Nutrient distributions in the Ria de Aveiro, Portugal. Preliminary results

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ABSTRACT

The Aveiro Lagoon, locally called «Ria de Aveiro», is a bar-built estuary situated in the northern Portugal, with a single mouth to the Atlantic Ocean . The distribution of nutrients (nitrate, nitrite, ammonium, phosphate and silicate) was studied together with water mass tracers (salinity, temperature) and with indicators of biological activity (dissolved oxygen, inorganic carbon and chlorophyll a). This was carried out by a study of the diel change of parameters at a central station in the Lagoon and by a survey of the distribution of subsurface parameters (8 sampling stations) at both low and high tides in March, April and June 1992. During diel cycles, nutrient variations are mostly induced by tidal mixing which hide variations due to biological activity. While the Lagoon basin as a whole is not highly eutrophic, nutrients are not limitating for the phytoplankton growth. Two trends emerge for the nutrient distribution in the Ria: 1) agriculture in the South, inducing high nitrate and phosphate concentrations, 2) industry and urban activity in the North, source of ammonium, nitrite and phosphate. Eutrophication seem to be limited to areas of relatively stagnant water and/or close to industrial effluents.

Key words : nutrients, lagoon, coastal zones, Portugal, Aveiro, nitrogen, phosphorus, silicon.

RÉSUMÉ

La Lagune de Aveiro, localement appelée «Ria de Aveiro», est un estuaire situé au nord du Portugal qui est caractérisé par une unique entrée à barre construite sur l'Océan Atlantique. La distribution des nutriments (nitrates, nitrites, ammonium, phosphates et silicates) a été étudiée en parallèle aux classiques traceurs de masses d'eau (salinité, température) et aux indicateurs d'activité biologique (oxygène dissous, carbone inorganique et chlorophylle a). Ceci a été réalisé par deux types de démarches expérimentales : l'étude des variations journalières des paramètres à une station centrale dans la lagune et l'étude de la distribution géographique des paramètres à huit stations de prélèvement lors des marées haute et basse en mars, avril et juin 1992. Durant les cycles journaliers, les variations dans les concentrations en nutriments sont principalement dues à l'effet de la marée et peu aux activités biologiques. Si l'ensemble du bassin lagunaire ne présente pas une eutrophisation marquée, les nutriments ne semblent pas limitants, pour la croissance phytoplanctonique. Deux tendances ressortent de la distribution des nutriments au sein de la Ria : 1° agricole au sud, caractérisée par des concentrations élevées en nitrates et phosphates, 2 ° industrialisée et urbanisée au nord, sources d'ammonium, nitrites et phosphates. L'eutrophisa-

tion semble limitée aux eaux relativement stagnantes et/ou proches d'effluents industriels.

Mots clés : nutriments, lagune, zones côtières, Portugal, Aveiro, azote, phosphore, silice.

INTRODUCTION

Rivers and their outlets to the sea are important interfaces between land and sea ecosystems with respect to biogeochemical cycling. These areas are characterized by marked changes in the chemical properties of water masses and usually by high biological activity, both of which significantly affecting the speciation of elements and transfer towards the adjacent coastal zones. This is particularly true in the case of nutrients and organic matter (Wollast,1983).

The major sources of nutrients include rainfall, freshwater flow, saltmarsh production, and sediment resuspension within the estuarine basin. The distribution of nutrients in estuarine water is controlled by physical, topographical, chemical, biological and sedimentological processes (Fan & Jin, 1989). In the Tamar Estuary for example, Morris et al. (1981, 1985) have demonstrated that the reduced species of nitrogen (ammonium and nitrite) show marked non-conservative behavior in contrast to the persistent apparent conservativeness of nitrate in this estuary. Nitrite is generated within the water column by bacterially mediated oxidation of ammonium. Ammonium distributions generally show a maximum in the middle to upper estuary which is attributed to release from interstitial water by tidal sediment disturbance. The silicate and phosphate salinity relationships also consistently indicate a non biological removal of these nutrients within the low (0-10%) salinity range of the Tamar Estuary but the exact removal mechanisms were not elucidated.

