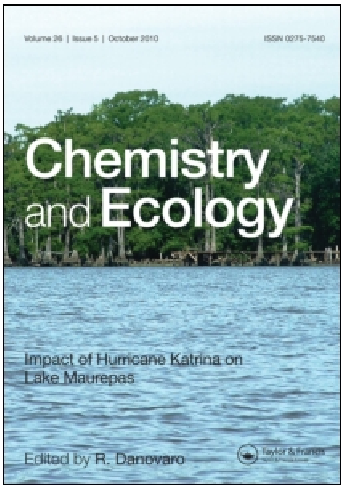

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Factors Affecting the Conservation of Nutrients in Estuarine Waters of the River Tiber

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The estuarine processes which can influence the release of nutrients of the River Tiber into the Tyrrhenian Sea have been studied. A conservative behaviour has been found for silicate in different hydrographic conditions.

For nitrogen, positive increments in respect of the dilution values were found in summer, due to regeneration processes; on the contrary a conservative behaviour was observed when seawater did not intrude into the river.

Dissolved phosphorus showed, in all the hydrographic conditions, a positive deviation in respect of the theoretical dilution values. This deviation has been attributed to regeneration processes which take place during the summer period. The chemical release of phosphate from particulate matter is predominant when the saline wedge is absent.

INTRODUCTION

The estuarine characteristics of the River Tiber, and many other rivers of the Mediterranean, are strongly dependent on seasonal conditions.

During periods of normal summer fluvial flows, seawater intrudes into River Tiber somewhat like a salt water wedge, maintaining a near-equilibrium state with the fluvial discharge and penetrating up to a maximum distance of 9 km upstream (Ghirlanda and Ronda, 1981; HRS report, 1977). The resulting two-layer structure may be a useful situation to investigate nutrient regeneration processes in the Tiber estuary (Peterson *et al.*, 1975; Wollast, 1978).

In other periods of the year, when there is no saline intrusion, the River Tiber flows into the sea as a jet-like stream, showing very sharp variations of salinity in the diffusion plume.

Physico-chemical processes should predominate in influencing nutrient distribution between soluble and particulate phases (Liss and Spencer, 1970; Burns and Salomon, 1969; Sholkovitz, 1976).

Whereas information on nutrient contents in the River Tiber and adjacent coastal waters has already been collected (Blundo *et al.*, 1978; La Noce *et al.*, 1980; Puddu *et al.*, 1981), this paper sets out to present some biochemical and physico-chemical processes representing important features of the mass-balance of nutrients in estuarine waters.

METHODS

Water samples were collected with 5 l Niskin bottles in the estuarine waters of the River Tiber, starting from station A at 8.8 km upstream from the mouth (Figure 1). The samples were then transferred to polyethylene bottles, stored at 4°C and filtered through 0.45 μm Millipore filters. The maximum time before filtration began and ended was from 3 to 8 h after collection. Aliquot volumes of the samples were stored unfiltered for total phosphorus analysis. Nutrient analysis was performed within one day after collection. The analytical methods used for the determination of nitrates, nitrites, ammonia and orthophosphates were those reported by Strickland and Parsons (1972). Reactive silicates, total soluble phosphorus and total phosphorus were analyzed following the methods reported by the F.A.O. manual (1975) and by Grasshoff (1976).

Analysis of samples was replicated from time to time in order to evaluate the scatter of the results. Variation Coefficients of variation, ranged from 2.0% to 3.5% for nitrate, nitrite, orthophosphate and silicate and from 3.5% to 5.5% for ammonia.

The total inorganic nitrogen (N_{toti}) has been calculated by summing nitrate, nitrite and ammonia values.

Dissolved oxygen (D.O.) measurements were performed according to the Winkler method. Salinity and temperature were determined by the E.I.L. MC 5 measuring bridge, while the pH measurements were performed by a portable pH-meter.

