, nitrite, ammonium and dissolved reactive phosphorus, using standard procedures. Macrophyte biomasses, primary production, benthic fluxes of oxygen and nutrients were also investigated (Baroli *et al.* 1996; Bondavalli *et al.* 1996).

Air temperature, wet deposition and hydrological data were obtained from the Meteorological Station of the International Marine Centre (IMC, Torregrande, Oristano) and from Guerzoni *et al.* 1995. See Guerzoni *et al.* 1999 for a review of the depositions in Mediterranean area.

<u>*Water and salt balance*</u>

The water and salt budget of S'Ena Arrubia Lagoon was calculated using the single box–single layer model since this lagoon is small and shallow. The two years investigated (1994 and 1995) differed from the meteorological point of view. Precipitation in 1994 was within the average values of the previous 10 years (410 mm yr^{-1}) while 1995 was very dry with scarce rainfall (215 mm yr^{-1}). As described below, this difference heavily affected the water budget of the lagoon.

Using a particularly complete data set, budgets are calculated on annual and seasonal (3 months) basis for both years.

The main water input to the lagoon is the discharge of the pumping station (V_Q), which is the only input from the catchment area. The discharge of Acque Medie and Santa Anna canals was considered zero because they are dry for most of the year and when they are in flood, their discharge is negligible compared to that of the pumping station. The water collected by the pumping station is brackish due to an input of marine water upstream of the pumping station. Precipitation data (V_P) are obtained from the Meteorological Station and evaporation (V_E) was calculated by the Hargreaves' equation. Evaporation largely exceeds precipitation in spring and summer while similar fluxes were calculated in autumn and winter. No data are available for groundwater inputs which were therefore assumed to be zero.

The water seasonal budgets for 1994-95 are summarised in Table 4.17. Additionally, separate budgets were calculated for October-November and for December 1995 periods due to the different hydrological regimes: very dry during the first, followed by high rainfall in December.

Since inputs to the lagoon are of brackish rather than freshwater, S_Q values for S'Ena Arrubia are greater than zero (Table 4.17) and therefore salt budgets were calculated from the general equation:

$$dV_{syst}S_{syst}/dt = +V_QS_Q + V_PS_P + V_GS_G + V_OS_O + V_ES_E + V_RS_R + V_X(S_{ocn} - S_{syst})$$

assuming steady state conditions and that S_P, S_G, S_O and S_E were zero, the equation was reduced to:

$$0 = +V_QS_Q + V_RS_R + V_X(S_{ocn} - S_{syst})$$

and

$$V_X = -(V_QS_Q + V_RS_R)/(S_{ocn} - S_{syst})$$

Table 4.17. Seasonal water budgets, salinity and water exchange time of the S'Ena Arrubia lagoon. Water flux in 10^3 m^3 d^{-1}, salinity in psu and water exchange time (t) in days.

Season/months	V_Q	V_P	V_E	V_R	S_Q	S_{syst}	S_{ocn}	V_X	t
Jan-Feb-Mar 94	11.1	2.8	-2.7	-11.2	2.2	13.3	37.0	10.9	36
Apr-May-Jun 94	15.9	1.7	-6.5	-11.1	1.4	20.3	37.0	17.7	28
Jul-Aug-Sep 94	18.0	1.0	-6.7	-12.3	1.4	19.1	37.0	17.9	27
Oct-Nov-Dec 94	58.7	3.6	-2.5	-58.9	1.8	21.3	37.0	104.3	5
Jan-Feb-Mar 95	15.4	1.1	-2.5	-14.0	2.2	24.8	37.0	32.7	17
Apr-May-Jun 95	6.5	1.7	-6.6	-1.6	2.2	31.8	37.0	7.9	84
Jul-Aug-Sep 95	4.8	0.6	-6.7	+1.3	6.5	43.9	37.0	12.2	59
Oct-Nov 95	2.9	0.0	-3.0	+0.1	3.5	44.0	37.0	2.0	381
Dec 95	7.1	3.7	-1.8	-9.0	1.7	33.0	37.0	75.8	9

The year 1994 was characterised by a similar scenario during the first 3 seasons, while the autumn was characterised by higher water flows which reduced the estimated water exchange time from about a month to about 5 days. A constant net export of water from the lagoon to the sea, indicated by negative V_R was observed throughout the year. In 1995, water inputs were rare in winter and very low from July to November. The consequences are evident from the lower net water exports from the lagoon and the net import from the sea from July to November (V_R positive). High salinity values, up to 50 psu, were measured in the lagoon from August to October and the theoretical water residence time increased to more than a year. Normal conditions were recovered from December onwards, when rainfall started and the estimated mean water exchange time was reduced to about 9 days.

Budgets of nonconservative materials

Table 4.18 summarizes the seasonal concentrations of dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen in the river, S'Ena Arrubia lagoon and adjacent ocean. Nonconservative fluxes of DIP and DIN were derived from the water budget in Table 4.17 and nutrient concentrations in Table 4.18.

Table 4.18. Seasonal nutrient concentrations (in mmol m^{-3}) for S'Ena Arrubia lagoon.

Season	DIP_Q	DIP_{syst}	DIP_{ocn}	DIN_{atm}	DIN_Q	DIN_{syst}	DIN_{ocn}
Jan-Feb-Mar 94	20.1	1.9	0.02	46	169	12	5
Apr-May-Jun 94	22.2	5.6	0.02	46	168	3	5
Jul-Aug-Sep 94	20.5	4.8	0.02	46	93	4	5
Oct-Nov-Dec 94	19.4	2.6	0.02	46	128	3	5
Jan-Feb-Mar 95	23.9	4.7	0.02	46	94	18	5
Apr-May-Jun 95	35.2	8.6	0.02	46	150	5	5
Jul-Aug-Sep 95	43.4	13.4	0.02	46	49	1	5
Oct-Nov 95	81.0	6.2	0.02	46	64	1	5
Dec 95	104.0	7.3	0.02	46	26	4	5

DIP balance

Data for the seasonal DIP budgets for 1994-95 are reported in Table 4.19. Atmospheric DIP inputs were estimated by direct measurements conducted in the 1997 and estimated to be 0.7 mol per day which is negligible compared to the DIP input from the discharge (V_QDIP_Q).

