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Application of the LOICZ Methodology to the Mediterranean Sea

Robert O. Strobl, José-Manuel Zaldívar Comenges, Francesca Somma, Adolf Stips and Elisa García Gorriz

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European Commission
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Contact information
Address: Via E. Fermi 1, TP 272
E-mail: robert.strobl@jrc.ec.europa.eu
Tel.: +39 0332789391
Fax: +39 0332785807

http://ies.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

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1. LOICZ METHODOLOGY

The coastal zone is an integral part of the catchment-ocean system and is subject to internal and external forcing from both natural and anthropogenic pressures. The Land-Ocean Interactions in the Coastal Zone (LOICZ) approach attempts to evaluate coastal change from a system perspective and assumes that the effects taking place are due to pressures within the whole basin. It assesses the physical, biogeochemical and human interactions influencing coastal change. The priority focus is on the transport of water and sediments as well as the cycling of nitrogen, phosphorus and carbon.

Pernetta and Milliman (1995) have summarized the key objectives of the LOICZ approach as follows:

• to gain a better understanding of the cycles of the key nutrient elements carbon (C), nitrogen (N) and phosphorus (P) on a local and ultimately on a global scale;

• to understand how the coastal zone affects material fluxes via biogeochemical processes; and

• to characterize the relationship of these fluxes to environmental change, including human intervention.

More specifically the goals of the LOICZ budget approach are stated in the Science Plan (Holligan and de Boois, 1993) and Implementation Plan (Pernetta and Milliman, 1995),

•To determine at global and regional scales:

(1) the fluxes of materials between land, sea and atmosphere through the coastal zone

(2) the capacity of coastal systems to transform and store particulate and dissolved matter

(3) the effects of changes in external forcing conditions on the structure and functioning of coastal ecosystems.

•To determine how changes in land use, climate, sea level and human activities alter the fluxes and retention of particulate matter in the coastal zone, and affect coastal morphodynamics.

•To determine how changes in coastal systems, including responses to varying terrestrial and oceanic inputs of organic matter and nutrients, will affect the global carbon cycle and the trace gas composition of the atmosphere.

•To assess how responses of coastal systems to global change will affect the habitation and usage by humans of coastal environments, and to develop further the scientific and socio-economic bases for the integrated management of the coastal environment.

The LOICZ methodology not only has the purpose of studying the impact of climatic change and human activities on fluxes of nutrients to coastal ecosystems, but also of addressing the increasing need of policy-oriented scientific information. Information on the impact of watershed processes on nearshore coastal environments is becoming increasingly important for the protection of biodiversity and sustainability of terrestrial aquatic ecosystems as well coastal systems under their influence. Such integrated systems require an approach that closely links science and policy for a more efficient development and implementation of EU Directives.

For constructing biogeochemical budgets for coastal waters LOICZ has developed a set of Guidelines (Gordon *et al.*, 1996) which concentrate on the simplest case where a seawater body is treated as a single box which is well-mixed both vertically and horizontally, and at steady state. The sequence of budgets follows four steps: water budget, salt budgets, nonconservative materials and stoichiometric linkages among nonconservative budgets. The budgets presented here can be referred to as 'stoichiometrically linked water-salt-nutrient budgets'. A convenient summary of sequential steps to be performed in the LOICZ budget approach is the following:

1. Water budget: Establish a budget of freshwater inflows (such as runoff, precipitation, groundwater, sewage) and evaporative outflow. There must be compensating outflow (or inflow) to balance the water volume in the system.
2. Salt budget: Salt must be conserved in the system. Therefore salt flux not accounted for by the salinities used to describe the freshwater flows in Step #1, above, must be balanced by mixing. If there is no salinity difference between the system of interest and adjacent systems, or if the pattern of water exchange is too complex to be amenable to be described by the combined water and salt budgets, some more complex form of circulation analysis will be required. Steps #1 and #2 describe the exchange of water between the system of interest and adjacent systems by the processes of advection and mixing.
3. Budgets of nonconservative materials: All dissolved materials will exchange between the system of interest and adjacent systems according to the criteria established in Steps #1 and #2, above. Deviations of material concentrations from predictions based on these two previous steps are quantitatively attributed to net nonconservative reactions of materials in the system.
4. Stoichiometric relationships among nonconservative budgets: It can often be assumed that the nonconservative flux of dissolved inorganic phosphorus is an approximation of net metabolism at the scale of the ecosystem, because there is no gas phase for phosphorus flux.

Nitrogen and carbon both have other major flux pathways (notably denitrification, nitrogen fixation, gas exchange across the air-sea interface, and [in some systems] $CaCO_3$ reactions). The deviation of the fluxes of these materials from expectation based on C:N:P composition ratios of reactive particles in the system can be assigned to other processes in a quantitatively reproducible fashion.

Elaboration of the individual budgets is given in the following subsections.

1.1 *Water budget*

The concept of the hydrological cycle is well established, and is often presented (both globally and locally) in terms of water budgets. The conceptual model may be represented by a simple box diagram (Figure 1). An accounting of freshwater inflows to a coastal marine system (such as runoff, precipitation, groundwater) and of evaporation from the system is often rather easy to accomplish. The fundamental concept behind the budgets, of course, is the conservation of water mass. If it is assumed that either water volume remains constant or that the change of water volume through time is known, then net water outflow from the system can be estimated by difference. This flow is known as "residual flow;" there are likely to be other flows, but the difference between inflows and evaporative outflow must be balanced by this residual flow. As examples of judgment about individual systems, it is often (but not always) legitimate to assume that the system volume remains constant. Groundwater, sewage discharge, and other freshwater sources may often, but not always, be ignored. Often, but not always, runoff overwhelms the direct meteorological fluxes of precipitation and evaporation. Simple calculations can usually be made to estimate whether terms such as these are likely to be significant above the errors in the other terms. Figure 1 illustrates the contributions of different sources in the water balance of a coastal system, which can be summarised as freshwater inflows: runoff, precipitation, groundwater; and evaporation from the system. Assuming either that the coastal volume is constant or its derivative (dV_1/dt) known, then the net water outflow from the system can be estimated by difference.

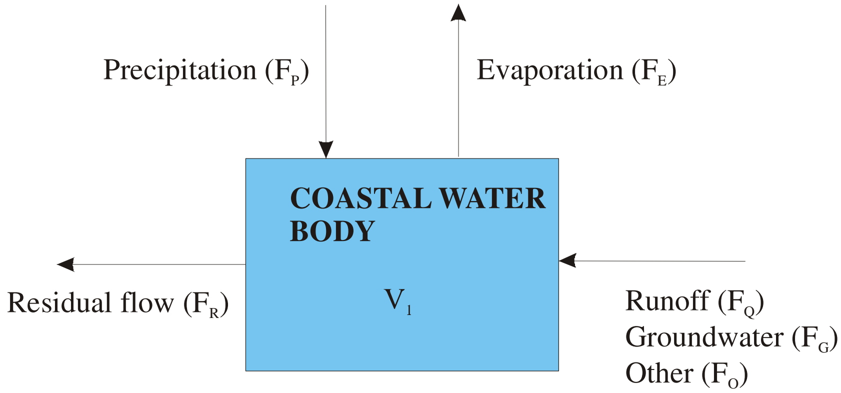

Figure 1. Water budget for a coastal water body of volume V1 (Gordon *et al.*, 1996).

1.2 *Budgets of conservative materials: Salt budgets*

Coastal marine systems have flows across the system boundaries in addition to the residual flow. For example, these systems can have water inflow and outflow associated with tides, winds, density, and large-scale circulation patterns. If the salinity of the system of interest as well as that of adjacent systems exchanging water with that system is known, then it may be possible to construct a salt budget (Figure 2) which includes these exchange flows in addition to residual flow. These exchanges are often modelled as mixing, rather than as advection. The salinity balance accounts for these additional exchange flows. In this case, note that any material in the water which is not changing by internal reactions within the system (in general, the salt of any abundant, highly soluble material) can be used in place of salinity. "Salinity", as defined by oceanographers, is in effect the sum of those salts and is readily measured. Because salt is not being either produced or consumed in the system, salinity is said to be "conservative" with respect to water within the system. Specific materials with similarly non-reactive properties (chloride is a common example) are said to be "conservative" with respect to salinity. Hence, a salt budget, see Figure 2, will allow to estimate the flow across the system boundaries, which is used afterwards for the calculation of non-conservative compounds as nitrogen and phosphorous.

The concept of "conservative" should be treated with some caution. On some time scales all of the salts in the ocean react. Therefore no salt dissolved in water is truly conservative with respect to water. Systems which include significant evaporate deposits may exhibit very nonconservative behaviour of salinity. In low salinity systems, ion ratios may vary significantly; the entire concept of "salinity" becomes qualitative. In such systems it may be safer to use a property which is more explicitly defined (for example, Cl). Having pointed to these cautionary notes with respect to salinity, it is useful to realise that salinities of streams or groundwater flowing into estuarine systems or the slight salt content of precipitation can be ignored in most cases. Again, simple calculations to evaluate this assumption are a useful precaution.

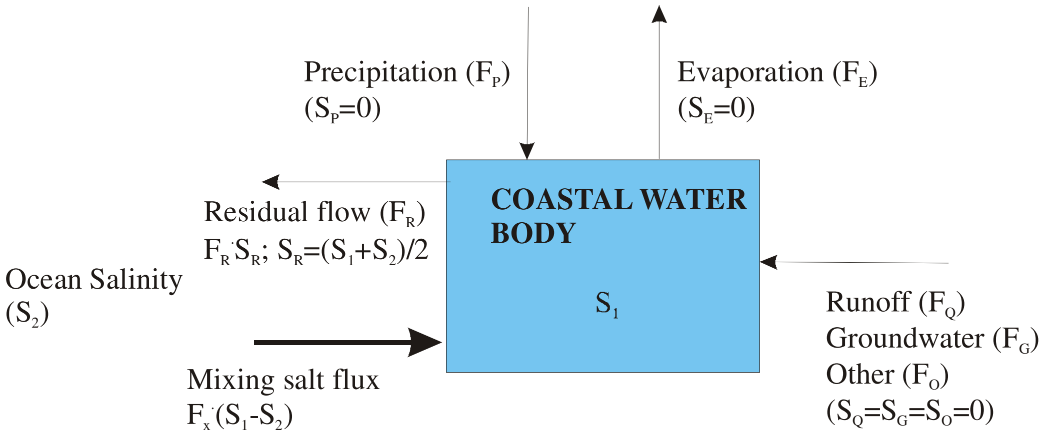

Figure 2. The salt budget for a coastal water body (Gordon *et al.*, 1996).

