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Nutrient budgets
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Nitrogen, phosphorus, and biogenic silicon budgets for the northern Adriatic Sea

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ABSTRACT

Proximate nitrogen, phosphorus and biogenic silicon budgets were calculated for the northern Adriatic, one of the most productive subregions of the Mediterranean Sea, and the main processes driving the biogeochemical cycle of these biogenic elements were ranked as to their relative importance. The calculations were based on an extensive data set ($n = 20\,000$) collected since 1966, and from results reported in the literature.

Contributions (N: $23{,}640 \times 10^6$, P: 910×10^6, and Si: $8{,}400 \times 10^6$ mol y^{-1}) and losses (N: $17{,}150 \times 10^6$, P: 750×10^6, and Si: $5{,}460 \times 10^6$ mol y^{-1}) were of the same order of magnitude. The results support the assumed importance of the nutrient contribution by the Po River (at least 50 % of the inputs) whose waters thereby influence a large part of the northern Adriatic. The loss by water mass transport is the principal mechanism balancing the nutrient budget in the northern Adriatic, although losses by denitrification in sediments account for a large part (about 40 %) of the nitrogen output. Atmospheric contributions are relatively minor, particularly for total phosphorus and orthosilicate, and nitrogen fixation does not contribute significantly to the total nitrogen budget. Phosphorus and silicon burial in the sediments represents a significant loss for these elements. Other losses (fish catches and production of nitrogen oxides) were not significant on the scale of these calculations.

Nutrient quantities equal to or higher than the yearly external input are biologically recycled annually in the northern Adriatic (N: $38{,}400 \times 10^6$, P: $1{,}065 \times 10^6$, and Si: $12{,}800 \times 10^6$ mol y^{-1}). The results quantify the importance of water column microheterotrophic activity as the principal mechanism of nitrogen and phosphorus regeneration in the northern Adriatic. Macrozooplankton and nekton excretion and benthic release together contribute less than 10 % of the total nitrogen and phosphorus remineralization. In contrast, the bulk of orthosilicate regeneration occurs in the sediments.

The high ratio of external contribution to regenerated nutrients clearly establishes that the former nutrient input is supporting a large part of the relatively high biological productivity of the region. This indicates that the northern Adriatic ecosystem is sensitive to further increases of anthropogenic nutrient load. The eutrophic impact of such loading could be critical during spring and early summer, when biological activity is the highest and the northern Adriatic behaves as a semienclosed sea due to eddy circulation.

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RÉSUMÉ

Les bilans en azote, phosphore et silicium biogénique de la mer Adriatique septentrionale

Les bilans en azote, phosphore et silicium biogénique sont établis pour l'Adriatique septentrionale, l'une des régions les plus productives de la mer Méditerranée. Les principaux phénomènes entrant dans le cycle biogéochimique de ces éléments biogéniques ont été classés selon leur importance relative en utilisant les nombreux

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résultats (20000) des analyses effectuées depuis 1966 et des résultats cités dans la littérature.

Les apports (N : 23640.10^6; P : 910.10^6; Si : 8400.10^6 mol.a^{-1}) et les pertes (N : 17150.10^6; P : 750.10^6; Si : 5460.10^6 mol.a^{-1}) sont du même ordre de grandeur. Les résultats confirment l'importance de l'apport de sels nutritifs par les eaux du Pô (au moins 50 % du total) dont l'effet s'étend à une grande partie de l'Adriatique septentrionale. La perte par transport de masse est le terme principal du bilan en éléments nutritifs, bien que la dénitrification soit importante dans les sédiments (environ 40 % des pertes d'azote). La contribution de l'atmosphère est relativement modeste, en particulier pour le phosphore total et l'orthosilicate; la fixation de l'azote élémentaire n'est pas significative. Les pertes de phosphore et de silicium sont importantes dans les sédiments; les autres pertes, dues à la pêche et à la production des oxydes d'azote, ne sont pas significatives dans les bilans établis ici.

Des quantités d'éléments nutritifs égales ou supérieures aux apports externes sont recyclées chaque année par des phénomènes biologiques (N: 38400.10^6; P: 1065.10^6; Si : 12800.10^6 mol.a^{-1}). Les résultats montrent que l'activité microhétérotrophique dans la colonne d'eau est le principal mécanisme de régénération de l'azote et du phosphore. L'excrétion du macrozooplancton et du necton, ainsi que la reminéralisation dans les sédiments, contribuent pour moins de 10 % à la reminéralisation totale de l'azote et du phosphore. Au contraire, la régénération de l'orthosilicate se produit surtout dans les sédiments.

Le rapport élevé entre la quantité d'éléments nutritifs d'origine externe et celle qui est régénérée montre que l'apport externe joue un rôle important dans la forte productivité biologique de cette région. L'Adriatique septentrionale est donc un écosystème sensible aux éventuelles augmentations de la charge anthropogénique en éléments nutritifs. L'impact eutrophisant de cette charge pourrait devenir critique au printemps et au début de l'été lorsque l'activité biologique est maximale, la circulation dans l'Adriatique étant alors celle d'une mer semi-fermée.

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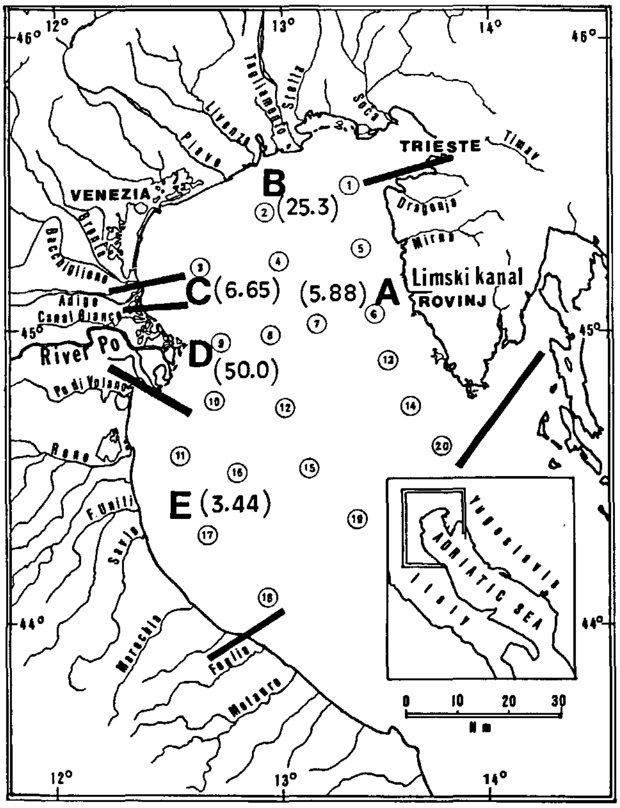
INTRODUCTION

The computation of a nutrient budget is the basic step in the study of the relative importance of the processes controlling the biogeochemical cycles of major plant nutrients. There are only a few coastal marine regions in the world for which budget calculations have been attempted: for example the Baltic Sea (Larsson *et al.*, 1985), the Gulf of Maine and Georges Banks, USA (*e.g.* Schlitz and Cohen, 1984), the Gulf of St. Lawrence, Canada (Coote and Yeats, 1979), Narragansett Bay, Rhode Island, USA (Nixon and Pilson, 1983), and the Mediterranean Sea as a whole (Bethoux and Copin-Montegut, 1986). Partial calculations have been made for some other coastal and estuarine areas (*see* Nixon and Pilson, 1983 for review). However, there are no regions where complete and fully reliable nutrient budgets are available.

The northern Adriatic Sea (18900 km^2) represents a small portion of the total area (139000 km^2) of the Adriatic Sea (Fig.), but it is one of, if not the most, productive regions in the Mediterranean (Sournia, 1973). The Po River (Italy), one of the largest in the Mediterranean, as well as various minor rivers, discharge their waters into the northern Adriatic. It was often assumed, but never quantified, that the Po River is the most important source of nutrients for the northern Adriatic. A preliminary budget calculation for



Figure

Positions of the oceanographic stations and subregions in the northern Adriatic Sea.