The global estimation of nutrient fluxes to oceans is complicated by the facts that there may be large seasonal fluctuations in their concentrations and that human activity has largely disturbed the natural fluxes. Except for dissolved silica, the concentration of the nutrients observed in freshwater are extremely variable, ranging from 0.4 to 60 μmol.l^{-1} for orthophosphate and from 3 to 800 μmol.l^{-1} for total dissolved inorganic nitrogen (Wollast, 1983). This wide range in concentrations mainly results from anthropogenic activity.

Among the many different types of outlets into the sea, lagoons are the least studied. The Lagoon of Aveiro (40°40'N, 9°45'W), locally called «Ria de Aveiro», is a bar-built estuary with a single mouth (Barra) on the Atlantic Ocean (figure 1).

Inland, the Lagoon has a complex topography including an intricate network of bays and channels of varying depths and shapes. It now covers a wet area of 47 km^2 and 43 km^2 respectively at high and low tides (Hall, 1980).

The water exchange with the ocean dominates the hydrological circulation to the Lagoon; this is mainly due to the low freshwater inputs compared to the seawater flow. Indeed, 60.10^6 m^3 of oceanic water enter the Lagoon for a mean tide (amplitude 2.5 m), while the average volume of freshwater incoming during a tide cycle is 2.10^6 m^3 (Barrosa, 1985). The main source of freshwater being the River Vouga (figure 1).

Beside domestic sewage and agricultural runoff, «Ria de Aveiro» receives effluents from a variety of industries, namely: food and drink, pulp and paper, fertilizers, chloralkali, iso-cyanates, aromatic and PVC (Santos et al, 1988).
Despite the potential importance of nutrients in contributing to eutrophication, so far nutrient contents in the Lagoon have not been investigated so far.

The aim of this study was to carry out an investigation of the nutrient content of the «Ria de Aveiro» in relation to the hydrological and biological context of the Lagoon. In order to achieve this, we simultaneously sampled nutrients and tracers of both water mass (salinity, temperature) and biological activity (dissolved oxygen, inorganic carbon and chlorophyll *a*).

MATERIALS AND METHODS

The sampling program included two parts: (i) a study of the diel change (36 hours, sampling every 3 hours) of parameters at a central sampling station in the Lagoon and (ii) a survey of the distribution of several parameters (8 sampling stations) at both low and high tides (figure 1). Diel cycles were carried out at station 6 in March, April and June 1992. Surveys were carried out in March and April 1992.
Salinity and temperature were determined using a field microprocessor conductometer WTW, LF 196.
The subsurface water concentrations in nitrate, nitrite, ammonium and silicate were measured using a multi-channel analyser ALLIANCE, model *evolution II*. The methods of determination and analytical circuits are similar to those described in Tréguer & Le Corre (1975), with slight modifications concerning the nature of the wetting agents. Precisions are 0.1 μmol.l^{-1} for N-NO_3^- , 0.01 μmol.l^{-1} for N-NO_2^-, 0.01 μmol.l^{-1} for N-NH_4^+ and 0.1 μmol.l^{-1} for Si. The phosphate concentration for the surveys and the third diel cycle were obtained by the methods described in Parsons et al (1984).
The pH was measured by a field pH meter (Jenway PWA4), calibrated against NBS buffers (4 and 7).
Total alkalinity and dissolved oxygen levels were analyzed using GRAN electrotitration (Gran, 1952) and WINKLER methods (in Parsons et al, 1984), respectively. Total inorganic carbon (TCO_2) was calculated from determination of both pH and total alkalinity using the equilibrium constants according to the NBS scale (Mehr-

