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Nutrient budget for the Eastern Mediterranean: Implications for phosphorus limitation

M. D. Krom[1]
Earth and Biosphere Institute, School of Earth Sciences, Leeds University, Leeds LS2 9JT, United Kingdom

B. Herut
Israel Oceanographic Limnological Research, Tel Shikmona, Haifa, Israel

R. F. C. Mantoura
Marine Ecology Laboratory, International Atomic Energy Authority, Monaco

Abstract

The eastern Mediterranean has a high nitrate to phosphate (N : P) ratio (~28 : 1) in the deep water and a highly unusual P limitation of the primary productivity. We present a detailed nutrient budget of inputs to the basin, which shows that there is a high N : P ratio (>16 : 1) in all the input sources, particularly from the atmospheric source, where the N : P ratio was 117 : 1. The high N : P ratio is retained within the system because there is no significant denitrification in either the sediments or intermediate water. This is because of the extreme oligotrophic nature of the system, which is caused by the unusual anti-estuarine flow at the Straits of Sicily. Support for this conclusion is provided by the observation that the only area of the eastern Mediterranean where the N : P ratio in deeper water is ~16 : 1 is the northern Adriatic, which is also the only area with significant denitrification. The N budget (total input to basin vs. net output at the straits of Sicily) balances closely. This N balance suggests that N fixation is an insignificant process in this P-limited system. The unusually light ^{15}N values in the deep water nitrate and particulate organic nitrogen can be explained by processes other than nitrogen fixation. These processes include a lack of significant denitrification in the basin and by particulate organic matter exported from surface waters during the P-limited winter plankton bloom.

The eastern Mediterranean is unusual in that it is phosphorus limited (Krom et al. 1991). The molar ratio of nitrate to phosphate in the deep water is ~28 : 1 (Krom et al. 1991; Kress and Herut 2001; Kress et al. 2003). After deep winter mixing, there is a winter phytoplankton bloom. This bloom ceases when the surface waters run out of phosphate and while there remains a measurable amount of nitrate (Krom et al. 1991, 1992). Furthermore, when the ^{15}N content of this nitrate was determined, it was found that it was significantly enriched in the heavy N isotope, which is characteristic of an ecosystem where primary production is terminated before completion, such as by P limitation (Struck et al. 2001). Additional evidence for P limitation of the surface waters of the eastern Mediterranean has been obtained from observations of phytoplankton and bacterial activity (Zohary and Robarts 1998). Results obtained during the recent CYCLOPS P addition experiment have shown that although the ecosystem response to P addition was complex, overall, the system showed a severe lack of phosphate (Krom et al. unpubl. data).

At present, there are two hypotheses to explain why the eastern Mediterranean is phosphorus limited. Krom et al. (1991) suggested that it was because phosphate but not nitrate was removed from the levantine deep water (LDW) by the adsorption of Saharan dust. The eastern Mediterranean has one of the highest fluxes of dust of any oceanic basin in the world (Chester et al. 1977). However, when detailed adsorption experiments were carried out using Saharan dust and Mediterranean seawater spiked with phosphate at similar concentrations to that found in LDW, insignificant amounts of phosphate were adsorbed (Herut et al. 1999; Pan et al. 2002; Ridame et al. 2003; Krom et al. unpubl. data). At present, the only alternative explanation for this unusual nutrient limitation is that there is excess N fixation in the system either by sea grasses or by N-fixing phytoplankton (Bethoux et al. 1992, 1998). Evidence for extensive N fixation has been suggested by Sachs and Repeta (1999) and by Pantoja et al. (2002), who interpreted the relatively light ^{15}N-NO_3 that they measured in the intermediate waters as being due to N fixation. Pantoja et al. (2002) calculated that ~90% of the nitrate present in the eastern basin was formed by this process. Koppelmann et al. (2003) similarly suggested that light ^{15}N-PON in mesozooplankton was due to consumption of phytoplankton, including a high proportion of N fixers.

In the present study, an alternative hypothesis is put forward to explain the unusual P limitation—that the nitrogen : phosphorus ratio supplied to the eastern Mediterranean is much greater than 16 : 1. Nutrient budgets for the eastern Mediterranean have been carried out previously (Sarmiento

[1] Corresponding author (M.D.Krom@earth.leeds.ac.uk).

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et al. 1988; Bethoux et al. 1992, 1998, 2002). These studies generally calculated the flux of dissolved inorganic nutrients across the Straits of Sicily and assumed steady state, calculating the atmospheric and terrestrial inputs (ATIs) into the eastern basin by the difference. This was because there were limited data available to measure directly the nutrient inputs to the eastern basin. Recent published data have enabled a far more accurate estimate of the total nutrient budget to be made. Specifically, over the past several years, detailed long-term measurements of the atmospheric inputs of both N and P into the eastern Mediterranean have been made for the first time (Mihalopoulos et al. 1997; Herut et al. 1999, 2002; Markaki et al. 2003). Better estimates are also now available for the flux of nutrients supplied by major rivers, such as the Po (Pettine et al. 1998; Degobbis et al. 2000) and the Nile (Nixon 2003). These data, together with a series of new measurements on current flows through the Straits of Sicily (Astraldi et al. 1999), mean that it is now possible to determine the flux of inorganic nutrients both into and out of the basin with more accuracy. In the present study, a total nutrient budget for the eastern Mediterranean using modern long-term data sets was carried out to determine the nitrogen and phosphorus loads to the basin and to examine whether they are significantly different from the Redfield molar ratio of 16 : 1.

However, even if such an imbalance were found, it would not be sufficient in itself to explain the unusual nutrient limitation found in this basin. The global supply of nutrients to the world's oceans has been estimated to be >50 : 1 (Galloway 2003; Ruttenberg 2003). Elsewhere, there are long-term biogeochemical mechanisms that cause N : P ratios to relax toward 16 : 1 (Redfield et al. 1963; Falkowski et al. 1998; Tyrell 1999). These mechanisms include N fixation for systems with excess P and denitrification and P recycling in suboxic/anaerobic zones for systems with excess N. Thus, even if there is an excess of N supplied to the basin, it is also necessary to explain why the normal biogeochemical feedback mechanisms for nutrient buffering to ~16 : 1 do not occur in the eastern Mediterranean.