Positions des stations océanographiques et des subrégions dans la mer Adriatique septentrionale.

Table 1

Ammonium (NH_4), nitrite (NO_2), nitrate (NO_3), total inorganic nitrogen (TIN), total nitrogen (TN), orthophosphate (PO_4), dissolved organic (DOP), particulate (PP), and total phosphorus (TP), and orthosilicate ($Si(OH)_4$) contributed by freshwaters discharged in subregions of the northern Adriatic Sea (% in parentheses).

Les apports en sels d'ammonium (NH_4), nitrite (NO_2), nitrate (NO_3), azote inorganique total (TIN), azote total (TN), orthophosphate (PO_4), phosphore organique dissous (DOP), particulaire (PP) et total (TP) et orthosilicate ($Si(OH)_4$) par les eaux douces déchargées dans le subrégions de l'Adriatique septentrionale (% entre parenthèses).

	Subregions					
Nutrient species	A Istria	B Northern coasts	C Adige River (10^6 mol y^{-1})	D Po River	E Emilia-Romagna	Total Northern Adriatic
NH_4	18	65	63	1 050	270	1 466
	(1)	(4)	(4)	(71)	(19)	(100)
NO_2	1.8	16	7.1	167	52	244
	(1)	(6)	(3)	(68)	(22)	(100)
NO_3	647	1 440	448	7 347	154	10 036
	(6.5)	(14)	(4.5)	(73)	(1.5)	(100)
TIN	667	1 521	518	8 564	476	11 746
	(6)	(13)	(4)	(73)	(4)	(100)
TN	806	–	–	–	–	–
PO_4	4.7	6.3	11.4	230	58	310
	(1.5)	(2)	(3.5)	(74)	(19)	(100.5)
DOP	–	–	1.3	17.5	–	–
PP	–	–	25.1	238	–	–
TP	7.1	30.0	37.8	495	110	680
	(1)	(4)	(5.5)	(73)	(16)	(100)
$Si(OH)_4$	400	875	660	5 990	412	8 340
	(5)	(10)	(8)	(72)	(5)	(100)
TIN/PO_4	142	241	46	37	8	38
$TIN/Si(OH)_4$	1.7	1.7	0.8	1.4	1.1	1.4
$Si(OH)_4/PO_4$	85	140	58	26	7	27

nitrogen alone indicated that the Po accounts for at least half of the total inputs of combined nitrogen (Degobbis *et al.*, 1986*a*), and that the relative importance of various nitrogen sources and sinks is essentially different than for the Mediterranean as a whole.

In 1966, a long term project was started to study the primary production of open waters of the northern Adriatic. In addition to biological measurements, hydrographic observations and nutrient analyses were carried out. The nutrient analyses generated an extensive data set ($n = 20000$) which was combined with results from the literature to calculate regional budgets for nitrogen, phosphorus and biogenic silicon. The main processes governing the biogeochemical nutrient cycles for all three elements were then evaluated in order to rank them as to their relative importance.

MATERIALS AND METHODS

The northern Adriatic is defined as that area lying north of the line from the southernmost extension of the Istrian peninsula in Yugoslavia to the southern border of the Emilia-Romagna region in Italy (Fig.). It has a surface of 18 900 km², a volume of 635 km³, and a mean (station) depth of 33.5 m.

The data used in developing nitrogen, phosphorus and biogenic silicon budgets came from approximately biweekly cruises from July 1972 to December 1973, quarterly cruises in 1974 and 1975, and from previous and subsequent cruises to 3-8 stations between Rovinj (Yugoslavia) and the Po River delta (Italy). The station positions (Fig.), sampling protocol, parameters measured, methods and techniques are described in detail elsewhere (Gilmartin *et al.*, 1972).

Analyses for nutrients were based on standard spectrophotometric methods (Strickland and Parsons, 1972). The indophenol blue technique was used for ammonium determination, while nitrite and nitrate were analyzed as a pink azo compound before and after reduction of the samples on columns filled with metallic cadmium filings coated with copper. Orthophosphate (reactive phosphorus) and orthosilicate (reactive silicate) were determined by molybdenum-blue techniques (reduction of molybdate complex with ascorbic acid and methol, respectively). The samples were collected by 5 l Niskin or Van Dorn samplers and the analyses were generally performed aboard immediately after collection. On infrequent occasions, due to equipment failure, samples (except for ammonium) were frozen at −30°C and subsequently analyzed ashore. In which case samples for ammonium determination were stabilized by adding the phenol-ethanol reagent (Degobbis, 1973). Absorbance readings were made on Beckman DU spectrophotometers with 10 cm cells.

RESULTS

Nutrient input to the region

The nitrogen, phosphorus and orthosilicate contributed by rivers and wastewaters discharging into the northern Adriatic (Tab. 1 and 2) was estimated separately for five major subregions (Fig. 1), in order to evaluate the spatial distribution of the terrestrial input of these compounds. These subregions were: A) the west Istrian coast of Yugoslavia (mainly karstic groundwater sources, and the small rivers Mirna, Dragonja, Rižana);

Table 2

Total nitrogen and total phosphorus loads in subregions of the northern Adriatic Sea (% in parentheses).

Les apports en azote et phosphore totaux dans les subrégions de l'Adriatique septentrionale (% entre parenthèses).

Subregions	Total nitrogen (10^6 mol y^{-1})	Total phosphorus (10^6 mol y^{-1})	Ratio N/P
Western Istrian coast (A)	900 (5)	19 (2)	47
Coast from Triest to Po river delta (B+C)	5 000 (25)	280 (31)	18
Po River (D)	11 575 (57)	495 (55)	23
Emilia-Romagna coastal region (E)	2 700 (13)	110 (12)	25
Total in the northern Adriatic	20 175 (100)	904 (100)	22

B) the region from Trieste to the Po Delta (the Soča, Stella, Tagliamento, Livenza, Piave, Sile, Brenta, and Bacchiglione rivers, and various drainage canals); C) the Adige estuary; D) the Po Delta; and E) the Emilia-Romagna region of Italy, just south of the Po Delta (the Reno, Lamone, Ronco, Montone, and Savio rivers, and various drainage canals).

In all regions river contributions were calculated from long-term averages of freshwater discharge rates (1956-1965 total average $92{,}173 \times 10^6$ m^3 y^{-1}; Cavazzoni Galaverni, 1972) and the concentrations of nutrient species. Total nitrogen and phosphorus loads were calculated from demographic and livestock production data, agriculture fertilizer utilization, and industrial wastewater discharge rates, combined with empirical coefficients estimating nitrogen and phosphorus inputs to the northern Adriatic from anthropogenic sources, and from natural soil erosion (Provini *et al.*, 1979). The calculation procedure essentially followed that used previously to estimate freshwater and wastewater nitrogen contributions (Degobbis *et al.*, 1986*a*).

Using published studies it was possible to compare the calculated nutrient loads with direct measurements of nutrient freshwater inputs to the northern Adriatic. Phosphorus load calculations for many bigger Italian watersheds (including the Adige and Po Rivers) agree very well with calculated inputs based on direct measurements of concentrations and flow rates (Garibaldi and Marchetti, 1982). Furthermore, the differences found between total nitrogen load and inorganic nitrogen contribution were of the order of 30-40 %, *i.e.* the same proportion of organic nitrogen to total nitrogen measured in many rivers of the world (Omernik, 1977; Van Bennekom and Salomons, 1981).