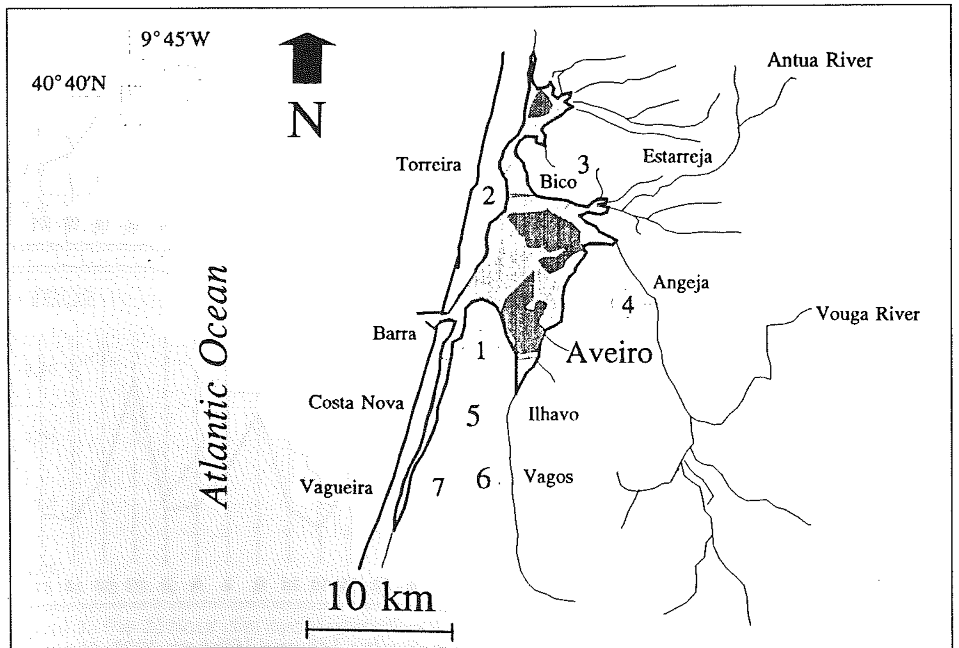


figure 1 : Map of the Aveiro Lagoon, its main urban centers and the 8 sampling stations.

bach et al, 1973).
Chlorophyll *a* concentrations were determined using the colorimetric method of Lorenzen & Jeffrey (1978).

RESULTS AND DISCUSSION

Results obtained during a diel cycle (June, 14th at 9 hour to June, 15th at 21 hour) at station 6 are presented in figure 2.
Salinity appears to be the master variable : its variation corresponds to a semi-diurnal tide (figure 2).
During the whole diel cycle, nutrients vary inversely with the salinity (figure 2). Many authors have studied the fate of freshwater components during the mixing process with the sea water in estuarine zones. For the ideal case in which the mixing components composition remained con-

