Carbonic-calcium system, nutrients and total organic nitrogen in continental runoff to the Galician Rías Baixas, NW Spain

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ABSTRACT

Biogenic element levels in continental runoff and their behaviour during estuarine mixing are studied in the Galician Rías Baixas for the upwelling season (May-October). Alkalinity, calcium, both with average concentrations of about 350 $\mu mol.kg^{-1}$, and reactive silica, with 105 $\mu mol.kg^{-1}$, show near conservative distributions along the estuarine side of the rías. A good agreement was found between values obtained by direct measurement in the river and those calculated by extrapolation to zero salinity from the mixing diagrams. On the other hand, nitrate (10-40 $\mu mol.kg^{-1}$) and mainly phosphate (1 $\mu mol.kg^{-1}$) are strongly affected by the biological activity of benthic algae during estuarine mixing. TON and ammonium in the innermost parts of the Ría de Arousa are also determined. The levels and time variations of these variables are very similar between stations with different water bodies. They show a tendency to increase in time during summer (from 20 to 50 $\mu mol.kg^{-1}$ for TON and from 15 to 25 $\mu mol.kg^{-1}$ for NH_4^+) independent of the water body present in the column.

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RÉSUMÉ

Système carbone-calcium, éléments nutritifs et azote organique total (TON) dans les apports d'eau continentale aux Rías Baixas, nord-ouest de l'Espagne

On étudie les concentrations d'éléments biogéniques dans les apports d'origine continentale et leur comportement pendant le mélange estuarien dans les Rías Baixas de la Galice au cours de la saison d'upwelling (mai-octobre). L'alcalinité, le calcium, présentant tous deux une concentration moyenne d'environ 350 $\mu mol.kg^{-1}$, et le silicate, avec 105 $\mu mol.kg^{-1}$, montrent une évolution quasi conservative dans la zone estuarienne des rías. De plus, une bonne concordance est obtenue entre les concentrations mesurées directement dans le fleuve et celles résultant de l'extrapolation des diagrammes de mélange au zéro de salinité. Cependant, les teneurs en nitrate (10-40 $\mu mol.kg^{-1}$) et principalement en phosphates (1 $\mu mol.kg^{-1}$) sont fortement influencées par l'activité biologique des

algues benthiques pendant le mélange estuarien. Les teneurs en TON et en ammonium sont aussi déterminées dans la zone la plus intérieure de la Ría de Arousa. On trouve que les niveaux et l'évolution temporelle de ces variables sont très similaires dans les stations avec différentes masses d'eau. Ils montrent une tendance à l'augmentation dans le temps pendant l'été (de 20 à 50 μmol.kg^{-1} en TON et de 15 à 25 μmol.kg^{-1} en NH$_4^+$) indépendamment de la masse d'eau présente dans la colonne.

INTRODUCTION

The Rías Baixas comprise four coastal embayments into the Galician coast, NW Spain, which behave as partially mixed positive estuaries (Beer, 1983). Two sides, oceanic and estuarine, can be distinguished (Fig. 1). The former, with salinity over 30, is volumetrically dominant in the rías. The latter include only the innermost and shallowest areas, where salinity is lesser due to continental runoff.

From May to October, an enhancement of the water interchange between the coastal shelf and the oceanic side due to wind-driven upwelling takes place. The colder nutrient-rich upper layer of the Eastern North Atlantic Central Water (ENAW) reaches the shelf and enters the rías, fertilizing them (Otto, 1975; Fraga, 1981; Blanton *et al.* 1987). As a result, upwelling is the main factor responsible for the high primary production found during spring and summer, from 700 to 1 200 mg C.m^{-2}.day^{-1} (Prego, 1990), which supports the most intensive raft

Figure 1

Location of the studied area. Stations R1, R2 and R3 are situated in the rivers Ulla, Umia and Oitaben respectively. E1, E2 and San Simón Bay (in the Ría de Vigo) are situated on the estuarine side of the rías (see the haline distribution in San Simón Bay). Station 01 is on the oceanic side of Ría de Arousa.

Localisation de la zone d'étude. Les stations R1, R2 et R3 sont respectivement situées dans les fleuves Ulla, Umia et Oitaben. E1, E2 et les stations de San Simón (dans la Ría de Vigo) sont situées dans la zone estuarienne des rías (voir la distribution haline dans la baie de San Simón). La station 01 est localisée dans la zone océanique de la Ría

culture of edible mussels in the world (Tenore *et al.*, 1982): 180 000 metric tons total wet weight during 1989, 90 % from Ría de Arousa.