In the absence of salinity gradients or adequate data to establish salt budgets or, in the presence of spatial distribution patterns which are too complex for simple water and salt budgeting, it may be feasible to develop 2-dimensional or 3-dimensional numerical models of water circulation (Haidvogel and Beckmann, 2000). The output from such numerical circulation models may subsequently be substituted for water and salt budgets in order to estimate water exchange.

It follows from the above analysis that the balance, or budget, of salt in the system of interest is defined by the following general equation describing the mass of material S in the system (dVS/dt), where SV_{in} and SV_{out} represent all of the hydrographic inputs and outputs (including in this case exchange flow in and out) of each water type and S_{in} and S_{out} represent the salinity of those water inputs and outputs:

$$\frac{d(VS)}{dt} = \sum V_{in} S_{in} - \sum V_{out} S_{out} \tag{1}$$

Expanding this equation:

$$V\frac{dS}{dt} + S\frac{dV}{dt} = \sum V_{in} S_{in} - \sum V_{out} S_{out} \tag{2}$$

Steady state assumptions of either *dS/dt* or *dV/dt* may simplify Equation (2). It is worth remembering at this point that various of the water sources entering the system are likely to have a salinity near 0 psu.

1.3 *Budgets of nonconservative materials*

The next step in the budgeting exercise involves developing the stoichiometric linkages among nonconservative budgets. In other words, to consider materials which may not behave conservatively with respect to salinity (Figure 3). While this might be done with any reactive material (for example, Si, which is actively involved in both biotic and abiotic reactions), the particular interest here is in the balance among the essential plant nutrient elements C, N, and P. The basic assumptions here are that net biogeochemical processes in coastal marine systems are dominated by a few specific chemical reactions; that the biogeochemical cycles of C, N, and P are intimately linked; and that the approximate stoichiometric relationships among these elements for the dominating reactions can be written. Water exchange, defined by the water and salt budgets, describes the exchange fluxes of these elements along with salt. Clearly, total C, N, and P are conserved, but these elements may be transformed from measured, such as dissolved, to unmeasured, such as particulate or gaseous, phases. All dissolved phases of these materials are known to be involved in biochemical and abiotic reactions, so they are not likely to be conservative with respect to salinity. In the case of salinity, the budget is exactly balanced by water exchange. In the case of dissolved C, N, and P, the budgeted exchange fluxes are likely to leave some residual flux which is not balanced by these calculations. This residual for each element is a measure of the net internal fluxes (that is, sources minus sinks) of these materials. In fact, “conservative behaviour” of these materials with respect to salt would be taken to reflect one (or perhaps both) of two conditions: either the exchange rates of these materials in the water are fast relative to the internal fluxes, or the “conservative behaviour” represents the sum of uptake and release fluxes which cancel one another out. If turnover dominates over net flux in the cycle of a particular material, then the proportionality between salinity and this material is likely to be accompanied by a great deal of scatter in the data, reflecting rapid turnover but little net change (see examples in Imberger et al., 1983).

Much of the flux of C, N, and P in coastal waters is attributed to production and consumption of organic matter, and the composition of organic matter tends to be relatively constant within the ocean. If plankton metabolism dominates, then the well-established “Redfield Ratio” (Redfield,

1934) is likely to be a reasonable approximation of the C:N:P ratio of locally produced (or consumed) organic matter. If the system metabolism is dominated by seagrass or benthic algal metabolism, then some other composition may be more appropriate (Atkinson and Smith, 1983). For systems in which sedimentary materials apparently dominate the local reaction, or in which particle inputs and outputs can be assumed to be small, then the sediment composition may be an appropriate compositional ratio to consider. In any case, some estimate can be made of the local organic matter composition. For the sake of linking the C, N, and P budgets, phosphorus may be considered to have the simplest chemical pathways. All phosphorus in the system can be considered to be in either the dissolved phase or the particulate phase, and phosphorus reactions involve transfers between these phases; there is no gas phase. In contrast, both nitrogen and carbon have prominent gas phases, and carbon and nitrogen fluxes involving the gas phases are known to be important in coastal systems. The working assumption is therefore made that the internal reaction flux of phosphorus is proportional to production and consumption of particulate material (generally dominated by organic matter). That is, phosphorus moves back and forth between dissolved and particulate material. N:P and C:P flux ratios are calculated from the budgetary analyses, and deviations of these flux ratios from proportionality with respect to the particle composition are attributed to gas-phase reactions for nitrogen and carbon.

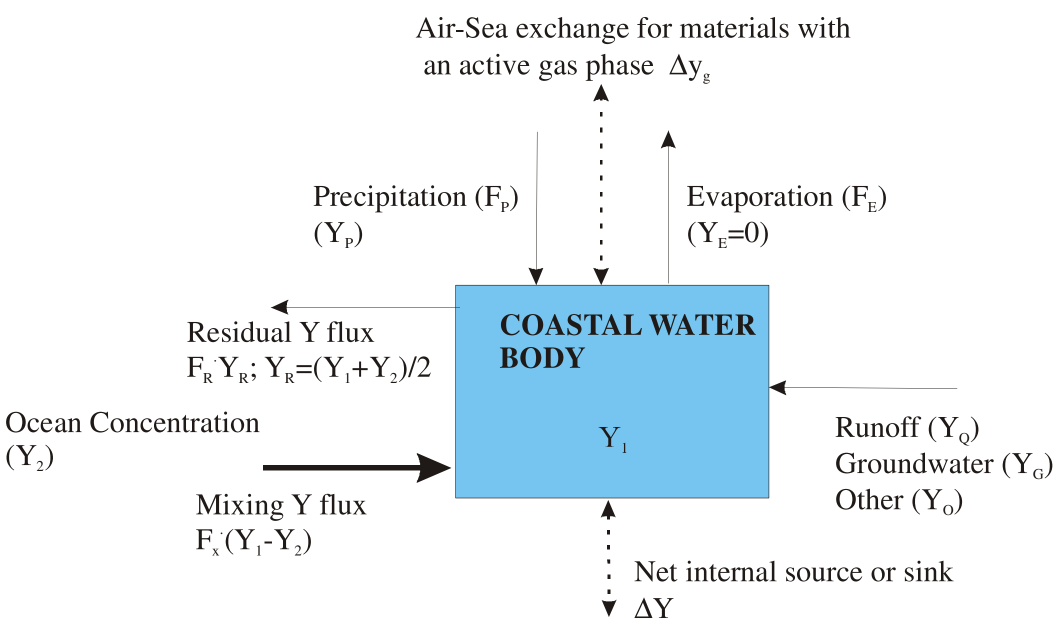

Figure 3. The budget for a non-conservative material, *Y*, in a coastal water body (Gordon *et al.*, 1996).

Two other cautions are in order here. Firstly, it was pointed out above that water input from processes like groundwater and sewage could often be ignored, and that the contributions of these terms to the salt balance could likewise usually be ignored. It is clearly not the case that the nutrient content of this water can be ignored; that should never be done for systems receiving significant sewage input and should be done only with some caution for groundwater and precipitation. If there is runoff, the nutrient input from that runoff must be included in the budget. Secondly, the budgets present here generally involve only dissolved materials. While there are methods to construct very useful budgets for particle fluxes, for example, sediment input by streams and deposition within the system, in general, salinity-based budgets must be treated with great caution in constructing budgets for particulate materials in shallow water systems. The reason is relatively simple. Dissolved materials have no gravitational component of flux within the water while particles do. Therefore particle distribution in the water column is likely to be extremely "patchy," with respect to both time and space, in areas subject to heavy loading with stream sediments, as well as in systems where wave mixing or active bioturbation is stirring the bottom sediments up into the water column. These processes can generate great heterogeneity in estimates of particle concentrations. While budgetary calculations for particles can be made according to the procedures to be outlined here, sampling artifacts may make the results quantitatively unreliable. As a result, the use of salt and water balance calculations are not generally useful to estimate particle budgets. It is worth recalling, however, that conservation of mass is a fundamental law of nature. Therefore, for materials without a gas phase, any deviation of dissolved forms of that material from conservative behaviour must represent net uptake or release with respect to particles. This point is used in the interpretation of output from the budgets.

In this context, there are two stoichiometries to be considered in the LOICZ budget:

(1) Nitrogen-Phosphorous stoichiometry: Nitrogen is present predominantly in seawater in the gaseous from. Conversion of N_2 gas to organic nitrogen is termed nitrogen fixation (*nfix*) whereas conversion from NO_3^- to N_2 is termed denitrification (*denit*). Both of these processes require biotic mediation (bacteria) and usually require anaerobic conditions to proceed in aqueous ecosystems. Significant amounts of nitrogen are transferred between the so-called fixed nitrogen (DIN, DON (Dissolved Organic Nitrogen), PN (Particulate Nitrogen)), which is normally measured and gaseous nitrogen (N_2), which is not. The net effect of this transfer has been termed by LOICZ as (*nfix-denit*). This value is often significant for the nitrogen budget, for this reason LOICZ methodology has proposed the following methodology to calculate it (Webb, 1981):

$$(nfix - denit) = \Delta N - \Delta P \cdot (N:P)_{part} \tag{3}$$

Assuming that the N:P ratio of particulate material in the system $(N{:}P)_{\text{part}}$ is known, the dissolved flux associated with production and decomposition of particulate material is the dissolved phosphorous flux ($\Delta P = \Delta DIP + \Delta DOP$) multiplied by $(N{:}P)_{\text{part}}$ minus the measured dissolved nitrogen flux ($\Delta N = \Delta NO_3^- + \Delta NH_4^+ + \Delta DON$) is the net effect of the nitrogen transfer (*nfix-denit*). As DOP and DON tend to be small when compared to DIN and DIP, it is possible to carry out the evaluation without these values (Gordon *et al.*, 1996).

(2) Phosphorous-carbon stoichiometry: According to LOICZ methodology (Gordon *et al.*, 1996) the ΔDIP scaled by $(C{:}P)_{\text{part}}$ ratio becomes a measure of net ecosystem metabolism NEM or (*p-r*).

$$(p - r) = -\Delta DIP \cdot (C:P)_{part} \tag{4}$$

A system with $\Delta DIP>0$ is interpreted to be producing DIC (Dissolved Inorganic Carbon) via net respiration ($p\text{-}r<0$), whereas a system with $\Delta DIP<0$ is interpreted to be consuming DIC via net organic production ($p\text{-}r>0$). This assumption is most likely not to work in systems with an anaerobic water column, or with sediments anaerobic to the sediment-water interface. Under either of these conditions, redox-mediated phosphorous desorption from inorganic particles is likely to occur.

