Hydrobiologia **373/374:** 237–246, 1998.
J. C. Amiard, B. Le Rouzic, B. Berthet & G. Bertru (eds),
Oceans, Rivers and Lakes: Energy and Substance Transfers at Interfaces.

The input of nutrients by the Rhône river into the Mediterranean Sea: recent observations and comparison with earlier data

T. Moutin, P. Raimbault, H. L. Golterman* & B. Coste
Laboratoire d'Océanographie et de Biogéochimie, Centre d'Océanologie de Marseille, Campus de Luminy, case 901, F-13 288 Marseille cédex 09, France
* *Mas dou Bòchi, Chemin de Tintarlot, F-13 200 Arles, France*

This paper is dedicated to the memory of Kees De Groot

Key words: nutrients, Rhône river, Gulf of Lions (Golfe du Lion), Mediterranean Sea

Abstract

The nutrient input by the Rhône river into the Mediterranean Sea was measured from June 1994 to May 1995. The various fractions of N and P (dissolved and particulate, organic and inorganic) as well as chlorophyll and dissolved silicate concentrations were measured twice a month at Arles, 40 km upstream of the river mouth, in this period. In addition, some samples were taken when the river was in high flood.

The study shows that nitrogen is mainly present as nitrate (76%). Dissolved and particulate organic nitrogen represent 8 and 9%, ammonium 5% and nitrite 1% of total nitrogen respectively. Almost half of the phosphate is particulate phosphate, the largest part of which is calcium-bound phosphate. Orthophosphate represents 31% of total phosphate.

We estimated the total input of nitrogen, phosphate and silicate as 115–127 kt y^{-1} (N), 6.5–12.2 kt y^{-1} (P) and 135–139 kt y^{-1} (Si) by different methods. For nitrogen an annual input of 92.3 to 96.1 kt of nitrate is found, 1.3 to 1.5 kt of nitrite, 6.3 to 6.7 kt of ammonium, 9.7 to 9.8 kt of dissolved organic nitrogen and 5.3 to 12.7 kt of particulate nitrogen; for phosphate the annual imput was 2.7 to 3.0 kt of orthophosphate, 1.3 to 1.7 kt of dissolved organic phosphate & polyphosphate and 2.5 to 7.5 kt of particulate phosphate. While the N-input was mainly in the form of nitrate, a large part of the phosphate input was particulate-P. Comparisons to previous estimations show that the mean annual nitrate concentration in the Rhône has increased by about 50% during the last two decades.

Introduction

Nutrient input by rivers contributes considerably to the nutrient balance of the Mediterranean Sea. The Rhône is the main river flowing into the western basin of the Mediterranean Sea. Its mean flow rate of 1690 $m^3\ s^{-1}$, estimated over a 30 y period, is three times higher than the sum of that of the Ebro (200 $m^3\ s^{-1}$), the Arno (103 $m^3\ s^{-1}$) and the Tiber (234 $m^3\ s^{-1}$) (Martin and Saliot, 1992).

The input of nutrients has a direct influence on primary production in the Golfe du Lion. On an annual basis, around 50% of the primary production in the Gulf can be attributed to terrigenous input (Coste, 1974, Morel et al., 1990). The nitrogen or phosphate concentration is generally considered to be a limiting factor for algal production in the Mediterranean (Berland et al., 1980). An increase in the input may cause a corresponding increase in primary production leading to changes in the functioning of the Mediterranean ecosystem. Therefore it is necessary to know the long-term variability of the input.

The aim of this work is to specify the concentrations of the various fractions (dissolved or particulate, organic or inorganic) of nitrogen and phosphate in the Rhône near the estuary, to estimate their input into