The obvious economic interest of this large-scale mussel farming has stimulated detailed investigation of water fluxes and biogenic element budgets along the oceanic side of the rías. Since the first study for Ría de Arousa by Otto (1975) using a two-layer box model, some others have been carried out (González *et al.*, 1979; Prego and Fraga, 1992; Ríos, 1992).

In order to run such circulation models it is necessary to know in advance the continental runoff and its chemical composition. However, strong biogeochemical processes occur on the estuarine side of the rías (Margalef, 1958), especially due to the activity of benthic algae like *Ulva* and *Fucus* and the marine angiosperm *Zostera* (Niell, 1977). Consequently, biogenic element levels associated with continental runoff can be affected during estuarine mixing (Bennekom and Salomons, 1981) and, therefore, direct measurements in the river can be unsuitable to the budget in the oceanic side of the rías.

The aim of this work is to establish the chemical composition of river inputs to the Rías Baixas and to determine how it is modified on their estuarine side during the upwelling season. Rivers Ulla and Umia, which enter the Ría de Arousa, and river Oitaben which enters the Ría de Vigo are studied (Fig. 1). Furthermore, the study will permit comparison of the Rías Baixas with other similar estuarine systems on the European Atlantic coast, away from industrial inputs.

MATERIAL AND METHODS

Sampling

From May to October 1989, water samples were collected every fifteen days (4 and 17 May, 6 and 21 June, 5 and 19 July, 2 and 28 August, 13 and 27 September and 11 and 25 October) at the bridges of Catoira (E1) and Padrón (R1) on the River Ulla and the bridges of Cambados (E2) and Caldas de Reis (R2) on the River Umia (Fig. 1), in collaboration with the Departamento de Química-Física of the Universidad de Santiago. Stations E1 and E2 lie on the estuarine side of Ría de Arousa where salinity is always greater than 5. Station R1 is in the lower course of the river Ulla and, at
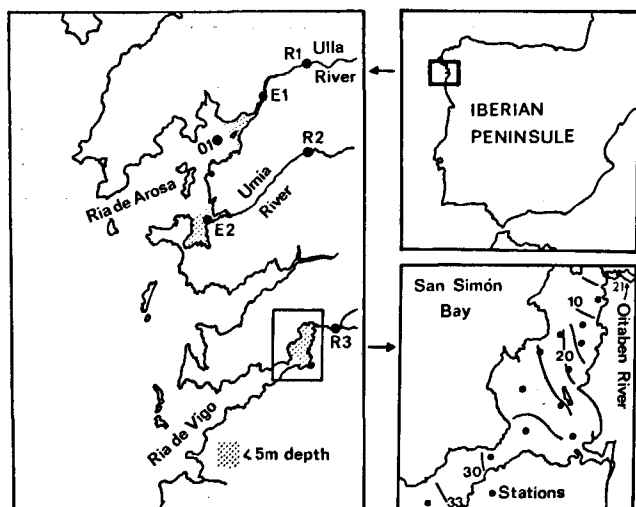
high tide, salinity is less than 2. Station R2, in the middle course of the river Umia, does not show any direct marine influence. All stations are very shallow, no more than 2 m deep. Samples were collected near the surface.

On the other hand, from January 1982 to November 1983, monthly samples from the River Oitaben were taken at Sotomaior (station R3), about 7 km from the river mouth. In addition, we use the data taken in San Simon Bay (Ría of Vigo) on 28 May 1983.

The basins of the rivers Ulla, Umia and Oitaben have a total surface area of 2 925, 450 and 350 km^2 and average rainfalls of 1 600, 1 900 and 2 500 $mm.year^{-1}$, respectively. Mean annual fluxes are 100, 21 and 22 $m^3.s^{-1}$ respectively, although during summer they are less than 30 % of these values (Rosón et al., 1991; Rios et al., 1992).