In mathematical terms, Equation 2 represents a salt balance for the system, whether determined by means of a water and salt budget or direct estimates of water advection and mixing. Materials which are not conservative with respect to water and salt can be assumed to be represented by the same hydrographic inputs and outputs as govern the water and salt. Thus, the advection and the mixing exchange derived for water and salt are equally well applied to these other materials (Figure 3). For any material *Y*, Equation 2 is modified to include the sum of the nonconservative processes acting in the system to add and remove *Y* (that is, Δ*Y*). It is assumed that the concentration of *Y* in evaporating water is 0, but it is not assumed that inputs of *Y* in the other water sources are 0.

$$V\frac{dY}{dt} + Y\frac{dV}{dt} = \sum V_{in}Y_{in} - \sum V_{out}Y_{out} + \Delta Y \tag{5}$$

Again, steady state assumptions may allow one or both of the derivatives on the left side of the equation to be dropped. In some cases individual fluxes may be directly available, rather than being the product of concentration and flow. For example, sewage input of *Y* may be directly known, without data on sewage volume. The summed nonconservative fluxes (ΔY) are the information desired and are derived by rearrangement:

$$\Delta Y = V\frac{dY}{dt} + Y\frac{dV}{dt} - \sum V_{in}Y_{in} + \sum V_{out}Y_{out} \qquad (6)$$

The units of ΔY are mass per time; generally presented in this report as moles (mol) or kilomoles per day. Note two aspects of this equation. In the first place, this derivation gives no information about the processes leading to ΔY, either the number of processes or the general form of those processes. Physical, abiotic chemical, or biotic chemical processes may contribute to ΔY, and they are indistinguishable from this derivation. Such information is derived through other considerations, as discussed in the next section and exemplified in the case studies. Some terms, again sewage is an example, may be directly entered as known values in Equation 6, or may be part of the term ΔY.

In the second place, while this budgeting procedure based on a salt balance is in principle applicable to any material in many situations, it often cannot be applied with much quantitative success to particulate materials. The concentrations of these materials tend to be so patchy both spatially and temporally in response to sedimentation and resuspension that they are not adequately sampled in the context of a budgetary procedure derived for application to tidally averaged data.

In general is useful to express ΔY per unit area, by dividing the value estimated according to Equation 4 by the system area, often expressed as mol or mmol m^{-2} d^{-1}.

2. THE MEDITERRANEAN SEA BASIN

2.1 *Study Area*

Although making up merely 1% of the total world ocean surface, the Mediterranean Sea is often used as a representative model of the world's oceans to assess the global change of the environment, due to its practically enclosed character. Thus, the Mediterranean Sea can be considered an important laboratory basin for water cycle, climate change and biota response in changing environments. The marked seasonal cycle, and in particular the timing and location of the winter storms, affect the regional hydrology (Peixoto *et al.*, 1982), its variability being also an important prerequisite for a correct understanding of the Sea's hydrology not only from an environmental but also from a socio-economic standpoint.

The Mediterranean Sea stretches at its widest cross-sections about 4,000 km and 900 km from west to east and south to north, respectively (Laubier, 2005). The surface area and volume are approximately 2.51×10^{12} m^2 and 4.67×10^6 km^3, respectively. The average depth is approximately 1,500 m. It is connected to the Black Sea via the Strait of Dardanelles (7 km width and 55 m average depth) and to the Atlantic Ocean via the Strait of Gibraltar (15 km width and 290 m deep sill). An artificial connection to the Red Sea is given through the Suez Canal. More than 130 million people live on a permanent basis along the Mediterranean coastline, this figure doubling during the summer tourist season (EEA, 2005). Figure 4 shows the topography of the Mediterranean Sea for an appreciation of its spatial depth distribution.

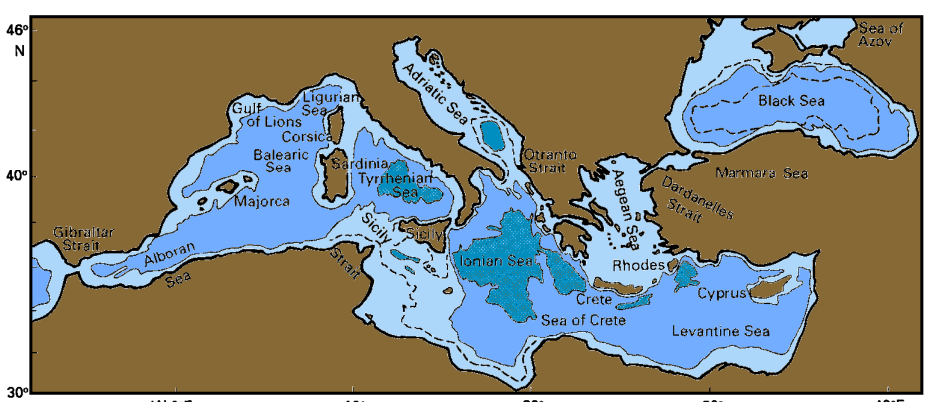

Figure 4. Topography of the Mediterranean Sea. The 1000 m contour is shown, and regions deeper than 3000 m are shaded. The 200 m contour is shown as a broken line where it departs significantly from the 1000 m contour. In addition, the 2000 m contour is shown as a broken line in the Black Sea (adopted from Tomczak and Godfrey (2003)).

The Mediterranean climate is marked by high winter and low summer precipitation, where the summer rainfall accounts for less than 10 percent of the annual total. A north-to-south gradient of the mean annual precipitation is evident, with precipitation decreasing towards the south. Especially in the Alpine and Pyrenean headwater areas, high precipitation (1,500 – 2,000 mm/yr) can be encountered. Thus, in the northern Mediterranean, the principal rivers are recharged via rather big basins, while the smaller basins usually experience floods. In the southern Mediterranean, on the other hand, there is a prevalence of very small rivers and flash floods are generally common (Laubier, 2005). In addition, the Mediterranean region is considered one of the most sensitive regions on Earth in the context of climate change as a consequence of its position between two different climate regimes in the North and the South (Somot *et al.*, 2006).

The largest river inflows come from the Nile, Rhône, Po and Ebro. The total riverine input to the Mediterranean Sea has been very roughly estimated at about 473 billion m^3/year (EEA/UNEP, 1999). For most parts of the Mediterranean Sea, evaporation exceeds the precipitation and river runoff inputs by over a 1 m, thereby causing a negative overall water budget. Thus, the Mediterranean Sea is often called an "evaporation basin", as it has a negative balance with the Atlantic Ocean. Thus the Mediterranean Sea can be considered a concentration basin. Theoretically, the sea level in the Mediterranean would decrease at a rate of about 0.5-1.0 m/yr if the Strait of Gibraltar became closed (Laubier, 2005). A consequence of this greater evaporation is that the water salinity increases, causing in the end a decrease in water temperature. Consequently, the two driving forces in the Mediterranean Sea which are responsible for the inflow of Atlantic surface water and the outflow of the Mediterranean deep water are the freshwater deficit and density increase. Generally speaking, the exchange between the Mediterranean Sea and the Atlantic Ocean occurs as the more saline and denser Mediterranean deep waters go out to the Atlantic Ocean, while the lighter Atlantic surface waters enter. The residence time for water entering through the Strait of Gibraltar is estimated to be between 80 and 200 years (Hopkins, 1999).

In the Mediterranean Sea, there are relatively strong vertical and lateral currents, therefore enabling relatively rapid mixing of introduced contaminants from the air, land or water compartments. The residence time for a basin is considered to be one of the indicators of how long contaminants may amass in a basin before mixing and then exiting a basin. The turnover time for the entire Mediterranean basin is estimated to range between 200 and 300 years (UNEP/MAP/MED POL, 2004).

As a result of the consequent water circulation due to the overall negative water balance of the Mediterranean Sea, the Atlantic Ocean receives great quantities of nutrients from the deep Mediterranean waters (Hopkins, 1985). Ultimately these deep water nutrient exports are completely lost for the internal primary production in the Mediterranean. Satellite studies have confirmed that zones of primary production can be found, on the other hand, near freshwater inputs in the Mediterranean coastal zones (Agostini and Bakun, 2002).

Land inputs of nutrients to the Mediterranean basin are originating principally from agriculture, animal husbandry and municipal sewerage. In other words, anthropogenic activities have contributed significantly to the existing nutrient enrichment and consequent eutrophication problems in the Mediterranean Sea. At the present, however, mainly because of the favorable circumstances regarding the hydrology, morphology and the absence of significant upwelling of the Mediterranean basin as a whole, severe eutrophication cases are limited to specific coastal areas (UNEP, 2003). An estimation of the percentage of each major anthropogenic factor contributing to the eutrophication problem has been made by the EEA/UNEP (1999). It was observed that the nonpoint sources of agricultural runoff as well as eroded soil are the root causes of nutrient enrichment in the Mediterranean, mostly from areas having a high degree of soil erosion (e.g. the Po and Rhône river basins). The total area of the basins draining into the Mediterranean comprises 3.91 million km^2. In the eastern Mediterranean Sea, nutrients are also being added via the receiving waters from the Black Sea, which has a net inflow of approximately 163 km^3/yr (UNEP, 2003).

Another possible source of nutrient input into the Mediterranean Sea is via seepage from coastal aquifers, such as unconfined sedimentary or karstic aquifers. It is estimated that approximately 25% of the total freshwater inflow into the Mediterranean Sea comes from seepage via coastal aquifers. However, no data is available on nutrient concentrations/loads entering by means of this pathway. Such coastal aquifers are known to be especially susceptible to pollution originating from the surface (UNEP/MAP/MED POL, 2004).

Figure 5 shows the area considered for the application of the LOICZ methodology.