In 1994, as for the water and salt budgets, similar scenarios were observed in the first three seasons while in autumn the maximal inputs of DIP were measured (more than 50% of the annual total). In 1995, the lower water fluxes led to high concentrations of DIP in the lagoon even though DIP inputs were lower than in 1994. Maximal 1995 inputs were observed in December coupled with the maximal annual water discharges from tributaries.

For the whole of the investigated period, S'Ena Arrubia lagoon acted as a sink for DIP since *DDIP* was always negative. Maximal negative values were measured in autumn 1994 in concurrence with the highest DIP inputs.

Table 4.19. Seasonal DIP budgets of the S'Ena Arrubia Lagoon.

Season	$V_Q DIP_Q$	$V_R DIP_R$	$V_X DIP_X$	$DDIP$	
	(mol d^{-1})			(mol d^{-1})	(mmol m^{-2} d^{-1})
Jan-Feb-Mar 94	223	-11	-20	-192	-0.10
Apr-May-Jun 94	353	-31	-99	-223	-0.11
Jul-Aug-Sep 94	369	-30	-85	-254	-0.13
Oct-Nov-Dec 94	1,139	-78	-269	-792	-0.40
Jan-Feb-Mar 95	368	-33	-153	-182	-0.09
Apr-May-Jun 95	229	-7	-68	-154	-0.08
Jul-Aug-Sep 95	208	+9	-163	-54	-0.03
Oct-Nov 95	235	0	-12	-223	-0.11
Dec 95	738	-33	-551	-154	-0.08

DIN balance

The data for the seasonal DIN budgets for 1994-95 are reported in Table 4.20. An average value of 46 μM for DIN for the precipitation was considered.

High DIN inputs, dominated by ammonium (73% of total DIN), were measured in autumn 1994. In the lagoon, DIN concentrations were maximal in winter of both years, in these cases, the dominant form was nitrate since ammonium concentrations were generally negligible. 1994 was characterised by higher DIN inputs and DIN_{syst} compared to 1995. Nonconservative flux of DIN (*DDIN*) was negative for the whole of the investigated period indicating a dominance of DIN removal processes (mainly assimilation) and the lagoon act as a net sink for DIN. As for *DDIP*, the maximal negative *DDIN* values were observed in autumn 1994.

Table 4.20. Seasonal DIN budgets of the S'Ena Arrubia Lagoon.

Season	$V_{atm}DIN_{atm}$	V_QDIN_Q	V_RDIN_R	V_XDIN_X	DDIN	
	(mol d^{-1})				(mol d^{-1})	(mmol m^{-2} d^{-1})
Jan-Feb-Mar 94	129	1,876	-95	-76	-1,834	-0.9
Apr-May-Jun 94	78	2,671	-44	+35	-2,740	-1.4
Jul-Aug-Sep 94	46	1,674	-55	+18	-1,683	-0.8
Oct-Nov-Dec 94	166	7,514	-239	+209	-7,650	-3.8
Jan-Feb-Mar 95	51	1,448	-161	-425	-913	-0.5
Apr-May-Jun 95	78	975	-8	0	-1,045	-0.5
Jul-Aug-Sep 95	28	235	+4	+49	-316	-0.2
Oct-Nov 95	0	186	0	+8	-194	-0.1
Dec 95	170	185	-41	+76	-390	-0.2

Stoichiometric calculations of aspects of net system metabolism

According to the assumption of the LOICZ Biogeochemical Model, the negative *DDIP* values can directly estimate DIP assimilation for the organic matter production. In this lagoon, the gap between DIP input and output is probably really related to the primary producer's uptake since the silico-clastic nature of the sediment and its low iron content should not permit high inorganic P adsorption (Lapointe *et al.* 1992; Golterman 1995). In fact the negative peak of *DDIP*, as well as for *DDIN*, was measured in autumn 1994 when a large phytoplankton bloom occurred, as indicated by high chlorophyll-*a* concentration (up to 100 µg l^{-1}) (Baroli *et al.*, 1996).

The lagoon was colonized by dense beds of floating macroalgae for most of the investigated period, with density peaks of up to 140 g DW m^{-2} (Baroli *et al.*, 1996). The measured N:P ratio's for the *Ulva curvata* thalli ranged from 10 and 35, although the mean value was close to the Redfield ratio which was used for all the following stoichiometric calculations (no data are available for C content of the macroalgae so Redfield CNP ratio of 101:16:1 was used) .

Results of the seasonal budgets are summarised in Table 4.21. The net nitrogen fixation minus the denitrification (*nfix-denit*) was calculated from the difference between the observed and expected *DDIN's*.

Table 4.21. Seasonal variation of (*nfix-denit*) and net ecosystem metabolism (*p-r*).

Season	$DDIP_{exp}$ (*mmol* m^{-2} d^{-1})	(nfix-denit) (*mmol* m^{-2} d^{-1})	(p-r) (*mmol* m^{-2} d^{-1})
Jan-Feb-Mar 94	-1.6	+0.7	+11
Apr-May-Jun 94	-1.8	+0.4	+12
Jul-Aug-Sep 94	-2.1	+1.3	+14
Oct-Nov-Dec 94	-6.4	+2.6	+42
Jan-Feb-Mar 95	-1.4	+0.9	+10
Apr-May-Jun 95	-1.3	+0.8	+9
Jul-Aug-Sep 95	-0.5	+0.3	+3
Oct-Nov 95	-1.8	+1.7	+12
Dec 95	-1.3	+1.1	+9

Expected *DDIN* was calculated by multiplying the *DDIP* by the N:P ratio of the organic matter produced.