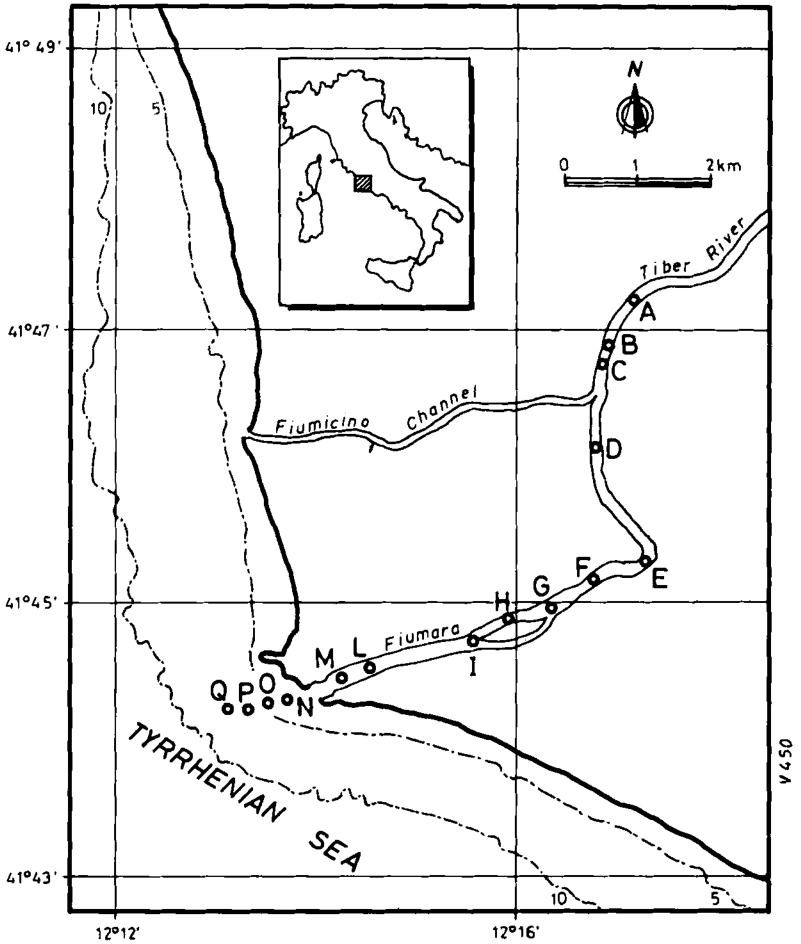

FIGURE 1 The investigated area.

RESULTS AND DISCUSSION

The two layers structure

The first survey was carried out on July 24, 1979, after a preliminary investigation allowed us to choose 10 sampling stations (A–L) and to ascertain that, in the zone studied, no other inputs complicated the field results (see Figure 1).

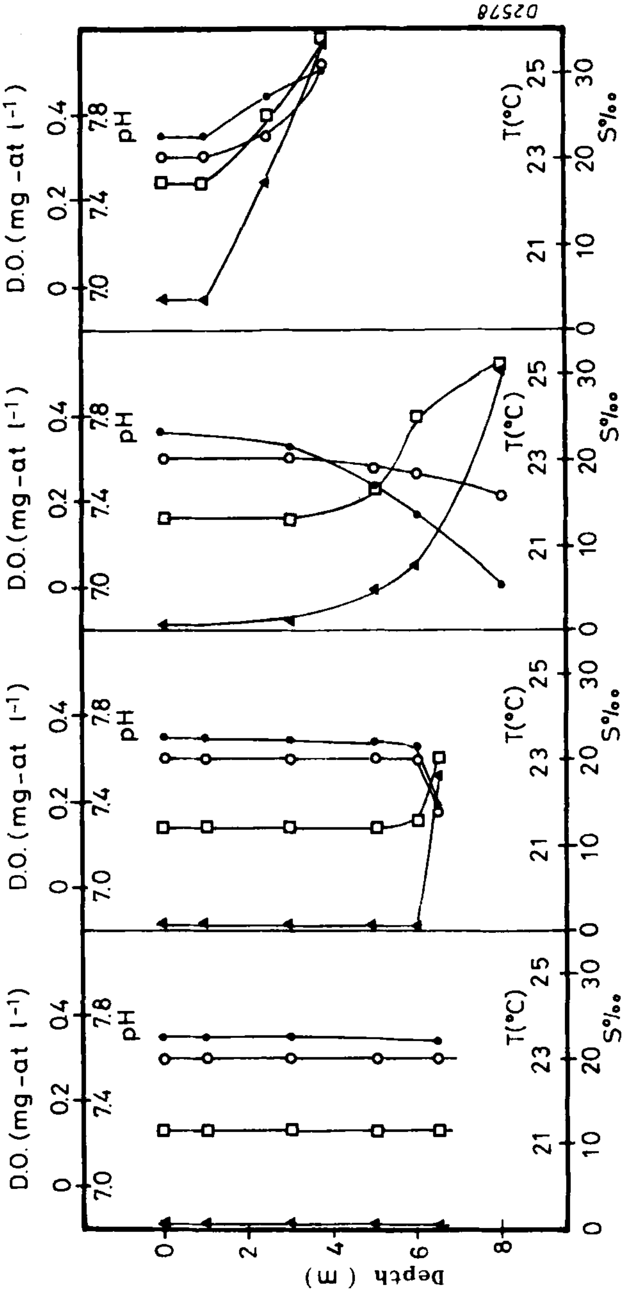

FIGURE 2 Hydrological characteristics S‰ (▲), T (□), pH (○), D.O. (●) of the stations A, B, D and L (July 24, 1979).

Figure 2 shows the vertical distribution of hydrological parameters, such as temperature, salinity, dissolved oxygen and pH, in the stations A, B, D and L.

Station A (8.8 km upstream) is characterized by a highly uniform distribution of hydrological parameters.