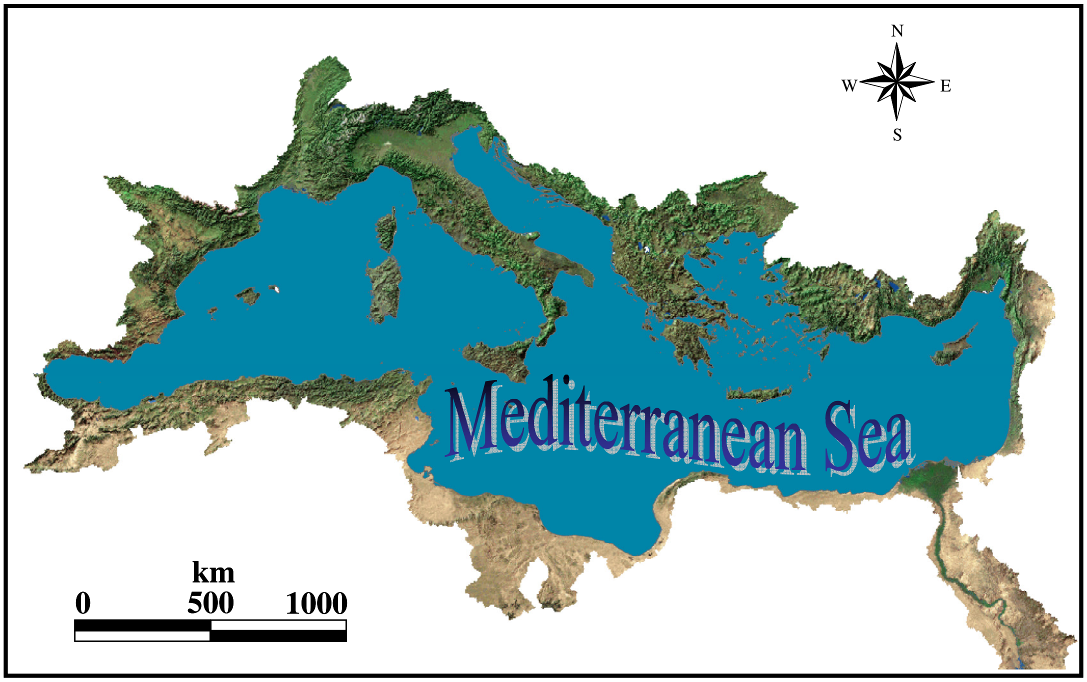

Figure 5. Boundary definitions for the LOICZ balance.

2.2 *Data Provision*

In order to perform the LOICZ budgeting approach to the Mediterranean Sea numerous input data were necessary. In addition, a preliminary watershed modelling exercise was indispensable in order to obtain an estimate of the total streamflow and nutrient inputs originating from the land surface into the Sea. The details of these model simulations and the related data sources have already been described in Strobl et al. (2008). The fluxes considered in the budgets were for streamflow, SGD, precipitation (wet and dry deposition) as well as interchange fluxes between the Mediterranean Sea and its neighbouring water bodies (i.e., Atlantic Ocean and Black Sea). The water budget included additionally the evaporation loss. No other input sources were considered. Table 1 depicts a summary of the data used for the LOICZ budget of the Mediterranean Sea.

Water budget input data

The AVGWLF model was used to estimate the total streamflow input for the time period 1996-2005 into the Mediterranean Sea. For the simulation, the watershed contributing areas to the Mediterranean Sea were divided into 65 units, and subsequently the computed streamflow was totalled from all units and added to an estimate for the Nile river of 3.91×10^{10} m^3/yr (Global Runoff Data Centre, 2008), which was not simulated with the AVGWLF model (see Strobl et al.,

2008) and represents the mean annual value for the Nile river for the period 1973 to 1984. The submarine groundwater discharge (SGD) to the Mediterranean Sea, on the other hand, was estimated from a study by Zekster and Dzhamalov (1988) on the world's oceans, and a time-invariant value was applied in the LOICZ budget.

Table 1. Summary of data used for the LOICZ budget of the Mediterranean Sea.

Data Type	Budget	Reference Year(s)	Spatial Reference	Data Source
Streamflow	Water	1996 - 2005	Land surface surrounding MED	AVGWLF Model Simulation (Evans *et al.* 2008)
Precipitation	Water	1996 - 2005	Over MED	
Evaporation	Water	1996 - 2005	Over MED	
SGD	Water	1988	MED	Zektser and Dzhamalov (1988)
Inflow from ATL to MED	Water	1991	MED-ATL Interface	Bryden *et al.* (1994)
Outflow from MED to ATL	Water	1991	MED-ATL Interface	Bryden *et al.* (1994)
Inflow from BLACK to MED	Water	unknown	MED-BLACK Interface	Pickard and Emery (1990)
Outflow from MED to BLACK	Water	unknown	MED-BLACK Interface	Pickard and Emery (1990)
Stream Salinity	Salt	n/a	MED	Assumed value
SGD Salinity	Salt	2002	Southeastern Sicily	Povinec *et al.* (2006)
MED Salinity	Salt	1874 - 2005	MED	Antonov *et al.* (2006)
ATL Salinity	Salt	1874 - 2005	ATL (area close to MED interface)	Antonov *et al.* (2006)
BLACK Salinity	Salt	1874 - 2005	BLACK (area close to MED interface)	Antonov *et al.* (2006)
Stream DIN	Nitrogen	1996 - 2005	Land surface surrounding MED	AVGWLF Model Simulation (Evans *et al.*, 2008)
SGD DIN	Nitrogen	2002	Southeastern Sicily	Povinec *et al.* (2006)
Deposition DIN	Nitrogen	2001-03	Average of various sites in MED	Markaki *et al.* (2008)
MED DIN	Nitrogen	1925 - 2005	MED	Garcia *et al.* (2006)
ATL DIN	Nitrogen	1925 - 2005	ATL (area close to MED interface)	Garcia *et al.* (2006)
BLACK DIN	Nitrogen	1925 - 2005	BLACK (area close to MED interface)	Garcia *et al.* (2006)
Stream DIP	Phosphorus	1996 - 2005	Land surface surrounding MED	AVGWLF Model Simulation (Evans *et al.* 2008)
SGD DIP	Phosphorus	2002	Southeastern Sicily	Povinec *et al.* (2006)
Deposition DIP	Phosphorus	2001-03	Average of various sites in MED	Markaki *et al.* (2008)
MED DIP	Phosphorus	1922 - 2005	MED	Garcia *et al.* (2006)
ATL DIP	Phosphorus	1922 - 2005	ATL (area close to MED interface)	Garcia *et al.* (2006)
BLACK DIP	Phosphorus	1922 - 2005	BLACK (area close to MED interface)	Garcia *et al.* (2006)

Abbreviations: ATL = Atlantic Ocean; MED = Mediterranean Sea; BLACK = Black Sea; DIN = dissolved inorganic nitrogen; DIP = dissolved inorganic phosphorus; SGD = submarine groundwater discharge.

Gridded precipitation-data sets are an essential base for many applications in geosciences and especially in climate research, as for instance global and regional studies on the hydrological cycle and on climate variability, verification and calibration of satellite based climate data or the evaluation of global circulation models (GCMs). As all applications require reliable high quality precipitation fields the underlying station data have to meet high demands concerning the quality of the observed precipitation data as well as the correctness of station meta data and also with respect to sufficient spatial station density and distribution. Concerning the use of regionally or globally gridded climate data for analyses of long-term climate variability it has to be ensured that station data used for gridding are as continuous and homogeneous as possible. In recent years various globally gridded data-sets of monthly terrestrial precipitation observations have been developed for example at the European Centre for Medium Range Weather Forecast (ECMWF), the National Center for Environmental Prediction (NCEP) or the Global Precipitation Climatology Centre (GPCC). For research purposes most of these data sets are available free of charge.

For the purpose of this study, model data from the reanalysis projects of ECMWF (ERA40) was used. This is also due to fact, that the gridded precipitation product of GPCC is based on measurement stations, which are located on land and are then extrapolated to cover the Mediterranean Sea. Such an extrapolation must be considered as rather doubtful, as the situation over sea is very different from that over land. Precipitation and evaporation estimates for the entire Mediterranean Sea were therefore derived from the ERA-40 reanalysis datasets, for a detailed description of the project see Uppala *et al.* (2005). This dataset is the results of a collective effort based on the ERA-40 re-analysis project, carried out by the (ECMWF), in collaboration with a number of institutions in Europe, Asia and North America. Very recently ECMWF has undertaken a new reanalysis effort called ERA-Interim, which most important is covering an extended time period going now until December 2008. The other for this study important point is that the complete humidity analysis was redone and thereby hopefully improved.

Meteorological observation from a number of different sources (stations, satellite, aircraft, radiosondes, ocean-buoys and other surface platforms), covering the period from September 1957 to August 2002, were collected and a global data assimilation system was set up and operated during the full period. These data are now available from the Meteorological Archival and Retrieval System (MARS), which is the main data repository at ECMWF. From the available global data in spectral representation an area covering the European area (25W-45E, 30S-67N) was selected and then interpolated to a grid with unique resolution of 0.5 x 0.5 degrees. Large Scale Precipitation

(LSP) and Convective Precipitation (CP) where both downloaded and aggregated in order to calculate Total Precipitation (TP). Evaporation (E) comprises evaporation and condensation. The sign convention used here for the data conversion, is so that precipitation and condensation are positive (water accumulation on land or sea), whereas real evaporation is negative (loss of water to the atmosphere). This is opposite to the typical sign convention in meteorology, where precipitation is considered a water loss of the atmosphere.

Precipitation and evaporation data as retrieved from MARS were accumulated into annual totals from the 6-hourly data (0:00, 6:00, 12:00, 18:00) for the period 1996-2002. For the remainder of the period (September 2002 to December 2005), pure model data derived from the operational model (IFS) of ECMWF were used. For comparison a second set of annual accumulated precipitation and evaporation data where calculated from the ERA-Interim product for the period from 1996 until 2008.

It should be mentioned that specifically the global modelling of precipitation despite the considerable progress made during the last decade still contains large uncertainties (see e.g. Troccoli and Kållberg, 2004) and even the measured data are not completely satisfactory. A recent model intercomparison of GCM's demonstrated that differences of up to 100% occurred (SCOR working group on fluxes and Turk *et al.* 2008). Fortunately, the most severe problems are apparent in the tropics and the southern hemisphere, whereas the arid climate of the Mediterranean Sea gives much more reliable precipitation estimates.

Estimates for the water exchange fluxes between the Mediterranean and Black Seas as well as between the Mediterranean Sea and Atlantic Ocean were obtained from Pickard and Emery (1990) and Bryden *et al.* (1994), respectively. These annual estimates were applied to all years in the time period of 1996-2005.