In the S'Ena Arrubia lagoon, nitrogen fixation inputs appears to dominate over losses via denitrification, since (*nfix-denit*) was positive over the whole investigated period . In both years, (*nfix-denit*) was lower than 2 mmol m^{-2} d^{-1} except in autumn when values of up to 2.6 mmol m^{-2} d^{-1} were calculated. These estimated maxims appear to be somewhat unexpected, since the high DIN concentrations would depress nitrogen fixation rates and suggests that other processes may effect the calculations, for example luxury N-uptake by macroalgal would reduce their C:N ratio to below that of the Redfield ratio used in the calculations.

The net ecosystem metabolism NEM or (*p-r*) was positive for the whole investigated period, even during the dry season when salinity increased to very high values and water exchange was very low. Thus in this lagoon, the production of organic matter seems more efficient than its oxidation, therefore the S'Ena Arrubia lagoon can be considered as an autotrophic system. In 1994, which was considered as typical year with normal water fluxes, the first 3 seasons were quite similar ((*p-r*) about 12 mmol m^{-2} d^{-1}) while in autumn when nutrients inputs were maximal, the net ecosystem metabolism was about 4 times higher (42 mmol m^{-2} d^{-1}). In the next year, the low precipitation and the consequently stressed conditions due to high salinity, affected (*p-r*) values which were reduced to 3 mmol m^{-2} d^{-1} in summer; a partial recovery was observed close to the end of the year.

4. COASTAL SYSTEMS OF FRANCE

The western Mediterranean Sea

The Mediterranean Sea is generally shallow, with an average depth of 1,501 m. Undersea ridges stretch from Tunisia to Sicily, dividing the Mediterranean into eastern and western basins, and between Spain and Morocco at the sea's outlet to the Atlantic Ocean. The narrow Strait of Gibraltar is also extremely shallow, restricting circulation and greatly reducing the tidal range of the sea. These factors, coupled with the high rate of evaporation, make the Mediterranean considerably saltier than the Atlantic.

The Gulf of Lions, a continental margin in the north-west Mediterranean, extends along the coast of southern France from the Spanish border on the west to Toulon on the east, and its coastline includes the eastern Pyrenees, some lagoons, the Rhone delta and limestone hills. The cold air which sweeps from the Alps through the Rhone Valley becomes a cold, dry northerly wind, the mistral, in the Gulf.

5.1 Gulf of Lions

X. Durrieu de Madron, L. Denis, F. Diaz, N. Garcia, C. Guieu, C. Grenz, M.D. Loÿe -Pilot, W. Ludwig, T. Moutin and P. Raimbault

Study area description

The Gulf of Lions (42-44°N, 3-6°E) has a large crescent-shaped continental shelf (Figure 5.1). More than ten rivers with a total watershed area of about 125,000 km^2 deliver significant water discharges into the gulf. The Rhône River on the north-eastern part of the gulf delivers about 80% of the total riverine water inputs. The shoreline is largely urbanized (ca. 1.5 million inhabitants), with one of the largest French cities, Marseilles (800,000 residents), at the north-eastern tip of the shelf.

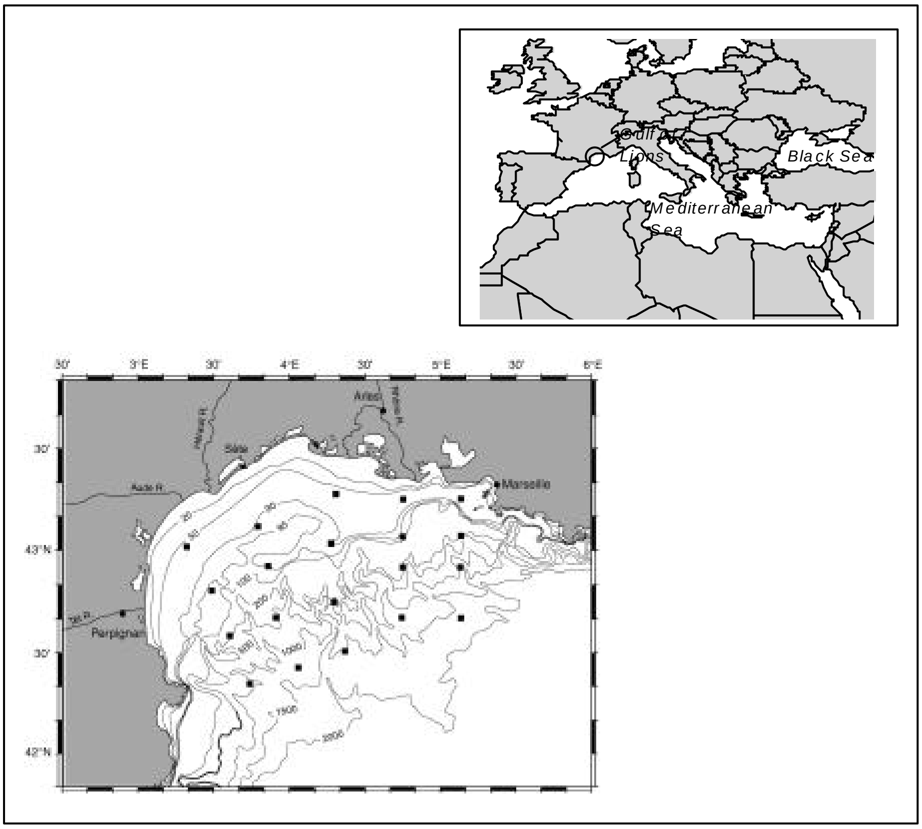

Figure 5.1. Map of the Gulf of Lions with the stations used to develop the budgets. The shelf region is delimited by the 200 m isobath.

The Gulf of Lions shelf has been the subject of intensive physical and biogeochemical oceanographic studies over the last 8 years. Water, salt, and nutrient budgets for the Gulf of Lions' shelf system were developed using data acquired in the French PNEC (Programme National Environnement Côtier) and European METRO-MED programs. Three surveys of the gulf were carried out in March and June 1988 and January 1999. Extensive data sets of dissolved inorganic and organic nutrients (NO_3^-, NO_2^-, NH_4^+ and PO_4^{-3}) were collected in combination with CTD data and studies of primary and new production (Diaz 2000; Raimbault 2000).