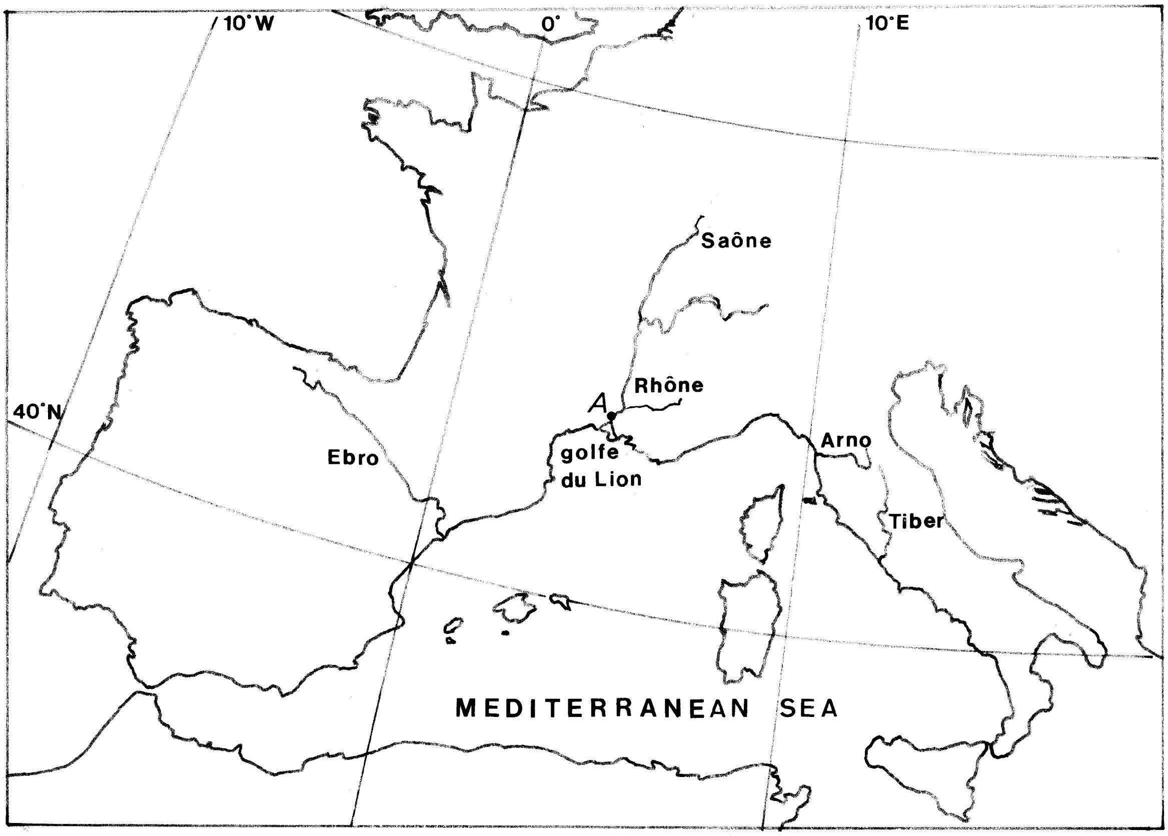

Figure 1. Map of the study area. A = Arles.

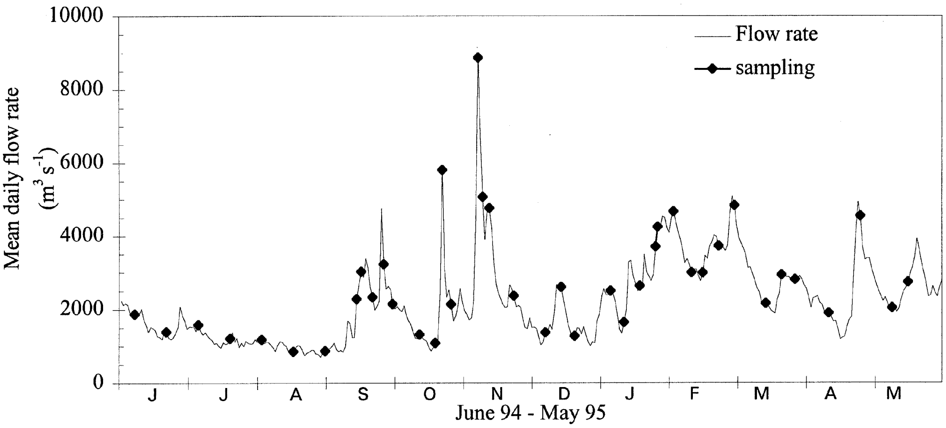

Figure 2. Mean daily flow rate and sampling date.

the Mediterranean Sea and to discuss their long term changes.

Material and methods

The study of the nutrient input by the Rhône into the Mediterranean Sea was carried out from 01/06/1994 to 31/05/1995. The various fractions of nitrogen and phosphate as well as dissolved silicate were measured twice a month in Arles (Figure 1). Additional results obtained from discrete sampling during flood are indicated in Figure 2. Chlorophyll *a* and phaeopigment concentrations were also measured. Samples were kept cooled and, if necessary, filtered over GF/F membranes and/or frozen at – 20 ˚C before analysis in the laboratory.

Chemical analyses

The methods used to determine nutrient (nitrate, nitrite, ammonium, orthophosphate and dissolved silicate) concentrations are described in Tréguer & Le Corre (1975). Particulate and dissolved organic nitrogen and phosphate are measured according to Pujo-Pay and Raimbault (1994). Tot-N and Tot-P correspond to the sum of these various fractions. Chlorophyll and phaeopigment concentrations are determined according to the fluorometric method described by Herbland et al. (1984).

An analysis of the various fractions of particulate phosphate has also been carried out on the suspended matter collected during four three-day sampling periods (14, 15 and 16 Oct. 92, March, May and June 1993). The protocol used is that of Golterman & Booman (1988) and of De Groot & Golterman (1990). Concentrations are expressed as mg l^{-1} (N, Si) or μg l^{-1} (P). N and P concentrations in particulate matter are expressed as mg g^{-1}. Loadings are expressed as t y^{-1} (N, P or Si).

Input calculation

The input into the Mediterranean Sea corresponds to the mass fluxes entering the estuary area (in tons per year). They have been estimated by the two most classical (Walling & Webb, 1985; Thomas & Meybeck, 1992) and two other methods ($*$) which only differ from the precedent in the estimation of the particulate fluxes.

Method 1: based on the calculation of weighted average

The fluxes are calculated from the concentrations C_i (mg f^{-1}) and c_i (mg g^{-1}) of the different variables listed above, the concomitant flow rates Q_i and suspended matter concentrations S_i, and the total water and solid flow rates over the year studied (respectively Q° et S°). The latter were estimated, from records of mean daily water and solid flow rates, at 70 10^9 m^3 and 14 10^6 t (Pont & Bombled, 1996).