Salt budget input data

As no estimates for the salinity of incoming streamflow for the Mediterranean Sea were available, an average salinity value of 5 psu was assumed for the streamflow entering the Mediterranean Sea for the entire budget time period. The salinity of the SGD was estimated on basis of salinity measured in southeastern Sicily in the Donnalucata area (see Figure 6). Due to lack of better measured data, this value was used for the entire budget time period and for the entire Mediterranean Sea. The World Ocean Database 2005 (Antonov *et al.*, 2006), on the other hand, was used to estimate the salinities for the Mediterranean and Black Seas as well as for the Atlantic Ocean. An average was calculated from 33 standard depths (from 0 m to 5500 m) using one degree gridded data. For the Black Sea and the Atlantic Ocean, only the sea/ocean areas near the Mediterranean interface were used in the calculations of the average salinity (within ca. 250 km of the interfaces).

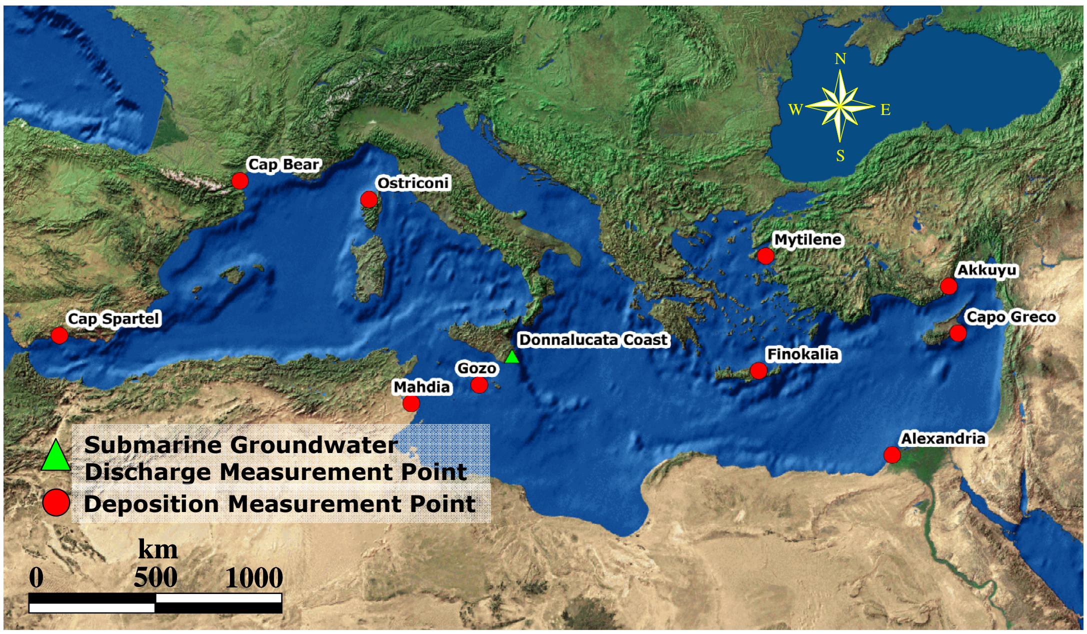

Figure 6. Nutrient deposition and SGD measurement points used for the LOICZ budget of the Mediterranean Sea.

Nitrogen budget input data

The AVGWLF model was used to estimate nitrogen load (as dissolved nitrogen) coming from the streams draining into the Mediterranean Sea (the Nile river was not included in the simulations). It was assumed that dissolved nitrogen represented mainly dissolved inorganic nitrogen (DIN). Dissolved nitrogen concentrations of SGD to the Mediterranean Sea were taken from nitrate estimates of the study by Povinec *et al.* (2006), representing the southeastern area of Sicily. Dissolved nitrogen estimates for precipitation (wet and dry deposition) falling on the Mediterranean Sea were obtained as an average from DIN measurements between 2001 and 2003 of ten coastal measuring points spread over the Mediterranean (see Figure 6). These measurements were performed in a study by Markaki *et al.* (2008) and were taken as far as possible from any local and regional influences in order that the results could be considered representative of long range transport and open sea deposition conditions. These estimates were assumed to be valid for the time period of 1996 to 2005. Similarly to the salinity estimates, the dissolved nitrogen estimates for the Mediterranean and Black Seas as well as for the Atlantic Ocean were computed from the World Ocean Database 2005 (Garcia *et al.*, 2006) where an average value was computed from 33 standard depths using one degree gridded data.

Phosphorus budget input data

As for the nitrogen budget, the AVGWLF model was utilized to obtain an estimate of the dissolved phosphorus (DP) coming from the land surface draining into the Mediterranean Sea. The DP originating from the SGD was estimated, similarly as for the DN estimate, from the study by Povinec *et al.* (2006) for southeastern Sicily and assumed to be applicable for the entire Mediterranean basin. The estimates of DP for wet and dry deposition were obtained from the study by Markaki *et al.* (2008). Computations from the data from the World Ocean Database 2005 (Garcia *et al.*, 2006) were performed to obtain an estimate for DP present in the Black and Mediterranean Seas and Atlantic Ocean and assumed to be representative for the time period of 1996 to 2005.

3. LOICZ BUDGET OF THE MEDITERRANEAN SEA

3.1 *Water Budget*

The water budget can be written as:

$$\frac{dV_{sys}}{dt} = F_Q + F_P - F_E + F_G + F_O + F_{R1a} - F_{R1b} - F_{R2a} + F_{R2b} \qquad (7)$$

where V_{sys} refers to the Mediterranean Sea volume, F_Q represents the inflows from stream runoff, F_P is the flow due to direct precipitation, F_E is the loss due to evaporation, F_G refers to the submarine groundwater discharge, F_O refers to other inflows such as sewage, and F_{R1a} and F_{R2b} are the flows due to hydrographically driven advective inflow from the Atlantic Ocean and Black Sea, respectively. Removals include evaporation, F_E, and advective outflow of water from the system into the Atlantic Ocean and Black Sea, F_{R1b} and F_{R2a}, respectively. It is useful to consider the difference between the incoming ($F_{in} = F_{R1a} + F_{R2b}$) and outgoing ($F_{out} = F_{R1b} + F_{R2a}$) advective f.lows into the system (i.e., the Mediterranean Sea) as the residual flow (F_R) driven by the water budget, see Figure 1. In fact, F_R can be obtained assuming $dV_{sys}/dt = 0$ as:

$$F_R = F_{in} - F_{out} = -F_Q - F_P + F_E - F_G - F_O \qquad (8)$$

Figure 7 shows a semi-schematic of the system under consideration along with the exchange fluxes considered in the budget of the Mediterranean Sea.

A comparison of the estimated amounts of streamflow, precipitation and evaporation over the Sea (Figure 8) confirms the well known fact that evaporation on average greatly exceeds precipitation by more than twice the amount, and even more so streamflow to the Mediterranean Sea (Mariotti *et al.*, 2002). This observation is quite central to the water circulation within the basin.

Table 2 shows the water budget for the Mediterranean Sea.

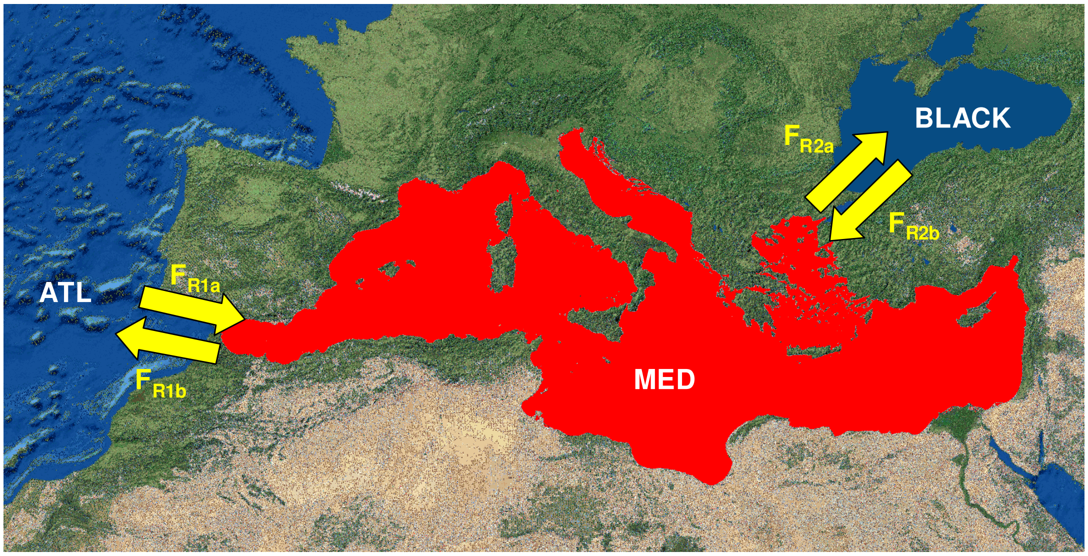

Figure 7. Semi-schematic of the system under consideration for the budget (where ATL = Atlantic Ocean; MED = Mediterranean Sea; BLACK = Black Sea; F_{R1a} = incoming flow from ATL to MED; F_{R1b} = outgoing flow from MED to ATL; F_{R2a} = outgoing flow from MED to BLACK; F_{R2b} = incoming flow from BLACK to MED).