Analytical methods

Salinity was calculated from conductivity measurements with an Autosal 8 400A (Unesco, 1981). Calcium was determined by potentiometric titration with a selective electrode, using EGTA as a complexing agent and borax as a buffer (Rosón and Pérez, 1991). Alkalinity was determined by potentiometric titration with HCl 0.13 N (Pérez and Fraga, 1987). Nutrient samples were frozen until they were analyzed by segmented flow spectrophotometric methods according to Hansen and Grasshoff (1983) with slight modifications (Mouriño and Fraga, 1985; Alvarez-Salgado et al., 1992) using a Technicon AAII. Total Nitrogen (TN) was determined for oxidation to nitrate with peroxidisulphate under UV light of a sample buffered with tetraborate also by Technicon AAII. The TON was calculated by substracting the Total Inorganic Nitrogen ($NO_3^-+NO_2^-+NH_4^+$) to the TN. All concentrations are expressed in $\mu mol.kg^{-1}$.

Data processing

The simplest method of estimating the input of each biogenic element associated with continental runoff to a ría is the measurement of their concentrations at places close to the mouth of the river but away from marine influence. However, this method can be unsuitable for the budgets on the oceanic side of the rías because they may be altered on the estuarine side by biogeochemical processes.

On the other hand, when measurements are carried out on the estuarine side, it can be assumed that the mixing of the continental and oceanic water bodies is linear with respect to a conservative parameter as salinity. The biogenic element vs. salinity plots can be a tool for undestanding the behaviour of such elements during estuarine mixing. If the resulting curve is close to a straight line, they behave conservatively and the extrapolation to zero salinity of the data fitted by linear regression can be used to estimate the concentrations in the river. On the other hand, deviations from linearity can be due to variability in the river and ocean end members (Loder and Reichard, 1981) and/or uptake-recycling as a consequence of biological activity and water-sediment exchange.

RESULTS AND DISCUSSION

Carbonic-calcium system

The variability of the carbonic-calcium system in the rías is due both to the photosynthesis-mineralization cycle and to the formation and dissolution of calcareous structures. As previously mentioned, on the oceanic side of the rías there are large numbers of mussel rafts which are capable of producing slight changes in the alkalinity and calcium distributions. To study these changes, it is necessary to take into account the runoff contributions, although these are very weak and furthermore decrease by dilution more than ten times in water of salinity higher than 33.

The calcium and alkalinity vs. salinity plots on the estuarine side of the rías -stations E1, E2 and San Simon Bay-fall on straight lines with $r^2 > 0.90$ (Fig. 2), and consequently behave conservatively during estuarine mixing. The concentrations by extrapolation at zero salinity are very low compared with other Iberian rivers (Catalán, 1981) and similar to the average dissolved
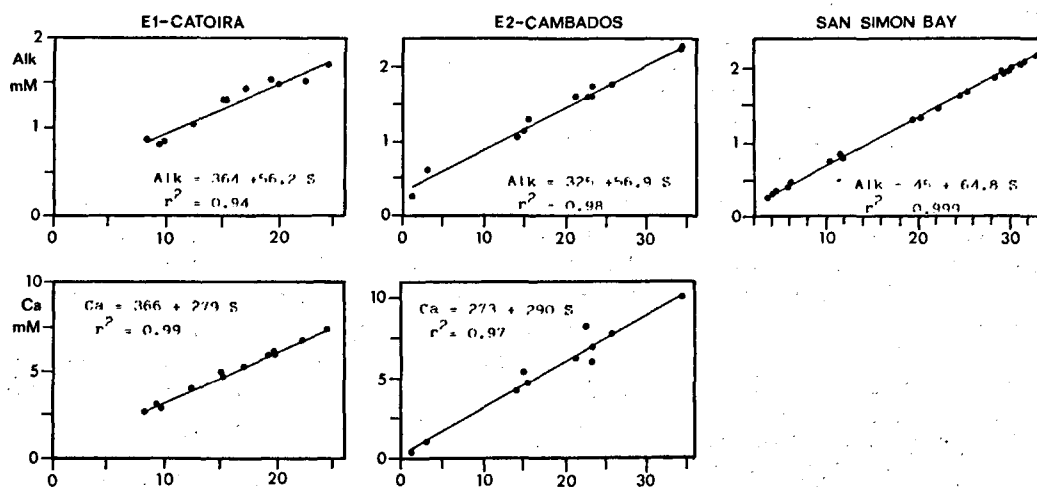

Figure 2

Alkalinity and calcium vs. salinity plots at stations E1 and E2 (May-October 1989) and in San Simón Bay (May 1983). Linear regression coefficients are expressed in the μM escale.