In subregion A, population data (total resident and tourist equivalent = 275,000) and wastewater discharge rates (5×10^6 m^3 y^{-1}; Anonyme, 1984) were used to estimate the anthropogenic nitrogen and phosphorus discharged directly to the sea from the coast of the western Istria region, in addition to freshwater contributions. Physiological human excretion rates of 320 mol y^{-1} per inhabitant for nitrogen and 23 mol y^{-1} per inhabitant for phosphorus (including detergent use) were assumed (Provini *et al.*, 1979). It was accepted that industrial wastewater discharges contained on average 1.2 mol m^{-3} of nitrogen and 0.065 mol m^{-3} of phosphorus (Bond and Straub, 1974). Nitrogen anthropogenic input (94×10^6 mol y^{-1}) was an order of magnitude smaller than the freshwater nitrogen contribution (Tab. 1). In contrast, the anthropogenic phosphorus contribution (12×10^6 mol y^{-1}) was about 70 % higher. These are maximum estimates, since a small part of the sewage is retained in septic tanks. No data were available to estimate agriculture nutrient contribution. However, this activity is poorly developed along the Istrian coasts, which also lacks significant surface drainage. Nutrient contributions from agriculture activities in the central parts of the Istria peninsula are included in the estimates of freshwater inputs (Tab. 1).

The estimates of freshwater nutrient inputs were based on studies in Limski kanal (Fig.), the major estuary in subregion A. Monthly measurements of nutrient concentrations were made from 1980-1986 in Limski kanal which receives freshwater from a watershed which covers the central part of the Istrian peninsula. Average concentrations of nutrient species (ammonium 3, nitrite 0.3, nitrate 110, total nitrogen 137, orthophosphate 0.8, total phosphorus 1.2, and orthosilicate 68 mmol m^{-3}) were estimated for freshwaters entering Limski kanal by extrapolating the concentrations measured from 1980 to 1986 in the estuary to zero salinity using linear regression analysis. Input data were only calculated for periods when low phytoplankon biomass and primary production occurred, and when the linear relationships were statistically very significant (probability levels <0.001) over large salinity ranges (4-36.2×10^{-6}; Degobbis, 1988), indicating that freshwater nutrient dilution strongly dominated biological nutrient utilization. A few analyses of spring waters from the region (on average NH_4 0.7, NO_2 0.4, NO_3 130, PO_4 0.9 and TP 1.25 mmol m^{-3}; Anonyme, 1988) were in good agreement with the extrapolation results.

The values, calculated from the intercepts of the regression lines, were assumed to be representative for the freshwaters of all western Istrian watersheds, whose total discharge rate is on average $5{,}881 \times 10^6$ m^3 y^{-1} (Cavazzoni Galaverni, 1972), and were thus used to estimate freshwater contribution of nutrient species from these sources to the sea (Tab. 1).

In general the total nutrient input from the western Istrian coast (from freshwaters and anthropogenic sources) is very low compared to the total nitrogen input to the northern Adriatic (Tab. 2). Thus, errors resulting from these calculations are relatively insignificant in terms of the regional nutrient budget.

Calculations for river nutrient input to subregion B (Tab. 1) was based in part on nutrient concentrations measured in 1976-1977 in the Soča (Isonzo) river ($6{,}430 \times 10^6$ m^3 y^{-1}; Bregant and Catalano, 1978), and in 1982-1984 in the Tagliamento river ($3{,}070 \times 10^6$ m^3 y^{-1}; Fossato *et al.*, 1987), the major streams (representing about 40 % of the total discharge rate) in the northern and northwestern coast from

Trieste to the Adige estuary. Nutrient concentrations in these two rivers were very similar, and their averages (ammonium 2.6, nitrite 0.65, nitrate 58, orthophosphate 0.25, and orthosilicate 35 mmol m^{-3}) were assumed to be representative for the minor rivers and drainage waters entering the Adriatic Sea in this subregion. Total phosphorus had not determined in the rivers of this subregion and the value determined in Limski kanal was used (1.2 mmol m^{-3}). The nutrient contribution from the entire subregion was calculated from these nutrient concentrations using the mean total freshwater discharge from the subregion ($25{,}273 \times 10^6\ m^3\ y^{-1}$; Cavazzoni Galaverni, 1972), and are presented in Table 1.

Calculations for river nutrient input to subregion C (Tab. 1) are based on nutrient data collected in 1977-1978 at Boara Pisani, 70 km upstream from the Adige river estuary (ammonium 9.5, nitrite 1.1, nitrate 67.5, orthophosphate 1.7, dissolved organic phosphorus 0.2, particulate phosphorus 3.8, total phosphorus 5.7 mmol m^{-3}; Provini *et al.*, 1980) and the average freshwater discharge rate of the Adige river ($6{,}649 \times 10^6\ m^3\ y^{-1}$; Cavazzoni Galaverni, 1972).

The nitrogen and phosphorus loads from the region from Trieste to the Po river delta (*i.e.* the combined subregions B and C) were calculated indirectly. Loads calculated independently for the Po river and Emilia-Romagna subregions (Chiaudani *et al.*, 1980) were subtracted from total loads calculated for the Italian side of the northern Adriatic (Provini *et al.*, 1979; Chiaudani *et al.*, 1982). Values thus obtained (Tab. 2, subregions B+C) were significantly higher (two times for nitrogen and four times for phosphorus) than those calculated as the freshwater contributions (Tab. 1; total for subregions B and C). However, the organic nitrogen contributed by freshwater was not directly measured, but was assumed to be similar to the Adige river (about 30 %).

Even correcting for organic nitrogen there is still a significant difference between the total load and river contributions ($2{,}916 \times 10^6$ mol y^{-1}) in the subregions B and C. The rest of the nutrients must thus be contributed by direct discharge of wastewaters into the sea. This would be expected, since in these subregions there are two large urban areas, with ports and industrial centers (Trieste and Venice). Their contributions (estimated from data reported by Olivotti *et al.*, 1986 and Cossu *et al.*, 1984) account for at least 25 % of the differences. In addition to these two centers (for which data exist), there are numerous smaller urban centers with heavily developed tourist and industrial activities, for which no data on direct wastewater discharges were available. Nutrient input from these unreported sources probably account for the remaining differences between total nitrogen and phosphorus loads and river contributions.

Fortunately, extensive and detailed nitrogen data are available for the Po river ($49{,}981 \times 10^6\ m^3\ y^{-1}$; Cavazzoni Galaverni, 1972), the major river entering the Adriatic Sea and the primary point source in subregion D. Several series of nutrient concentration measurements exist, most collected at Polesella or Pontelagoscuro, 74 and 90 km respectively from the delta (*see* Marchetti *et al.*, 1985 for review). Averages for the period 1981-1984 (ammonium 21, nitrite 3.35, nitrate 147, orthophosphate 4.6, dissolved organic phosphorus 0.35, particulate phosphorus 4.77, total phosphorus 9.9, and orthosilicate 120 mmol m^{-3}) were used to calculate the Po river contribution of nutrient species (Tab. 1). The inorganic nitrogen contribution represents 74 % of the total Po river nitrogen load (Anonyme, 1977), and, thus, the total nitrogen input from this source is $11{,}600 \times 10^6$ mol y^{-1} (Tab. 2).