The method amounts to the estimation of the yearly dissolved flux F_d from a water discharge weighted average concentration CE_d, and of the yearly particulate flux F_p from a sediment discharge weighted average concentration CE_p.

For dissolved compounds:

$$CE_\mathrm{d} = \frac{\sum_{i=1}^{n} Q_i \cdot C_i}{\sum_{i=1}^{n} Q_i}$$

For particulate compounds:

$$CE_\mathrm{p} = \frac{\sum_{i=1}^{n} S_i \cdot c_i}{\sum_{i=1}^{n} S_i}$$

with *n*: number of samples and $F_\mathrm{d} = Q^\mathrm{o} \cdot CE_\mathrm{d}; F_\mathrm{p} = S^\mathrm{o} \cdot CE_\mathrm{p}$.

Method 1*: As method 1 but considering particulate fluxes as dissolved fluxes.

Method 2: based on a linear interpolation

The annual flux is the sum, over the year, of the product for each period j between two samples, of the mean value for two successively measured concentrations $\overline{C}_{\mathrm{d}j}$ (or $\overline{c}_{\mathrm{p}j}$) by the mean value of the mean daily flow rate $\overline{Q}_i$ (or solid flow rate $\overline{S}_j$) measured during this time interval:($\mathrm{k}_j - 1$) days (i.e. extrapolation of concentration).

For dissolved compounds:

$$F_\mathrm{d} = \sum_{j=1}^{n-1} \overline{C_\mathrm{d} j}, \overline{Q_j}(k_j - 1)$$

For particulate compounds:

$$F_\mathrm{p} = \sum_{j=1}^{n-1} \overline{c_\mathrm{p} j}, \overline{S_j}(k_j - 1)$$

Method 2**:* As method 2 but considering particulate fluxes as dissolved fluxes.

For methods 1 or 2, the total input of a compound is equal to the sum of its dissolved and particulate fluxes: $F = \Sigma F_\mathrm{d} + \Sigma F_\mathrm{p}$

Methods 1^* & 2^* do not take into account the state (dissolved or particulate) of the compounds studied. The fluxes are calculated by adding up the fluxes of the various compounds all calculated as if they were dissolved coumpounds.

Results and discussion

Hydrology

The mean flow rate of the Rhône river calculated for the period 1961–1994 is 1690 $m^3\ s^{-1}$ (s.d. = 320, $n = 34$). the minimum and maximum annual discharge measured being 1064 and 2388 $m^3\ s^{-1}$ respectively.

The annual cycle studied is characterized by a mean annual flow rate of 2220 $m^3\ s^{-1}$ which corresponds to a high flow rate, by a minimum flow rate of about 1000 $m^3\ s^{-1}$ and by numerous floods, one of which was exceptional on the 6th of November 1994: the probability of this event is once in 30 yr. Figure 2 gives daily flow rate and times of sampling.

The yearly inputs are calculated from concentrations and flow rates. Concentrations are measured at Arles and flows at Beaucaire, the distance between the two places is about 20 km (Figure 1). The branching off of the Rhône river near the mouth is considered to have no influence on the input, as the water flow is divided but the concentrations are similar in the 'Petit Rhône' and in the 'Grand Rhône'.

Several reservoirs are located even in the lower part of the Rhône basin, which influence the relation between flow rate and suspended matter. The lake of Geneva which intercepts about 7000 km^2 of the drainage area retains the major part of the suspended matter of glacier origin.

Otherwise, inter-annual variations of the flow rate are significant: the mean annual flow rate can double as the values of the minimum and maximum show during the period 1961–1994. This means that extrapolation to other years is only allowed if the relation between concentration and flow rate is known.

Concentration analysis:

The results obtained for the different variables measured between June 1994 and May 1995 are given in Table 1. They concern arithmetic means as well as standard deviations, minimum and maximum values, weighted average concentrations, medians and quantiles, and total number of analyses. The discharge-weighted averages of Tot-N, Tot-P and dissolved silicate are respectively 1.73 mg l^{-1} (N), 0.12 mg l^{-1}(P) and 1.99 mg l^{-1}(Si). Nitrogen is mainly present as nitrate (76%). Org-N_{diss} and N_{part} account respectively for 8% and 9% of Tot-N, ammonium for 5% and nitrite for 1%. The major part of the phosphate is P_{part}. o-P represents only 31% of Tot-P.

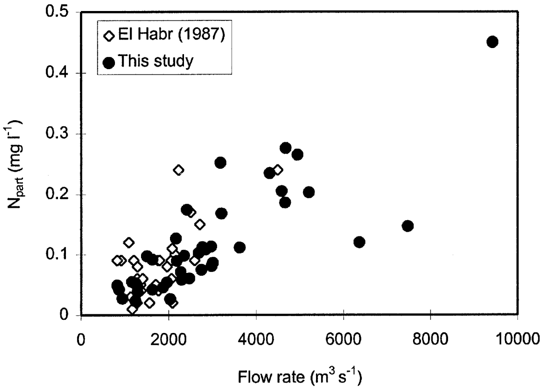

Figure 3. N_{part} concentration versus *Q*. Data from El Habr (1987) and from this study.