This work complements the carbon budgets (Durrieu de Madron *et al.* 2000; Sempéré *et al.* 2000) as well as the physical and biogeochemical modeling (Pinazo *et al.* 1996, Tusseau-Vuillemin *et al.* 1998; Diaz 2000) already performed for this area.

Freshwater and freshwater nutrient sources

Terrestrial sources of nutrients from sewage treatment waters, runoff and rivers bring significant supply of nutrients in the form of nitrate and phosphate to the gulf. Minas and Minas (1989) showed that the Rhone River inputs significantly enhance the primary productivity on the shelf.

Extensive water flux data are available for the Gulf of Lions' rivers, through the Compagnie Nationale du Rhône and the HYDRO data bank of the French ministry of environment. Dissolved inorganic nutrients (DIP, DIN) concentrations are available for all rivers through water agencies for the last 20 years. Dissolved organic nutrients (DOP, DON) concentrations are available only for the Rhône River. These values are used to extrapolate the river inputs of organic nutrients from all rivers. Freshwater inputs and DIN concentrations strongly decrease during the summer season (June-October) (Figure 5.2). Compared to the long term monthly average, DIP concentrations during the year 1998 are 2 to 4 times lower than the climatological average (Figure 5.2).

Significant discharges of treated sewage effluent occur at Marseilles. Although the water volume of sewage is small relative to other freshwater inputs, total N and P are highly concentrated in the effluent (data from the Service d'Assainissement of city of Marseilles, personal communication). We use the following stoichiometric ratios between the dissolved and total fractions: DIN:TN = 0.38 and DIP:TP = 0.5 (San Diego-McGlone *et al.* 2000) to estimates the discharges coefficients (water : 0.3 m^3 d^{-1} per person, DIP : 19 mmole d^{-1} per person, DIN : 419 mmole d^{-1} per person). Sewage discharges to the sea by the total population living along the coast (1.5 million) are evaluated using these discharge coefficients.

Evaporation and precipitation are estimated from a high-resolution re-analysis of the ECMWF model outputs made by the CERFACS in Toulouse (data from Siefridt *et al.*, personal communication). The net balance of precipitation and evaporation remains negative all year long, with rainfall decreasing during summer and evaporation decreasing during spring (Figure 5.3).

Aerosols transported to the Gulf of Lions consist of anthropogenic-rich "background" materials supplied continuously from the nearby land, upon which sporadic pulses of Saharan terrigenous dust are superimposed. Inorganic nitrogen is almost entirely anthropogenic (industrial combustion, vehicle traffic and intensive livestock breeding) and contributes to new production. Crustal inorganic phosphorus may represent half of total deposition but its solubility and bioavailability are uncertain. The only dry and wet atmospheric deposition of inorganic nitrogen for the Gulf of Lions region were measured in 1988-89 (Alarcon and Cruzado 1990; Loÿe-Pilot *et al.* 1991; Guieu 1991; Loÿe-Pilot *et al.* 1993). Likewise, the only recent atmospheric deposition of total phosphorus was measured at the atmospheric sampling station of Ostriconi in Corsica in 1999-2000. The DIP flux was estimated to represent 20% of the total atmospheric deposition (Ridame, personal communication 2001); this percentage is probably underestimated because a fraction of the dry deposition of anthropogenic origin will dissolve in seawater and so far, no data are available to quantify this dissolution.

Saltwater and marine nutrient sources

A cyclonic current that composes the northern branch of the general circulation in the western Mediterranean essentially drives the movement of the water masses. Whereas the main outer branch permanently flows south-westward along the slope (water flux about 1-2x10^6 m^3 sec^{-1}), a shallow branch of this current occasionally penetrates over the shelf under the effect of wind (Millot 1990; Estournel *et al.* submitted) and exchanges dissolved inorganic and organic nutrients between the ocean and the shelf. The hydrological structures present also a well-marked seasonality as a result of surface heat fluxes. In summer, the solar heating of the surface layer causes the formation of a seasonal thermocline around 20-40 m depth. In winter, cold and continental winds as well as air-sea temperature differences induce evaporation and heat loss from the sea. The sustained cooling and mixing of the surface layer lead to a relatively homogeneous water column and the formation of dense waters on the shelf that cascade down the slope. This latter process was not observed during the winter/spring surveys, but is considered as a major export mechanism (Tusseau-Vuillemin *et al.* 1998, Béthoux *et al.* submitted). The upward transport of nutrients by vertical mixing in winter explains the relative importance of primary productivity rates in the Gulf of Lions compared to those generally measured in the Mediterranean Sea (Diaz *et al.* 2000).

Flux of nutrients at the sediment/water interface was measured at the shelf stations for the three surveys (Denis 1999; Denis *et al.* 2001). A significant release of inorganic nitrogen and phosphorus was observed over the whole shelf area.

System description

We chose a single box system to describe the unstratified water column observed for the January and March cruises. This unstratified condition prevails from November to early May. As the system in June changes to a stratified water column, we used a two-layer system to describe the summer water and nutrient dynamics. This stratified situation lasts from June to October. The annual approximation of the budget has thus three periods corresponding to the different field surveys: a winter period from November to February, a spring period from March to May and a summer period from June to October.

The system is delimited by the shelfbreak, which is delineated by the 200 m isobath (Figure 5.1) and divides the shelf waters from the slope waters offshore. In survey data, gradients of salinity and nutrients are associated with this boundary, reflecting the dilution of the riverine freshwater and nutrient inputs on the shelf. The shelf system has a surface area of 12,000 km^2, and a total volume of 910x10^9 m^3. While the shelf has a sloping bottom down to 200 m, the average depth for the one-layer model is about 76 m. For the two-layer models the surface layer thickness was 30 m, and the deep layer average depth was 46 m.