In subregion E the total discharge rate of the Emilia-Romagna rivers ($3{,}437 \times 10^6\ m^3\ y^{-1}$) is small compared to the other rivers, although very high nutrient concentrations were found in several small rivers. During 1977 nutrients were measured in almost all of the small rivers and drainage canals (Anonyme, 1978). The Savio river was monitored more intensively during 1977 and 1978 (Hadrill *et al.*, 1983). The mean values obtained for each stream were weighted by the discharge rates and overall average values were calculated, which were assumed to be representative for freshwaters of the subregion (ammonium 81, nitrite 15, nitrate 45, orthophosphate 17, total phosphorus 32 mmol m^{-3}). Orthosilicate was not monitored, so the value for the Po river was used. The freshwater contribution of total phosphorus thus obtained (Tab. 1) and the calculated load (Tab. 2; Chiaudani *et al.*, 1980) were identical. This could be expected, since wastewaters, even those from coastal urban and tourist centers, are discharged into these small rivers, mostly very near the mouth (Anonyme, 1978). This fact also accounts for the high ratio of ammonium to oxidized nitrogen (nitrate; Tab. 1) and the big difference between the nitrogen load (Tab. 2) and the inorganic nitrogen contributed by freshwaters (Tab. 1). Furthermore, in the Emilia-Romagna region organic nitrogen sources, *i.e.* sewages, livestock production, food industries, and tanneries are relatively more important (62 % of the total nitrogen load) than agriculture which contributes mainly nitrate (38 %). In comparison, for example, the Po river watershed contributes 44 and 56 %, respectively (Provini *et al.*, 1979). The freshwater and wastewater total contributions of nutrients are presented in Table 3.

The land also contributes nitrogen (Tsunogai, 1971) and phosphorus (Graham and Duce, 1979) to the sea through the atmosphere, and all the subregions of the northern Adriatic are strongly under terrestrial influence. Atmospheric nitrogen and phosphorus contributions were calculated from annual means based on long term precipitation data records for the northern Adriatic (1956-1965; Cavazzoni Galaverni, 1972), and analyses of nutrient concentrations in rainwater. In 1984-1985 inorganic nitrogen species and orthophosphate were measured in 89 rain samples collected at Rovinj (western Istrian coast). Average values were: ammonium 48, nitrite 3.5, nitrate 67, orthophosphate 0.25 mmol m^{-3} of rainwater. In some coastal and estuarine areas (*e.g.* Williams, 1967; Correl and Ford, 1982) organic nitrogen accounted for about a third of

Table 3

Nitrogen (TN), phosphorus (TP) and orthosilicate ($Si(OH)_4$) budgets for the northern Adriatic Sea (% in parentheses).

Les bilans de l'azote (TN), du phosphore (TP) et de l'orthosilicate ($Si(OH)_4$) pour l'Adriatique septentrionale (% entre parenthèses).

Terms	TN	TP (10^6 mol y^{-1})	$Si(OH)_4$
Inputs			
Po river	11 575 (49)	495 (55)	5 990 (<71)
Minor rivers and wastewaters	8 600 (36)	409 (44)	2 400 (>29)
Rainfall	3 300 (14)	10 (1)	?
N_2 fixation	135 (1)	–	–
TOTAL	23 610 (100)	914 (100)	8 390
Output			
Water transport	9 220 (54)	430 (59)	4 360 (80)
Denitrification in the sediment	7 100 (42)	–	–
Sedimentation	260 (1.5)	260 (36)	1 100 (20)
Fish catches	370 (1.5)	40 (5)	0
N_2O and NO production	200 (1)	–	–
TOTAL	17 150 (100)	730 (100)	5 460 (100)
Recycled			
Assimilated	21 300	600	–
Regenerated			
in the water	26 900-35 900	780-1 040	>70
in the sediment	2 500	25	12 700

the total rainfall nitrogen. It was assumed that the same ratio is valid for rainfall in the northern Adriatic. The organic phosphorus (determined by digestion of samples with persulfate) was found to account for approximately half of the total phosphorus content of rainwater (*e.g.* Williams, 1967; Faganeli and Tušnik, 1983). In the atmosphere about 30 % of the total phosphorus is present in a very refractory form (Graham and Duce, 1979). This fraction was not taken into account in the calculated phosphorus contribution presented in Table 3. Very few data on orthosilicate concentration were available for the Rovinj rain samples (ranging from 2-5 mmol m^{-3}), and no reliable estimate of atmospheric contribution could be made. In the northern Adriatic the nutrient contribution from the atmosphere to the sea by dry deposition (*i.e.* dust) is not known. In nonpolluted coastal areas this nutrient source can contribute up to 20 % of the total nitrogen, and up to 15 % of the phosphorus (Barrie and Sirois, 1986; Savoie *et al.*, 1987). However, because of the large uncertainties involved no estimates of dry deposition were included in these calculations.

Atmospheric nitrogen gas fixation probably does not occur in the water column to a significant degree in the northern Adriatic. No major concentrations of microplanktonic Cyanophytes, able to fix molecular nitrogen in appreciable quantities (Capone and Carpenter, 1982), have been reported for the northern Adriatic in modern times (Revelante, 1985). Bethoux and Copin-Montegut (1986) have hypothesized that in the Mediterranean Sea, the seagrass *Posidonia oceanica* may be able to fix nitrogen and significantly influence the local nitrogen budget. However, this plant does not occur in the northern Adriatic. In contrast, N_2 fixation by sediment bacterial populations is possible. If a rate of 7 mmol m^{-2} y^{-1}, characteristic for ocean coastal areas (Capone and Carpenter, 1982) is assumed, the northern Adriatic sediments could fix a relatively modest 135×10^6 mol y^{-1} (Degobbis *et al.*, 1986*a*), the amount used in these calculations.

Nutrient losses

The rate of loss to the sediments were estimated using sedimentation rates and nitrogen and phosphorus concentrations in the surface sediments of the northern Adriatic. The total nitrogen content of the northern Adriatic sediments (Brambati *et al.*, 1967), varies significantly depending on the sediment type. Therefore, the region was subdivided into three parts with different sediment nitrogen characteristics (Tab. 4). The eastern subregion includes stations 1, 5, and 6 (Fig.), the central subregion includes stations 2, 4, 7, 12, and 16, while stations 3, 8, 9, 10, 11, 17, 18 comprised a western subregion. In contrast the total phosphorus distribution in sediments was more homogenous, and one mean value was used for all subregions (Tab. 4). In the southern part (stations 13, 14, 15, 19 and 20; Fig.) of the eastern subregion, characterized by sandy sediments, no appreciable sedimentation occurs (Brambati *et al.*, 1983), and the region was consequently excluded from the sediment loss calculations.

A sedimentation rate of 1 mm y^{-1} was assumed for the northern Adriatic, as an approximation of values (average 1.2 mm y^{-1}) obtained by radiodating (^{14}C) 1 m sediment cores collected on a profile extending from the area off the Po Delta to the center of the northern Adriatic (Collantoni *et al.*, 1979). This rate was extrapolated to obtain estimates of total annual sedimentation in the subregions using a specific weight of 1 740 kg m^{-3} obtained from the value of 1 170 kg m^{-3} for sediment with water content of 33 % (Van Straaten, 1970). According to Emery *et al.* (1955) 50 % of the sedimented nitrogen is remineralizated during diagenesis before it is sequestered in sediments of the Southern California basins, and therefore, in absence of better information, the calculated quantity of nitrogen sedimented in the northern Adriatic was divided by a factor of two. The nitrogen and phosphorus loss rates in the sediments were estimated accordingly and are presented in Table 4.

Table 4

Calculations of nitrogen and phosphorus losses by burial in sediments of the northern Adriatic Sea.

Calculs des pertes d'azote et phosphore dans les sédiments de l'Adriatique septentrionale.

	Subregions			Total northern Adriatic
	Eastern	Central	Western	
Area (10^9 m^2)	3.13	6.05	3.96	13.14
Mean N content (% dry sediment)	0.018	0.037	0.061	–
Mean P content (% dry sediment)	0.037		0.0535	–
Sedimentation rate (10^{12} g y^{-1})	5.4	10.5	4.0	–
N loss (10^6 mol y^{-1})	35	140	85	260
P loss (10^6 mol y^{-1})	190		70	260

No data for biogenic silicon dioxide were available for the northern Adriatic. In the part of Chesapeake Bay in which the sedimentation rate is approximately the same as in the northern Adriatic the silicon burial rate is 0.08 mol m^{-2} y^{-1} (D'Elia *et al.*, 1983). Applying this rate to the northern Adriatic an annual total loss of 14×10^6 mol y^{-1} was calculated (Tab. 3).