Distributions de l'alcalinité et du calcium vs. salinité dans les stations E1 et E2 (mai-octobre 1989) et dans la baie de San Simón (mai 1983). Les coefficients des régressions linéaires sont donnés en μM.

Table 1

Recorded averages, standard deviations, maximum and minimum values of salinity (USP), alkalinity, calcium, nitrate, phosphate and silicate ($\mu mol.kg^{-1}$) at the river stations R1 and R2 (Padrón and Caldas in the rivers Ulla and Umia respectively) from May to October 1989.

Valeurs moyennes, déviation standard, maxima et minima de salinité (USP), alcalinité, calcium, nitrate, phosphate et silicate ($\mu mol.kg^{-1}$) dans les stations R1 et R2 (Padrón et Caldas dans les fleuves Ulla et Umia respectivement) de mai à octobre 1989.

	S	Alk	Ca^{2+}	NO_3^-	PO_4H^{2-}	SiO_2	NH_4^+
R1							
Mean	0.478	392	200	22	0.39	89	11
Std		127	180	5	0.48	21	16
Min	0.040	146	79	12	0.04	63	1
Max	1.941	635	614	31	1.79	137	16
R2							
Mean	0.020	146	35	41	2.5	29	13
Std				13	1.3	14	6
Min	0.010	69	9	13	0.04	9	5
Max	0.030	254	88	57	4.26	54	25

contents of surface waters discharging to the ocean (Meybeck, 1981). Alkalinity shows standard deviations close to one-fifth of its values, while calcium concentrations are very higher.

With regard to the concentrations obtained in the river basins during the same period (Tab. 1), at station R1 (river Ulla) the mean alkalinity (392 $\mu mol.kg^{-1}$) is similar to those obtained by extrapolation to zero salinity at E1 (364 $\mu mol.kg^{-1}$) . However, the average alkalinity in the middle reach of the river Umia, station R2, is lower (146 $\mu mol.kg^{-1}$) than those obtained by extrapolation at E2 (325 $\mu mol.kg^{-1}$). This may be due to the fact that station R2 is far from the river mouth, about 20 km, and the drainage basin between R2 and E2 is not taken into account. Since the extrapolated values at E1 and E2, and the measurements made at R1 are not significantly different, an average alkalinity of 366 ± 91 $\mu mol.kg^{-1}$ is obtained for the continental runoff to Ría de Arousa by regression of all these data.

On the other hand, the alkalinity in the river Oitaben (station R3) was 68 $\mu mol.kg^{-1}$ two weeks after sampling in San Simón Bay, where the calculated value by extrapolation to zero salinity was very similar (45 $\mu mol.kg^{-1}$), lower than those measured in the basins of the Ría de Arousa.

Calcium at stations R1 and R2 shows large standard deviations (Tab. 2). The average values obtained in the river Ulla (200 $\mu mol.kg^{-1}$) are similar to those extrapolated to zero salinity at E1 (366 $\mu mol.kg^{-1}$). However, the average values at R2 (35 $\mu mol.kg^{-1}$) are lower than those obtained by extrapolation at E2 (273 $\mu mol.kg^{-1}$), E1, or that measured at R1. These were the same as we observe for alkalinity.

Except for the R2 measurements, the average concentration of calcium in the continental runoff to Ría

de Arousa is 0.3 ± 0.2 $mol.m^{-3}$. Rivers Ulla and Umia had a total average flow of 35 $m^3.s^{-1}$ (Rosón et al., 1991) from May to October 1989 (about $500 \cdot 10^6$ m^3) which means a total input of 5,800 tons of calcium, more than a half that withdrawn by mussels from the oceanic side of the ría, assuming that calcium represents 15 % of total wet weight of mussels (Rosón, 1992).

Nutrients

The nitrate vs. salinity plots of the data recorded at stations E1, E2 and in San Simón Bay are shown in Figure 3. At station E2, with $r^2 = 0.97$, a conservative mixing pattern can be observed and the nitrate extrapolated to zero salinity (42 $\mu mol.kg^{-1}$) coincides with the average concentration at station R2 (41 $\mu mol.kg^{-1}$). However, in San Simón Bay, and mainly at station E1, strong biogeochemical processes leads to a non conservative behaviour of nitrate, enhanced by low and variable concentrations in the rivers, as we shall see below.