Salinity and nutrient data were depth-averaged at each station for the different layers considered. Only data shallower than 150 m depth were used since exchanges between the shelf and the slope occur mainly within this layer. The data were then horizontally averaged separately for the shelf region and the slope region.

The budgetary analysis was performed using the LOICZ Biogeochemical Modelling Guidelines (Gordon *et al.* 1996), and is presented in Figures 5.4 to 5.8.

<u>*Water and salt balance*</u>

Water and salt balance allowed the estimation of volume transports between the shelf and the slope, as well as between the surface and deep shelf layers during the stratified period. The Gulf of Lions shelf has a low residual export compared to the large mixing exchanges between the shelf and the slope water. Shelf-slope exchanges represent less than 20% of the along-slope circulation water transport.

Balance of nonconservative materials

Nonconservative dissolved inorganic phosphorus (DIP) and nitrogen (DIN) fluxes and dissolved organic phosphorus (DOP) and nitrogen (DON) fluxes were calculated using the estimated volume transports. The Gulf of Lions shelf apparently took up DIP, DIN and DOP during the three surveys. Minimum values were observed during the March survey (spring bloom period). The system also took up DON during the spring survey, but liberated DON during the winter and summer surveys.

Stoichiometric calculations of aspects of net system metabolism

The parameter (*nfix-denit*) is estimated using all inorganic and organic imbalances (*DDIP*, *DDIN*, *DDOP*, *DDON*). With the assumption that the system is dominated by phytoplankton and using the Redfield ratio of N:P (16:1) (Redfield *et al.* 1963), the (*nfix-denit*) obtained is negative for the three surveys and its annual average is about -1 mmol N m^{-2} d^{-1} (Table 5.1). The denitrification process slightly dominates the N_2 fixation process and the Gulf of Lions appears to be a sink of fixed nitrogen. Furthermore, based on the C:P (106:1), the system is interpreted to be autotrophic (*p-r*) by about +16 mmol C m^{-2} d^{-1} (Table 5.1) and appears to be a net producer of organic matter.

Table 5.1. Summary of water exchange time, nonconservative nutrient fluxes, apparent net metabolism (*p-r*) and nitrogen fixation minus denitrification (*nfix-denit*) for the three surveys and the annual approximation. Results for the June 98 survey correspond to the sum of surface and deep layers.

Parameters	***January 99*** (winter)	**March 98** (spring)	**June 98** (summer)	**Annual**
Area (10^9 m^2)	12	12	12	12
Mean depth (m)	76	76	76	76
Volume (10^9 m^3)	910	910	910	910
t (days)	28	60	108	70
DDIP(10^3 mol d^{-1})	-3,083	-684	-1,392	-1,800
DDIP(mmol m^{-2} d^{-1})	-0.26	-0.06	-0.12	-0.15
DDIN(10^3 mol d^{-1})	-88,753	-30,124	-43,474	-55,200
DDIN(mmol m^{-2} d^{-1})	-7.4	-2.5	-3.6	-4.6
DDOP(10^3 mol d^{-1})	-533	-64	-155	-260
DDOP(mmol m^{-2} d^{-1})	-0.04	-0.005	-0.01	-0.02
DDON(10^3 mol d^{-1})	+18,258	-1,932	+4,160	+7,300
DDON(mmol m^{-2} d^{-1})	+1.5	-0.2	+0.3	+0.6
$(p\text{-}r)_{plankton}$ (mmol m^{-2} d^{-1})	+28	+6	+13	+16
$(nfix\text{-}denit)_{plankton}$ (mmol m^{-2} d^{-1})	-1.1	-1.7	-1.2	-1.3

