Seasonal variations of nutrients 
(NO$_3^-$, NO$_2^-$, NH$_4^+$, PO$_4^{3-}$ and Si(OH)$_4$) 
and suspended matter 
in the Rhone delta, France

Véronique DENANT, Alain SALIOT 
Laboratoire de Physique et Chimie Marines, Université Pierre-et-Marie-Curie, UA­ CNRS n° 353, Tour n° 24-25, 4, place Jussieu, 75252 Paris Cedex 05, France.

Received 21/10/88, in revised form 26/6/89, accepted 18/8/89.

ABSTRACT
Nutrient concentrations studied in the upstream Rhone delta showed very different variations according to the season and to the nutrient considered. Nitrate and silicate varied by a factor of 1.6, whereas phosphate and total dissolved phosphorus varied within a wider range, by a factor of 2.1-2.6. The largest variations were observed for ammonia whose concentration varied from 0.011 mg/l in November 1984 to 0.180 mg/l in February 1985. Nutrient concentrations were highest in winter and decreased in spring. In February and the beginning of May 1985 the behaviour of nutrients was practically conservative in the delta, from the river to marine waters. A slight nutrient deficit was observed for low salinity waters for other seasons. An estimation of the annual input of nitrogen/nitrate (N-NO$_3^-$) discharged by the Rhone river was determined from a re-examination of previous data; it was approximately 7.5 x 10$^4$ metric tons/year. Rhone river waters showed suspended matter concentrations varying in the range 7-62 mg/l. Higher values occurred in October and in November, corresponding to higher river flow values (>2000 m$^3$s$^{-1}$) due to autumn mediterranean rains. The relationship between suspended matter and particulate organic carbon, expressed in percentage of particulate matter, was similar to that observed for most world rivers.


RéSUMÉ
Variations saisonnières des éléments nutritifs [NO$_3^-$, NO$_2^-$, NH$_4^+$, PO$_4^{3-}$ et Si(OH)$_4$] et des matières en suspension dans le delta du Rhône

L'étude des variations saisonnières des éléments nutritifs dans la partie amont du delta du Rhône montre des amplitudes de fluctuation très différentes selon l'élément considéré. Alors que les nitrates et la silice montrent une faible amplitude de variation d'un facteur 1,6, les phosphates et le phosphate total dissous varient dans une gamme plus importante (2,1 - 2,6). L'ammonium fluctue plus largement, de 0,011 mg/l en novembre 1984 à 0,180 mg/l en février 1985. Dans l'ensemble les concentrations des éléments nutritifs sont maximales en hiver, puis chutent au printemps. En février et début mai 1985, le comportement des éléments nutritifs, dans le delta et son débouché en milieu marin, est pratiquement conservatif. Un léger déficit est observé pour les autres campagnes pour les eaux de faible salinité. Pour ces années 1984-1985, l'apport en azote/nitrate (N-NO$_3^-$) du Rhône à la Mer Méditerranée serait de 7,5 x 10$^4$ t par an. Le Rhône se situe dans la moyenne des fleuves mondiaux quant à la relation existant entre les matières en suspension et le carbone organique particulaires, exprimé en pourcentage des suspensions. Les teneurs en matières en suspension observées dans le fleuve varient dans une large gamme (7-62 mg/l). Les fortes valeurs rencontrées en octobre et novembre 1984 correspondent à de forts débits du fleuve, associés aux pluies méditerranéennes automnales.

INTRODUCTION

Although the Mediterranean Sea is a semi-enclosed area, it is considered a good model for studying biogeochemical cycles. The northwestern basin has been the subject of assessment of budget of different chemical species such as nutrients (Bethoux, 1981). In the last few years, several programs have studied the biogeochemistry of the northwestern basin and focused on the impact of inputs from rivers and from the atmosphere (Programs Pelagolion, Écomarge, Dyfamed, Greco Ico, Eros2000). In this context the Rhone river, which is the largest river entering the Mediterranean Sea, plays a major role in terms of inputs of water, dissolved material and suspended matter originating from natural and anthropogenic riverine and atmospheric mobilization and remobilization of solid materials deposited as sediments into the northwestern basin.