At stations R1 and R2, the minimum nitrate values were recorded in autumn, showing a standard deviation of 23 % and 32 % of the mean value, respectively (Tab. 1). At station R3 the average nitrate for the two years' sampling is 11 $\mu mol.kg^{-1}$ with a standard deviation of only 4 (36 %). Maximum values were recorded in January and the two lowest values in September and June.

Nitrate contributions of these Galician rivers to the oceanic side of the rías are relatively low: about 10 to 40 $\mu mol.kg^{-1}$. These values are much lower than those in other European rivers. Thus, Denant and Saliot (1990) give values of 74 to 134 μM in the Rhone delta describing a similar pattern with minimum values during autumn and a seasonal variation of about 30 %; Tréguer and Quéguiner (1989) show values between 90 and 464 μM (60 %) for the river Aulne. Although certain domestic inputs exist,

Table 2

Average values of salinity and nutrients on the oceanic side of Ría de Arousa (station O1).

Valeurs moyennes de salinité et des nutriments dans la zone océanique de la Ría de Arousa.

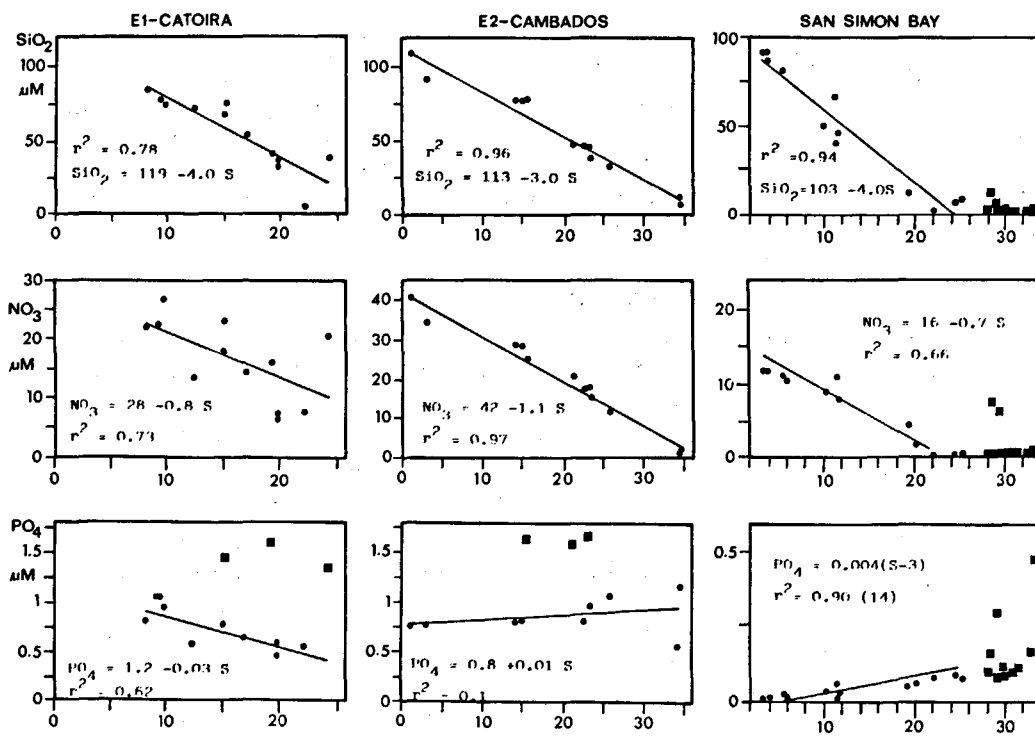|	S	NH_4^+	TIN	PO_4H^{2-}
12 May	33.701	0.74	0.88	0.20
22 May	34.246	1.48	1.76	0.36
8 June	35.012	1.17	2.37	0.41
26 June	34.564	1.80	2.49	0.64
6 July	34.793	0.47	1.45	0.34
17 July	35.322	1.15	2.86	0.25
3 August	35.481	1.08	5.09	0.49
24 August	35.477	1.22	6.07	0.64
14 September	35.374	1.12	7.58	0.69
28 September	35.141	1.70	4.29	0.57
13 October	35.466	1.95	7.92	0.55
27 October	34.791	6.83	10.52	0.79
MEAN	34.95	1.73	4.44	0.50
STD	0.54	1.59	2.91	0.18