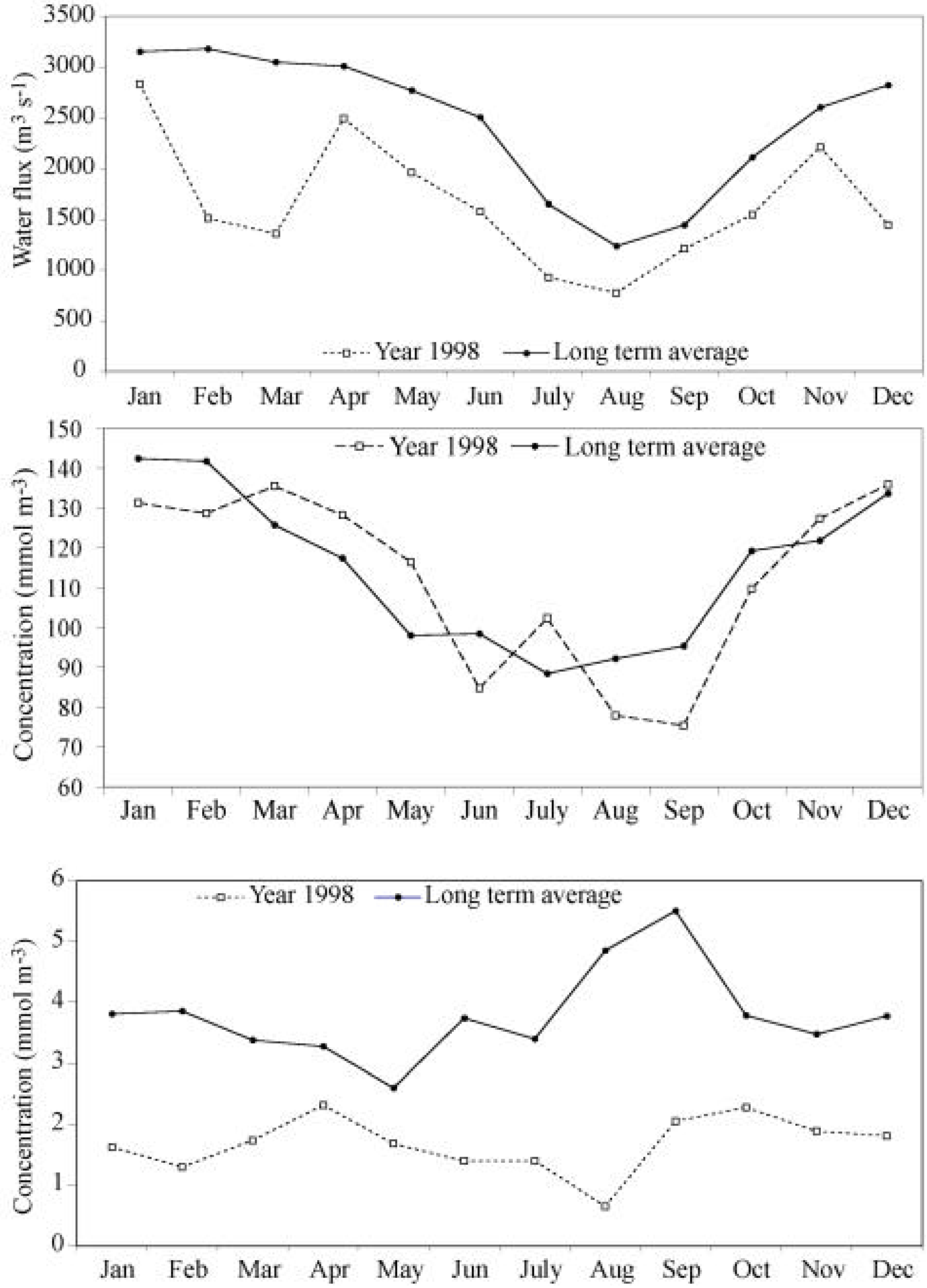

Figure 5.2. Monthly-average riverine discharge of freshwater (A), DIN (B) and DIP (C) concentrations in 1998 and for the long term average.

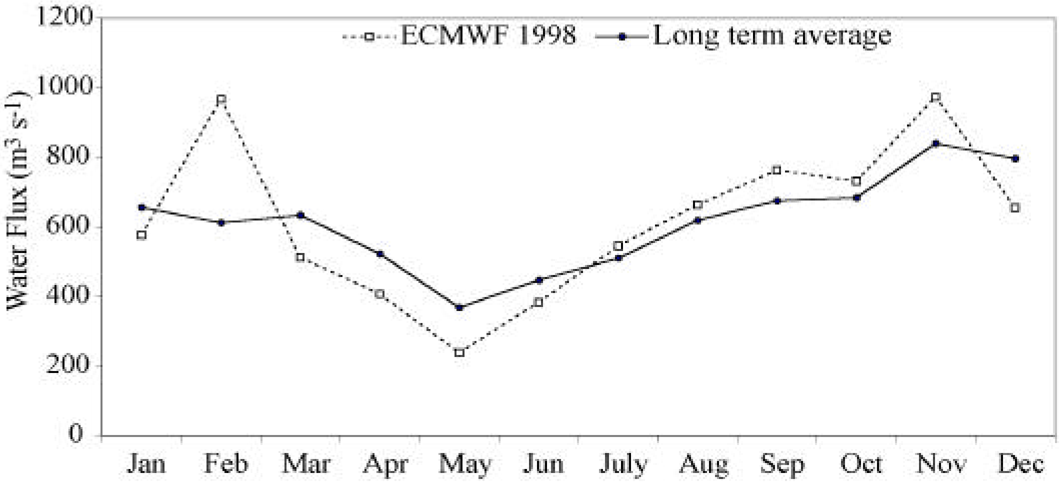

Figure 5.3. Monthly average evaporation (upper) and precipitation (lower) on the Gulf of Lions in 1998 and the long term average.

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Figure 5.4. Water and salt budgets of the Gulf of Lions for the three surveys. Water and salt fluxes in 10^6 m^3 d^{-1}. Salinity is dimensionless since it is computed from a conductivity ratio.

Abbreviated indexes have the following meanings : Q (river), O (urban sewage), G (ground water), E (evaporation), P (precipitation), R (residual), X (horizontal mixing), Z (vertical mixing), syst (system), ocn (ocean), s (surface), d (deep).

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Figure 5.5. DIP budgets of the Gulf of Lions for the three surveys. Fluxes are in 10^3 mol P d^{-1}. Abbreviated indexes have the following meanings : Q (river), O (urban sewage), sed

(sediment), atm (atmosphere), R (residual), X (horizontal mixing), Z (vertical mixing), syst (system), ocn (ocean), s (surface), d (deep).

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Figure 5.6. DIN budgets of the Gulf of Lions for the three surveys. Fluxes are in 10^3 mol N d^{-1}. Abbreviated indexes have the following meanings : Q (river), O (urban sewage), sed (sediment), atm (atmosphere), R (residual), X (horizontal mixing), Z (vertical mixing), syst (system), ocn (ocean), s (surface), d (deep).

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Figure 5.7. DOP budgets of the Gulf of Lions for the three surveys. Fluxes are in 10^3 mol P d^{-1}. Abbreviated indexes have the following meanings : Q (river), O (urban sewage), sed (sediment), atm (atmosphere), R (residual), R (horizontal mixing), Z (vertical mixing), syst (system), ocn (ocean), s (surface), d (deep).

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Figure 5.8. DON budgets of the Gulf of Lions for the three surveys. Fluxes are in 10^3 mol N d^{-1}. Abbreviated indexes have the following meanings : Q (river), O (urban sewage), sed (sediment), atm (atmosphere), R (residual), X (horizontal mixing), Z (vertical mixing), syst (system), ocn (ocean), s (surface), d (deep).

5. ESTUARINE SYSTEMS OF MOROCCO

Morocco, on the north-west corner of Africa (21-36°N), has nearly 3000 km of low-relief Atlantic Ocean coast and 500 km of rocky shores along the Mediterranean Sea. Four mountain ranges run across the country, including the Middle Atlas and High Atlas, the highest mountain chains in northern Africa. From the Atlas Mountains, plains extend west to the Atlantic, while desert and semi-desert plateaux spread south-east and east. The main rivers (Loukkos, Bouregreg, Sebou, Oum Rbia and Souss) rise in the mountains and flow to the Atlantic; only one major river, the Moulouya, flows to the Mediterranean.