Results

Atmospheric flux to the eastern Mediterranean—Atmospheric inputs of nutrients to marine ecosystems have received increasing attention recently, because it has become apparent that such inputs may be important, especially in oligotrophic areas (Duce et al. 1991). The eastern Mediterranean basin is located at the southern edge of Europe. It receives air masses from central and eastern Europe during most of the year (at least 70% of the time). Although there are natural sources of fixed nitrogen to the atmosphere in western Europe, the main sources of fixed nitrogen to the atmosphere are anthropogenic (NO_x) from industrial combustion and vehicle traffic, HNO_3 from vehicle traffic, and NH_3 emissions from intensive farming (Guerzoni et al. 1999). In this budget, an attempt has been made to determine bioavailable nutrient fluxes. Thus all the N input (dissolved inorganic nitrogen [DIN], dissolved organic nitrogen [DON], and leached DIN [LDIN]) is assumed to be bioavailable, whereas only the dissolved and leachable inorganic P (DIP and LDIP) was included as being initially bioavailable. This is because a significant fraction of the total P passes through the system and is buried in the sediment without interacting with the biological cycle (Eijsink et al. 2000). However, as is discussed below, it is possible that this assumption may be too conservative for P, and some fraction of the refractory P may be transformed into bioavailable P by biogeochemical processes in the water column or sediment.

Almost all of the rainfall in the eastern Mediterranean occurs during winter (October–May). The value for inorganic wet deposition of nitrogen (DIN) is rather similar across the entire eastern Mediterranean, at an average of 20.5 ± 3.8 (1 s; $n = 6$) mmol N m^{-2} yr^{-1} and a total range of 16–24 mmol N m^{-2} yr^{-1} (Table 1). By comparison, the atmospheric flux of inorganic nitrogen in the northwestern Mediterranean, which is the most complete data set previously available in the region, is higher by a factor of slightly more than two (Migon et al. 1989). This is not surprising, considering that the area of the south of France where this was sampled has a higher annual rainfall and is closer to the principal sources of atmospheric pollution in western Europe.

Despite P being the critical nutrient controlling primary productivity in the Eastern Mediterranean (Krom et al. 1991), fewer data are available for the wet deposition of phosphate to the basin than for nitrogen. Herut et al. have measured the wet deposition of dissolved phosphate (DIP) in Israel and obtained estimates of 220 and 260 μmol P m^{-2} yr^{-1} for the periods of 1992–1995 and 1992–1998 (Herut and Krom 1996; Herut et al. 1999*a*, 2002). Markaki et al. (2003) determined the wet deposition rate of DIP in eastern Crete and southern Turkey (Erdemli) as 65 and ~135 μmol P m^{-2} yr^{-1} for 1 yr (1999–2000), respectively. Estimates of the wet deposition of P from Cap Ferrat in the northwestern Mediterranean bracket those determined in Israel (150–500 μmol P m^{-2} yr^{-1} (Migon et al. 1989; Migon and Sandroni 1999). Given the relatively short period of time of sampling in Crete and Erdemli at present, it was considered reasonable to take the average value from the two long-term data sets, Israel and the northwestern Mediterranean (280 μmol P m^{-2} yr^{-1}) and use that as the wet depositional flux for the eastern Mediterranean in this calculation. Wet deposition was calculated from dissolved phosphate (DIP) determinations and included all bioavailable phosphate.

The dry deposition of nutrients is particularly important in the eastern Mediterranean, because it has one of the largest inputs of dust for any region of the ocean (Chester et al. 1977). It has been recognized by several workers that it is necessary to estimate separately the total dry flux of nitrogen (TN) and phosporus (TP) and that fraction of the atmospheric input which is leachable into seawater (LDIN and LDIP) and thus is available for biological productivity in surface waters (e.g., Bergametti et al. 1992; Herut et al. 2002; Ridame and Guieu 2002). In the western Mediterranean, wet deposition is considered to be a highly effective mechanism of dust deposition (Guerzoni et al. 1997; Guieu et al. 2002), where it is characterized by short-lived events of high magnitude. Thus, for the western Mediterranean there are no separate estimates of dry deposition, and dust input is in-

Table 1. Measured atmospheric input of nitrogen and phosphorus to the eastern Mediterranean. N fluxes are given in mmol N $m^{-2}yr^{-1}$, and P fluxes are given in μmol P $m^{-2}yr^{-1}$. The average values used in subsequent total flux calculations are marked in boldface italics. See text for justification of the choices made.

Location	Nitrogen flux	Phosphorus flux	Reference
Wet deposition			
Israel	26	220	Herut and Krom 1996
Israel	16	*260*	Herut et al. 1999
Heraklion, Crete	24		Kouvarakis et al. 2001
Finokalia, Crete	17		Kouvarakis et al. 2001
Finokalia, Crete	20	65	Markaki et al. 2003
Erdemli, S. Turkey*	—	168 (135)	Markaki et al. 2003
Average used	***20.5***	***280***	
Northwest Mediterranean	43–51	150–500	Migon et al. 1989
Sardinia	15–20		Lebolloch and Guerzoni 1995
Sardinia		165	Migon and Sandroni 1999
Dry deposition: leachable			
Israel		320	Herut et al. 1999
Israel	54†	400	Herut et al. 2002
Finokalia, Crete	23‡/53§		Kouvarakis et al. 2001
Crete	12	125	Markaki et al. 2003
Erdemli, S. turkey	44	168	Markaki et al. 2003
Average used	***54***	***350***	
Corsica		400–1000	Bergametti et al. 1992
Cap Ferrat		150–500	Migon et al. 1989

* Total reactive P and DIP in parenthesis (under the assumption of DIP = 0.8TRP in the reported average pH of 6).
† Of which 34 was associated with nitrate and 20 with ammonium.
‡ Measured using aerosol concentration and an assumed depositional velocity.
§ Measured at the same sight using a marbles tray to catch total dry deposition.

cluded within wet deposition estimates (DIN and DIP). By contrast, in Israel, it is considered that conventional dry deposition of dust particles onto the sea surface is the most important pathway. As a result, Herut et al. (2002) measured the concentration of aerosol in the air and calculated the depositional flux using standard estimates of deposition rate. The amount of nutrients leached from this dry dust into Mediterranean surface seawater was then determined by experimentation (LDIN and LDIP). Markaki et al. (2003) also leached nutrients from dry deposition but used Milli-Q water to leach N and P and thus determine the bioavailable LDIP and LDIN flux from dry deposition. In Table 1, leachable, and thus bioavailable, nutrient fluxes are presented.