A few previous analyses of nutrients have been performed in the Rhone river by Coste and Minas (1967), Blanc et al. (1969), Coste (1974), Coste et al. (1977) and Coste et al. (1984). In order to complete budgets of matter entering the Mediterranean Sea through the Rhone river, we present a study of seasonal variations of nutrients and suspended matter. This study was performed in the river itself and in the Rhone delta to assess the pathway of nutrients within the salinity gradient at some five key hydrological periods.

MATERIAL AND METHODS

Sampling sites

Since the erection of the Assouan dam on the Nile river, the Rhone river has become the major river entering the Mediterranean Sea, with an average annual water flow of 1570 m$^3$s$^{-1}$. It enters the sea through a complex deltaic system, the left branch of which (or Grand Rhone) collects approximately 90% of the total Rhone flow. The hydrological regime of the river is mainly influenced by: a) rains of oceanic origin, predominating from January to March; b) waters originating from the melting of alpine ice-fields, leading to spring high waters; c) rains of mediterranean origin, occurring roughly from October to December, bringing large and sudden variations of the river flow.

Five sampling cruises were carried out from October 1984 up to May 1985 (Fig. 1). This permitted collection of samples belonging to different key hydrological periods (Tab. 1). For example, the water flow varied from 1300 m$^3$s$^{-1}$ in May 1985 to 2431 m$^3$s$^{-1}$ in November 1984.

Analytical methods

Nutrients

The water was filtered through pre-combusted glass fibre Whatman GF/F filters (0.7 µm pore size) and kept at T<4°C after addition of chloroform. Nutrient determination was carried out in the land-based laboratory within a few days. References for methods, limits of detection and precision are reported in Table 2.

Suspended matter (SM), particulate organic carbon (POC)

These parameters were measured on particulate matter collected from the filtration of water through pre-combusted Whatman GF/F glass fibre filters, rinsed several times with distilled water. SM was determined by weighing the filters before and after filtration. POC was measured after decarbonation of particulate matter by phosphoric acid using a Leco analyzer.

RESULTS AND DISCUSSION

Nutrients in the river

Nutrient data obtained in the riverine zone are given in Table 3. The riverine station corresponds to the minimum salinity value encountered, here less than 33 mg l$^{-1}$. The position of this station varies between Barcarin and Port Saint Louis du Rhone (Fig. 1),...
NUTRIENTS AND SUSPENDED MATTER IN THE RHONE DELTA

Table 1
General characteristics of the five sampling cruises carried out in the Rhone delta in the period 1984-1985: date, river flow and characteristics of reference riverine and marine stations.

<table>
<thead>
<tr>
<th>Sampling cruise</th>
<th>River flow (m³ s⁻¹)</th>
<th>Riverine station</th>
<th>Marine station</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 3-4, 1984</td>
<td>2 134-2 332</td>
<td>Barcharin</td>
<td>Roustan buoy</td>
</tr>
<tr>
<td>November 29, 1984</td>
<td>2 431</td>
<td>Barcharin</td>
<td>River mouth</td>
</tr>
<tr>
<td>February 23-25, 1985</td>
<td>1 570-1 285</td>
<td>Barcharin</td>
<td>Station “large”</td>
</tr>
<tr>
<td>May 2, 1985</td>
<td>1 300</td>
<td>Port Saint Louis</td>
<td>Roustan buoy</td>
</tr>
<tr>
<td>May 28, 1985</td>
<td>1 760</td>
<td>Port Saint Louis</td>
<td>Roustan buoy</td>
</tr>
</tbody>
</table>

pk: kilometric point: distance from the city of Lyon.
Cl⁻: chlorinity.
T°C: temperature.

Table 2
Characteristics of analytical methods used for the determination of nutrients.