Climatically, Morocco has maritime, mountain and desert influences. There are two distinct seasons, a hot, dry summer and a cool to cold winter. Rainfall is extremely variable in space and time. Average rainfall varies from north (700 mm) to south (25 mm) and from west (600 mm) to east (100 mm), with the most rain falling on the Rif and Atlas mountains (2000 mm). Most of the rain (95% falls in October-May, with rare storms in summer in the mountains.

Water resources are scarce and 70% of the available water is used for irrigation. With a population of 28 million (1999), 55% of them in cities and towns, and an estimated population growth of 1.35% per year, Morocco is already in a water-stress situation (<1,000 m^3/person/year) and by 2020 this will be critical (<500 m^3/person/year). The main towns and cities are along the Atlantic coast, as are industries, tourism and some agriculture. Fishing is good and diverse but the coastal zone is under increasing pressure, particularly near the mouth of the Sebou River and offshore of major urban agglomerations.

Source: Maria Snoussi

6.1 Moulay Bousselham Lagoon, Atlantic coast

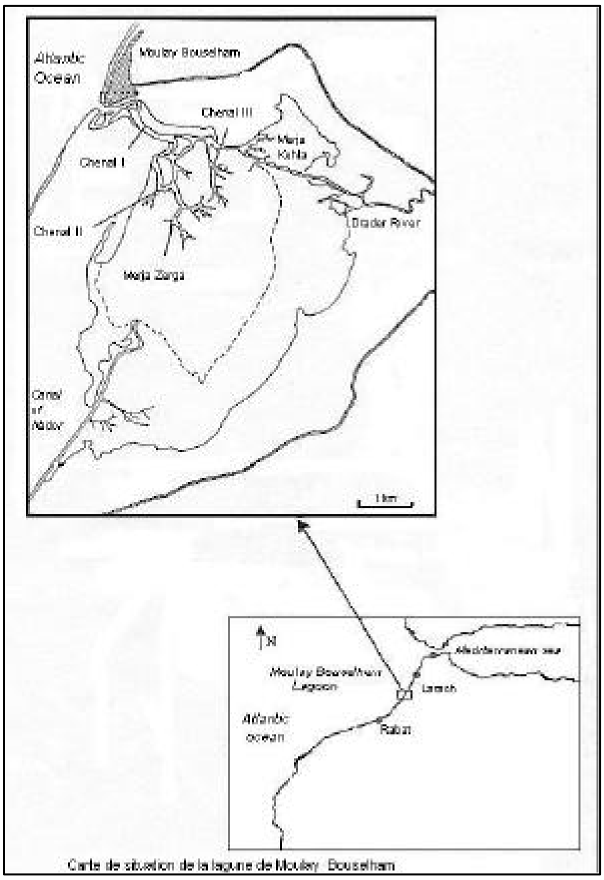
M. Snoussi and L. Ouaknine

Abstract
The Moulay Bousselham coastal lagoon is a Biosphere reserve, Ramsar site and protected wetland on the Atlantic north coast of Morocco. However, the pressures of the increasing population and activities around the lagoon are threatening the system. Available physico-chemical data was compiled to construct a preliminary nutrient budget applying the LOICZ biogeochemical approach. Based on water and salt budgets, the water exchange time was estimated at about 14 days. The net nonconservative fluxes of dissolved inorganic phosphorus and nitrogen (*DDIN* and *DDIP*) show that the system is slightly net source for DIP and a net sink for DIN. The system appears to be net denitrifying and net heterotrophic. These preliminary budgets need to be completed with more DIP and DIN data for the whole year.

Study area description

The Moulay Bousselham Lagoon is situated on the Atlantic north coast of Morocco (34.83ºN, 6.27ºW; Figure 6.1). The lagoon has an ellipsoidal shape in a north-south direction, is 9 km in length and 5 km wide in its widest portion; its area is 35 km^2. The Drader River channel divides the lagoon into two sub-basins, Merja Kahla to the north with an average depth of 0.3-0.5 m and Merja Zerga to the south with 1-1.5 m depth. The outer channels are 4-5 m deep. The inlet communicates with the ocean intermittently, as sediment accumulation after strong storms closes its mouth. Studies done since 1928 have reported that closure of the inlet occurs every 3-5 years (Beaubrun 1976). The mouth is now kept permanently open by artificial means.

The lagoon has a semi-diurnal tidal cycle. Tide amplitudes at the entrance ranges from about 1.5 m at neap tide to about 1 m at spring tide. Intertidal zones cover 96% of the area and represent the main vegetation types, with *Spartina densiflora,, Salicornia, Sarcoconia, Juncus rigidus* and seagrass (Benhoussa 2000).



Carte de situation de la lagune de Moulay Bousselham

Figure 6.1. Location and map of Moulay Bousselham Lagoon, Morocco.

Climatic data from 1983-1992 give an annual precipitation average of 600 mm with a strong seasonal and interannual variability and an annual average evaporation of 1,360 mm. Average temperature is about 18°C.

The lagoon system receives drainage mainly from the Drader River to the east and the Nador Canal to the south. The Drader River has a drainage area of 750 km^2 and an annual runoff volume of about $31x10^6\ m^3\ yr^{-1}$ or $85x10^3\ m^3\ d^{-1}$ (Beaubrun 1976). The Nador Canal was built in 1953 to drain flooded depressions and cultivated areas of the Rharb coastal plain. Its mean annual discharge to the Moulay Bousselham lagoon has been estimated to be $150x10^6\ m^3\ yr^{-1}$ or $411x10^3\ m^3\ d^{-1}$ (Carruesco 1989).