Herut et al. (2002) estimated the flux of leachable LDIN to be 54 mmol N m^{-2} yr^{-1}, of which leachable inorganic nitrate ($LINO_3$) was 34 mmol N m^{-2} yr^{-1} and leachable ammonium ($LINH_4$) was 20 mmol N m^{-2} yr^{-1}. The sum of seawater leachable inorganic nitrogen species was similar to that of total N, which suggests that there was no significant organic N or other N phases in the dry deposition. Kouvarakis et al. (2001) estimated the ammonia and nitrate content of aerosols collected at Finokalia, Crete, from October 1996 to September 1999. They estimated their flux in two ways. Using depositional velocities from the literature in a similar manner to Herut et al., they estimated the depositional flux of LDIN as 23 mmol N m^{-2} yr^{-1}. Using a set of glass beads within an impaction tray that was sampled only during the dry period from April to September, their estimate of LDIN was 53 mmol N m^{-2} yr^{-1}.

The flux of bioavailable P (LDIP) calculated by Herut et al. (1999*a*, 2002) are similar to one another (320 and 400 μmol P m^{-2} yr^{-1}; Table 1). In calculating this mean value, Herut et al. (2002) corrected for the observation that the input during dust events have high total flux but relatively small percentages of N and P, where the background dry deposition flux is much lower but the percentage of N and P is higher. The mean values are in a similar range to the calculated value for Corsica obtained by Bergametti et al. (1992) of 400–1000 μmol P m^{-2} yr^{-1} (DIP) and for Cap Ferrat of 150–500 μmol P m^{-2} yr^{-1} (DIP; Migon et al. 1989). Markaki et al. (2003) obtained lower estimates for LDIP of 60–100 μmol P m^{-2} yr^{-1} on the basis of data collected for 1 yr of sampling in eastern Crete. The fluxes used later in calculating the total nutrient flux to the eastern Mediterranean are given in bold in Table 1. The best estimate for the bioavailable N load (LDIN) is 75 mmol N m^{-2} yr^{-1}, and that for bioavailable P (LDIP) is 630 in μmol P m^{-2} yr^{-1}. On the basis of these data, the total bioavailable nutrient inputs to the eastern Mediterranean from the atmosphere are 111×10^9 mol N yr^{-1}, whereas those for P are 0.95×10^9 mol yr^{-1}. This calculation, however, does not take into account any gas-phase deposition that might occur, because no data are currently available. If such data were added, it would further increase the N : P ratio of the atmospheric input and also reduce further the potential importance of N fixation to the system.

The average values used in the present study involve the use of data from Israel and Crete, with data from the northwestern Mediterranean, where appropriate. This choice, although based pragmatically on the best long-term data sets available, was shown to be consistent with the modeled geographical variability of atmospheric nitrogen flux over the eastern Mediterranean (Erdman et al. 1994).

Flux of nutrients from river runoff into Eastern Mediterranean—The most detailed studies of nutrient input from rivers have been carried out for the river Po and adjacent catchments areas supplying the northern Adriatic (Degobbis and Gilmartin 1990; Pettine et al. 1998; Degobbis et al. 2000). In the most recent of these estimates, DeGobbis et al. (2000) measured the total dissolved N (TDN) and total dissolved P (TDP) in all the rivers discharging into the northern Adriatic. They used a data set sampled periodically between 1966 and 1995 that included five stations of the Rovinj-Po delta sampled biweekly to seasonally during this period. On the basis of this extensive data set, they determined that TDN was 20.2×10^9 mol yr^{-1} and TDP was 0.9×10^9 mol yr^{-1}. Of this value, the Po river itself contributes ~50% of the total nutrients transported to the basin (Degobbis and Gilmartin 1990).

No similar detailed data set exists for the other rivers flowing into the basin. Vollenweider et al. (1996) created a model to calculate the N and P inputs from all rivers to the Mediterranean on the basis of an analysis of the land use and population in each catchment area. That model used best estimates for the river discharges and then assumed the same export coefficients for nitrogen (1.25×10^3 kg N km^{-2} yr^{-1}) and phosphorus (0.17×10^3 kg P km^{-2} yr^{-1}) for all exports. These export coefficients were calculated for four Italian rivers plus the Rhone and then assumed to be valid for all Mediterranean rivers. This resulted in total input to the basin of 28.9×10^9 mol N yr^{-1} and 1.09×10^9 mol P yr^{-1}. When the model was carried out for the river Po catchment alone, they calculated an input of 24.3×10^3 kg N d^{-1} and 1.7×10^3 kg P d^{-1} (5.9×10^9 mol N yr^{-1} and 0.2×10^9 mol P yr^{-1}). These estimates were smaller than the measured values for the Po of ~10 and 0.45×10^9 mol yr^{-1} calculated by Degobbis et al. (2000) from measurements made within the basin. To estimate the nutrient load to those areas of the Mediterranean where better direct measurements are not available, we used two different assumptions. In the first estimate, the estimated flux input to the Ionian, Aegean, and Levantine basins (excluding the input from the river Nile) as given in Vollenweider et al. (1996) was used. This resulted in N and P loads of 16.8 and 1.1×10^9 mol yr^{-1}, respectively.

Alternatively, it was assumed that Degobbis et al.'s measured estimate for the nutrient load from the Po catchment is correct and that it represents the same percentage of the total input as in Vollenweider et al.'s calculation (i.e. 42%). We then recalculated the total load of N and P from non-Po and Nile sources to the eastern basin to be 27.9 and 1.2×10^9 mol yr^{-1}.