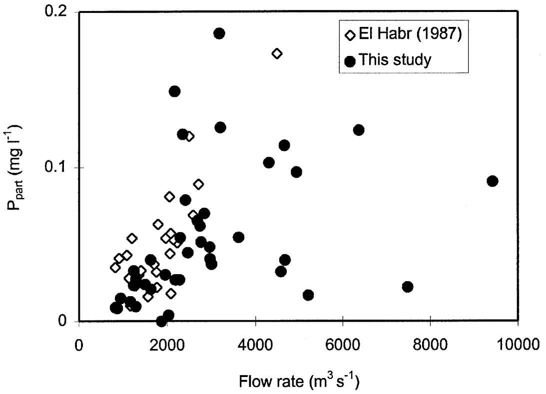

Figure 4. N_{part} concentration versus *Q*. Data from El Habr (1987) and from this study.

Considering the importance of P_{part}, it seems essential to specify the various forms present, in order to estimate their fate in the Golfe du Lion. Table 2 gives the results of four analyses of the P-fractions carried out on the suspended matter sampled between Oct. 92 and June 1993. All flow rates were somewhat below the average, but not exceptionally. Iron-bound P ranged between 5–34%, Ca-bound P between 43–56%, Acid Soluble Organic P between 6–28% and NaOH Soluble Organic P between 11–13%. Ca-bound P is therefore the largest fraction, which is due to $CaCO_3$ being formed in the Rhône. The ratio between Iron-bound P and Iron extracted can not be explained: two values fall in the usual range (1:10–1:20), but especially the very high value in June can not be explained. It seems likely that the system is not yet in chemical equilibrium. Many more data are needed in order to predict the quantity of bio-available P transported by the Rhône. In

Table 1. Characteristics of variable measured in the Rhone river during the period June 1994 – May 1995.

Variables	Units	Arithmetic mean	Standard deviation	Minimum	Maximum	Water-discharge weighted average concentration	Sediment-discharge weighted average concentration	Median and quantiles					*n*
								Q_{10}	Q_{25}	Q_{50}	Q_{75}	Q_{90}	
Instantaneous flow rate	m^3 S^{-1}	2847	1702	836	9431			1238	1635	2448	3420	4707	40
Suspended matter	mg l^{-1}	311	848	8.5	5200	683		14	31	70	285	694	39
Nitrate	mg l^{-1} (N)	1.34	0.43	0.82	2.26	1.32		0.90	0.99	1.15	1.72	1.96	40
Nitrite	mg l^{-1} (N)	0.020	0.005	0.010	0.034	0.019		0.015	0.016	0.020	0.023	0.026	39
Ammonium	mg l^{-1} (N)	0.09	0.05	0.004	0.18	0.091		0.020	0.061	0.097	0.134	0.148	39
org-N_{diss}	mg l^{-1} (N)	0.14	0.08	0.00	0.51	0.14		0.07	0.09	0.13	0.17	0.21	38
N_{part}	mg l^{-1} (N)	0.12	0.09	0.02	0.45	0.16		0.04	0.05	0.09	0.16	0.24	40
N_{part}	mg g^{-1} (N)	1.69	1.51	0.09	7.47		0.38	0.25	0.76	1.27	2.08	3.28	39
Tot-N (Sum)	mg l^{-1} (N)	1.70	0.49	1.04	3.01	1.73		1.16	1.32	1.53	2.10	2.40	37
o-P	μg l^{-1} (P)	44	29	9	195	38		19	29	41	53	61	40
org-p_{diss} & poly P	μg l^{-1} (P)	23	12	2	55	19		9	13	22	31	36	36
P_{part}	μg l^{-1} (P)	55	43	4	186	67		12	24	40	76	121	40
P_{part}	mg g^{-1} (P)	0.76	0.51	0.02	2.17		0.18	0.07	0.39	0.72	0.97	1.34	39
Tot-P (Sum)	μg l^{-1} (P)	117	50	43	231	124		63	80	110	143	195	34
Silicate	mg l^{-1} (Si)	1.89	0.50	0.84	2.74	1.99		1.20	1.59	2.06	2.25	2.46	39
Chlorophyll *a*	μg l^{-1}	2.2	2.1	0.4	13.3			0.7	1.2	1.8	2.7	3.6	40
Phaeopigments	μg l^{-1}	1.5	1.4	0.1	8.4			0.3	0.6	1.3	1.8	2.6	40

Table 2. Characteristics of 4 samples of suspended matter collected in 1992/1993, with special attention to fractionation of P_{part}.

Variables	Units	Oct 92	March 93	May 93	June 93
Flow rate	$m^3\ s^{-1}$	1100	780	1350	1590
Suspended matter	$mg\ l^{-1}$	400	230	182	179
org-C	$mg\ g^{-1}$	4.2	8.2	29.0	17.0
org-N	$mg\ g^{-1}$	0.3	0.9	2.8	2.1
Tot-Fe	$mg\ g^{-1}$	4.6	7.4	15.0	23.0
Tot-P	$\mu g\ g^{-1}$	200	490	454	1200
$Fe(OOH)_{extr}$	$\mu g\ g^{-1}$	400	770	40	510
$Fe(OOH) \approx P$	$\mu g\ g^{-1}$	47	30	20	405
$CaCo_3 \approx P$	$\mu g\ g^{-1}$	90	210	250	570
Acid Soluble Organic P (1)	$\mu g\ g^{-1}$			123	73
Residual Organic P (2)	$\mu g\ g^{-1}$			50	150
(1) + (2)	$\mu g\ g^{-1}$	70	150	173	223
Sum of fractions	$\mu g\ g^{-1}$	207	390	443	1198

the Golfe du Lion, a shift may occur from iron-bound P to calcium-bound P due to the greater salinity and high calcium concentration and higher pH of the sea water, while most of the incoming o-P may precipitate as both inorganic forms.