In the other downstream stations the saline intrusion causes a sharp change of all the parameters at the interfacial zone, which separates the fresh water from the seawater layer. Anoxic conditions were found at stations B and D in the lower layer near the bottom, characterized also by a decrease of pH of 0.3 and 0.2 units respectively. Higher oxygen concentrations and higher pH values of deep waters with respect to surface waters were observed in the stations I and L, respectively at 2.2 and 0.8 km from the sea. These observations indicate that seawater entering the outfall channel in the lower layer is almost saturated with oxygen. As the seawater moves landward in the lower layer it becomes steadily depleted in dissolved oxygen, due to the oxidation of organic matter.

Table I shows the concentration of nutrients together with salinity and dissolved oxygen values: compare the nutrients and dissolved oxygen concentration of Riber Tiber and Tyrrhenian sea water before mixing (Table II). When the concentration of silicates is expressed as a function of salinity the following linear relationship is obtained:

$$SiO_2 - Si(\mu g\text{-at } l^{-1}) = 191.8\text{–}5.06\ S‰ \quad \sigma = \pm 6.1; \qquad (1)$$

with -0.99 as correlation coefficient for 34 data points. This equation fits, within the σ value, with the dilution line shown in Figure 3. This is in agreement with the results obtained by Wollast (1973) and Liss (1976), according to whom the removal of silicates in estuaries occurs generally when their concentrations are greater than 14 mg l^{-1} of SiO_2. The SiO_2 concentration in the present survey as well as the mean freshwater concentration of SiO_2, evaluated from data collected in the period 1976–1979, were lower than 14 mg l^{-1}.

As regards nitrogen and phosphorus both the nutrients are generally characterized by a positive deviation in respect of the theoretical dilution line, the highest deviations occurring in the deepest water samples of stations B and D where anoxic conditions are responsible for the strong increase of ammonia concentration.

The algebraic increments ($\pm \Delta$) of the experimental concentration of nutrients and dissolved oxygen respect to the theoretical values are reported in Table III for stations B, D, E, G, I and L affected by

TABLE I
Results of the survey of July 24, 1979

Station	Depth (m)	NH_3—N μg–at l^{-1}	NO_2—N μg–at l^{-1}	NO_3—N μg–at l^{-1}	PO_4—P μg–at l^{-1}	SiO_2—Si μg–at l^{-1}	Salinity ‰	D.O. mg–at l^{-1}
A	0	55.55	4.85	61.31	10.53	190.81	0.5	0.35
A	−1	63.14	5.07	43.97	9.23	197.22	0.5	0.35
A	−3	56.14	5.63	55.62	10.20	193.41	0.5	0.35
A	−6.5	51.92	5.82	61.90	9.17	198.39	0.5	0.34
B	0	59.21	5.63	51.97	10.20	195.08	0.5	0.35
B	−3	60.71	5.63	50.80	10.30	192.7	0.5	0.34
B	−5	55.55	6.01	60.93	9.84	194.12	0.5	0.34
B	−6	45.50	5.63	55.86	9.00	192.23	0.5	0.33
B	−6.5	137.78	6.01	48.47	17.40	105.83	18.0	0.18
C	0	61.64	5.45	52.93	10.23	190.31	0.5	0.35
D	0	50.07	5.45	45.54	10.59	182.02	0.5	0.36
D	−3	62.21	5.63	55.86	11.01	183.19	1.0	0.33
D	−5	71.64	5.63	52.35	11.23	173.01	5.0	0.23
D	−6	80.71	5.26	56.62	11.65	160.66	7.6	0.17
D	−8	96.21	2.82	4.18	10.91	27.05	31.0	0.00
E	0	54.28	5.82	51.85	9.29	187.25	0.9	0.36
E	−1	57.07	5.26	55.45	9.91	183.19	0.8	0.36
E	−3	56.71	5.07	37.74	9.33	182.98	1.0	0.35
E	−4	39.14	4.13	41.79	9.00	137.87	10.5	0.25
F	0	63.43	5.63	61.30	11.27	182.02	0.5	0.35
G	0	49.78	6.01	53.15	10.26	189.85	1.4	0.38
G	−1	56.78	5.82	52.94	10.20	173.01	1.7	0.37
G	−2	54.00	6.20	49.46	10.10	169.45	3.5	0.34
G	−3.5	63.42	4.85	48.47	9.75	153.79	9.0	0.32
H	0	65.85	6.39	51.60	10.27	183.44	0.5	0.35
I	0	75.00	6.01	48.87	11.68	180.84	3.4	0.37
I	−1	52.78	5.07	36.57	10.23	169.66	3.2	0.36
I	−2	64.64	5.45	51.37	10.39	162.54	4.5	0.35
I	−3	52.78	3.95	29.91	7.29	108.22	18.5	0.46
I	−5	10.64	1.13	4.71	2.00	21.82	33.0	0.49
L	0	68.57	6.20	51.79	9.46	166.82	3.5	0.35
L	−1	66.78	5.63	53.50	10.04	164.47	3.5	0.34
L	−2.5	47.93	4.13	33.23	6.84	102.52	17.0	0.44
L	−3.8	7.85	0.75	5.40	1.68	26.09	33.2	0.51