Polat and Tugrul (1995) measured the net annual flux of total N (DIN, particulate organic nitrogen [PON], and DON) and total P (DIP, PP [particulate phosphorus], and dissolved organic phosphorus [DOP]) from the Black Sea into the Sea of Marmara. For the purposes of this budget, the Sea of Marmara is considered to be part of the eastern Mediterranean. The nutrient and water flux data were obtained during a series of cruises between 1986 and 1992. There was a net output of N from the Black Sea of 1.25×10^8 kg N yr^{-1} (8.3×10^9 mol N yr^{-1}) to the Sea of Marmara. There was no net influx of P into the Mediterranean from the Black Sea.

Nixon (2003) calculated the annual flux of dissolved nutrients to the Mediterranean using nutrient data collected from the Nile in Cairo principally by Abdin (1948). Concentrations of DIP averaged 2.9 μmol L^{-1} during the flood and 1.9 μmol L^{-1} during the remainder of the year. Using known values for the Nile flow during the flood and during the rest of the year, Nixon calculated a dissolved P flux of 0.1×10^9 mol P yr^{-1}. In addition to the transport of dissolved phosphate, there was almost certainly a significant flux of exchangeable inorganic P on the fine-grained sediment carried by the Nile flood. Recently, Pan et al. (2002), having carried out detailed adsorption-desorption experiments on Nile sediments, estimated the amount of additional phosphate supplied from desorption from particles during the Nile flood to be 0.10–0.15×10^9 mol P yr^{-1}. As far as we know, no data for TDP prior to 1965 are available for the Nile system.

Nixon (2003) determined the annual flux of nitrogen to be 0.48×10^9 mol N yr^{-1} based only on nitrate measurements (Abdin 1948). Abdel-Hamid et al. (1992) measured total DIN, DIP, TDN, and TDP in the river Nile over an annual cycle and showed that the N : P molar ratio in the river in winter varied from 80 to 290, with measured ammonium values in the river approximately an order of magnitude greater than nitrate values. In the present study, we have used an intermediate N : P ratio of 150 : 1 for the Nile river to represent the value for dissolved nutrients supplied to the southeastern levantine basin prior to 1965. The estimated flux of dissolved N is thus 15×10^9 mol N yr^{-1}, and P flux is 0.25×10^9 mol P yr^{-1} derived from DIP plus desorbed P. Nixon (2003) concluded, in the absence of modern direct measurements, that the present-day nutrient flux is likely to have matched and possibly exceeded the pre-Aswan values. In the absence of direct published data, we have assumed that the modern input is similar to our best estimate of the pre-Aswan input. This represents a maximum value as is discussed below. Fortunately, as will be seen below, the amount of nutrients supplied to the basin from the river Nile is a rather small fraction of the total inputs, and significant errors in this estimate will not have a major effect on our overall budget.

Nutrient flux through the Straits of Sicily—Astraldi et al. (1999) showed that there are systematic seasonal changes in both water flux and the depth of the upper layer of the outflowing Levantine Intermediate Water (LIW) through the Straits of Sicily. The flux is higher in winter than in summer. Also in winter, the outflowing water is present only below 200 m, whereas, in summer and autumn, water flowing out of the eastern Mediterranean is found much closer to the surface. Although Astraldi et al. (1999) presented the flux of water out of the Eastern Mediterranean through the Tunisian and Sicilian passages separately, in our calculations only the summed monthly flux for both passages together was used. This was because the fluxes for each passage were similar (0.54 ± 0.58 and $0.55 \pm 0.17 \times 10^6$ m^3 s^{-1}), and no

Table 2. Nutrient concentrations in the Straits of Sicily as determined by Denis-Karafistan et al. (1998) and Karafistan et al. (2002). n.m. = not measured.

	Surface water (0–50 m)				Deep water, all year
	Winter, Jan–Mar	Spring, Apr–Jun	Summer, Jul–Sep	Autumn, Oct–Dec	
Nitrate	0.5	0.5	0.2	0.15	5.5
Phosphate	0.075	0.1	n.m.	n.m.	0.225

separate data exist for the nutrient concentrations in these two passages. This value is similar to the estimate of total outflow through the Strait of Sicily of 1.2×10^6 m^3 s^{-1} (Bethoux 1980) based on salinity balance. Astraldi et al. (1999) stated that the inflow into the eastern Mediterranean cannot be measured directly using current meters because it is dominated by mesoscale features. To maintain the salinity balance of the basin, there must be 4% more water flowing into the eastern Mediterranean at the Straits of Sicily than are flowing out. It was therefore calculated that the total annual inflow into the Eastern Mediterranean was 1.13×10^6 m^3 s^{-1}.

All the water that flows into the eastern basin is surface water with the nutrient characteristics of water within the photic zone. During winter (December–March), only intermediate and deep water below 200 m flows out of the eastern Mediterranean (Astraldi et al. 1999). For the rest of the year, the outflowing water is much closer to the surface. In our calculations, it was assumed that half of the surface water above 200 m is flowing out of the basin and half of the surface water is flowing into the basin. These assumptions seem reasonable on the basis of the stick diagrams of individual current flows presented in Astraldi et al. (1999).

Denis-Karafistan et al. (1998) summarized the nitrate data archived at the National Oceanic Data Center for all of the Mediterranean during 1945–1987. This includes all the data sampled close to or within the Straits of Sicily. On the basis of these data, they have created a set of contour maps for the seasonal nitrate distribution in the upper 50 m and at depth for the entire year. Karafistan et al. (2002) carried out a similar exercise for the DIP data, except that their data set continues until 1993. The phosphate data have more data in the area of the straits of Sicily; thus, the averages they obtained in this area are likely to have greater level of confidence than those for nitrate. The nutrient distribution within the eastern Mediterranean has a clear seasonal distribution (Krom et al. 2003). Although there are no published nutrient profiles within the Straits of Sicily or in the western Ionian Sea, Provero et al. (1990) measured nutrient distributions in the eastern Tyrrhenian Sea just outside the Straits of Sicily. They sampled in October and November 1984 and found constant low values in the upper 100 m (the photic zone), a nutricline to 200 m, and then constant higher values in the deep water below 200 m. In our calculations, these depths (100 and 200 m, as appropriate) are used to define the critical depths for changes in nutrient concentration.