E1-CATOIRA

SiO_2
100
μM
50

$r^2 = 0.78$
$SiO_2 = 119 - 4.0\ S$

0   10   20

E2-CAMBADOS

100

50

$r^2 = 0.96$
$SiO_2 = 113 - 3.0\ S$

0   10   20   30

SAN SIMON BAY

100

50

$r^2 = 0.94$
$SiO_2 = 103 - 4.0S$

10   20   30

30
NO_3
20
μM
10

$NO_3 = 28 - 0.8\ S$
$r^2 = 0.73$

0   10   20

40
30
20
10

$NO_3 = 42 - 1.1\ S$
$r^2 = 0.97$

0   10   20   30

20

$NO_3 = 16 - 0.7\ S$
$r^2 = 0.66$

10

10   20   30

PO_4
1.5
μM
1

0.5

$PO_4 = 1.2 - 0.03\ S$
$r^2 = 0.62$

0   10   20

1.5

1

0.5

$PO_4 = 0.8 + 0.01\ S$
$r^2 = 0.1$

0   10   20   30

0.5

$PO_4 = 0.004(S-3)$
$r^2 = 0.90\ (14)$

10   20   30

Figure 3

Silicate, nitrate and phosphate vs. salinity plots at stations E1 and E2 (May-October 1989) and San Simón Bay (May 1983). The square dots have not been taken for the linear regression.

Distributions du silicate, nitrate et phosphate vs. salinité dans les stations E1 et E2 (mai-octobre 1989) et dans la baie de San Simon (mai 1983). Les carrés n'ont pas été utilisés dans le calcul des régressions lineaires.

these findings indicate the "quasi-unpolluted" character of the rivers studied (Meybeck, 1982).

With regard to reactive silica, this behaves conservatively and gives high correlation coefficients and similar y-axis intercept values vs. salinity for the three estuarine areas (Fig. 3): 119, 113 and 103 $\mu mol.kg^{-1}$ for rivers Ulla, Umia and Oitaben, respectively. The values recorded directly in the river are slightly lower at R1 (89 $\mu mol.kg^{-1}$), and much lower at R2 (29 $\mu mol.kg^{-1}$). From May to October 1983 the average value of reactive silica at R3 was 105 ± 36 $\mu mol.kg^{-1}$, and the value measured at the same time in San Simón Bay was 136 $\mu mol.kg^{-1}$, slightly higher than estimates by extrapolation. Pérez et al. (1987) calculated by extrapolation reactive silica concentrations of 95 $\mu mol.kg^{-1}$, for the continental input to the Ría de Vigo. Therefore, excepting again R2 values, the continental input to the Rías Baixas has a mean Si $(OH)_4$ concentration of 105 $\mu mol.kg^{-1}$. These results are somewhat higher than those in the river Rhône, 50 to 80 $\mu mol.kg^{-1}$ (Denant and Saliot, 1990). These high reactive silica values are a consequence of the geological composition of the Galician river basins, and are practically unaffected by biological activity on the estuarine side of the rías, leading to the conservative behaviour of this nutrient during estuarine mixing.

At E2, except for samples taken on 19 July, 27 September and 25 October (represented by squares in Fig. 3), the phosphate shows nearly constant levels (0.9 ± 0.2 $\mu mol.kg^{-1}$). Thus the phosphate runoff contribution to the oceanic side of the rías seems to be small if the dilution is taken into account. Only when there is strong mineralization, independent of salinity, are the inputs significant from the estuarine side.

Sampling in San Simón Bay was carried out at the end of May, during a period of high photosynthetic activity. Under these conditions, the silicate distribution in San Simón Bay testifies to biological activity at salinities above 26, where its concentration falls to zero. At salinity lower than 26, estuarine mixing is sufficiently rapid, with respect to photosynthesis, to maintain a conservative silicate distribution. Similar patterns occur with nitrate and phosphate plots (Fig. 3), showing good agreement in their y-intercept values with measurements in the river (13 and 0.05 $\mu mol.kg^{-1}$ of NO_3^- and HPO_4^{2-}, respectively, 17 May 1982 at station R3). Nitrate seems to be the limiting nutrient on the more saline side of San Simón Bay.