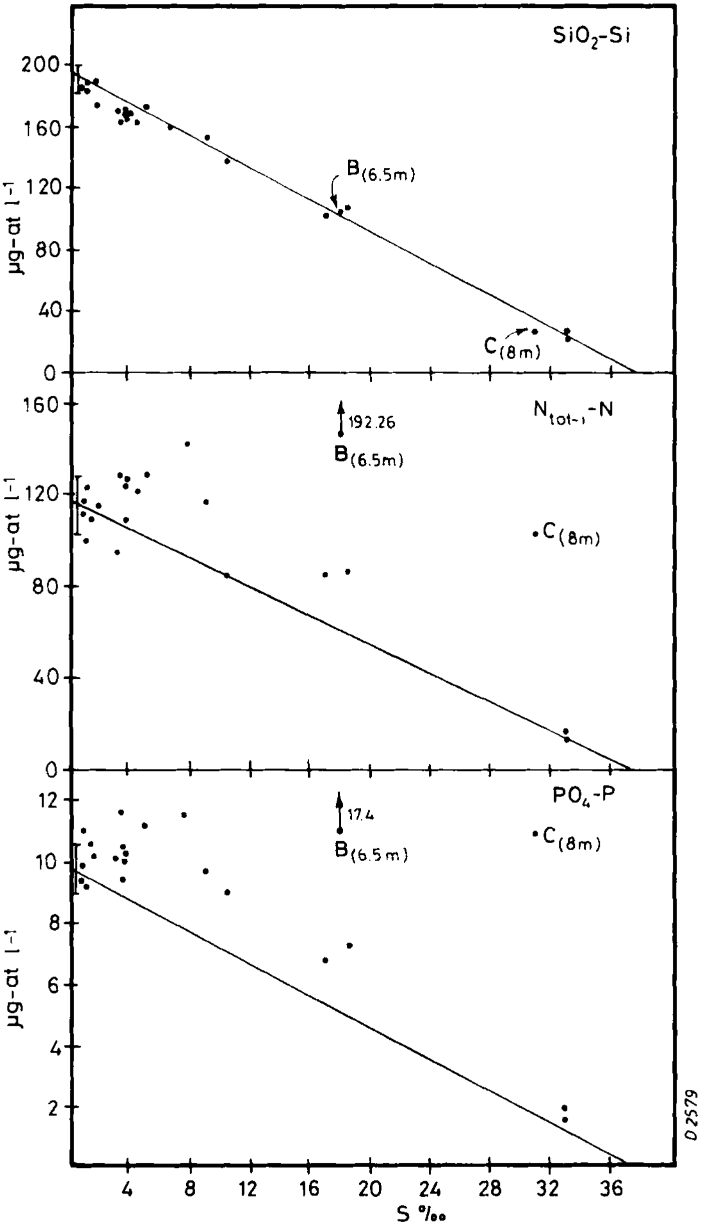

FIGURE 3 Behaviour of silicates (SiO_2—Si), total inorganic nitrogen (N_{tot_i}) and reactive phosphates (PO_4—P) in function of salinity (July, 1979).

TABLE II

Nutrients and dissolved oxygen concentrations of River Tiber and Tyrrhenian Sea waters before mixing

	Tiber	Tyrrhenian
NO_3—N (μg-at l^{-1})	54.9	0.6
NO_2—N (μg-at l^{-1})	5.3	0.05
NH_3—N (μg-at l^{-1})	57.2	0.3
PO_4—P (μg-at l^{-1})	9.8	0.03
$Si0_2$—Si (μg-at l^{-1})	195	1.0
Dissolved oxygen (mg-at l^{-1})	0.35	0.5
Salinity (‰)	0.5	37.5

TABLE III

Increments ($\pm\Delta$) of nitrate, nitrite, total inorganic nitrogen, reactive phosphate and dissolved oxygen

		ΔN_{toti} μg-at	ΔNO_3—N μg-at	ΔNO_2—N μg-at	ΔPO_4—P μg-at	ΔO_2 μmoles
B	0	−0.9	−3	0.3	0.4	0
B	−3	0.8	−3.5	0.4	0.6	−6
B	−5	5.3	6.3	0.7	0.1	−5.5
B	−6	−9	1.7	0.4	−0.6	−11
B	−6.5	128.2	18.5	3.1	12.1	−122[a]
C	0	5.1	−0.7	0.2	0.7	−2
D	0	−8.8	−5.7	0.5	1.5	−0.5
D	−3	13.1	4.3	0.6	1.8	−15
D	−5	25.1	3.6	0.9	2.6	−69[a]
D	−6	45.5	11.3	0.8	3.6	−104[a]
D	−8	86.5	−3.7	2	9.6	−244.5
E	0	−1.1	−0.9	0.7	−0.1	2
E	−1	7.2	3.9	0.2	0.7	0
E	−3	−10.9	−13.8	0.1	0.2	−5
E	−4	1.7	2.9	0.3	2.1	−73.5[a]
F	0	20.5	10	0.6	2.1	−5.5
G	0	−5.7	−0.3	0.8	0.7	13
G	−1	11.1	4.2	1.1	1.5	1
G	−2	7.3	1.7	1.6	1.6	−15.5
G	−3	23.8	5.1	0.6	2	−32[a]
H	0	13.1	−0.1	1.4	1.1	−5
I	0	20.7	−2.1	1.1	2.6	4
I	−1	−8	−11.2	0.4	1.7	−5.5
I	−2	23.3	5.6	1	2.2	−13.5
I	−3	21.1	−0.7	1	1.9	19
I	−5	3	−1.7	0.5	0.9	−1.5
L	0	25.8	4.8	1.6	1.1	−11.5
L	−1	26.6	7.1	1.1	1.8	−17.5
L	−2.5	23.2	4.2	1.3	1.7	7
L	−3.8	−2.1	−2.2	0	0.4	10.5