Moulay Bousselham Lagoon is one of the most important ornithological sites in Morocco. Many species of migratory birds (110 species according to Benhoussa 2000) use the lagoon as a stopover from Europe to the south. Despite its protected status under the Ramsar Convention as a coastal wetland of international importance, the abundance and diversity of flora and fauna are threatened by human activities (El Agbani *et al.* 1998).

The population in Moulay Bousselham Lagoon and adjacent area is about 154,000. The main activities are land cultivation and cattle raising (practised by more than 90% of the population), artisanal fishing and shellfishing (15%) (Benhoussa 2000) and summer tourism, an important income source for the local people. Agro-chemicals are used in 78% of the cultivated area around the lagoon. These activities are increasing without enough consideration of the environmental impacts on biodiversity and other aspects of ecological change.

Construction of the Nador Canal, the damming of the Drader River in 1979 for irrigation purposes, together with the agricultural activities and the closure/artificial opening of the inlet, put at risk the basic structural functions of the ecosystem and its resources.

For budgetary calculations, data for water and salinity were obtained from various sources (Beaubrun 1976; Zarzozo 1982; Carruesco 1989). The dissolved inorganic phosphorus (DIP) and dissolved inorganic nitrogen (DIN) data for the lagoon and the inshore ocean are from Badour (1987), based on 40 water surface samples collected between March and June 1987 at 5 stations. Data on groundwater are from the DRPE (1998). DIN represents NO_3^- + NO_2^- + NH_4^+. The fluxes of water, salt, DIP and DIN were calculated using simple box models following Gordon *et al.* (1996).

Water and salt balance

The box model (Figure 6.2) represents the terms used for calculating the average annual water and salt budgets. Freshwater flow (V_Q) is estimated by adding the flows of the Drader and Nador streams (496×10^3 m^3 d^{-1}). Considering the inundated area of the system (23×10^6 m^2), precipitation (V_P) and evaporation (V_E) are estimated as 38×10^3 m^3 d^{-1} and 85×10^3 m^3 d^{-1}, respectively. Groundwater input (V_G) is estimated as 96×10^3 m^3 d^{-1}. Sewage inflow (V_O) is assumed to be zero (but may be higher, especially in the summer period). Using equations from Gordon *et al.* (1996), the system shows substantial net residual outflow of water (V_R), as freshwater inputs to the system exceed evaporation. The water exchange time of water in Moulay Bousselham lagoon for the summer period can be calculated from equation (1), where V_{syst} is the total volume of the system, $|V_R|$ the absolute value of V_R and V_X the mixing volume.

$$t = V_{syst}/((V_R(+ V_X) \qquad (1)$$

Water exchange time was 14 days.

Budgets of nonconservative materials

Assuming steady state and considering runoff and groundwater as the important terrigenous inputs to the lagoon, the general equation for calculating nonconservative fluxes of dissolved element Y is :

$$DY = -V_Q Y_Q - V_G Y_G - V_R Y_R - V_X (Y_2 - Y_1) \qquad (2)$$

The nonconservative fluxes, *DDIP* and *DDIN* are calculated from data in Table 6.1 and illustrated in Figures 6.3 and 6.4. We have only data from March to June 1987. Nevertheless, we use these data as at least an approximation of the annual average fluxes.

Table 6.1. Water inputs, salinity, DIP and DIN concentrations for Moulay Bousselham lagoon. (*Badour, 1987; **DRPE, 1998).

	Volume Flux (10^3 m^3 d^{-1})	Salinity (psu)	DIP (mmol m^{-3})	DIN (mmol m^{-3})
Lagoon		26.8	0.2*	21*
Adjacent Ocean		36.6	0.2*	1.8*
Drader River	85	0 (assumed)	0.2*	2.2*
Nador Canal	411	0 (assumed)	0.2*	5.8*
Groundwater (V_G)	96	0 (assumed)	0 (assumed; may not be correct)	808**

DIP and DIN balance

The system appears to be a net source for DIP; *DDIP* = +10 mol d^{-1}. Extrapolating over the entire area, the rate is close to zero; *DDIP* = +0.0004 mmol m^{-2} d^{-1}.

Dissolved inorganic nitrogen concentration and flux are very high in groundwater. It can be seen that the system takes up most of the DIN delivered to the system, it is therefore a net sink for DIN. The observed flux per unit area is *DDIN* = -1.7 mmol m^{-2} d^{-1}.

The rates of nonconservative DIP and DIN fluxes can be used to estimate the apparent rate of nitrogen fixation minus denitrification (*nfix-denit*) as the difference between observed and expected *DDIN*. Expected *DDIN* is *DDIP* multiplied by the N:P ratio of the reacting particulate organic matter. We assume that this reaction is the Redfield N:P ratio of 16:1, for plankton.

$$(nfix\text{-}denit) = DDIN_{obs} - DDIN_{exp} = DDIN_{obs} - (N{:}P)_{part} \times DDIP \qquad (3)$$

Thus the system appears to be denitrifying at a substantial rate; *(nfix-denit)* = -1.7 mmol m^{-2} d^{-1}.

The calculation of the net ecosystem metabolism, that is, the difference between organic carbon production (p) and respiration (r) within the system (*p-r*), is made through equation (4):

$$(p\text{-}r) = - DP \times (C{:}P)_{part} \qquad (4)$$

Assuming again that organic oxidation is the primary source of nonconservative DIP flux, this rate is estimated as the Redfield ratio of the reacting organic matter (C:P = 106:1)

$$(p\text{-}r) = -0.04 \text{ mmol m}^{-2} \text{ d}^{-1}$$

This result indicates that the Moulay Bousselham Lagoon is slightly net heterotrophic.

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Figure 6.2. Water and salt budgets for Moulay Bousselham Lagoon. Water fluxes in 10^3 m^3 d^{-1} and salt fluxes in 10^3 psu-m^3 d^{-1}.

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Figure 6.3. DIP budget for Moulay Bousselham Lagoon. Fluxes in mol d^{-1}.

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Figure 6.4. DIN budget for Moulay Bousselham Lagoon. Fluxes in mol d^{-1}.

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