The nutrient concentrations varied during the period studied. The maximum factor of variation is 3 for Tot-N, 6 for Tot-P and 3 for dissolved silicate. These fluctuations are much greater if one considers the various fractions of nitrogen and phosphate, the maximal fluctuations concerning the dissolved and particulate organic fractions. The concentrations of nitrate show a maximum in winter and a minimum in summer whereas there is no marked seasonal variation in the other nitrogen compounds as was already noticed by Coste & Raimbault (1993). The other variables measured during the period of study do not show significant seasonal variations either. Furthermore, there is no linear relationship between the mean daily flow rate and any of the variables studied, except for N_{part} which showed a significant relationship. Figures 3 and 4 show the concentrations of N_{part} and P_{part} as functions of the flow rate (data of El Habr (1987) and from this study). With a linear regression of the type $y = ax$, a slope of 3.7 to 4.5 10^{-5} is obtained for N_{part} and of 1.5 to 2.1 10^{-5} for P_{part} at the 95% confidence threshold ($R^2 = 0.60$ for nitrogen ($n = 69$) and 0.06 for phosphate ($n = 66$)). The relation obtained for P_{part} is not significant, due to the fact that P_{part} comprises several organic and inorganic compounds, while N_{part} is mainly organic.

Comparison with other rivers

Table 3 indicates the median value of the frequency distributions of concentrations found in other rivers. It shows that the concentrations of dissolved nutrients in the Rhône are clearly higher than those measured in 60 non-polluted major rivers (Meybeck, 1995), particularly as far as nitrogen is concerned (12, 20 and 7 times higher for nitrate, nitrite and ammonium, respectively). The median value is 4 times higher for o-P. On the contrary, for particulate fractions, nitrogen and phosphate are about 2 times less concentrated in the turbid Rhône river. This is partly related to the fact that N_{part} and P_{part} median values are actually much different from the sediment discharge averages because of increasing sampling during flood period.

Input in the Mediterranean Sea

Table 4 presents the mass fluxes estimated according to the four methods proposed. Considering the maximum and minimum values obtained by these methods of estimation for each variable, an annual N-input of 92.3 to 96.1 kt as nitrate is found, 1.3 to 1.5 kt as nitrite, 6.3 to 6.7 kt as ammonium, 9.7 to 9.8 kt as org-N_{diss} and 5.3 to 12.7 kt as N_{part}; an annual P-input of 2.7 to 3.0 kt as o-P, 1.3 to 1.7 kt as org-P_{diss}/poly-P and 2.5 to 7.5 kt as P_{part}.

The input of Tot-N is 115-127 kt and the input of Tot-N is 6.5-12.2 kt for the year studied. The nitrate input represents about 80% of the Tot-N input while that of o-P is only about 25-45% of the Tot-P. There-

Table 3. Medians of frequency distributions of nutrient concentrations or contents for: (1) 60 non-polluted rivers (Watershed $> 100\,000$ km^2) (Maybeck & Helmer 1989 in Meybeck, 1995). (2) References in Meybeck 1993; (3) This study.

	Nitrate mg l^{-1}	Nitrite mg l^{-1}	Ammonia mg l^{-1}	org-N_{diss} mg l^{-1}	N_{part} mg l^{-1}	N_{part} mg g^{-1}	o-P mg l^{-1}	org-P_{diss} & poly P mg l^{-1}	P_{part} mg l^{-1}	P_{part} mg g^{-1}	Silicate* mg l^{-1}
Non-polutted rivers (a)	0.1	[0.001]	0.015	0.26	0.35	2.3	0.01	[0.015]	0.17	1.1	5.0
Mackenzie (2)	0.1			0.1	0.2						1.4
Amazone (2)	0.17		< 0.02	0.2	0.32		0.024	[0.015]	[0.16]		3.2
Seine (2)	4.3		1	0.5	0.3		0.40				
Rhône (3)	1.15	0.02	0.10	0.13	0.09	1.3	0.041	0.022	0.040	0.6	2.06

* Transformed in mg l^{-1} of Si in this table.

Table 4. Estimation of nutrient input (kt of N, P or Si per year) by the Rhône river into the Mediterranean Sea using different calculation methods: methods 1* & 2* as method 1 & 2 but assuming the same transport model for particulate and dissolved compounds (see method section).

	Nitrate	Nitrite	Ammonia	org-N_{diss}	N_{part}	Tot-N	o-P	org-P_{diss} & poly P	P_{part}	Tot-P	Silicate
Method 1	92.3	1.3	6.3	9.7	5.3	115	2.7	1.3	2.5	6.5	139
Method 1*					11.2	121			4.7	8.7	
Method 2	96.1	1.5	6.7	9.8	12.7	127	3.0	1.7	7.5	12.2	135
Method 2*					8.7	123			3.8	8.5	
Minimum	92.3	1.3	6.3	9.7	5.3	115	2.7	1.3	2.5	6.5	135
Maximum	96.1	1.5	6.7	9.8	12.7	127	3.0	1.7	7.5	12.2	139

fore the o-P flux represents less than half of the Tot-P input into the Mediterranean Sea. Given the rapidity of the exchanges between the particulate and the dissolved fractions of phosphate (De Groot, 1992; Moutin, 1992), it is necessary to calculate the Tot-P input as the sum of all fractions.