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Reference</th>
<th>Limit of detection (mg l⁻¹)</th>
<th>Precision % for a concentration of (mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻</td>
<td>*E-P-A</td>
<td>0.001 (N)</td>
<td>5</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>Reference AFNOR T90013 11/1985</td>
<td>0.001 (N)</td>
<td>5</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>Reference AFNOR T90015 08/1975 (indophenol method)</td>
<td>0.002 (N)</td>
<td>0.100 (N)</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>Reference AFNOR T90023 09/1982</td>
<td>0.001 (P)</td>
<td>3</td>
</tr>
<tr>
<td>Si(OH)₄</td>
<td>Industrial Method No. 7-68W</td>
<td>0.02 (Si)</td>
<td>1.0 (Si)</td>
</tr>
</tbody>
</table>


Table 3
Chemical characteristics of Rhone river surface waters collected at the riverine reference station in the period 1984-1985: Cl⁻: chlorinity; NO₃⁻: nitrate; NO₂⁻: nitrite; NH₄⁺: ammonia; PO₄³⁻: phosphate; P: total phosphorus; Si(OH)₄: silicate; n.d.: not determined.

<table>
<thead>
<tr>
<th>Riverine reference Station</th>
<th>Cl⁻ (mg l⁻¹)</th>
<th>NO₃⁻ (mgNl⁻¹)</th>
<th>NO₂⁻ (mgNl⁻¹)</th>
<th>NH₄⁺ (mgNl⁻¹)</th>
<th>PO₄³⁻ (mgPl⁻¹)</th>
<th>Total P (mgPl⁻¹)</th>
<th>Si(OH)₄ (mgSil⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barcharin 4.10.84</td>
<td>33.00</td>
<td>1.04</td>
<td>n.d.</td>
<td>0.050</td>
<td>0.068</td>
<td>n. d.</td>
<td>1.40</td>
</tr>
<tr>
<td>Barcharin 29.11.84</td>
<td>18.50</td>
<td>1.86</td>
<td>n. d.</td>
<td>0.011</td>
<td>0.205</td>
<td>0.209</td>
<td>1.53</td>
</tr>
<tr>
<td>Barcharin 25.02.85</td>
<td>18.80</td>
<td>1.87</td>
<td>0.018</td>
<td>0.180</td>
<td>0.146</td>
<td>0.150</td>
<td>2.27</td>
</tr>
<tr>
<td>Port St Louis 2.05.85</td>
<td>19.20</td>
<td>1.29</td>
<td>0.019</td>
<td>0.065</td>
<td>0.148</td>
<td>0.152</td>
<td>1.41</td>
</tr>
<tr>
<td>Port St Louis 28.05.85</td>
<td>23.80</td>
<td>1.24</td>
<td>0.017</td>
<td>0.058</td>
<td>0.092</td>
<td>0.098</td>
<td>1.72</td>
</tr>
</tbody>
</table>

According to the river flow. These data lead to the following comments: seasonal variations show very different ranges from one nutrient to another. Nitrite shows fairly constant and low concentrations representing less than 1.5% of nitrogen/NO₃⁻. Nitrate and silicate show a narrow seasonal variation range, characterized by factors of 1.60 and 1.65 respectively. Phosphate and total phosphorus have a wider variation range (2.13-2.56). Ammonia has the widest variation range, from 0.011 mg l⁻¹ in November 1984 up to 0.180 mg l⁻¹ in February 1985, corresponding to a factor of 16.

With the exception of nitrite, nutrients exhibit higher concentrations in winter, followed by a decrease in spring.

Pathway of nutrients in the Rhone river delta

In order to study the fate of nutrients during freshwater/seawater mixing where strong chemical gradients should control how and at what rate nutrients are transported to the sea, other samples were collected and analyzed from the riverine reference station up to the river mouth (Roustan They), to Roustan Buoy or even to station “Large”, 12 km off the river mouth (corresponding to a chlorinity > 18 g l⁻¹).