[a] Bottom samples considered for the determination of Δ ratios.

saline intrusion. The theoretical values have been calculated according to the relationship:

$$m_i = m_{RW} X + m^{SW} (1 - X) \qquad (2)$$

where m_i are the moles of a constituent i per kg of a solution formed by mixing river water and seawater having a concentration equal to m_{RW} and m_{SW} respectively (Millero, 1978). The river fraction (X) was computed according to equation (3),

$$X = \frac{m_i - m_{SW}}{m_{RW} - m_{SW}} \qquad (3)$$

inferred from the relationship (2), by using the concentration of silicates as a conservative parameter.

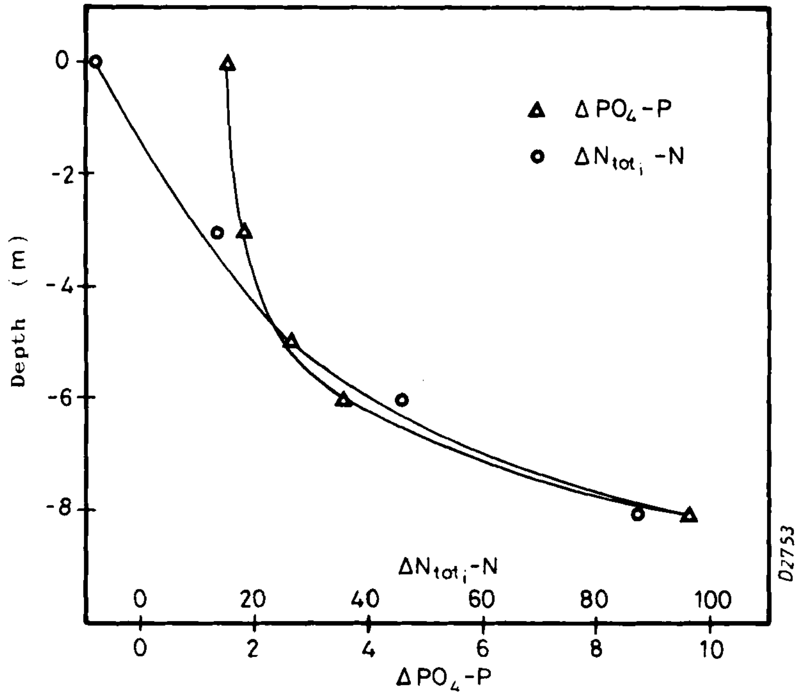

FIGURE 4 Trend of the calculated Δ values for N_{tot_i} and PO_4—P as function of depth at D station (July, 1979).

Salinity has not been used since it has been determined from conductivity measurements (Millero *et al.*, 1981).

Since the difference between values expressed in μg–at l^{-1} and μg–at kg^{-1} is not significant when taking into account the experimental error, the m_{RW} and m_{SW} values, used for the two end members in the equation (2) and (3) are those reported in Table II. The analysis of the increments ($\pm\Delta$) shows that the positive values represent the general tendency, the negative ones being probably related to biological uptake.

Figure 4 shows the increase of Δ values with depth in the station D. This increase is related to the regeneration of phosphorus and nitrogen from organic matter.

The strong stratification between seawater intrusion and the surface river waters in the stations B and D is responsible for the high Δ values found in bottom samples, characterized by very low or zero dissolved oxygen concentrations.

The regression analysis of Δ values versus oxygen shows an inverse significant correlation, which support the strong influence of biochemical processes on the nitrogen and phosphorus concentrations. The observed correlation coefficients were -0.72 and -0.66 for phosphorus and nitrogen respectively with 30 data pairs.