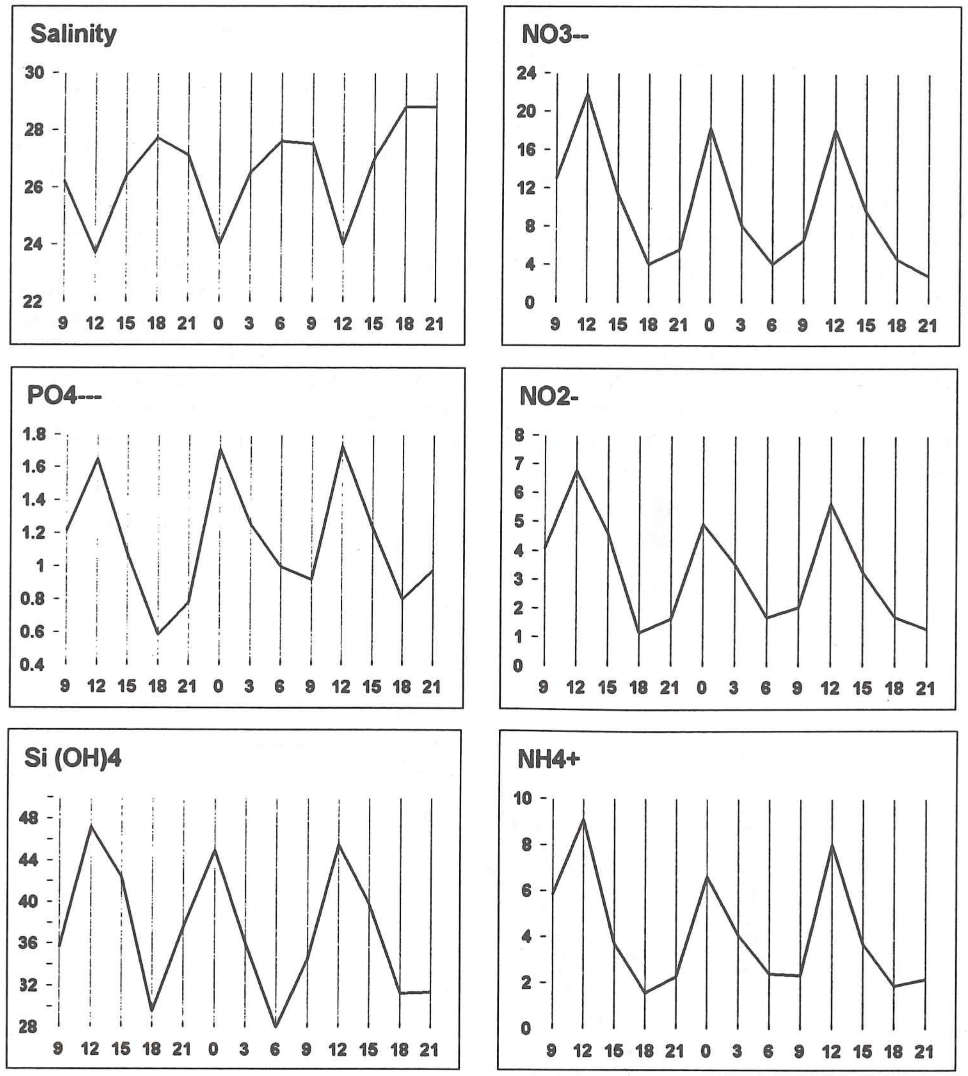


figure 2 : The 36 hour diel cycle at station 6 (Bico) during the 14th and 15th June 1992. Abscissa is in hours. Salinity is in psu. Nitrate, nitrite, ammonium, phosphate and silicate are in µmol.l⁻¹.

stant throughout the time necessary to generate the observed estuarine mixture, a linear constituent-salinity correlation (conventional termed the theoretical dilution line) would be produced by dilution processes alone (Morris et al, 1981). The correlation coefficients (r^2) between salinity and nutrients are, on average, close to 0.8 (table 1). Nutrients are then mainly supplied by freshwaters and variations in their concentrations are mainly due to tidal mixing with sea water.
In spite of this dilution, the concentrations remain very high, especially for nitrate and nitrite (up to 21.8 $\mu mol.l^{-1}$ N-NO_3^- and 6.7 $\mu mol.l^{-1}$ N-NO_2^-). On average, they are much higher than those measured e.g. in June in the Venice Lagoon, an area considered nevertheless highly eutrophic (Pavoni et al, 1990). This may result from the proximity of an industrial complex (Estarreja, figure 1), a source of polluted waste waters. However, certain areas of the Venice Lagoon are richer in phosphate and ammonium than this Aveiro site (5.92 compared to 1.7 $\mu mol.l^{-1}$ P-PO_4^{3-} at maximum, and 13.67 compared to 9 $\mu mol.l^{-1}$ N-NH_4^+ at maximum).
From the pH, total inorganic carbon (TCO_2), dissolved oxygen and chlorophyll *a* data (figure 3), it is evident that high biological activities exist in the Lagoon waters. Photosynthesis induces an increase in pH and in dissolved oxygen concentrations and a decrease in TCO_2. Respiration, which predominates during the night, has an inverse effect upon those parameters. As can be seen, variations in chlorophyll *a* and the other parameters are influenced by *in situ* processes and not by tidal variations, as demonstrated by the low correlation coefficients (table 1) of these parameters with salinity.
Compared to the adjacent Atlantic Ocean waters, the water in the Lagoon is more acid, contains less carbonate, is undersaturated in oxygen and contains more dissolved carbon dioxide.
For this cycle at this site it is obvious that dilution by ocean water causes most of