The two methods used to estimate the dissolved compounds fluxes give essentially equivalent results (Table 4). This is mainly related to the relatively dense sampling which makes the choice of the method to estimate the fluxes less crucial. On the contrary, for the particulate compounds, there is a difference of about a factor 3 between the maximum and minimum values obtained by the four methods of estimation. This is awkward in the case of phosphate for which the particulate fraction is far from negligible. The transport is different for dissolved and particulate compounds which led us to use two different calculations to evaluate their respective fluxes: one based on the evaluation of the total water flow rate over the year and the other based on the evaluation of the total solid flow rate (method 1). In the second case, it implies that there is a constant relationship between the variables studied and the concentration of suspended matter. That is true when the concentration of suspended matter does not exceeds 150 mg l^{-1}. In this case, N_{part} concentration in suspended matter is equal to 2.28 mg g^{-1} with a confidence interval of 0.34 and the P_{part} concentration in suspended matter is equal to 1.16 mg g^{-1} with a confidence interval of 0.11 ($\alpha = 0.05$). On the contrary, when the concentration of suspended matter exceed 150 mg l^{-1}, it seems that it is poor in nitrogen (Figure 5) and the relationship with P_{part} is not linear (Figure 6): method 1 probably underestimates N_{part} and P_{part} inputs. The fact that P_{part} & N_{part} concentrations (mg.l^{-1}) increase more or less linearly with flow (Figures 3 and 4) lead us to prefer methods 1* or 2* to method 1 to estimate particulate nutrient fluxes. Method 2, which permits to take into account the variability of the fluxes of suspended matter, seems to be the most appropriate for the quantification of particulate fluxes (N_{part} & P_{part}) and total fluxes (Tot-N & Tot-P). For dissolved compounds, good results are obtained with method 1 which is of easy use.

Long-term pattern of nitrate input

Figure 7 represents the nitrate input by the Rhône river into the Mediterranean Sea:

(1) calculated by Coste & Raimbault (1993) at four periods (1968, 1984, 1989, 1990),

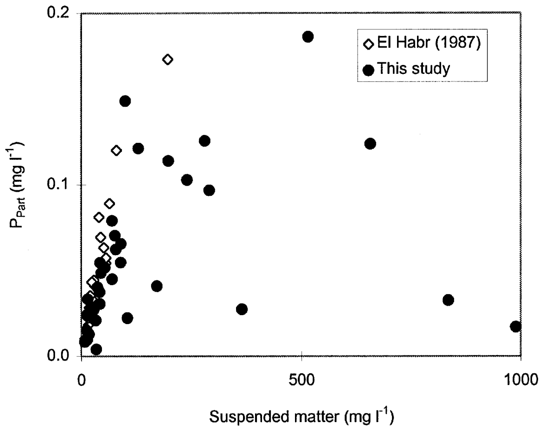

Figure 5. N_{part} concentration versus suspended matter concentration. Data from El Habr (1987) and from this study, one sample omitted ($x = 5200$; $y = 0.45$).

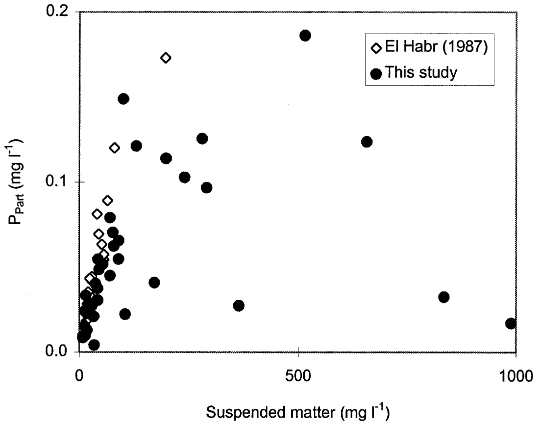

Figure 6. N_{part} concentration versus suspended matter concentration. Data from El Habr (1987) and from this study, one sample omitted ($x = 5200$; $y = 0.09$).

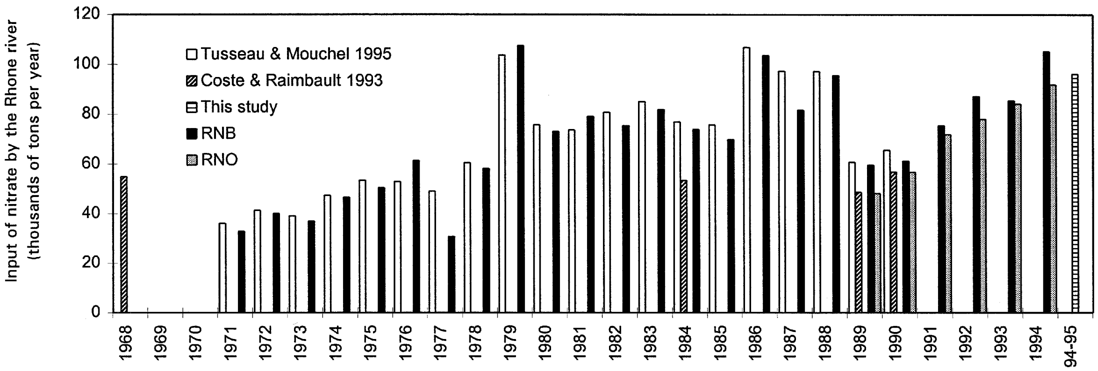

Figure 7. Input of nitrate by the Rhône river into the Mediterranean Sea since 1968.