The net flux out of the eastern Mediterranean was calculated in two different ways. The first was the simple flux calculation used previously for this calculation (Sarmiento et al. 1988; Bethoux et al. 1998), in which the total water flux out the eastern Mediterranean was multiplied by the concentration of nutrients (nitrate and phosphate) in deep water from the eastern Mediterranean. The only difference between the numbers in the present study and those carried out previously is that the total water flux value used was the more recent estimate of Astraldi et al. (1999) and the nutrient value at depth was that given by Denis-Karafistan et al. (1998) for nitrate and by Karafistan et al. (2002) for phosphate. This resulted in net fluxes of 203×10^9 mol N yr^{-1} and 8.3×10^9 mol P yr^{-1}. In the second calculation, the seasonal flow rates from Astraldi et al. (1999) were used together with the nutrient value given in Denis-Karafistan et al. (1998) and Karafistan et al. (2002), as shown in Table 2. The net flux results are given in Table 3. The flux results used in subsequent calculations (142×10^9 mol N yr^{-1} and 4.4×10^9 mol P yr^{-1}) take into account the seasonality of water flow and nutrient distribution used in the total budget. These values are within the range of values determined by Ribera D'alcala et al. (2003).

Determination of the burial flux of N and P in sediments—Eijsink et al. (2000) calculated the total P burial rate in the eastern Mediterranean. The total area of the eastern Mediterranean is 150×10^4 km^2 of which 90% is estimated as being the deep basin and 10% the continental shelves, of which 2% is the Egyptian-Israeli shelf. Using measured values for total P, the particle burial rates calculated from the linear sedimentation rate, and bulk density, the burial rate of total P for major sedimentary provenances across the eastern Mediterranean was calculated. In the present study, the burial rate for organic P as determined by SEDEX extraction was used as the measure of the biologically available P (Eijsink et al. 2000). A series of literature values were used for the molar total N : P ratio of sediment for each of the major sediment provenances used in Eijsink et al. (2000).

Table 3. Calculated flux of nitrate and phosphate through the Straits of Sicily (in 10^9 mol yr^{-1}).

	Nitrate	Phosphate	Method used in calculation
Flux out of the eastern Mediterranean	158	6.6	Seasonal water flux × seasonal concentration given in Denis-Karafistan et al. (1998) and Karafistan et al. (2002)
Flux into the eastern Mediterranean	16	2.2	Seasonal water flux × seasonal surface water concentration in Denis-Karafistan et al. (1998) and Karafistan et al. (2002)
Net flux out of the eastern Mediterranean	142	4.4	

Table 4. Molar ratio of total N : total P in sediments from the major sedimentary provenances across the eastern Mediterranean (Eijsink et al. 2000).

Location	Total N (%N)	Total P (mg kg^{-1})	Molar N : P	No. of samples	Reference
Egyptian-Israeli shelf	0.14	540	5.4 : 1	26	El Sabrouti et al. 1990
Northern Adriatic shelf	0.13	516	5.2 : 1	14	Faganeli et al. 1994
Coastal Margins (mid-Adriatic)	0.103	489	4.4 : 1	25	Faganeli et al. 1994
Ionian and Aegean Seas and Levantine basin	0.175	553*	6.8 : 1	1	Wakefield and O'Sullivan 1996
Ionian and Aegean Seas and Levantine basin	(0.64–0.95)†	(0.48–0.72)‡	1.3 : 1	1	Nijenhuis et al. 2001

* Value for Total P is not given. The concentration used was that for BC03 (Eijsink et al. 2000), which is a location south of Crete close to that given in Wakefield and O'Sullivan (1996).
† Burial flux of N calculated from the C_{org} accumulation rate (g m^{-2} yr^{-1}), divided by the $C_{org} : N_{org}$ ratio given in Nijenhuis et al. (2001).
‡ Burial flux of P is given in Eijsink et al. (2000) for the stations location closest to the ODP core locations of 969 and 974 presented by Nijenhuis et al. (2001).

These were then multiplied by the total P burial flux to calculate the N burial flux.

El Sabrouti et al. (1990) measured both total N and P for a series of sediment samples ($n = 26$) across the Egyptian shelf (Table 4). Faganeli et al. (1994) presented values for total N (%N) and total P (ppm) for surficial sediments for a series of stations across the Adriatic sea. In the present study, the values for the most northerly stations (zone 1) are taken as those representative of the northern Adriatic shelf, which is adjacent to the Po estuary. The average values for the remaining areas of the Adriatic (zones 2–4) are used to represent the molar ratio for the rest of the Adriatic and also for coastal margins of the eastern Mediterranean away from the influence of the Nile and the Po.

There are few values for total N available for the deeper basins of the eastern Mediterranean and none where total N and P were measured on the same samples. Wakefield and O'Sullivan (1996) presented total N values for a station on the Mediterranean ridge south of Crete very close to Sta. BC03 measured in Eijsink et al. (2000). Likewise, although Nijenhuis et al. (2001) presented values for organic carbon burial flux and an organic C : N ratio from which the organic N burial flux can be calculated, they did not present any P data for these samples. In Table 5, the molar ratio (N : P) was determined by combining results from these two studies. This procedure resulted in molar ratios of 6.8 : 1 and 1.3 : 1. The former seems rather high compared with values obtained from the coastal shelves and the later seems rather low compared with values that are normally found in deep-sea sediments. Fortunately, the total N and P content of these sediments is so low that it does not have a major effect on the burial flux of the eastern Mediterranean as a whole. The calculations result in a N sediment burial flux of 27 × 10^9 mol N yr^{-1} and an organic P sediment burial flux of 1.0 × 10^9 mol P yr^{-1}.