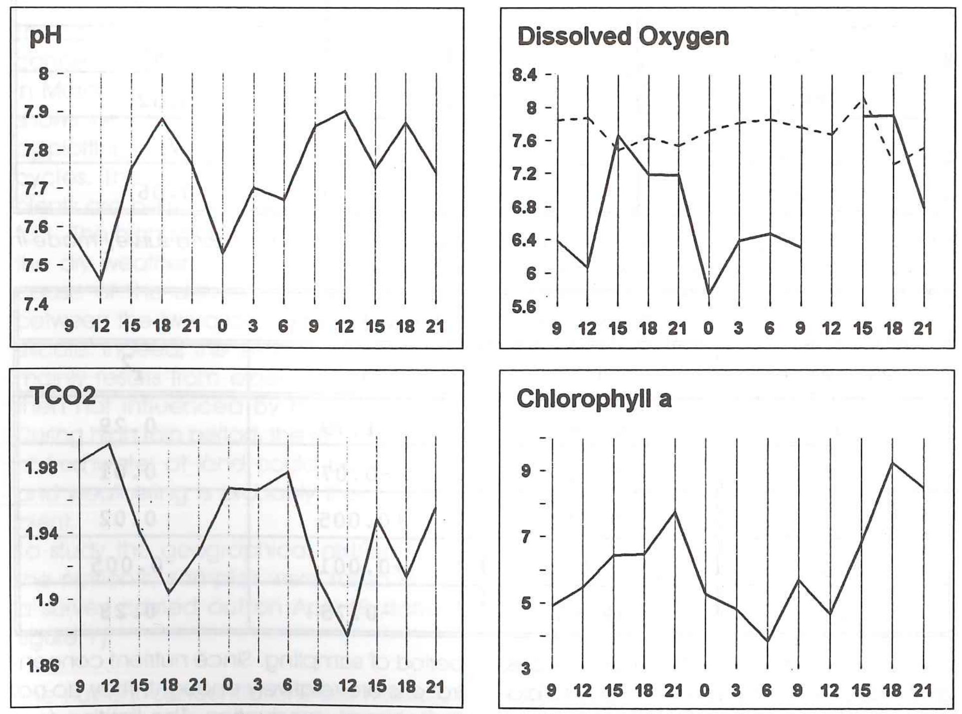


figure 3 : The 36 hour diel cycle at station 6 (Bico) during the 14th and 15th June 1992. Abscissa is time in hours. On the oxygen graph, the saturation level is drawn by a dotted line. pH is on the NBS scale, dissolved oxygen in mg.l⁻¹, TCO_2 in mmol.kg⁻¹ and chlorophyll a in µg.l⁻¹.

table 1 : Linear regression obtained by plotting parameters versus salinity for diel cycle of June 1992.

Parameter A + B * Salinity			
Parameter	A	B	r^2
NO_3^-	103.16	-3.51	0.92
NO_2^-	29.5	-0.98	0.84
NH_4^+	4.03	-0.13	0.88
PO_4^{3-}	6.2	-0.19	0.79
Si	124.3	-3.27	0.78
pH	6.6	+0.04	0.27
TCO_2	2.04	-0.03	0.03
O_2	-0.31	+0.26	0.34
chla	-0.36	+0.54	0.3

table 2 : r^2 obtained by plotting nutrients versus salinity on a linear regression. Diel cycles of March and April 1992.