The attempt to interpret the nitrogen and phosphorus increments in terms of dissolved oxygen depletion gave the following relationships:

$$\Delta O_2 : \Delta NO_3 : \Delta PO_4 = -138 : 14.1 \pm 7.6 : 7.2 \pm 4 \qquad (5)$$

$$\Delta O_2 : \Delta(NO_3 + NO_2) : \Delta PO_4 = -138 : 16 \pm 8.6 : 7.2 \pm 4 \qquad (6)$$

The analysis was limited to the deepest samples characterized by a significant dissolved oxygen depletion, except the sample D(-8 m) where anoxic conditions were evident. All the concentration changes in the above relations have been normalized to a ΔO_2 of -138, in order to enable the comparison with the stoichiometry proposed by Richards (1965). This comparison results in a reasonable agreement with the stoichiometric Δ value of nitrates and nitrates + nitrites, while higher Δ values for reactive phosphate were found. This fact suggests that the nutrients enrichment are not simply related to dissolved oxygen consumption but also to the concurrence of anoxic regeneration processes at sediments level which involve the reduction of nitrates and sulphates and release of ammonia and phosphates. These compounds would diffuse from the bottom into the upper layers, thus altering the $\Delta O_2 : \Delta PO_4$ ratio.

This interpretation is coherent with the enrichment of ammonia and phosphates in the deepest samples of B and D stations which are the most representative of such processes (see Table III and Figure 4).

Nutrients behaviour in absence of saline wedge

In order to have a more complete picture of the nutrient behaviour in all the possible hydrographic conditions, other cruises were accomplished in the winter season when the saline intrusion did not occur.

A characteristic situation was found on November 22, 1979, when the river was in flood (385 $m^3\ sec^{-1}$). The saline intrusion reached only a few hundred meters upstream from the mouth, while the suspended load and the nitrate concentration were significantly increased compared to the corresponding values of July 24. This increase, ranging from 20 to 213 mg l^{-1} for the suspended matter and from 0.78 to 3.34 mg l^{-1} for the nitrate concentration, is due to the heavy effect of drainage waters. Since in these conditions the mixing of freshwater with seawater inside the river is very limited, some samples were also collected in the seawater stations M to Q (see Figure 1).

The nutrients behaviour as a function of salinity is shown in Figures 5 and 6.

From Figure 5 it is apparent that silicate and total inorganic nitrogen are conservative. This behaviour is represented by the linear equations:

$$SiO_2 - Si\ (\mu g\text{-at}\ l^{-1}) = 234\text{–}6.04\ S‰\quad \sigma = \pm 16.9;\ r = -0.98 \qquad (7)$$

$$N_{toti} - N\ (\mu g\text{-at}\ l^{-1}) = 267.9\text{–}6.79\ S‰\quad \sigma = \pm 20.1;\ r = 0.97 \qquad (8)$$

The same figure shows the positive deviation of reactive phosphate with respect to the dilution line.

Figure 6 shows the trend of total phosphorus (TP) and total suspended solid (TSS) in function of salinity. From this figure both total phosphorus and total suspended solids appear to be not conservative but strongly correlated each other. In particular samples (a), collected near the bottom and in the station M, are characterized by higher total phosphorus and particulate matter concentrations, while samples