Sedimentary denitrification—The process of bacterial denitrification requires suboxic/anaerobic conditions. Globally, this occurs predominantly in organic-rich coastal sediments and in the oxygen-minimum zones of the Arabian Sea and the eastern central Pacific. Within the eastern Mediterranean, the observed oxygen minimum is far too small (Kress and Herut 2001) to allow nitrate reduction to occur. The only significant area of organic-rich sediment is the northern Adriatic (Degobbis and Gilmartin 1990). Other researchers estimated a denitrification rate of 1.4 mmol m^{-2} d^{-1}, equivalent to 7.1 × 10^9 mol N yr^{-1} for the region. All of the other coastal margin areas of the basin, which are estimated to represent 10% of the total area of the eastern Mediterranean, have low carbon productivity (Krom et al. 2003) and are floored with sediments that are low in organics (<1% organic C; Christensen et al. 1988). Christensen et al. (1988) carried out a detailed study of sedimentary N dynamics from the Israeli continental shelf. They showed that although the sediments represent a small net source of N to the basin, overall, a minor amount of denitrification does occur. Their estimated denitrification rates of 5.9–14 mmol N m^{-2} yr^{-1} results in a total denitrification rate for the continental shelves in the entire basin of 0.9–2 × 10^9 mol N yr^{-1}. Over the remaining deep water of the eastern Mediterranean, the redox boundary is related to buried sapropels that were formed >5,000 yr ago. Typically, the present-day suboxic

Table 5. Total N and P burial flux across the eastern Mediterranean (Eijsink et al. 2000). Values were calculated from the burial flux of total P given in Eijsink et al (2000) and the molar ratios given in Table 4.

Location	Area (10^4 km^2)	Calculated burial flux of total P (10^9 mol P yr^{-1})	Calculated burial flux of organic P (10^9 mol N yr^{-1})	Calculated burial flux of total N (10^9 mol N yr^{-1})
Egyptian-Israeli shelf	3.0	3.0	0.6	16
Northern Adriatic shelf	0.3	0.3	0.06	1.
Coastal margins	12	1.0	0.2	4.4
Ionian and Aegean Seas and Levantine basin	135	1.2	0.18	1.6–8.1
Total	150	5.5	1.0	24–30

Table 6. Calculated nutrient inputs into the eastern Mediterranean basin. All values are given in 10^9 mol yr^{-1}. NA: not applicable.

Source	N input/output	P input/output	Molar N : P ratio
Best estimates for the nutrient fluxes into the basin			
Atmospheric input	111	0.95	117
Riverine input (Po and adjacent area of the northern Adriatic)	20	0.9	22
Nile input	15	0.25	60
Riverine input from rest of basin	28	1.25	23
Black Sea	8	0	—
Total input to basin	180	3.4	54
Best estimates for nutrient fluxes out from the basin			
Straits of Sicily	142	4.4	32
Sediment deposition	27	1.0	27
Sediment denitrification	10		NA
Total output from basin	179	5.4	33

zone occurs at >25 cm depth within the sediment (De Lange et al. 1999). Using the measured nitrate gradient with zero nitrate at 25 cm and assuming simple Fickian diffusion, the total denitrification flux over the deep basin is 0.8×10^9 mol N yr^{-1}. In the budget, the maximum denitrification rate of $10 (7 + 2 + 0.8) \times 10^9$ mol N yr^{-1} is used, which, as will be seen below, has only a small effect on the overall N : P ratio.

Discussion

The total budget shows that the biologically available N load to the basin is significantly more than 16 times the biologically available P load to the basin (Table 6). The calculated N : P ratio of the total input is 54. Furthermore, the N : P ratio of all the individual input sources are all greater (and, in the case of the atmospheric input, very much greater) than 16 : 1. In simple terms, because all the inputs to the system are significantly in excess of the Redfield ratio of 16 : 1, the entire basin has a shortage of phosphorus. It does not require in situ processes such as N fixation by sea grasses and/or phytoplankton (Bethoux et al. 1992, 1998) or P removal by Saharan dust (Krom et al. 1991) for the system to have a surplus of N over P. This imbalance between N and P in the supply is sufficient to explain the unusual N : P ratios that accumulate within the deep water of the basin and that are exported as the steady-state flux through the Straits of Sicily. It is this unusual nitrate : phosphate ratio in the deep waters of the basin, which, when mixed into the euphotic zone during deep winter mixing, results in the major annual phytoplankton bloom being P limited (Krom et al. 1991).

This conclusion remains robust even after other reasonable alternative assumptions are made in the budget calculations. Thus, the dominant term in this nutrient budget is the atmospheric flux, which has an estimated N : P ratio of 117 : 1. It is likely that, at present, the atmospheric N input is increasing to this system as a result on increased fluxes of NO_x from car use and NH_3 from agriculture. Any estimate of the nitrogen flux to the system is likely to be larger than the one presented here, especially if direct gas exchange is added to the flux estimate. It is possible that the bioavailable fraction of P in Saharan dust has been underestimated. It is assumed here that only seawater LDIP is biologically available. There have been some very tentative observations to suggest that this might be too conservative. When the concentration of TP in Saharan dust that affects the eastern Mediterranean (~25 μmol g^{-1}) was compared with the calculated fraction of Saharan dust–derived sediment remaining in the sediment (17 μmol g^{-1}), it was found that the amount lost in transit was approximately double that leached from the dust in the surface layers (3 μmol g^{-1}; Eijsink et al. 2000). Additional P may be mobilized from the dust in the acidic guts of zooplankton or by microbial remobilization in surface sediments. Although this additional P would go a considerable way to closing the P budget for the system, it would still leave an N : P ratio in the atmospheric input of >50 : 1. The second largest flux into the system is from the Po river system. As a result of recent changes in water management in the catchment, there is even less P being discharged into the northern Adriatic, which results in an increased N : P ratio (Degobbis et al. 2000). The estimate for the flux from the river Nile assumes that the flux has returned to pre-Aswan levels. Hamza et al. (2003) presented an alternative flux estimate of 45×10^6 mol N yr^{-1} and 2.7×10^6 mol P yr^{-1}, with an N : P ratio of 16 : 1. These estimates are similar to those presented in the Gemswater Atlas of 1.7×10^9 mol N yr^{-1} and 30×10^6 mol P yr^{-1} (http://www.gemswater.org). This estimate includes only nitrate and phosphate and has an N : P ratio of 57 : 1. These flux estimates are much lower than those used in the present study. If included, they would have no effect on the overall conclusion regarding the excess of N over P in the supply to the basin. They would however result in a moderate shortfall in the N budget of $\sim 15 \times 10^9$ mol N yr^{-1}. However, no account is taken in this budget of direct groundwater fluxes into the basin, which, it has been suggested, might be significant, especially at the Nile delta, because no data exist anywhere that estimate the magnitude or nature of this flux.