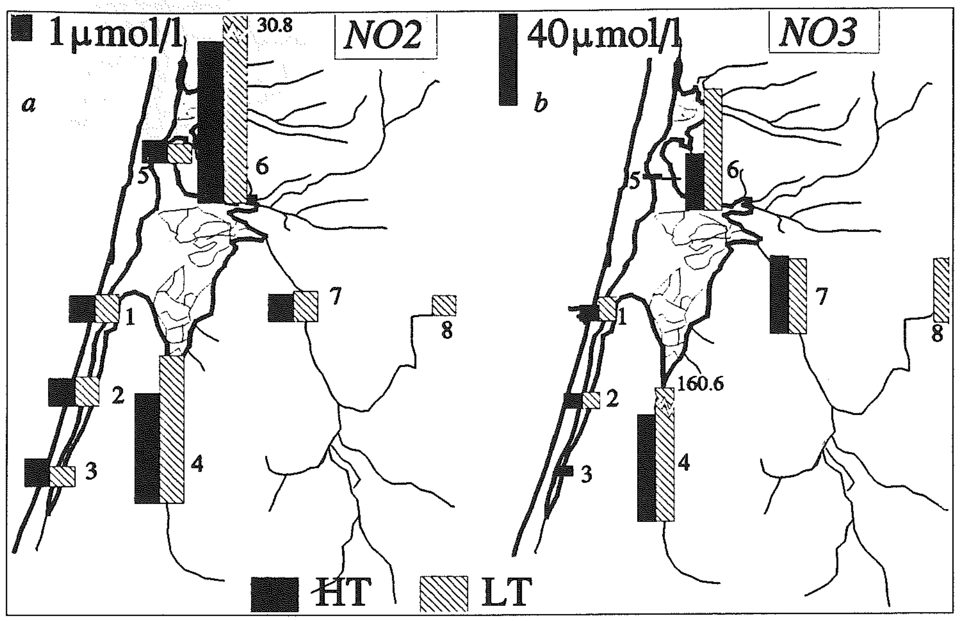
Parameters	r^2 in March	r^2 in April
NO_3^-	0.96	0.70
NO_2^-	0.92	0.68
NH_4^+	0.93	0.62
PO_4^{3-}	/	/
Si	0.95	0.06

table 3 : Linear regression obtained by plotting nutrients versus salinity for a survey made in April at 8 sampling stations at both low and high tides.

Parameter A + B * Salinity			
Parameter	A	B	r^2
NO_3^-	60.31	-1.79	0.29
NO_2^-	4.60	-0.07	0.01
NH_4^+	0.41	+0.005	0.02
PO_4^{3-}	0.44	+0.001	0.005
Si	39.55	-0.75	0.28

the variation in the nutrient concentrations, and in fact hide any variations due to biological activity. Indeed, the results from other parameters clearly show that there is significant biological activity during the period of sampling. Since nutrient concentrations are relatively enought, they do not limit primary production. The limiting factor for growth is probably light due to the high level of turbidity of the lagoon wa-

figure 4 : Nitrite (a) and nitrate (b) concentrations in µmol.l⁻¹ at low (LT) and high (HT) tides during the April survey.



ters (no data).

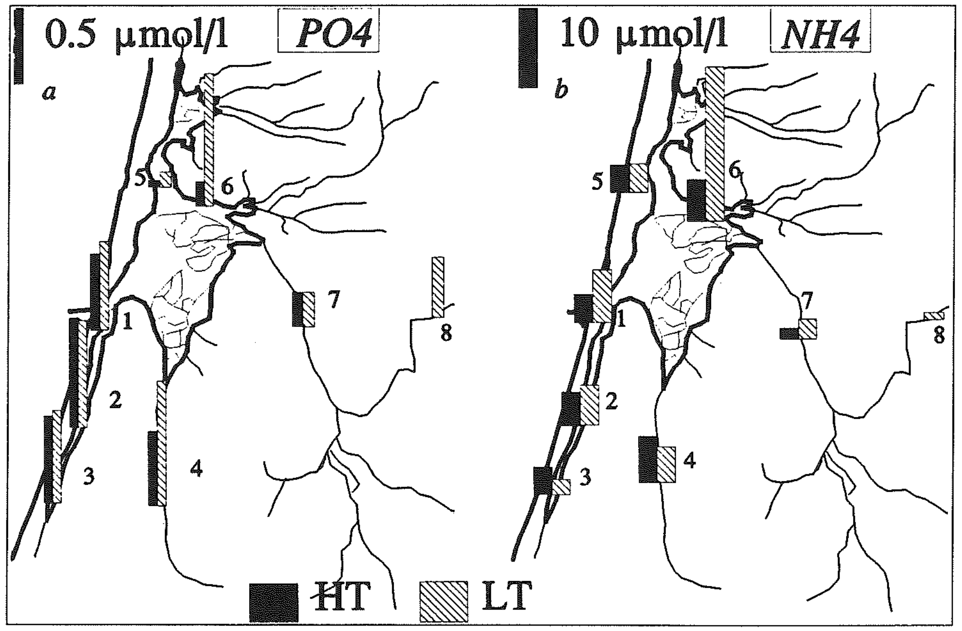
The same conclusion can be proposed concerning diel cycles previously made in March and April 1992. Indeed, table 2 shows the correlation coefficient obtained by plotting nutrients versus salinity for those cycles. The observed correlation coefficients are better in March and very close to 1. The high rainfall in April compared to the dry weather in March is probably the cause of the difference observed on r^2 between the two cycles, especially for the silicate. Indeed, the silicate water content mainly results from erosion of rock and is then not influenced by human impact. During high rain period, the residence time of freshwater at land could be very short and weathering is probably then less efficient.