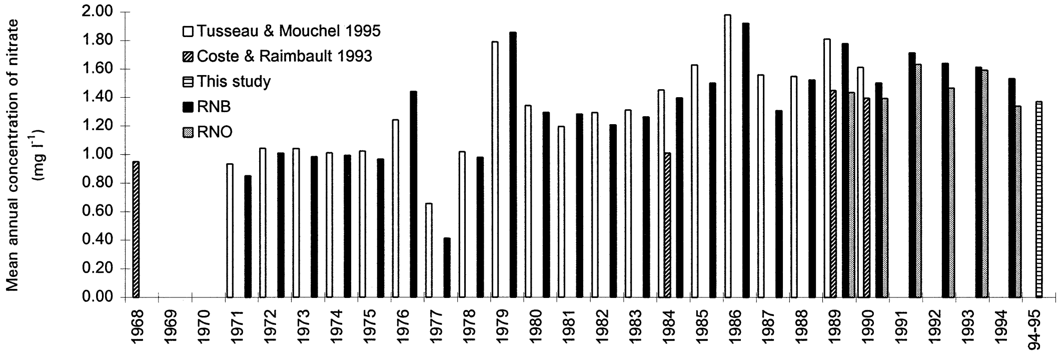

Figure 8. Mean annual concentration of nitrate in the Rhône river near the estuary since 1968.

(2) estimated by Tusseau and Mouchel (1995) from a statistical method and using the data provided by the Agence de l'Eau Rhône-Méditerranée-Corse for the period 1971–1990 (Réseau National de Bassin (RNB), a French river water survey),

(3) calculated with method 1 from the data of this study,

(4) calculated with method 1 from the data provided by the Agence de l'Eau Rhône-Méditerranée-Corse for the period 1971–1990 (RNB),

(5) calculated with method 1 from data obtained from sampling near the estuary for the period 1989–1994 (Réseau National d'Observation (RNO), a French coastal water survey).

Coste & Raimbault (1993) mentioned that there is no significant increase in the nitrate flux during their study period (1968–1990). Tousseau & Mouchel concluded, from the analysis of their data, that the input increased. These contradictory conclusions are based on different approaches and data sets, more precisely on a different number of observations due to a different sampling frequency.

To evaluate the possible increase of the nitrate input, we calculated the mean annual concentration of nitrate in the Rhône as the mass flux calculated by method 1 divided by the mean annual flow rate. This in order to get rid of the inter-annual variability of the flow rates. In all cases, it seems that the mean annual concentration of nitrate in the Rhône has increased during the two last decades (Figure 8). The presence of a trend was tested with a non parametric permutation test using a Wald and Volfowitz's statistic (Good, 1994): the hypothesis of an absence of trend has to be rejected ($\alpha = 0.0022$). The least square estimate of the increase rate of N is 0.029 mg l^{-1} $y^{-1}$with a standard deviation of 0.006. The steady state noted by Coste & Raimbault (1993) must be related to the particular hydrological features of the years included in their study.

Comparison to the total inputs in the Mediterranean Sea

According to Helmer (1977), the annual load carried by rivers into the Mediterranean Sea in the early 1970's was 600–1000 kt of N and 200–400 kt of P. The input by the Rhône river may represent about 10–20% of the Tot-N and 2–6% of the Tot-P. These fluxes are considerable with regard to the global nutrient balance and primary production in the Mediterranean Sea, more especially as Helmer's estimation is based on data from a UNEP report (1977) which seem to be overestimated (Coste et al., 1988).

Conclusion

Input of Tot-N, Tot-P and dissolved silicate by the Rhône river into the Mediterranean Sea was evaluated during a one-year period to 115–127 kt of N, 6.5–12.2 kt of P and 135–139 kt of dissolved silicate (Si). The N-input is mainly as nitrate (92.3–96.1 kt y^{-1}) while that of P is for an important part in particulate form. These quantities can play an essential role in the nutrient balances and the primary production in the Golfe du Lion and a non-negligible role at the scale of the Mediterranean Sea.

The analysis of our data and of the previous estimations leads us to conclude that the mean concentrations of nitrate in the Rhône increased during the two last decades by about 50%. It is necessary to prolong these studies and to establish the relation between the nutrient concentration and flow rate more precisely, and to study the influence of this increase in nitrate input on the primary production of the Golfe du Lion.

Acknowledgements

We want to thank B. Bombled, N. Garcia, D. Pont coordinator of the program, M.C. Bonin and Mrs J. C. Golterman-Hardenberg for help in preparation of the manuscript and M. Meybeck and J.P. Durbec for helpful comments. Financial support was provided by the Agence de l'Eau Rhône-Méditerranée-Corse and the Agence Régionale pour l'Environnement Provence-Alpes-Côte d'Azur.