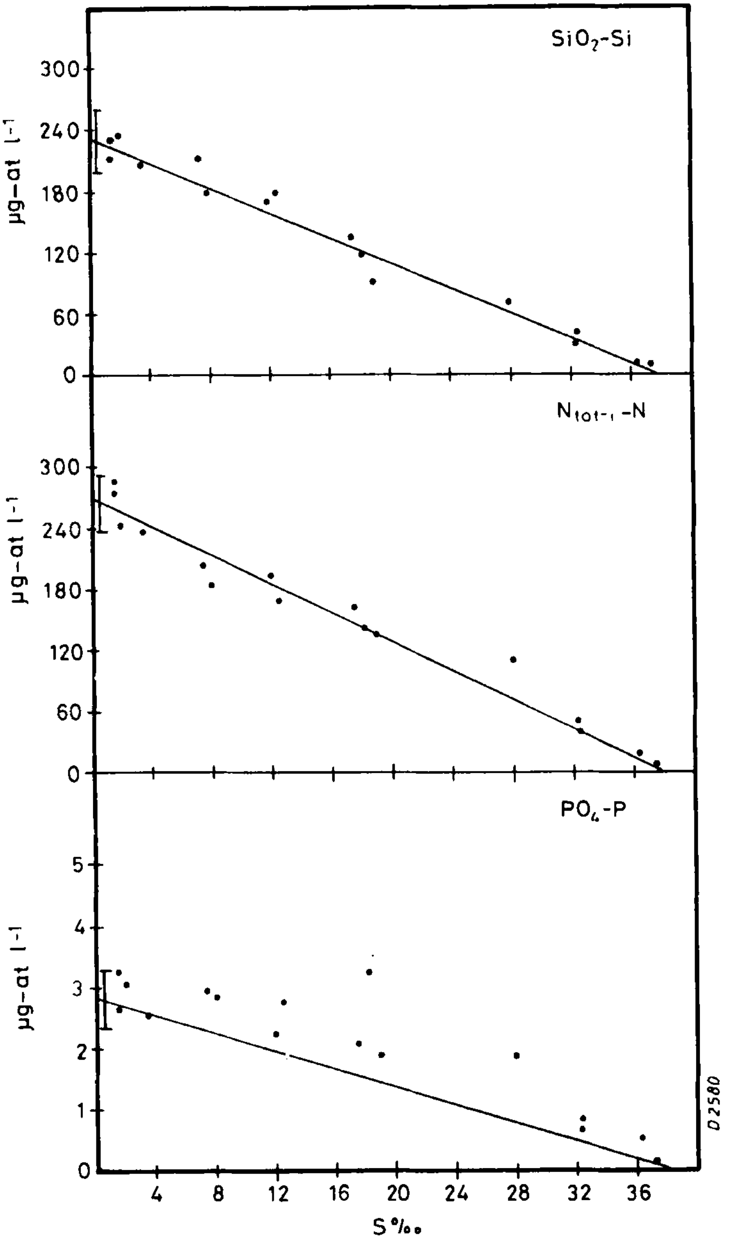

FIGURE 5 Behaviour of silicates (SiO_2—Si), total inorganic nitrogen (N_{toti}) and reactive phosphates (PO_4—P) in function of salinity (November, 1979).

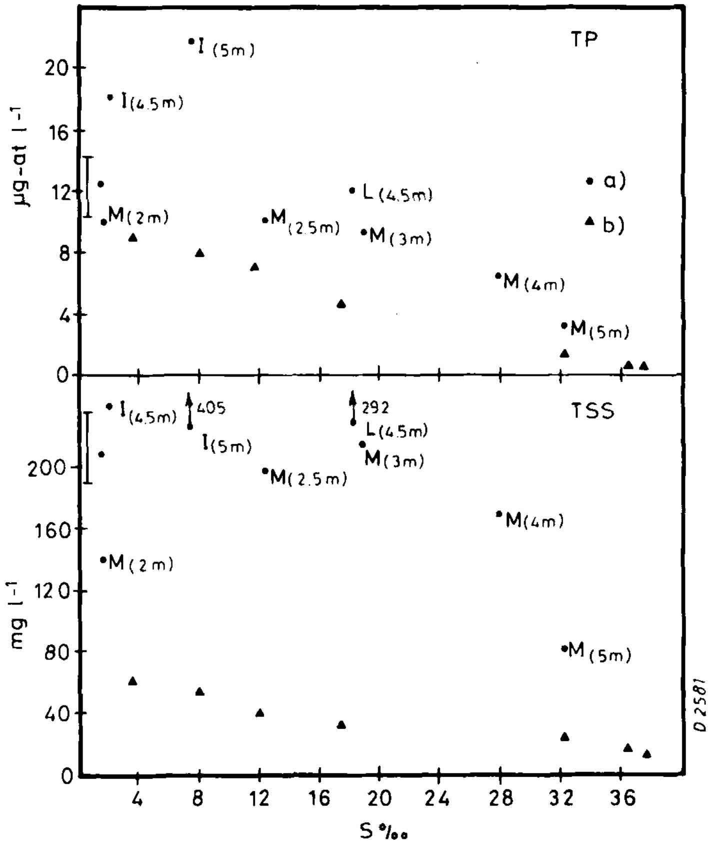

FIGURE 6 Behaviour of total phosphorus (TP) and total suspended solids (TSS) in function of salinity (November, 1979), for the stations I to M (a) and the stations N to Q (b).

(b) collected in stations N–Q show lower concentrations in respect of the dilution values.

These results indicate that the high solid load, which is typical of flood periods has to be considered the main factor controlling the total phosphorus concentration in the Tiber estuary in these conditions.

In order to verify the above results in other hydrographic conditions with a comparable saline intrusion a more accurate procedure of sampling was used. The body of river water was tagged by releasing a series of drogues at the river mouth. Some samples from within this body of river water were collected as they mixed