The nitrogen, phosphorus and biogenic silicon losses in fish catches were estimated from the catch in the Adriatic, which averages 230×10^6 kg y^{-1} (1980-1985; GFCM, 1987). It was assumed that 76 % of the catch was taken in the northern Adriatic, as calculated for the period 1957-1967 (Štirn, Kubik, 1974). The nitrogen content of the fish was assumed to be 3×10^{-2} (wet mass fraction) for sardines, the largest biomass component of the catch (Krvarić-Škare, 1955). The average phosphorus and silicon content of fishes are 10^{-2} and 7.5×10^{-6} (wet mass fractions), respectively (Vinogradov, 1953). From these data total losses were calculated for the northern Adriatic (nitrogen 375, phosphorus 56, and silicon 0.05×10^6 mol y^{-1}; Tab. 3).

Other losses occur during biochemical reactions involving nitrogen, but no direct measurements of these processes are available for the northern Adriatic. Nitrogen losses by gas production during bacterial nitrification and denitrification processes, as well as by photochemical nitrification at the sea surface, may occur. In the northern Adriatic denitrification can occur at least in summer in the sediments which are quite reduced immediately below the surface (Giordani and Angiolini, 1983). This is verified by the AOU/N regenerative mean ratio of 40 measured in the bottom layer of the northern Adriatic (Degobbis, 1990), which is significantly higher than the stoichiometric ratio for nitrogen regeneration in the ocean (17; Redfield *et al.*, 1963) due to the loss of nitrate during denitrification. Thus, the difference of nitrogen regeneration rates estimated from oxygen changes or, alternatively, from inorganic nitrogen changes observed in the bottom layer of the northern Adriatic (*see* following text and Tab. 6) can be ascribed to nitrogen loss due to denitrification. This difference is 0.13 mmol m^{-3} d^{-1}. Given the thickness of the bottom layer (Tab. 6) this means that the denitrification flux at the sediment-water interface is on average 1.4 mmol m^{-2} d^{-1}, or $7{,}100 \times 10^6$ mol y^{-1} when extrapolated to the surface area of the northern Adriatic where significant sedimentation occurs (Tab. 6). The denitrification rate calculated for the northern Adriatic lies in the range reported for coastal sediments elsewhere (0-3.5 mmol m^{-2} d^{-1}; *e.g.* Payne, 1983; Reeburgh, 1983; Seitzinger *et al.*, 1984; Kaspar *et al.*, 1985). During denitrification N_2O is also produced, but at rates at least two order of magnitude lower than N_2 (Seitzinger *et al.*, 1984).

N_2O is one of the secondary products of nitrification and is produced in an atomic ratio to oxidized NH_4 of 1 to 350 (Elkins *et al.*, 1978), a ratio that lies in the range given by Cohen and Gordon (1979) for several ocean areas. From the estimate of regeneration rate in the northern Adriatic, based on inorganic nitrogen changes in the bottom layer (Tab. 6), it follows that 130×10^6 mol y^{-1} of N_2O could be produced by this mechanism. This value is almost surely an overestimate. The ratio of regenerated ammonium which is directly assimilated by phytoplankton to that which is oxidized by bacteria (leading to a concurrent production of N_2O) is unmeasured for the northern Adriatic. But, for example in Cook Strait (New Zealand) only 30 % of biologically available ammonium is oxidized (Priscu and Downes, 1985). During nitrification NO is also produced in an atomic ratio to N_2O of 1.5 (Lipschultz *et al.*, 1981), which could account for an additional nitrogen loss of up to 200×10^6 mol y^{-1}.

Nutrient exchange by water circulation

Nutrient advective fluxes, due to water mass exchange between the northern Adriatic and the rest of the Adriatic sea, were calculated assuming the generally accepted cyclonic circulation pattern (Zore-Armanda, 1963; Mosetti, 1967; Hendershott and Rizzoli, 1972). The nutrient concentrations found at the southeastern boundary of the investigated area were considered typical for the inflowing current, while those measured on the southwestern side were assumed to be characteristic of the outflowing current. A water exchange rate of 10^5 m^3 s^{-1}, obtained from geostrophic calculations (Zore-Armanda, 1963), was used. Mean water column values were derived from data on inorganic and organic nitrogen and phosphorus species, as well as on orthosilicate, for eastern and western boundary stations (Tab. 5). The data for inorganic nutrient species were collected during 1972-1975; those for dissolved organic nitrogen and total phosphorus during 1981-1984, and for particulate organic nitrogen in 1978, 1980, and 1982 (*see* also Degobbis *et al.*, 1986*a*).

From these data the amount of nitrogen transported yearly by inflowing and outflowing water was calculated. The difference between the two calculated transport rates indicated a net loss of all nutrient species from the northern Adriatic (Tab. 5). The degree of accuracy of this nutrient loss estimate from the northern Adriatic depends on a number of factors which are discussed in detail elsewhere (Degobbis *et al.*, 1986*a*).

Table 5

Water column integrated means of nutrient concentrations (number of data in parentheses) at southwestern and southeastern stations, and exchange rates by water mass transport between the northern and central Adriatic Sea.

Valeurs moyennes intégrées des concentrations en sels nutritifs (nombre des données dans les parenthèses) dans la colonne d'eau aux stations sud-occidentales et sud-orientales; transport par les masses d'eau entre l'Adriatique septentrionale et centrale.

	Western side		Eastern side		Exchanged		
Nutrient species	Station	Concentration (mmol m^{-3})	Station	Concentration (mmol m^{-3})	Output	Input (10^6 mol y^{-1})	Losses
NH_4	18	0.75 (108)	20	0.58 (147)	2350	1850	500
NO_2	18	0.20 (84)	20	0.13 (121)	640	390	250
NO_3	18	1.08 (84)	20	0.41 (121)	3390	1290	2100
TIN	18	2.08 (84)	20	1.08 (121)	6560	3400	3160
DON	9, 10	3.33 (130)	6	2.86 (68)	10500	9000	1500
PON	9-11	3.35 (59)	6, 13, 20	1.90 (40)	10560	6000	4560
TN					27620	18400	9220
PO_4	18	0.06 (79)	20	0.02 (69)	195	72	123
TP	9, 10	0.27 (104)	6	0.13 (60)	855	425	430
$Si(OH)_4$	18	3.22 (68)	20	1.83 (69)	10150	5890	4360
TIN/PO_4	–	–	–	–	33	49	–
TN/TP	–	–	–	–	32	43.5	–
$TIN/Si(OH)_4$	–	–	–	–	0.6	0.6	–
$Si(OH)_4/PO_4$	–	–	–	–	52	80	–

Recycling terms

The annual quantity of nutrients assimilated by phytoplankton (Tab. 3) was estimated from monthly *in situ* primary production measurements by the ^{14}C technique at station 6 (Fig.), in the eastern part of the northern Adriatic, and at station 9 in the western part during 1972 and 1973 (Revelante, 1975). The annual primary production was 63 gC m^{-2} y^{-1} at station 6 and 104 gC m^{-2} y^{-1} at station 9. These *in situ* values were proportionally weighted on the basis of the distributions of chlorophyll *a* concentrations and primary production rates measured in "standard" light incubators, throughout the entire region (*see* Degobbis *et al.*, 1986*a* for the calculation procedure) leading to an average value of 89.6 g m^{-2} y^{-1} of carbon. This estimate of fixed carbon was converted to nitrogen utilization rate (Tab. 3) using the atomic C:N ratio of 106:16 (Redfield *et al.*, 1963).