References

Berland, B., D. J. Bonin & S. Y. Maestrini, 1980. Azote ou phosphore? Considérations sur le paradoxe nutritionnel de la Méditerranée. Oceanologica Acta 3: 135–142.

Coste, B., 1974. Rôle des apports nutritifs minéraux rhodaniens sur la production organique des eaux du Golfe du Lion, Téthys 6: 727–740.

Coste, B., P. Le Corre & H. J. Minas, 1988. Re-evaluation of the nutrient exchanges in the strait of Gibraltar. Deep-Sea Res. 35: 767–775.

Coste, B. & P. Raimbault, 1993. Recent data on the nutrient input into the Mediterranean Sea by the Rhône river. In Martin J.-M. & H. Barth (eds), EROS 2000. NERC, Plymouth, U. K., Wat. Pollut. Res. Rep. 30: 47–50.

De Groot, C. J., 1992. Flux et transformations du phosphate et de l'azote dans les zones humides: la Camargue (Delta du Rhône). Thèse de l'Université Claude Bernard (Lyon I). Thèse et articles de la thèse.

De Groot, C. J. & H. L. Golterman, 1990. Sequential extraction of sediment phosphate. Hydrobiologia 192: 143–148.

El Habr, H., 1987. Les éléments nutritifs du Rhône; leur devenir dans les canaux d'irrigation et les marais en Camargue. Thèse de l'Université Claude Bernard (Lyon I), 150 pp.

Golterman, H. L. & A. Booman, 1988. Sequential extraction of iron-phosphate and calcium-phosphate from sediments by chelating agents. Verh. int. Ver. Limnol. 23: 904–909.

Good, P., 1994. Permutation tests. A practical guide to resampling methods for testing hypotheses. Springer series in statistics. Springler-Verlag New York, 228 pp.

Helmer, R., 1977. Pollutants from land-based sources in the Mediterranean. Ambio 6: 312–316.

Herbland, A., A. LeBouteiller & P. Raimbault, 1984. Size structure of phytoplankton biomass in the Equatorial Atlantic Ocean. Deep-Sea Res. 32: 819–836.

Martin, J. M. & A. Saliot, 1992. Bilan des apports fluviatiles et atmosphériques d'éléments et composés chimiques en Méditerranée Occidentale. 3ème rencontre de l'Agence Régionale pour l'Environnement Provence-Alpes-Côte d'Azur, 24–27 septembre 1991: 61–66.

Meybeck, M., 1995. Les lacs et leur bassin. In Pourriot, R. & M. Meybeck (eds), Limnologie générale. Masson, Paris: 6–59.

Meybeck, M., 1993. C, N, P and S in rivers: from sources to global inputs. In Wollast R., F. T. Mackenzie & L. Chou (eds), Interaction of C, N, P and S Biogeochemical Cycles and Global Change. Springer Verlag: 163–193.

Meybeck, M. & R. Helmer, 1989. The quality of rivers: from pristine stage to global pollution. Global Planet. Change 75: 283–309.

Morel, A., A. Bricaud, J. M. André & J. Pelaez-Hudlet, 1990. Spatial-temporal evolution of the Rhône river plume as seen by CZCS imagery: Consequences upon primary productions in the Gulf of Lions. In Martin J. M. & H. Barth (eds), EROS 2000. NERC, Plymouth, U. K., Wat. Pollut. Res. Rep. 20: 45–62.

Moutin, T., 1992. Contribution à l'étude du cycle du phosphate dans les écosystèmes lagunaires. Thèse de l'Université de Montpellier II, 251 pp.

Pont, D. & B. Bombled, 1996. Estimation du débit solide. In Evaluation des charges polluantes du Rhône à la Méditerranée. Rapport Agence de l'Eau Rhône-Méditerranée-Corse, 15 pp.

Pujo-Pay, M. & P. Raimbault, 1994. Improvement of the wet-oxidation procedure for simultaneous determination of particulate organic nitrogen and phosphorus collected on filters. Mar. Ecol. Prog. Ser. 105: 203–207.

Thomas, R. L., & M. Meybeck, 1992. The use of particulate material in Water Quality and Assessments, D. Chapman (ed.), Chapman and Hall, London: 121–170.

Tusseau, M. H. & J. M. Mouchel, 1995. Nitrogen inputs to the gulf of Lions via the Rhône river. In Martin J.-M. & H. Barth (eds), EROS 2000. NERC, Plymouth, U.K., Water Pollution Research Report 32: 49–60.

Tréguer, P. & P. LeCorre, 1975. Manuel d'analyse des sels nutritifs dans l'eau de mer (Utilisation de l'autoAnalyseur II). 2ème ed., Laboratoire d'Océanographie chimique, Université de Bretagne Occidentale, Brest, 110 pp.

Walling, D. E. & B. W. Webb, 1985. Estimating the discharge of contaminants to coastal waters by rivers: some cautionary comments. Marine Poll. Bul. 16: 488–492.

UNEP (United Nations Environnement Programme), 1977. Preliminary report on the state of pollution of the Mediterranean Sea. UNEP Preliminary Report IG.11/INF. 4.