As with all previous budgets (Sarmiento et al. 1988; Bethoux et al. 1992, 1998), no account is made of DON or DOP because no relevant values of DON and DOP and its seasonal variability and vertical distribution exist at present. Recent values of DON and DOP have been measured in May in the southeastern levantine basin (Spyres et al. unpubl. data). These show somewhat higher values of the DON : DOP ratio in the surface waters than at depth, which is consistent with the pattern found in oligotrophic waters elsewhere. Spyres et al. (pers. comm.) also suggested that dissolved organic matter (DOM) values are likely to vary, from constant in winter, during mixing, to a maximum in summer. This means that it is necessary to have a complete seasonal data set before sensible fluxes could be calculated. However, if DON and DOP values had been included in our budget, the N : P value of the input to the basin are likely to have been even higher.

In our budget, although essentially all the N input to the system is accounted for on the outflow, there is more bioavailable P fluxing out at the Straits of Sicily than is measured in the inputs. One possible explanation for this discrepancy is that, although all of the measured major chemical forms of N inputs (NO_3, NH_4, and DON) have been included and are bioavailable, some P species may have been missed. Some of the P may be transported as particulate P, which was not adequately measured. In addition, part of the P cycle involves refractory inorganic compounds. The information on the bioavailability of such compounds, especially in the context of a P-starved system as the eastern Mediterranean, is poor.

This budget is effectively a steady-state budget. Some of the inputs are changing with time. Riverine fluxes such as the Po have decreased in phosphate content with time. Such changes might contribute to the ''missing'' P. There are also changes in circulation, particularly the formation of deep water in the Aegean Sea and the resulting eastern Mediterranean transient, which may affect the storage of nutrients within the system and are not taken into account in this budget. Another possible effect of changing inputs of N is that it is likely that the atmospheric input has increased considerably over the past 50 yr. If the average residence time of nutrients in the system is long enough, then it may be appropriate to use a significantly lower N input from the atmosphere. The corrected budget might then be consistent with some N fixation.

The calculation that the input flux of bioavailable nutrients to the eastern Mediterranean is $\gg$16 : 1 is not, however, sufficient on its own to explain why the system has retained this high nutrient ratio. A recent compilation of nutrient fluxes to the global ocean have calculated that the total fixed nitrogen supplied to the oceans (atmosphere and river input) is 4.6×10^{12} mol N yr^{-1} (Galloway 2003), whereas the total dissolved P input is 5.6×10^{10} mol N yr^{-1} (Ruttenberg 2003). This represents an N : P availability ratio of 82 : 1. Yet most of the world's oceans have a nitrate : phosphate ratio of ~16 : 1 (Redfield et al. 1963). This is because competing biologically mediated processes, particularly nitrogen fixation and denitrification, interact with the terrestrial nutrient input, oceanic circulation, and sedimentation and tend to push the N : P ratio of the dissolved inorganic and particulate organic nutrients toward the Redfield ratio of 16 : 1 (Tyrell 1999). It is therefore necessary to answer the question of why these feedback mechanisms function so successfully in many other regions of the world but apparently do not operate in the eastern Mediterranean.

In the situation where there is an excess of nitrogen in the system, two adjacent mechanisms occur to drive the system back toward 16 : 1. Seitzinger and Giblin (1996) showed that denitrification losses in the ocean are on the order of 9.2×10^{12} mol N yr^{-1}, which exceeds the known oceanic nitrogen inputs. More than half of this denitrification takes place in sediments, particularly in the coastal zones (Wollast 1998), with the remainder occurring in pelagic oxygen minimum zones. In the coastal zones, much of the excess organic matter produced accumulates in the sediment. This results in a redox boundary close to the sediment water interface, which sets up a nitrification-denitrification couple that converts fixed nitrogen into nitrogen gas, which is vented from the system. In sediments where the redox boundary is close enough to the sediment-water interface, phosphate is also more efficiently recycled. Inorganic phosphate, which is bound to labile iron oxyhydroxides on passage through the redox boundary, releases a large fraction of the phosphate (Krom and Berner 1981). Both of these processes result in a reduction in the N : P ratio within the oceanic water column.

In the eastern Mediterranean, this mechanism does not operate, because the system is too ultraoligotrophic to allow significant export carbon production because of the unusual anti-estuarine circulation in the basin. That is, surface water, with depleted nutrients, flows in at the Straits of Sicily (and at Gibraltar), whereas intermediate and deep water with enhanced nutrient content flow out. The pelagic oxygen minimum is only ~70% saturation (Kress and Herut 2001), which is far above the suboxic conditions required for pelagic denitrification to occur. There are almost no areas in which the amount of organic matter exported to the sediment is large enough to allow significant accumulation in the surface layers and, hence, cause the redox boundary to approach the sediment water interface. The only moderately large exception is the northern Adriatic (Zago et al. 2000). In this budget, it has been shown that even a maximal estimate for sedimentary denitrification in the system of 10×10^9 mol N yr^{-1} is insufficient to significantly modify the N : P ratio within the basin.

The most widespread alternative explanation for the unusual N : P ratio in the eastern Mediterranean is that it is due to widespread N fixation (Bethoux et al. 1992, 1998, 2002*a;* Ribera D'alcala et al. 2003). Pantoja et al. (2002) suggested that 90% of the N found in the eastern Mediterranean is the result of N fixation. However, there has been as yet no field data showing evidence of N fixation in the eastern Mediterranean. *Trychodesmium,* the most important N-fixing marine organism, has not been observed in the eastern Mediterranean (Thingstad et al. pers. comm.). The only potential N-fixing organism found in the eastern Mediterranean in significant numbers is *Synnechoccus,* and it is unclear at present whether this is capable of fixing N_2 under the conditions found in the basin.