During spring, in the Rade de Brest, Tréguer and Quéguiner (1989) found a similar pattern in nitrate distribution. Nitrate stops behaving conservatively at salinities above 29. Furthermore, in the Rhône Delta, Denant and Saliot (1990) have shown a non-linear behaviour in the spatial distribution of nitrate, phosphate and silicate in May and October. They have also suggested that the loss of nutrients is due to uptake by biota.

When nutrient vs. salinity plots do not fall in a straight line, as is the case at E1, anomalies from the conservative mixing line can be estimated from the salinity and nutrient values at E1, R1 and on the oceanic side of the ría, O1 (Tab. 2). Thus, for each measurement made at E1, the nutrient anomaly, &N, can be calculated (Liss, 1976) from equation (1).

$$\&N = [N]_{E1} - \frac{(S_{O1}-S_{E1})\ [N]_{R1}+(S_{E1}-S_{R1}).[N]_{O1}}{S_{O1}-S_{R1}} \quad (1)$$

where S_{O1}, S_{E1} and S_{R1} are the salinities at stations O1, E1 and R1, and $[N]_{O1}$, $[N]_{E1}$ and $[N]_{R1}$ the nutrient
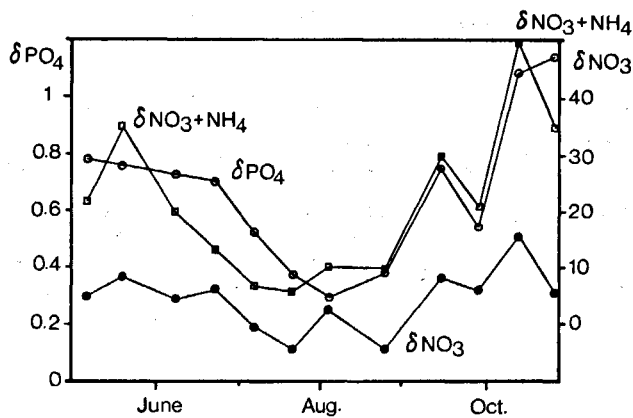
Figure 4

Temporal variations of PO_4H^{2-}, NO_3^-, and TIN anomalies with regard to theoretical mixing at E1.

Variations temporelles de PO_4H^{2-}, NO_3^-, et des anomalies du TIN par rapport au mélange théorique en E1.

concentrations at stations O1, E1 and R1, respectively. Actually, according to Loder and Reichard (1981), these anomalies also include the deviation from linearity due to the end-member variability.

The change in time of these nutrient anomalies at E1 can be seen in Figure 4 (nitrite is included in the &NO_3 estimate). All samples at E1 show HPO_4^{2-} and NO_3^- values higher than those estimated by mixing (*i. e.* &N positive) except for NO_3^- on 19 July and 23 August, when there were remarkable inputs of these nutrients to the water column. An important increase of nutrient concentrations during the late spring and autumn can be observed in this figure.

&NO_3 and &PO_4 show a similar pattern of variation with a significant correlation between themselves ($r^2 = 0.56$). But, if we take into account the variation of the Total Inorganic Nitrogen (TIN) not due to estuarine mixing at E1, *i. e.* $NH_4 + NO_3 + NO_2$, the correlation *vs.* &PO_4 is higher ($r^2 = 0.74$), giving a N:P ratio of 51 ± 8. In this sense, Faganeli *et al.* (1986) studied the C:N:P ratios of the benthic marine algae *Ulva rigida* and *Fucus virsoides* obtaining N:P ratios of 52 ± 22 for these algae in the Gulf of Trieste. Similar species of benthic algae have been described by Niell (1977) on the sheltered shore of the Ría de Vigo: *Fucus spiralis, Fucus vesiculosus, Ascophyllum nodorum and Ulva* sp. In the annual cycle of benthic algae, maximum biomass occurs during spring and decays during late summer and autumn. According to this - with the Loder and Reichard limitation - in our study the stronger recycling of nutrients seems to come from the mineralization of estuarine and benthic biota, chiefly in September and October.

TON and ammonium

Measurements of TON were also carried out at stations R1, E1 and E2. The levels and changes in time of TON recorded are very similar at the three stations (Fig. 5 *a*).