There is evidence that in many coastal and estuarine areas (*e.g.* Nixon, 1981; Fisher *et al.*, 1982; Kaufman *et al.*, 1983), including eastern Mediterranean bays (Friligos, 1986), the assimilation rate ratios between carbon and nutrients are on average very close to Redfield's stoichiometric model, despite the fact that in those areas the *in situ* nutrient concentration ratios in the water are frequently very different. This is particularly true for C/N assimilation ratios. The C/P and C/Si ratios vary much more widely, depending on environmental conditions (Dugdale and Hopkins, 1974). For instance, in the Ebrie lagoon (Ivory Coast; Lemasson *et al.*, 1980) and Lake Constance (F. R. Germany; Uehlinger and Bloesch, 1987) the C/P assimilation ratio was higher than 300 under conditions where very low phosphorus concentrations were assumed to limit phytoplankon activity. In most of the northern Adriatic (if river plumes are excluded) orthophosphate concentrations are often very low (below 0.05 mmol m^{-3}; Ivančić and Degobbis, 1987). Thus, it would be expected that C/P assimilation ratio would be higher than the stoichiometric model.

In laboratory experiments, natural phytoplankton community samples from the eastern part of the northern Adriatic were enriched with 30 mmol m^{-3} nitrate and 1 mmol m^{-3} phosphorus compounds. At the end of the experiments (about 10 days) no excess of nitrate over the "optimal" nutrient assimilation ratio of 16 (Redfield *et al.*, 1963) was found in the media (Ivančić, 1985). This indicates that the phytoplankton community in the northern Adriatic can take up inorganic nitrogen despite an apparent relative deficiency in phosphorus (according to the Redfield model). The AOU/P regeneration ratio for the bottom layer averaged about 610 (Degobbis, 1990), thus, assuming that the AOU/C ratio = 276/106, the C/P ratio should equal 230, leading to a phosphorus assimilation estimate of 600 × 10^6 mol y^{-1} (Tab. 3). This estimate is about two times lower than that obtained using Redfield's ratios (*i.e.* 1,300 × 10^6 mol y^{-1}).

The C/Si assimilation ratio varies greatly depending on the relative proportion of phytoplankton species requiring silicon (*e.g.* diatoms) in the total community. Unfortunately this ratio was not known for the northern Adriatic phytoplankton community at the time nutrients were sampled, and no silicon assimilation rate could be calculated.

Nutrient regeneration rates were calculated from increases in nutrient concentrations and decreases of oxygen concentrations in the bottom layer during periods when the layer was quasi-isolated by strong pycnoclines. Under conditions of high water column stability, which prevail in the northern Adriatic from about March to November, a steady decrease in oxygen concentration is usually observed in the bottom layer. Nitrogen and phosphorus regeneration rates were calculated from observed decreases in oxygen and increases in inorganic nitrogen and orthophosphate concentrations in the bottom layer between cruises. During these periods the physical structure of the water column was not significantly altered, as evidenced by the vertical distribution of density anomaly values. An additional conservative filter was used by restricting calculations to those periods when the chlorophyll *a* standing crop was less than 0.5 mg m^{-3}, in order to reduce errors due to nutrient assimilation processes. Orthosilicate regeneration rates were only calculated directly from changes in concentrations. Decreases in dissolved oxygen concentrations, combined with a AOU/Si ratio, were not used because of the time lag introduced by silica frustules dissolution.

The ranges and average nutrient regeneration rates are presented in Table 6. The calculations are based on data collected in the northern Adriatic between 1966 and 1987, and are reported separately for western stations (at which pelite predominates) and for eastern stations (where admixtures of pelite and sand prevail; Brambati *et al.*, 1983).

Subsequently, weighted means for the entire northern Adriatic were obtained based on the relative surface area of the respective subregions.

Estimates of inorganic nitrogen regeneration rates were obtained by converting oxygen changes to nitrogen changes using weighted mean atomic O/N ratios. These were calculated using the Redfield *et al.* (1963) stoichiometric model of nutrient regeneration, without (O/N ratio 212:16) and with (276:16) nitrification, by weighting with the mean nitrate percentage in the total inorganic nitrogen measured in the bottom layer of the northern Adriatic (Tab. 6). Significant differences occurred between estimates calculated from oxygen changes and those obtained directly from changes in inorganic nitrogen concentrations. The differences arise because a significant portion of the regenerated nitrate is subsequently denitrified in the sediments before it is advected to the upper layers of the water column. This creates an apparent nitrogen scarcity relative to the observed changes in the oxygen concentrations. Consequently, while total nitrogen regeneration rates can be estimated from oxygen changes, only the portion estimated from direct inorganic nitrogen changes is available for phytoplankton assimilation. In contrast, phosphorus regeneration rates are based on changes in orthophosphate concentrations, since it is likely that organic matter in the bottom layer of the northern Adriatic is poorer in phosphorus with respect to other biogenic elements compared to the world ocean.

The estimates obtained reflect both *in situ* water column and benthic regeneration processes. Data for benthic regeneration rates in the open northern Adriatic are not available. However, in the region off the Emilia-Romagna coast (northwestern Adriatic) nitrogen release from the sediments has been measured using *in situ* benthic chambers (Hammond *et al.*, 1984). These were deployed up to 20 km offshore, at depths from 8 to 28 m, on different sediment types, ranging from sandy to pelitic. The results obtained for ammonium averaged 0.5, for orthophosphate 0.005, and for orthosilicate 2.5 mmol m^{-2} d^{-1}. Similar values for ammonium and orthosilicate were also reported for other coastal regions (*e.g.* Davies, 1975; Raine and Patching, 1980: Van Der Loeff *et al.*, 1984; Enoksson and Samuelsson, 1987). In contrast, orthophosphate fluxes in the northern Adriatic were considerably lower than in other moderately or highly productive coastal areas (*e.g.* from 0.1 mmol m^{-2} d^{-1} in San Francisco bay, USA, Hammond *et al.*, 1985, to 0.3 mmol m^{-2} d^{-1} in Narragansett Bay, USA, Nixon *et al.*, 1980). Lastly, release rates of organic nitrogen and phosphorus from the sediment are an order of magnitude lower than inorganic fluxes (*e.g.* Hartwig, 1976; Nixon, 1981) and were therefore disregarded for these calculations.

Table 6

Calculations of nutrient regeneration rates (mmol m^{-3} d^{-1}) from temporal changes of oxygen and inorganic nutrient concentrations in the bottom layer of the northern Adriatic during marked water column stratification (n, number of data; x, means; R, ranges).

Calculs des vitesses de la régénération des sels nutritifs (mmol m^{-3} d^{-1}) basés sur les changements des concentrations de l'oxygène et des sels nutritifs dans la couche du fond de l'Adriatique septentrionale pendant la période de stratification de la colonne d'eau (*n*, nombre des données; *x*, valeurs moyennes; R, ranges).

		Subregions		Total
		Pelitic sand	Pelite and sandy pelite	northern Adriatic
Stations		1-6, 12, 16	7-11, 17, 18	1-12, 16-18
Area (10^6 m^2)		7534	6354	13888
Thickness of the bottom layer (m)	*n*	48	92	140
	x	10.5	11.0	10.7
	R	5-20	5-20	5-20
% nitrate of total inorganic N	*n*	20	44	64
	x	35	32	33
	R	6-95	5-95	5-95
O/N/P ratio		236/16/1	230/16/1	234/16/1
N regeneration rate (from oxygen changes)	*n*	55	111	166
	x	0.18	0.23	0.20
	R	0.01-1.0	0.03-0.7	0.01-1.0
P regeneration rate (from oxygen changes)	*n*	55	111	166
	x	0.011	0.015	0.013
	R	0.001-0.043	0.002-0.045	0.001-0.045
N regeneration rate (from TIN changes)	*n*	25	58	83
	x	0.05	0.10	0.07
	R	0.01-0.1	0.01-0.6	0.02-0.8
P regeneration rate (from PO_4 changes)	*n*	19	73	92
	x	0.003	0.008	0.005
	R	0.001-0.011	0.001-0.047	0.001-0.047
Si regeneration rate (from $Si(OH)_4$ changes)	*n*	32	85	117
	x	0.14	0.33	0.23
	R	0.033-0.36	0.037-2.75	0.033-2.75

Based on the data from the Emilia-Romagna coastal region it was assumed that the nutrient flux from regeneration within the sediments of the northern Adriatic, in the area where appreciable sedimentation occurs (13 000 km^2), was 2,500 × 10^6 for ammonium, 25 × 10^6 for orthophosphate, and 12,700 × 10^6 mol y^{-1} for orthosilicate (Tab. 3).