The requirements for such N fixation are abundant sunlight and sufficient iron supply to meet the high iron requirement of N-fixing phytoplankton. It is a matter of active debate at present whether shortage of N is an additional requirement for significant N fixation to occur. Where N fixation has been shown to be a major process in tropical surface waters, the surface waters are either seasonally N limited (Wu et al. 2000) or there is evidence of temporary multiyear N limitation (Karl and Bjorkman 2002). The eastern Mediterranean represents a location in which there is abundant sunlight and a high concentration of iron in the surface waters (Statham and Hart unpubl. data) supplied by Saharan dust, but a drastic shortage of bioavailable phosphate (Krom et al. 2003). N-fixing organisms, including *Synnechoccus*, have been shown to require P to fix nitrogen (Sanudo-Wilhelmy et al. 2001). Hence, it is likely that the P-limited status of this region will act to suppress N fixation. In the present study, the N input to the basin balances the outflow. This balance occurs without any N fixation being included in the calculated total N budget. In their most recent study, Bethoux et al. (2002*a*) used a budget calculation for the eastern basin to conclude that N fixation is the reason for the unusual N : P ratio. However, they did not present any atmospheric input data in their budget, which we have shown is the major source of nutrients to the basin. In addition, they used an estimate for the terrestrial discharges to the entire Mediterranean (Helmer 1977) of 6.2 : 1, which is much older and less detailed than the budget for the eastern Mediterranean that we used, which was carried out by Vollenweider et al. (1996). Furthermore, the N : P ratio suggested in Helmer (1977) is far lower than the detailed measurements made subsequently by Degobbis and Gilmartin (1990), Degobbis et al. (2000), and others.

Pantoja et al. (2002) found that $\delta^{15}N\text{-}NO_3$ in the eastern basin (2.4 $\pm$ 0.1‰) is significantly lighter than the level of deep-ocean nitrate in the world's oceans in general and in the Atlantic Ocean in particular (+4.8–5‰). They assumed that this low $\delta^{15}N$ fixed N was due to N fixation and calculated that N fixation supplies 90% of the nitrate to the basin. Sachs and Repeta (1999) also reported low nitrate $\delta^{15}N$ in the eastern basin (-0.7‰) and estimated that N fixation could supply 46–70% of the nitrate to the eastern basin. This represents an N fixation term of 80–160 $\times$ 10^9 mol N yr^{-1} on the basis of the known export of DIN from the basin (Bethoux et al. 1998). Such a large missing term is incompatible with the N budget calculated in the present study. Sachs and Repeta (1999), Pantoja et al. (2002), and Koppelmann et al. (2003) all assumed that N fixation is the only process that could result in the light values of $\delta^{15}N\text{-}NO_3$ and $\delta^{15}N$-PON. In the eastern Mediterranean, there are a number of possible alternative explanations that are compatible with existing isotopic data and with our N budget.

During the winter bloom, primary productivity ceases when phosphate is entirely consumed in the surface waters. This has been shown to result in isotopically light PON (3.5–4.0‰) being found and heavy nitrate remaining (17–20‰; Struck et al. 2001). As in all oceanic systems, the most important pulse of organic matter from the surface waters to the intermediate and deep waters occurs during the annual phytoplankton bloom. In the eastern Mediterranean, this results in light PON being exported, which would result in the light values for zooplankton (2–3.1‰) observed in sediment traps and plankton tows carried out at the end of the winter period (Koppelmann et al. 2003). When this PON is remineralized at depth, it results in light nitrate. It has been suggested that the excess nitrate left over in surface waters after the winter bloom is converted to DON (Thingstad et al. unpubl. data). This explanation would predict that the DON in the eastern Mediterranean would be unusually heavy.

An alternative explanation for the light nitrate in the deep water is that denitrification is known to remove light nitrate preferentially (Owens 1987). Thus, the isotopic signal of the deep nitrate in the Pacific Ocean and Arabian Sea, which has been modified by denitrification in the water column, will be isotopically heavier. Denitrification in the Atlantic Ocean occurs in sediments on the continental shelf. The effect of this on the isotopic signal is not as clear. Nevertheless, the combination of denitrification on the shelf and mixing with water that had seen the Pacific and/or Indian Oceans would tend to create a heavy nitrate residual. It is thus not unreasonable to expect that, in a region such as the eastern Mediterranean, where denitrification is relatively unimportant, the residual nitrate will be lighter than the global average.

Finally, no systematic data exist on the isotopic composition of nutrient inputs to the basin; thus, it is not possible to assume that the input to the basin has the same ratio as the inputs to the North Atlantic or other oceans.

A test of the new hypothesis to explain the reason for P limitation in the eastern Mediterranean is to see whether there are any areas where the N : P ratio in the deep water approaches 16 : 1. The only area where the nutrient ratio in mid- and deep waters are ~15 : 1 (Degobbis and Gilmartin 1990; Zavatarelli et al. 1998) is in the northern Adriatic, which is also the only area where there is sufficient nutrient input for organic matter accumulating in the sediment to result in significant denitrification. There is only one other region of the world's oceans at present where the N : P ratio in the deep waters is greater than 16 : 1—the Red Sea, where the ratio is 21 : 1 (Naqvi et al. 1986). This is also the only large body of water which is ultraoligotrophic because of an anti-estuarine circulation.

The eastern Mediterranean is characterized by a high N : P ratio in the deep water (Krom et al. 1991), which results in the highly unusual P limitation of primary productivity. The total nutrient budget calculation carried out in the present study suggests that the high N : P ratio is due primarily to the high biologically available N : P ratio in all the input sources but particularly from the atmosphere (117 : 1). The high N : P ratio is retained within the system because the normal biological feedback mechanisms that operate on the global oceanic system, denitrification in coastal sediments and/or intermediate water, do not operate in the eastern Mediterranean. This is because of the extreme oligotrophic nature of the system caused by its unusual anti-estuarine circulation. This hypothesis is supported by the observation that the only area of the eastern Mediterranean that has significant denitrification, the northern Adriatic, is also the only area where the N : P ratio in deeper water is 16 : 1. In addition, the only other area of the ocean that has N : P ratio >16 : 1 is the Red Sea, which is the only other large area with anti-estuarine circulation. The calculation carried out in the present study suggests that the N budget balances without any significant input from N fixation. The unusually light ^{15}N values in the deep-water nitrate and PON, which were found by Sachs and Repeta (1999) and by Pantoja et al. (2002), can be explained by the unusual characteristics of this system—namely P limitation of primary productivity during the winter plankton bloom and a lack of significant denitrification in the basin.

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