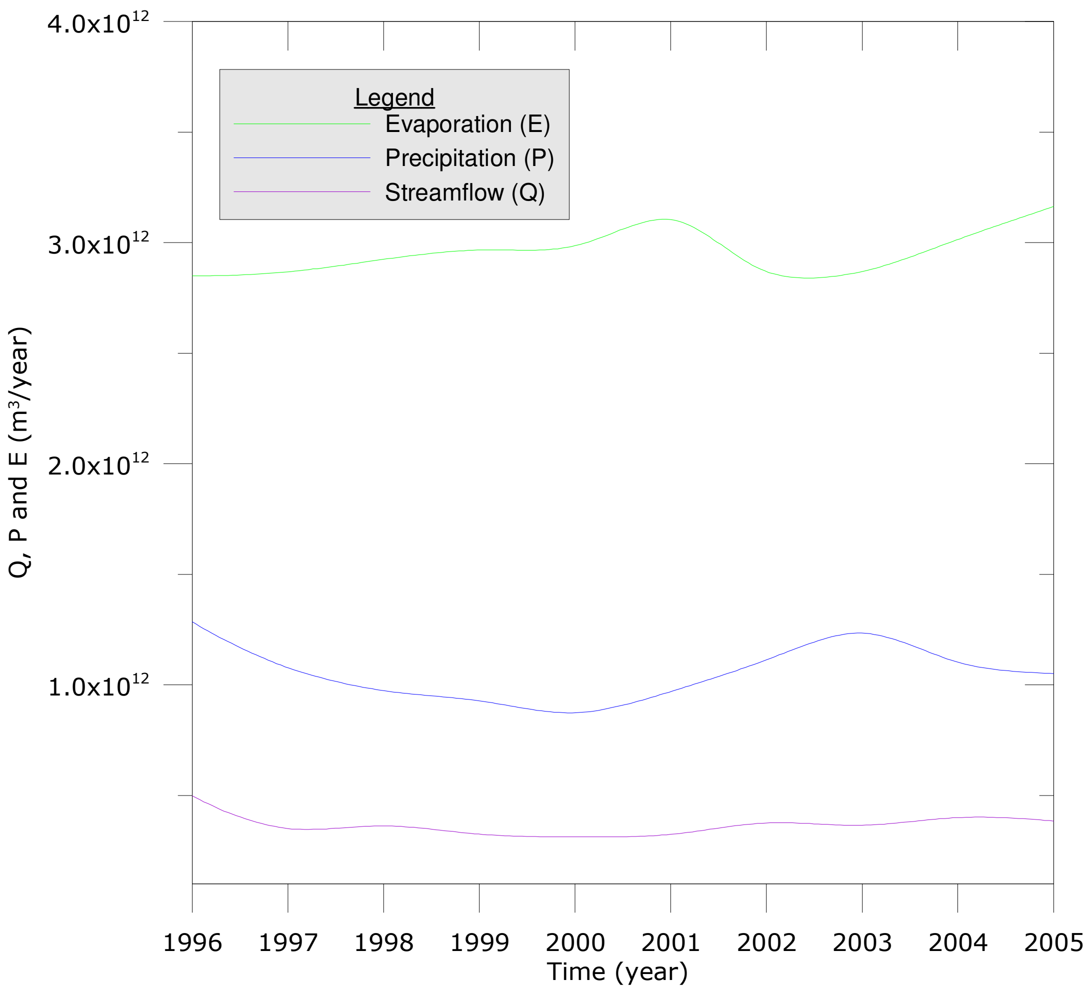

Figure 8. Estimated streamflow, precipitation and evaporation for the Mediterranean Sea.

Table 2. Water budget for the Mediterranean Sea.

Year	F_Q (m^3)	F_P (m^3)	F_E (m^3)	F_G (m^3)	F_O (m^3)	F_{R1a} (m^3)	F_{R1b} (m^3)	F_{R1} (m^3)	F_{R2a} (m^3)	F_{R2b} (m^3)	F_{R2} (m^3)	F_R (m^3)
1996	5.32E+11	1.29E+12	-2.85E+12	1.40E+08	0	2.16E+13	-2.29E+13	-1.33E+12	-1.90E+11	4.11E+11	2.21E+11	-1.11E+12
1997	3.84E+11	1.08E+12	-2.87E+12	1.40E+08	0	2.15E+13	-2.28E+13	-1.32E+12	-1.89E+11	4.10E+11	2.21E+11	-1.10E+12
1998	3.96E+11	9.74E+11	-2.92E+12	1.40E+08	0	2.15E+13	-2.28E+13	-1.32E+12	-1.89E+11	4.10E+11	2.21E+11	-1.10E+12
1999	3.58E+11	9.28E+11	-2.97E+12	1.40E+08	0	2.15E+13	-2.28E+13	-1.32E+12	-1.89E+11	4.10E+11	2.21E+11	-1.10E+12
2000	3.46E+11	8.73E+11	-2.99E+12	1.40E+08	0	2.16E+13	-2.29E+13	-1.33E+12	-1.90E+11	4.11E+11	2.21E+11	-1.11E+12
2001	3.58E+11	9.70E+11	-3.10E+12	1.40E+08	0	2.15E+13	-2.28E+13	-1.32E+12	-1.89E+11	4.10E+11	2.21E+11	-1.10E+12
2002	4.09E+11	1.11E+12	-2.87E+12	1.40E+08	0	2.15E+13	-2.28E+13	-1.32E+12	-1.89E+11	4.10E+11	2.21E+11	-1.10E+12
2003	3.99E+11	1.23E+12	-2.87E+12	1.40E+08	0	2.15E+13	-2.28E+13	-1.32E+12	-1.89E+11	4.10E+11	2.21E+11	-1.10E+12
2004	4.34E+11	1.10E+12	-3.01E+12	1.40E+08	0	2.16E+13	-2.29E+13	-1.33E+12	-1.90E+11	4.11E+11	2.21E+11	-1.11E+12
2005	4.18E+11	1.05E+12	-3.16E+12	1.40E+08	0	2.15E+13	-2.28E+13	-1.32E+12	-1.89E+11	4.10E+11	2.21E+11	-1.10E+12

Table 3. Overall flow exchange as computed from Pickard and Emery (1990) and Bryden *et al.* (1994) as well as from Equation 7.

Source	*Pickard and Emery (1990) & Bryden et al. (1994)*	*Equation 7*	
Year	F_R (m^3)	F_R (m^3)	Difference (m^3)
1996	-1.11E+12	-1.03E+12	-7.42E+10
1997	-1.10E+12	-1.41E+12	3.02E+11
1998	-1.10E+12	-1.55E+12	4.51E+11
1999	-1.10E+12	-1.68E+12	5.77E+11
2000	-1.11E+12	-1.77E+12	6.59E+11
2001	-1.10E+12	-1.78E+12	6.73E+11
2002	-1.10E+12	-1.35E+12	2.43E+11
2003	-1.10E+12	-1.24E+12	1.32E+11
2004	-1.11E+12	-1.48E+12	3.71E+11
2005	-1.10E+12	-1.70E+12	5.92E+11

Using the streamflow estimates of the AVGWLF model simulation along with the precipitation and evaporation data from the reanalysis projects of ECMWF (ERA40), as well as the SGD estimates, a water budget for the time period 1996 to 2005 could be undertaken. However, using these input parameters only, merely permits the computation of the overall exchange (i.e., F_R) between the system (i.e. the Mediterranean Sea) and its neighbouring water bodies (the Atlantic Ocean and Black Sea). In order to achieve this, the term dV_{sys}/dt in Equation 3 is assumed to tend to zero. This assumption is justifiable as the water budget has been performed on an annual basis. Nonetheless, using only these data does not allow for a more accurate evaluation of the term F_R. In other words, the incoming and outgoing flows between the Mediterranean Sea and the Atlantic Ocean and Black Sea cannot be obtained. However, Pickard and Emery (1990) and Bryden *et al.* (1994) have estimated these incoming and outgoing flows for the Black Sea and Atlantic Ocean, respectively (see Table 2). Table 3 shows the overall flow exchange for the Mediterranean Sea using Pickard and Emery's (1990) and Bryden *et al.*'s (1994) estimates as well as a comparison of the F_R as calculated via Equation 7. As can be observed, the differences for the time period 1996 to 2005 range from absolute values of approximately $4 \cdot 10^{10}$ to $6 \cdot 10^{11}$ m^3/yr. This represents differences of one to two magnitudes lower than the estimated values and can be considered to be within acceptable limits for a water budget calculation for the Mediterranean basin.

On an annual basis, it is seen from Table 2 that the Mediterranean Sea has an overall water addition from the Black Sea and water loss to the Atlantic Ocean. Table 2 also shows that the major water flows into and out of the Mediterranean basin are from the interface with the Atlantic Ocean.

3.2 *Salt Budget*

The salt budget can be written as:

$$V_{sys} \frac{dS_{sys}}{dt} = F_Q S_Q + F_G S_G + F_O S_O + F_{R1a} S_{ATL} - F_{R1b} S_{sys} - F_{R2a} S_{sys} + F_{R2b} S_{BLACK} \quad (9)$$

where S_{sys} refers to the Mediterranean Sea salinity, S_Q is the salinity of the incoming streamflows, S_G refers to the salinity of the submarine groundwater discharge, S_O is the salinity of other incoming flows (e.g. sewage flow), S_{ATL} is the salinity of the Atlantic Ocean at the Strait of Gibraltar, and S_{BLACK} is the salinity of the Black Sea near the entrance to the Mediterranean Sea. In this equation, the mixing terms F_{in} and F_{out} remain as the unknowns. It was assumed that the salinity input due to deposition was negligible.

Using the salinity estimates available for the Mediterranean system, a salt budget was performed and is presented in Table 4.

Table 4. Salt budget for the Mediterranean Sea.

Year	S_Q (psu)	S_G (psu)	S_O (psu)	S_{sys} (psu)	S_{ATL}(psu)	S_{BLACK} (psu)	$\frac{dS_{sys}}{dt}$ (psu)
1996	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.25E-02
1997	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.26E-02
1998	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.26E-02
1999	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.26E-02
2000	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.27E-02
2001	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.26E-02
2002	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.25E-02
2003	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.26E-02
2004	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.26E-02
2005	5.00E+00	3.70E+01	0.00E+00	3.86E+01	3.59E+01	2.12E+01	-2.25E-02

The calculation of $\frac{dS_{sys}}{dt}$ in Table 4 confirms that the estimated salinity values for streamflow, SGD, etc. along with the computed salinity values computed for the Mediterranean Sea, Atlantic Ocean and Black Sea from the World Ocean Database 2005 data are acceptable as the long-term expected change in the system should approach zero. It can also be observed that the salinity of the Black Sea is less than that of the Atlantic Ocean and Mediterranean Sea. Due to the high evaporation and low runoff from streams, the salinity value for the Mediterranean Sea is much higher than for the Black Sea. This is also can be explained from the fact that the Mediterranean Sea is a concentration basin, whereas the Black Sea is considered a dilution basin since it receives great freshwater inputs from the Danube river. However, it should be noted that there a few parts of the Mediterranean Sea that receive great freshwater input, such as the Adriatic Sea from the Po river, which hence locally represents a dilution basin.