The nutrient flux values were divided by the thickness of the bottom layer in which (under conditions of high water column stability) the nutrients released from the sediments were assumed to be distributed. The thickness of this layer averaged 11 m for the periods from which the regeneration rate was calculated from the oxygen and nutrient concentration changes (Tab. 6). Fluxes for ammonium of 0.045, orthophosphate 0.00045, and orthosilicate 0.23 mmol m^{-3} d^{-1} was derived and subtracted from the estimates calculated from the observed oxygen changes (Tab. 6). Thus, nitrogen and phosphorus regeneration rates due to the total water column heterotrophic activity (macrozooplankton and microheterotrophs) were obtained (0.155 and 0.0045 mmol m^{-3} d^{-1}, respectively). To calculate the annual regeneration rate in the water column, these value were multiplied by the total volume of the region (635×10^9 m^3). However, the annual rates were derived from data collected during the stratified period, *i. e.* during the warmer periods of the year, and are surely overestimates. In fact, it can be expected that the winter regeneration rate is lower, since heterotrophic activity is reduced due to lower temperatures and lower concentrations of organic matter (living and dead). Assuming as an extreme case that in winter the regeneration rate is zero, the annual values calculated above would be reduced by 25 %. The calculated regeneration rates are presented as ranges in Table 3. Notheworthy, the orthosilicate release rate from the sediments was approximately the same as that estimated from concentration changes in the bottom layer.

In order to independently evaluate the magnitude of possible errors, nitrogen regeneration rates were also calculated by another approach, using macro- and microzooplankton biomass data, nitrogen excretion rates, and microheterotrophic regeneration rates measured in the northern Adriatic or similar marine environments (Degobbis *et al.*, 1986*a*). The estimates obtained by both approaches are in good agreement, to at least an order of magnitude.

DISCUSSION

The Po watershed is very large ($75{,}000 \times 10^6$ m^2; Cati, 1981), and includes the most highly developed regions in Italy. In the watershed live 15 million people, with an industry equaling an additional 40 million equivalent inhabitants (Anonyme, 1977). The Po valley is intensively cultivated with heavy use of natural and artificial fertilizers. Consequently, the northern Adriatic receives about 50 % of the total nutrient load, and 60-70 % of the inorganic nutrient load, from the Po river (Tab. 3). The adjacent Adige river nutrient contribution is much smaller, but significant because it discharges in an area just north of the Po delta. The combined discharge of the Po and Adige ($58{,}100 \times 10^6$ m^3 y^{-1}) is not only greater than the combined discharge of all other rivers ($34{,}600 \times 10^6$ m^3 y^{-1}), but it is concentrated in a small coastal area (Fig.) where it functions as a point source that influences areas far distant from the Po delta. The Po and Adige freshwaters are often transported over the entire northern Adriatic by currents, especially from spring through summer when the region is semi-isolated by eddy circulation (Franco *et al.*, 1982; Gilmartin *et al.*, 1990).

Thus, the Po river has a wide ranging eutrophicating influence, which can be very marked, especially during peak discharge periods (Degobbis *et al.*, 1979). In marked contrast, other freshwater sources, such as minor rivers, water drainage outfall and wastewater discharging directly to the sea, are widely distributed along the coast and do not function as a strong point source. In most cases their effect is localized, although environmental problems are developing in the Emilia-Romagna coastal region (Montanari *et al.*, 1984) and Venice Lagoon (Degobbis *et al.*, 1986*b*).

The freshwater discharge rate in the coastal region of Emilia-Romagna is about one half that from the Istrian watershed, or one eighth that from the subregion between Trieste and the Adige estuary. However, the Emilia-Romagna contribution of ammonium and orthophosphate (the nutrient species dominating in sewage) is an order of magnitude higher than in the other coastal subregions. It is the opposite for nitrate, which in karstic rivers and groundwaters represents almost all the inorganic nitrogen, and orthophosphate concentrations are at a minimum. This is clearly evident considering the contribution ratios of nutrient species (Tab. 1). The TIN/PO_4 ratio varies from 200 in the Istrian watersheds to only 10 in the Emilia-Romagna coastal region. The local enrichment of the marine environment with phosphorus, often assumed to be the limiting element over most of the northern Adriatic (*e. g.* Chiaudani *et al.*, 1980) may significantly influences the level of primary production in Emilia-Romagna coastal waters.

The atmospheric nitrogen contribution (Tab. 3), even if an order of magnitude smaller than the Po River contribution, is still significant and can be important at times. This is particularly true for periods of the year with maximum rainfall, or when nitrogen in the surface layer of the water column has been heavily reduced by high rates of primary production. In contrast atmospheric contributions of phosphorus, and perhaps orthosilicate, are minimal and probably not a factor in regional primary production. Nitrogen fixation is two orders of magnitude lower, and does not significantly influence the nitrogen budget of the northern Adriatic.

Water mass exchange (Tab. 3) plays a dominant role as the principal process controlling the nutrient output from the northern Adriatic, influencing all nutrient species. Denitrification almost equals water mass exchange as a mechanism of nitrogen loss. In contrast, burial in the sediments represents no significant loss for nitrogen (mainly present in refractory organic form), but is more important for phosphorus and silicon (36 and 20 % of the total loss, respectively; Tab. 3). Other losses, *i. e.* N_2O and NO production and fish catches, play only small roles in the nutrient budgets of the northern Adriatic.

Interestingly, loss mechanisms affecting all nutrient species led to relatively higher losses for phosphorus than for the other nutrients, tending to balance the loss of inorganic nitrogen by denitrification. Thus the TIN/PO_4, TN/TP, and $Si(OH)_4/PO_4$ concentration ratios are much higher in seawater entering the northern Adriatic, than in seawater leaving the northern Adriatic (Tab. 5), while the TIN/$Si(OH)_4$ ratio is essentially the same. This is due to phosphorus enrichment by wastewater contributions along the western coast, particularly from the Emilia-Romagna region, compared to the eastern regions. In addition, a much larger portion of the total phosphorus input (almost

30 %) is buried in the sediment than is the case for nitrogen (only 1 %). As a result, the ratio of total inputs of nitrogen to phosphorus into the northern Adriatic (26) is on average very close to the output ratio (23; Tab. 3).

The calculated nutrient inputs significantly exceed nutrient outputs. Although uncertainties in calculation may partially explain the discrepancies, other processes leading to nutrient losses probably occur. These processes were not considered in these budget calculations due to lack of data. For instance, it is well known that at the freshwater-seawater interface orthosilicate can be involved in adsorption and coprecipitation reactions with the sedimenting particulate matter (iron and aluminium hydroxides, degraded clays, organic matter, *etc.*) and are thus scavenged from the water column (*e.g.* Aston, 1978). A biological removal of orthosilicate is not significant in many estuaries (*see* Aston, 1978 for review) or may account for 10-20 % of river contributions to estuaries in Great Britain (Liss and Spencer, 1970; Burton *et al.*, 1970) and in the Netherlands (Helder and De Vries, 1986). If locally important, such a mechanism could explain a significant part (up to an half) of the difference obtained between orthosilicate inputs and outputs in the northern Adriatic. Unfortunately, no data are available indicating the rates of these processes in the northern Adriatic.