Figures 2, 3 and 4 show the variations of nitrate, phosphate and silicate concentrations as a function of chlorinity. With respect to the extreme riverine and marine reference points, nitrate shows a conservative pathway during the mixing process in May 2, 1985.
Figure 3
Relationship between phosphate (\(P - PO_4^{2-}\)) and chlorinity. Relation entre phosphates (\(P - PO_4^{2-}\)) et chlorinité.

Figure 4
Relationship between silicate (\(Si - Si(OH)_4\)) and chlorinity. Relation entre silice (\(Si - Si(OH)_4\)) et chlorinité.

through the whole chlorinity range and, in February 1985, so far as measurements are available, through the chlorinity range 0-7 g l\(^{-1}\). In contrast, data obtained at the end of May 1985 and in October 1984 suggest a loss in nitrate in the low chlorinity range resulting from uptake reactions related to other processes other than mixing, such as uptake by deltaic biota or removal to the sediment interface.

A reasonable number of points in the 0-20 g l\(^{-1}\) chlorinity range suggests a conservative pathway for phosphate in February and beginning of May with a close value observed for the slope of the two mixing curves. The limited number of samples obtained for other cruises in the medium chlorinity range does not permit conclusions concerning a conservative pathway. A slight deficit is observed at the end of May 1985 in the 0.5 g l\(^{-1}\) chlorinity range, as previously observed for nitrate. The same trends are encountered for silicate. These data confirm previous observations by Blanc et al. (1969) and Coste et al. (1977) suggesting a quasi-conservative behaviour of nutrients in the Rhone delta. Chlorophyll \(a\) concentrations were slightly higher at the end than at the beginning of May 1985 (3.2-19.4 \(\mu g l^{-1}\) in the river, 2.5-10.5 \(\mu g l^{-1}\) in marine waters and 0-6 \(\mu g l^{-1}\) in the river; 1.9-4.3 \(\mu g l^{-1}\) in marine waters respectively). The higher biological activity revealed by the chlorophyll \(a\) and total pigment concentrations encountered at the end of May, indicators of the pressure of the biological utilization of primary nutrients, N, P, Si (Sharp et al., 1984; Church, 1986) could explain the change of behaviour of nutrients leading to the observed deficit, whereas chlorophyll \(a\) concentrations are in the same range in October 1984 (0.8-1.6 \(\mu g l^{-1}\) in the river; 1.6 \(\mu g l^{-1}\) in marine waters) and in February 1985 (0.1-1.9 \(\mu g l^{-1}\) in the river; 0.1-1.6 \(\mu g l^{-1}\) in marine waters).

A tentative assessment of the Rhone river inputs to the Mediterranean Sea necessitates considering chemical species concentrations as a function of river discharge at a given time point. A serious difficulty here is the great variability of the river flow as measured on a daily, weekly, or monthly basis. Such a budget has been established by Coste in 1974 for Rhone inputs of nitrate and phosphate for the year 1968. This period was characterized by more marked seasonal variations than those observed by Parde (1925) over forty years. Comparing values obtained for nitrate during the five periods sampled with those reported by Coste shows that our values are higher by 26% in February, by 55% in November, the yearly average being 40% higher. This suggests that during the period 1984-1985 where river discharge values were similar in winter and in spring but higher in autumn than mean values over a 40-year period, the annual input of the Rhone river in nitrogen/nitrate (N - NO\(_3^-\)) could be estimated at a 40% higher level than that evaluated by Coste, i.e., approximately 7.5 x 10^4 metric tons N - NO\(_3^-\).