3.3 *DIP Balance*

The following equation represents a mass balance for the system in the case where compound(s) undergo chemical transformations inside the coastal lagoon:

$$V_{sys}\frac{dY_{sys}}{dt} = F_Q Y_Q + F_P Y_P + F_G Y_G + F_O Y_O + F_{R1a} Y_{ATL} - F_{R1b} Y_{sys} - F_{R2a} Y_{sys} + F_{R2b} Y_{BLACK} + \Delta Y \qquad (10)$$

where *Y* refers to the concentration of the species, and *ΔY* represents the net internal source or sink. The definition of the subscripts is as previously defined. In this case we are interested in the last term of Equation 10 which will give us an idea on the behaviour of our system, i.e. sink or source, in relation to a particular species. However, it is clear that *R* is the sum of all processes (physical, chemical or biological) taking place, i.e.:

$$R = \sum_{i=1}^{n} \nu_i \cdot r_i \qquad (11)$$

where ν_i is the stoichiometric coefficient for the *i-th* transformation, and hence, in principle, the mass balance will not give us any information concerning the number of processes (*n*) and their relative importance (r_i/r_j).

In order to estimate the dissolved inorganic phosphorous for the Mediterranean Sea, the AVGWLF model (Evans *et al.*, 2008) has been employed as reported in Strobl *et al.* (in press). DP concentrations were assumed to be approximately equal to DIP concentrations and indeed this is usually the case. The calculated annual mean dissolved phosphorous loads in streamflow entering the Mediterranean Sea for the period 1996 to 2005 can be seen in Figure 9.

ΔDIP is therefore calculated in the following manner:

$$\Delta DIP = \frac{R \cdot V_{sys}}{S_{sys}} = V_{sys}\frac{dDIP_{sys}}{dt} - F_Q \cdot DIP_Q - F_P \cdot DIP_P - F_G \cdot DIP_G - F_O \cdot DIP_O - F_{R1a} \cdot DIP_{ATL} + F_{R1b} \cdot DIP_{sys}$$
$$+ F_{R2a} \cdot DIP_{Hsys} - F_{R2b} \cdot DIP_{BLACK} \qquad (12)$$

The calculated *ΔDIP* budget for the Mediterranean Sea is shown in Table 5. As can be seen, for the selected time period the estimated *ΔDIP* is relatively constant. On a yearly basis, the Mediterranean Sea acts as a sink of phosphorous. For a more precise definition of a general behaviour throughout different periods of the year, a monthly or seasonal balance would have been required. A graphical representation of *ΔDIP* for the time period 1996 to 2005 is shown in Figure 10.

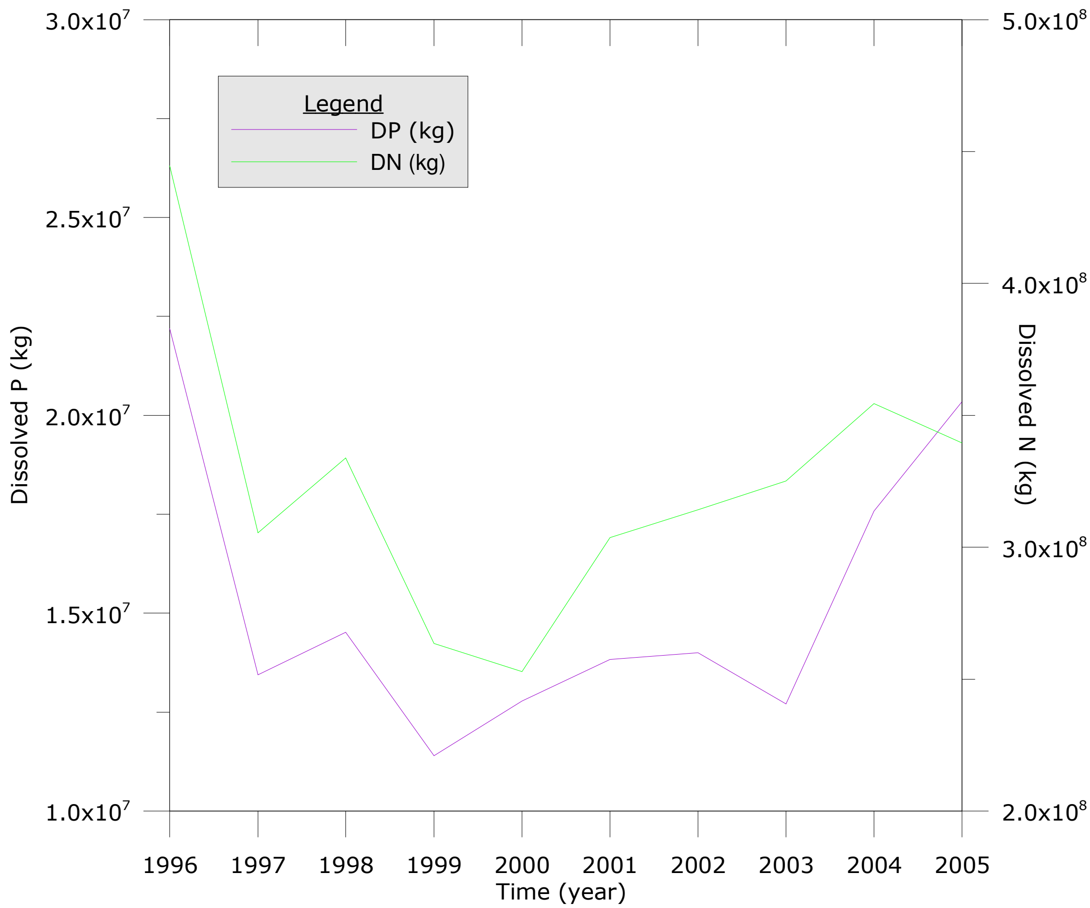

Figure 9. Calculated annual amount of dissolved phosphorous and dissolved nitrogen (in kg) discharged to the Mediterranean Sea from its catchments.

Table 5. *ΔDIP* and *ΔDIN* budgets for the Mediterranean Sea for the time period 1996 to 2005.

Year	ΔDIP (kg/yr)	ΔDIP (mmol/m^2/d)	ΔDIN (kg/yr)	ΔDIN (mmol/m^2/d)
1996	4.05E+08	1.38E-02	4.26E+09	3.32E-01
1997	3.96E+08	1.35E-02	4.11E+09	3.20E-01
1998	3.97E+08	1.35E-02	4.14E+09	3.23E-01
1999	3.93E+08	1.34E-02	4.07E+09	3.17E-01
2000	3.96E+08	1.35E-02	4.07E+09	3.17E-01
2001	3.96E+08	1.35E-02	4.11E+09	3.20E-01
2002	3.96E+08	1.35E-02	4.12E+09	3.21E-01
2003	3.95E+08	1.35E-02	4.13E+09	3.22E-01
2004	4.01E+08	1.36E-02	4.17E+09	3.25E-01
2005	4.02E+08	1.37E-02	4.15E+09	3.23E-01

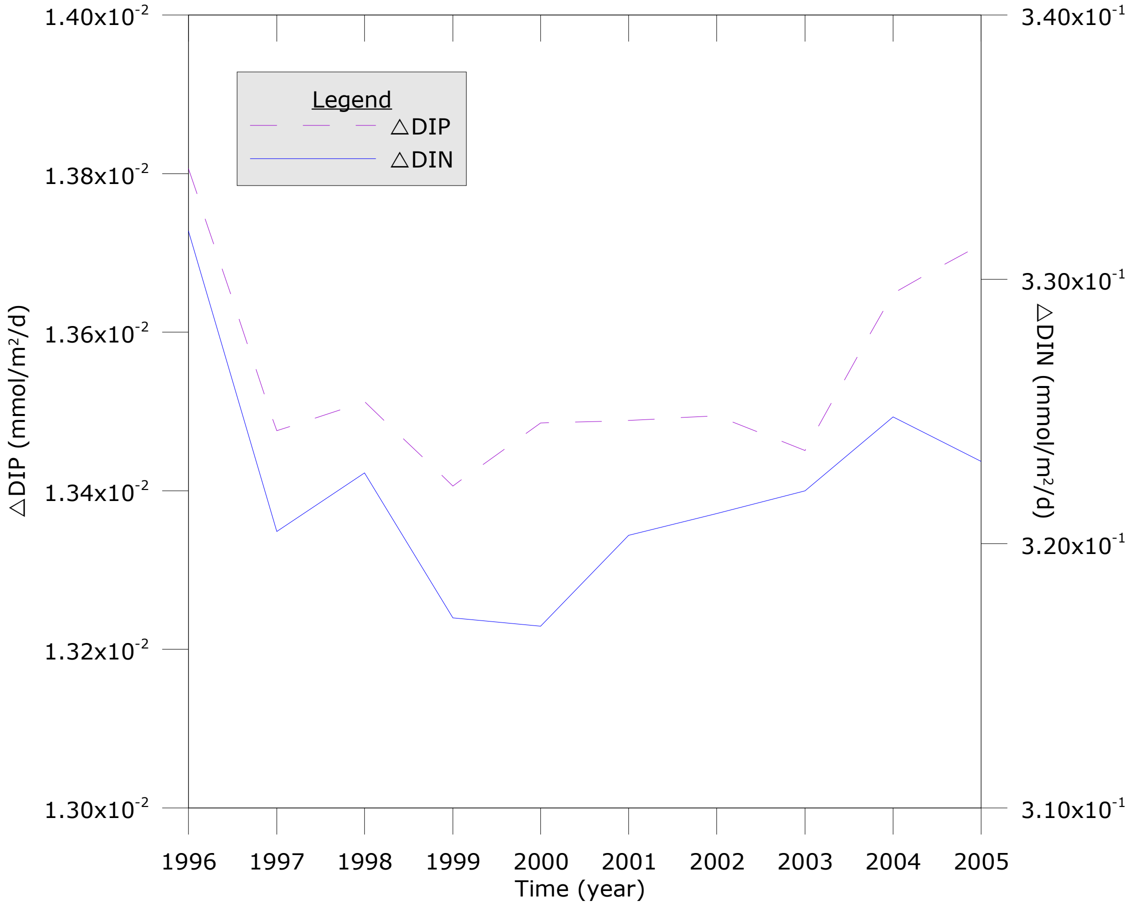

Figure 10. Estimated *ΔDIP* and *ΔDIN* for the time period 1996 to 2005.