A large portion of total phosphorus carried by northern Adriatic rivers is in particulate form (Tab. 1), part of which is quickly sedimented in the estuary or delta regions. Noteworthy, the sedimentation rate within the nearshore prodelta area of the Po river (up to 2 Nm off the delta) is as high as 2-4 cm y^{-1} (Boldrin *et al.*, 1988), compared with values an order of magnitude lower further off the delta (Colantoni *et al.*, 1979). If locally important, such a mechanism could account for the observed discrepancy in the phosphorus budget, even if some desorption of orthophosphate occurs from particulate matter due to increasing salinity along estuaries (Froelich, 1988). Unfortunately, insufficient data are available for such calculations, particularly concerning extremely variable sedimentation rates, and the estuarine surface areas of increased sedimentation. Data reported by Nelson (1972) indicated that the suspended solid content of the water column was reduced about 30 % from the Po river mouths to 2 Nm offshore. If this is the case for other northern Adriatic rivers and if particulate phosphorus is sedimented in the same ratio as total suspended solids, the phosphorus loss would be somewhat less (because of possible orthophosphate desorption) than $180 \times 10^6 \mathrm{mol\,y^{-1}}$, and accounts for almost the total difference between the calculated phosphorus inputs and outputs in the northern Adriatic (Tab. 3).

From the results it is evident that different nutrient species are regenerated in the northern Adriatic by different mechanisms. The role of sediment regeneration of phosphorus is probably not significant on an annual basis. Orthosilicate is regenerated almost entirely in the sediments by the relatively slow dissolution of sedimented silica frustules produced by diatoms, and other phytoplankton and protozoan species. Sediment regeneration was also the dominant mechanism for orthosilicate regeneration in other shallow coastal regions (*e.g.* Narragansett Bay, USA, Nixon and Pilson, 1983; and Chesapeake Bay, USA, D'Elia *et al.*, 1983). In contrast, nitrogen and phosphorus are mostly regenerated in the water column during the sinking of organic matter, mainly by a microheterotrophic (bacterial and protozoan) food web (*see* calculations for nitrogen; Degobbis *et al.*, 1986*a*).

Recycling rates are probably much faster during summer, when they occur at higher temperatures in a microplankton dominated food web (nannophytoplankton, protozoans, heterotrophic bacteria) than in winter, when temperatures are lower and biological activity is minimal in a food web with less nano and microplankton elements. Furthermore, biogenic silica diatom skeletons dissolve much faster at higher temperatures (*e.g.* Kamatani, 1982).

When the assimilation and regeneration terms in the nutrient budgets are compared they are unbalanced. This is not surprising for nutrient assimilation-regeneration cycles in open systems like the northern Adriatic, where external contributions of both inorganic and organic compounds (which are at least in part regionally remineralized) combine. The regeneration processes provide sources of nutrients for phytoplankton assimilation, while concurrently significant losses are caused by flushing and loss to the sediments.

Furthermore, the amounts of nutrients calculated as assimilated yearly by phytoplankton must be carefully qualified. It is based on primary production estimates from ^{14}C data, a method for which many artifacts (both positive and negative) have been reported (*e.g.* Carpenter and Lively, 1980; Colijn *et al.*, 1983). In addition, the C:N:Si:P assimilation ratios are not precisely known for the northern Adriatic phytoplankton community.

The concept of "new" and "regenerated" (*i.e.* "old") primary production in the ocean (Dugdale and Goering, 1967) has been extended to the coastal marine environment (Nixon, 1981; Kemp *et al.*, 1982). "New" production depends on external nutrient contributions. In the northern Adriatic these are freshwater, wastewater, and rain contributions. The total external annual contribution of nutrients is of the same order of magnitude as the regeneration rate. This is unusual. Even for estuaries the external contribution is usually smaller than regeneration rate by at least a factor of two (*e.g.* Kemp *et al.*, 1982). This high ratio between "new" and "regenerated" production is the reason for the increased biological productivity of the region compared with the rest of the Adriatic, which is typically oligotrophic. The major impact of external nutrients on the primary production of the region is in spring and early summer, when the freshwater discharge is at a maximum, closed circulation patterns prevail, and regenerated nutrients are mostly trapped in the bottom layer of a markedly stratified water column (Gilmartin *et al.,* 1990). In contrast, during the fall and winter, when vertical mixing in the water column is significant, and freshwater nutrients are largely transported out of the northern Adriatic along the west Italian coast, regeneration becomes relatively a more important source of nutrients.

A high ratio of external input of nutrients to regeneration rates means that the northern Adriatic ecosystem is sensitive to changes of anthropogenic nutrient inputs and/or to the hydrographic conditions controlling exchange rates with the rest of the Adriatic. As an example, in spring and summer 1977 unusual hydrometeorological conditions prevailed leading to extremely high freshwater discharge and minimal water exchange with the central Adriatic. Freshwaters "flooded" the entire area markedly increasing the stratification of the water column (Degobbis *et al.,* 1979). During this period a series of phytoplankon blooms produced "surplus" organic matter which could not be consumed by the extant food web. The excess organic matter sedimented, and was decomposed in a bottom layer separated from the upper part of the water column by very strong pycnocline. This caused a higher than normal oxygen demand, and created near anoxic conditions in the bottom waters of a large part of the northwestern Adriatic. These conditions affected benthic fisheries (*e.g.* Froglia and Gramitto, 1982). Subsequently, very low oxygen concentrations were also measured in the Gulf of Trieste (northeastern Adriatic) in September 1983, with the appearance of hydrogen sulfide and massive mortality of benthic fauna (Faganeli *et al.,* 1985). Finally, during summer and fall 1988 near anoxic conditions occurred again in the entire northern Adriatic, even if the Po nutrient influence was at average levels, but the water circulation was greatly reduced (Degobbis, 1989).

Thus synergistic interactions between unusual hydrometeorological conditions, water column stratification, water mass exchange rates, and external nutrient input can cause anoxic events in the bottom waters of the northern Adriatic. From anecdotal evidence these appear to have occurred more frequently in the past two decades. In a relatively open region, like the northern Adriatic, nutrients and organic matter do not accumulate from year to year. During winter increased water mass exchange, and low primary production, reestablishes an ecosystem equilibrium (at least at the annual nutrient budget level). Nevertheless, the degree of eutrophication in such a system can be defined. The frequency at which phytoplankton blooms, or anoxic events, occur under given oceanographic conditions can be statistically quantified. A subsequent increase in the frequency of such events would signal a significant threat to the ecological equilibrium of the region, which would probably include negative consequences for fisheries.

It must be emphasized that the mechanism which controls the biogeochemical cycles of nutrients in the northern Adriatic is not yet fully quantified. More investigations both field and laboratory, are needed. In the field, better estimates of the nutrient flux by water mass exchange between the northern region and the remainder of the Adriatic deserve priority attention, as well as improved estimates of phytoplankton assimilation by non-^{14}C methods. In the laboratory the assumptions regarding the importance of denitrification in the sediments, and geochemical processes at the freshwater-salt water interface involving nutrients, need to be more fully tested experimentally.

CONCLUSIONS

From this assessment of nutrient budgets for the northern Adriatic we concluded the following:

1) The major nutrient input to the northern Adriatic is by river contribution, mainly from the Po river.

2) Nutrients are primarily exported from the northern Adriatic by water mass transport along the western side. Denitrification (for nitrogen) and burial in the sediments (for phosphorus and silicon) also represent significant mechanisms of nutrient loss from the region.

3) Nitrogen and phosphorus in the northern Adriatic are recycled mainly in the water column. In contrast regeneration of orthosilicate occurs mostly at the sediment-water interface.

4) Annual nutrient inputs to the northern Adriatic, primarily from freshwater contributions, approximate the quantity of nutrients regenerated through biological cycle. This unusually high ratio of "new" *vs.* "regenerated" primary production makes the northern Adriatic a unique marine environment, and particularly susceptible to hypereutrophication by increases in the anthropogenic nutrient load to the Po river watershed.

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