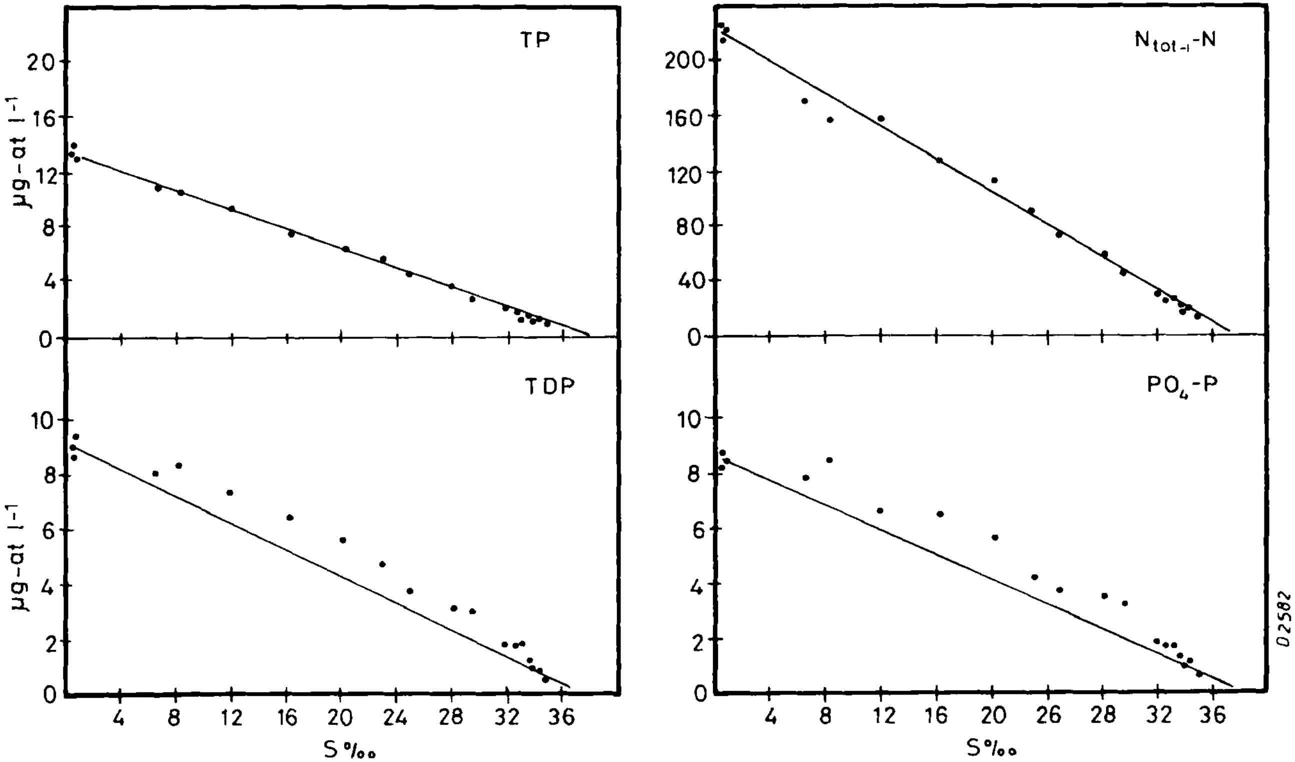

FIGURE 7 Behaviour of total phosphorus (TP), total inorganic nitrogen (N_{toti}), total dissolved phosphorus (TDP) and reactive phosphates (PO_4—P) in function of salinity (March, 1981).

progressively with the coastal sea waters, following the plume centre drogue movement. Such a procedure allows one to reduce the short-term variability in the nutrient concentrations during river water sampling.

The results of two surveys carried out in December 1980 and March 1981 confirmed, except that for total phosphorus, the results obtained in November 1979.

Data in Figure 7, obtained during the March 1981 cruise, show the relationship between total inorganic nitrogen and phosphorus versus salinity. From these results the conservative behaviour of total phosphorus is demonstrated in these conditions.

As far as the dissolved phosphorus is concerned, both reactive phosphate and total dissolved phosphorus show a positive deviation with respect to the theoretical dilution line. Since a short contact time characterizes the mixing and a high percentage of total dissolved phosphorus is represented by reactive phosphate, the increase of the concentration of the dissolved species of phosphorus with respect to the dilution values is probably due to a physico-chemical rather than biochemical process. Such a process should consist in a release of phosphate from suspended matter in order to maintain the equilibrium between the phosphate concentration in suspended matter and in solution, where the concentration of phosphate tends to decrease as a function of salinity (Carritt and Goodgal, 1954). The increasing competition of other anions, such as chloride and sulphate, with the phosphate adsorption process would increase the release (Carritt and Goodgal, 1954; Burns and Salomon, 1969). The slight pH variation, from 7.7 to 8.1, and the consequent dissociation of the phosphoric acid species should have only a minor effect.

CONCLUSIONS

Processes which can influence the nutrients behaviour in the Tiber river estuarine waters have been investigated in different hydrographic river conditions.

During periods of normal summer fluvial flows the seawater intrudes into both outfall channels as a salt wedge which remains in a state of quasi-equilibrium with the fluvial discharge, the amplitude of the tidal variation being about 30 cm (Istituto Idrografico della Marina, 1973).

In these conditions, while silicates show a conservative behaviour, higher concentrations of total inorganic nitrogen and reactive phosphorus, in respect of the expected dilution values, have been found at the river mouth. These positive increments in the lower layer waters and their relationships with oxygen depletion indicate the occurrence of nutrient regeneration.

However the latter process is not simply related to the dissolved oxygen, but also to the anoxic regeneration occurring at sediment levels.

In periods when the saline intrusion is practically absent, mixing between the freshwater and seawater occurs in the river plume.

Under these conditions silicate and total inorganic nitrogen follow a conservative pattern as a function of mixing, while dissolved phosphorus shows a positive deviation with respect to the dilution values. The positive deviation of dissolved phosphorus has been attributed to a chemical release of phosphate from particulate matter with the increase of salinity.

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