3.4 *DIN Balance*

In order to carry out a mass balance of dissolved inorganic nitrogen (DIN) for the Mediterranean Sea, Equation 10 has been rearranged accordingly:

$$\Delta DIN = \frac{R \cdot V_{sys}}{S_{sys}} = V_{sys}\frac{dDIN_{sys}}{dt} - F_Q \cdot DIN_Q - F_P \cdot DIN_P - F_G \cdot DIN_G - F_O \cdot DIN_O - F_{R1a} \cdot DIN_{ATL} + F_{R1b} \cdot DIN_{sys}$$
$$+ F_{R2a} \cdot DIN_{Hsys} - F_{R2b} \cdot DIN_{BLACK} \qquad (13)$$

Table 5 and Figure 9 show the estimated *ΔDIN* budget for the period of 1996 to 2005. Similarly to the *ΔDIP* budget the annual mean values remain constant throughout the selected time period. The budget shows that on an annual basis, the Mediterranean Sea can be considered a sink of nitrogen. For the DIN there is no specific trend, similarly to the case of DIP.

3.5 *Stoichiometrically Linking the Nonconservative Budgets*

One procedure to gain insight into the main processes responsible for the non-conservative fluxes is to study the relationships between them and to see if it is possible to link them stoichiometrically according to well-known processes in the coastal zone. In the case of the whole Mediterranean, we can assume that plankton metabolism dominates, then the "Redfield Ratio" is likely to be a reasonable approximation of the C:N:P ratio of locally produced (or consumed) organic matter. Figure 11 shows the variation of *nfix-dnit* for the selected 10-year time period, as well as the corresponding production-respiration NEM (Net Ecosystem Metabolism) balance. As can be observed, the Mediterranean Sea shows a positive balance between nitrogen fixation and denitrification during the analyzed years. On the contrary, NEM is always negative indicating that there is a net production of dissolved inorganic carbon (DIC).

It is important to underline that the linking of stoichiometric budgets, due to the absence of relevant data, is based only on the inorganic N and P compounds; therefore, it would be necessary to validate the contribution of the organic N and P cycles to the overall budget of the Mediterranean to validate these values.

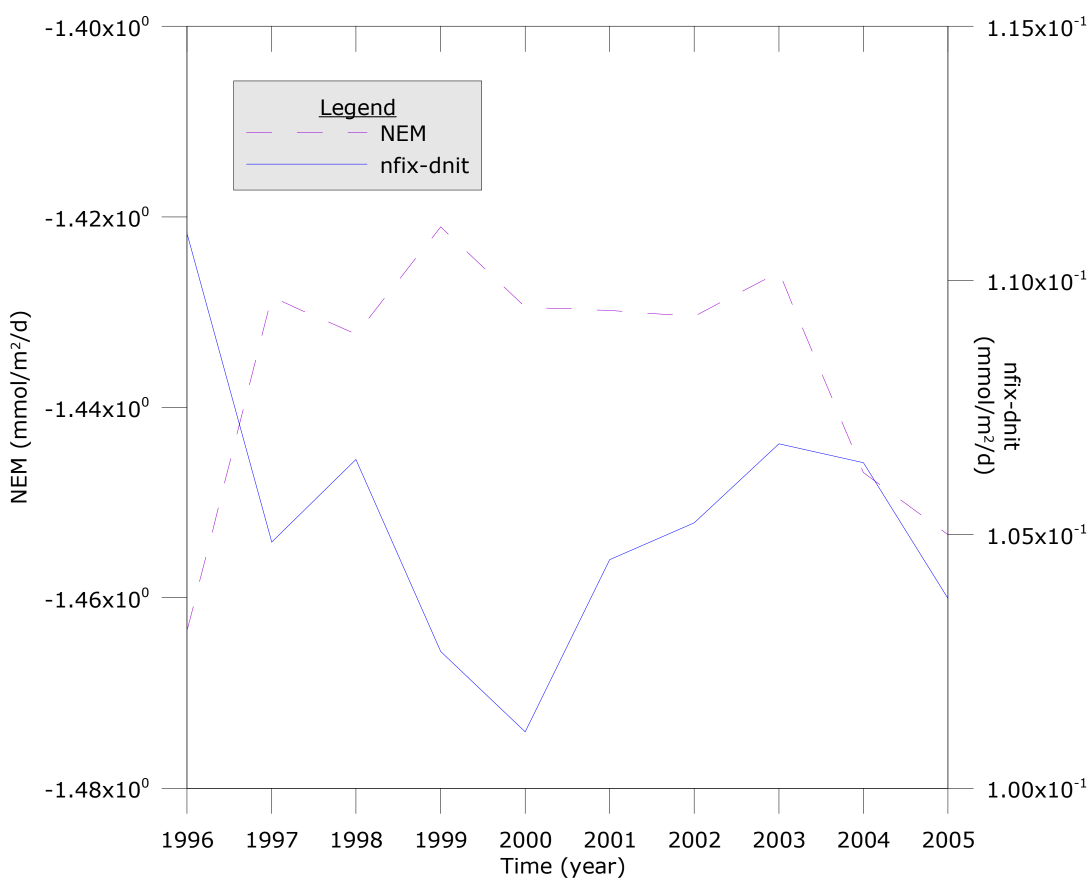

Figure 11. NEM balance and *nfix-dnit* variation for the Mediterranean Sea (1996-2005).

4. DISCUSSION AND CONCLUSIONS

The LOICZ methodology has proven to be extremely valuable in the use and analysis of data from several sources on different aspects of a complex system. Furthermore, it has provided some insights into the biogeochemical cycles of the Mediterranean Sea.

Even though the LOICZ methodology has been developed having in mind to use the minimum amount of data, there is still a gap between LOICZ data requirements and the standard monitoring practices in the coastal zone. This has especially become apparent when having to extrapolate single data to represent greater areas of the Mediterranean Sea, or when having to use temporally sparse data for a longer time period under study. For this case study, for example, some input parameters (e.g. SGD salinity, SGD DP, etc.) to the LOICZ budget were only available for a limited spatial extent span and hence were extrapolated to the entire Sea in order to run the budget. This imbalance between spatial sampling was also present for some parameters in a temporal context with measured values of some input parameters (e.g. SGD, DP from deposition, etc.) only available for specific time periods or years. In reality, the application of the LOICZ methodology requires careful consideration of the large spatial gradients and temporal variability of the parameters that are usually characteristic of regional seas, such as the Mediterranean Sea. Ideally, the boundary concentrations of N and P, the corresponding long-term inputs of N and P and the internal concentrations need to be known.

On average over the time period 1996 to 2005, the phosphorous and nitrogen budgets of $1.35 \cdot 10^{-2}$ mmol m^{-2} d^{-1} and $3.22 \cdot 10^{-1}$ mmol m^{-2} d^{-1}, respectively, suggest an excess of release over uptake. The budget calculations translate to the fact that on average the Mediterranean Sea acts as a sink of phosphorous and nitrogen. In order to know if specific areas of the Mediterranean Sea act as sources, the Sea needs to be analyzed on a more local level, such as on the Mediterranean subbasin level. This will constitute a further research activity.

A closer visual look at the LOICZ budget results for phosphorous and nitrogen (e.g. Figure 9) do not indicate any specific trend in order to possibly make a specific statement about if the water quality and ecosystem functioning of the Mediterranean Sea are changing or remain stationary. A more in-depth statistical analysis in this respect using linear regression to detect if trends could be perceived for ΔDIP and ΔDIN for the time period 1996 to 2005 has been performed. The results clearly show that the mean ΔDIP and ΔDIN values do not differ along different years for this chosen time period (i.e., null hypothesis at the 95% confidence level cannot be reject and thus no linear trend). Tables 6 and 7 show the results of this statistical analysis for ΔDIP and ΔDIN, respectively.

The stoichiometric linkage of C, N and P through the Redfield ratio indicates that nitrogen fixation and production of dissolved inorganic carbon dominate over denitrification and consumption of dissolved inorganic carbon via net organic production.

Table 6. Trend analysis for *ΔDIP* for the time span of 1996 to 2005.

SUMMARY OUTPUT for ΔDIP (mmol m-2 d-1)

Regression Statistics	
Multiple R	0.045567726
R Square	0.002076418
Adjusted R Square	-0.12266403
Standard Error	0.000136782
Observations	10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	3.11433E-10	3.114E-10	0.01664591	0.900527318
Residual	8	1.49674E-07	1.871E-08		
Total	9	1.49986E-07			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.013539341	8.03941E-05	168.41223	1.73E-15	0.013353952	0.0137247	0.01335395	0.01372473
X Variable	1.94292E-06	1.50592E-05	0.129019	0.900527	-3.2784E-05	3.667E-05	-3.2784E-05	3.66695E-05

Table 7. Trend analysis for *ΔDIN* for the time span of 1996 to 2005.

SUMMARY OUTPUT for ΔDIN (mmol m-2 d-1)

Regression Statistics	
Multiple R	0.156677428
R Square	0.024547817
Adjusted R Square	-0.097383706
Standard Error	0.004434851
Observations	10

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	1	3.95963E-06	3.96E-06	0.20132461	0.665558252
Residual	8	0.000157343	1.967E-05		
Total	9	0.000161303			

	Coefficients	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*Lower 95.0%*	*Upper 95.0%*
Intercept	0.323027329	0.002606601	123.92666	2.01E-14	0.317016496	0.3290382	0.3170165	0.329038161
	-0.000219079	0.000488261	-0.4486921	0.665558	-0.00134501	0.0009069	-0.00134501	0.000906853

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Abstract

From a broad perspective, the LOICZ (Land-Ocean Interactions in the Coastal Zone) approach attempts to evaluate coastal change from a system perspective and assumes that the effects taking place are due to pressures within the whole basin. The LOICZ methodology was applied to the Mediterranean Sea in order to estimate its water, salt and nutrient budget, as well as to gain insights into its biogeochemical cycles. In order to undertake this budget approach, various input data relative to the three budgets were gathered for the time period of 1996 to 2005. In the case of the Mediterranean Sea, it was seen that there is still a gap between LOICZ data requirements and the standard monitoring practices in the coastal zone, both from a spatial as well as temporal viewpoint. The results show that on average over the time period 1996 to 2005, the phosphorous and nitrogen budgets of $1.35 \cdot 10^{-2}$ mmol m^{-2} d^{-1} and $3.22 \cdot 10^{-1}$ mmol m^{-2} d^{-1}, respectively, suggest an excess of release over uptake. The budget calculations translate to the fact that on average the Mediterranean Sea acts as a sink of phosphorous and nitrogen. No specific, statistically relevant trend of the water quality and ecosystem functioning of the Mediterranean Sea was observed. An examination of the stoichiometric linkage of C, N and P through the Redfield ratio indicates that nitrogen fixation and production of dissolved inorganic carbon dominate over denitrification and consumption of dissolved inorganic carbon via net organic production.

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