The linear correlation between the data recorded at R1 and E1 is high, $r^2 = 0.88$, with a slope of 1.0. The TON values at E2 also show a high linear correlation with respect to those recorded at E1, $r^2 = 0.85$, where the slope is 1.2 (excepting 27 September). At R1, salinities are always less than 2, therefore only continental water exists. At E1, however, the range of salinity was from 8 to 24. Thus, it is very hard to explain why TON follows the same pattern at E1 and R1 when the TON input at R1 is strongly diluted at E1 by sea water. If the same levels and variations exist at the river and on the oceanic side of the rías, it would be possible to find the same global pattern at E1, R1 and R2. However this would imply that the effect on the nitrogen cycle is the same in different water columns. On the other hand, the tide seems to have some effect on the change in time of TON (Fig. 5 *a*). But, to analyse these processes, a more extensive study is necessary than that reported here.

At the same time, ammonium at E1 correlates poorly with salinity ($r^2 = 0.02$), while there is a stronger correlation with &NO_3 ($r^2 = 0.48$). Furthermore, it shows a time variation similar to that of TON (Fig. 5 *b*) and the correlation between the data recorded at R1 *vs.* those at E1 is also high ($r^2 = 0.67$) with a slope of 1.1.

Nitrite behaves similarly to ammonium ($r^2 = 0.76$ at E1), giving poor correlations with salinity. At E1 and E2 it shows a moderate correlation with phosphate ($r^2 = 0.60$).

This behaviour of nitrogen compounds in the internal parts of the rías shows again that the distributions of TON, NH_4^+ and NO_2^- are strongly influenced by biological activity of the estuarine and benthic biota. Their seasonal growth usually declines in late summer and autumn, and
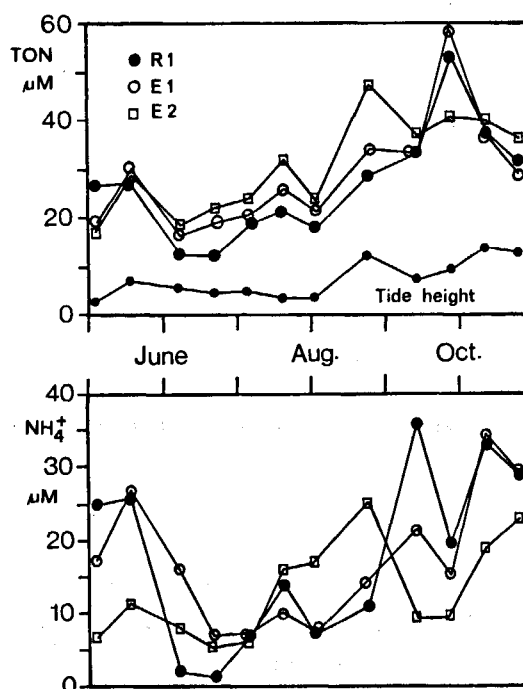

Figure 5

Temporal variations of (a) TON and (b) NH_4^+ concentrations at stations R1, E1 and E2.

Variations temporelles des concentrations en : a) azote organique total ; et b) ammonium dans les stations R1, E1 et E2.

this can be produced over all the estuarine side of the rias where they account for an important amount of biomass. Furthermore these biological processes could increase dissolved organic matter as well as other nitrogen compounds in the water column during the biomass decay. However, the covariability found between nitrate and salinity at E2 indicate that the latter is also marked by the estuarine mixing process.

which also behave conservatively during the mixing. The silicate input is about 9 Tm-Si.d^{-1} and play an role on the diatoms dominance in the Rías Baixas (Margalef, 1958).

On the other hand, the low nitrate (0.2-0.6 g-N.m^{-3} and 0.6-1.8 T-N.d^{-1}), and phosphate (0.02 g-P.m^{-3} and 0.06 T-P.d^{-1}) concentrations found are an indication of low industrial or agricultural pollution. The levels of these nutrient salts from late spring to autumn are mainly determined by a high biological activity, relatively similar from place to place, that can result in identical concentrations and time variations at stations with different water bodies.

CONCLUSIONS

The main rivers that flow into the Galician Rías Baixas are characterized by very low alkalinity and calcium levels, both about 350 μmol.kg^{-1}, which behave conservatively during estuarine mixing. The input of calcium by runoff to Arousa from May to October 1989 represents 65 % of the total amount uptake by mussel rafts on the oceanic side of the ría.

These rivers, due to the mineralogical composition of their basins, have high silicate levels (about 100 μmol.kg^{-1})

Acknowledgements

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