Phosphate concentrations are approximately twice those reported by Coste (1974). The comparison here is only possible for three months and does not allow any yearly extrapolation. Nevertheless, it could be possible to use the mean value of N/P atomic ratios from concentrations in nitrate and phosphate as shown in Table 3. This gives a ratio of 26:5 with a coefficient of variation of 25%. According to this hypothesis, the tentative evaluation of annual phosphate input would be 6.45 x 10^4 metric tons P - PO\(_4^{2-}\). This estimation is 35% higher than that proposed by Coste in 1974: 4.8 x 10^3 tons P - PO\(_4^{2-}\). We can note that the value of the N/P atomic ratios, 26:5, is close to that given by Coste (1974) (25:6) with a coefficient of variation of 55% and to that given by McGill (1965), 23:4 with a coefficient of variation of 15.2% for the Ligurian Sea.

Suspended matter and particulate organic carbon

Riverine waters show suspended matter concentrations varying from 7 mg l\(^{-1}\) at the beginning of May 1985 up to 62 mg l\(^{-1}\) in November 1984, as measured at the riverine reference station (Tab. 4). High values encountered in October and in November correspond to higher flow values (> 2000 m\(^3\) s\(^{-1}\)), associated with autumnal Mediterranean rains. Suspended matter concentrations of surface waters show generally slight variations in the river between Barcarin and waters influenced by dilution with seawater (chlorinity > 1 g l\(^{-1}\)). These variations illustrated in Figure 5 are as follows:

a) 23-34 mg l\(^{-1}\) (mean = 29 ± 17%) in October 1984; at this season much higher concentrations, up to 84 mg l\(^{-1}\) have been observed between Arles and pK 310, probably related to local influences such as
Table 4
Chemical characteristics of Rhone river surface waters collected at the riverine reference station in the period 1984-1985; SM: suspended matter in mg/l; POC: particulate organic carbon; POC/SM (%): percentage of suspended matter in organic carbon; Chl a: chlorophyll a in µg/l.

<table>
<thead>
<tr>
<th>Riverine reference Station</th>
<th>SM (mg/l)</th>
<th>POC (µgC/l)</th>
<th>POC/SM (%)</th>
<th>Chl a (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barcarin</td>
<td>4.10.84</td>
<td>23.0</td>
<td>6.8</td>
<td>2.96</td>
</tr>
<tr>
<td>Barcarin</td>
<td>29.11.84</td>
<td>62.0</td>
<td>2.96</td>
<td>4.75</td>
</tr>
<tr>
<td>Barcarin</td>
<td>25.02.85</td>
<td>12.6</td>
<td>1.01</td>
<td>8.05</td>
</tr>
<tr>
<td>Port St Louis</td>
<td>2.05.85</td>
<td>7.0</td>
<td>0.41</td>
<td>5.75</td>
</tr>
<tr>
<td>Port St Louis</td>
<td>28.05.85</td>
<td>16.0</td>
<td>0.74</td>
<td>4.49</td>
</tr>
</tbody>
</table>

The existence of a relation between suspended matter load and organic carbon content in suspended matter (POC in %). Variation of POC content results, as in most large rivers, from two opposite trends: the decrease of POC % with suspended matter load and the increase of suspended matter with water discharge, the latter process being dominant.

The Rhone river belongs to the mean variation range of POC % versus suspended matter relationship as determined for world rivers by Meybeck (1982). As an exception, note that values representative of marine waters collected in February 1985 are outside the mean variation range window. This is not surprising as the mean variation range window has been established from river waters and not from coastal marine waters. The existence of a relation between suspended matter POC content and suspended matter load could help in evaluating transport budgets for different organic chemical species associated mainly with suspended matter such as hydrocarbons or pesticides (Marchand et al., 1986; Saliot et al., in press) using the suspended matter concentration, a routinely determined parameter in most river monitoring programs.

Acknowledgements

This study has been performed as part of the GRECO Interactions Continent/Ocean Program with the financial support of the CNRS. We thank Dr. J.-M. Martin, leader of the ICO program, Dr. M. Meybeck for stimulating help during the realization of the program, Dr. G. Cauwet for help in carbon analysis, Dr. C. Carrio for help during sampling and Dr. B. Coste for his comments on the manuscript.
REFERENCES