To study the geographical distribution of the nutrients, samples were taken during a survey carried out on April (8 stations, figure 1).

The nutrient concentrations are heterogeneously distributed in the lagoon waters (figure 4,5). The weak correlation coefficients (r^2, table 3) indicate that salinity, and hence the tides, is not the main factor determining the variations in nutrient concentrations for the whole lagoon.

As showed during the diel cycles, nitrate is the most predominant of the nitrogen measured here (figure 4b), in particular at station 4 (Vagos) (up to 160 $\mu mol.l^{-1}$). This could be explained by the input in this channel of effluents draining the southern agricultural zone. The relatively high nitrate contents in the water at station 6 (Bico) and 7 (Angeja) are close to the one analysed in the Vouga River (station 8), a probable source of nitrate due to important local seawage.

Nitrite concentrations are lower than 1 $\mu mol.l^{-1}$, except at station 6 (Bico) and 4 (Vagos) (figure 4a). The three diel cycles at station 6 also present high nitrite and ammonium (figure 5b) levels, which indicates that the nitrite and ammonium sources are close to station 6. The origin of the high content of ammonium in the water at station 6 (Bico) could be from waste water of the industrial complex at Estarreja. Nevertheless, in the lagoon water mean nitrite contents are not so high (except for stations 4 and 6) compared with the surface water obtained by Elskens *figure 5 : Phosphate (a) and ammonium (b) concentrations in µmol.l⁻¹ at low (LT) and high (HT) tides during the April survey.*



et al(1992), in the upwelling area off Spanish coast (0.2 μmol.l^{-1} N-NO_2^- and 0.15 μmol.l^{-1} N-NH_4^+).

From the phosphate data, it appears that each freshwater input is a source for the Lagoon (figure 5a). High values at stations 6 (Bico) and 4 (Vagos) could be due respectively to detergents in industrial waste water from Estarreja and to the use of fertilizer for agriculture. Data from the open sea off the Spanish coast show an average surface concentration of 0.25 μmol.l^{-1} P-PO_4^{3-} (Elskens et al, 1993), i.e. about half the value observed in the lagoon. The Ria then acts as a probable source of phosphate to coastal waters.

Two trends are evident from the lagoon nutrient distributions ; the first is that the agricultural activity to the South leads to the inputs of high concentrations of nitrate and phosphate, and the second, the industrial - urban band to the North leads to inputs of ammonium and nitrite in addition to phosphate.

Even if the nutrients do not appear to be limiting for the phytoplankton growth, the whole lagoon basin is not highly eutrophic. Large quantities of these elements are probably transported towards the ocean following the important flows of water leaving the lagoon. Eutrophication will be limited to areas of relatively stagnant waters or close to polluting factories.

CONCLUSIONS

In view of this preliminarily analysis, the «Ria de Aveiro» is an heterogeneous and display moderate nutrients levels. The original sources of the nutritive elements are either natural (rivers, land runoff) or anthropogenic (urban, industrial or agricultural). These multiple sources of nutrients break the homogeneity of the seawater flow entering the Lagoon by a single mouth.

The nutrient flow from the lagoon and its potential influence on the coastal area remain to be quantified.

Once obtained, such data will allow a definition of the exact role that this environment plays as an interface between the land and sea.

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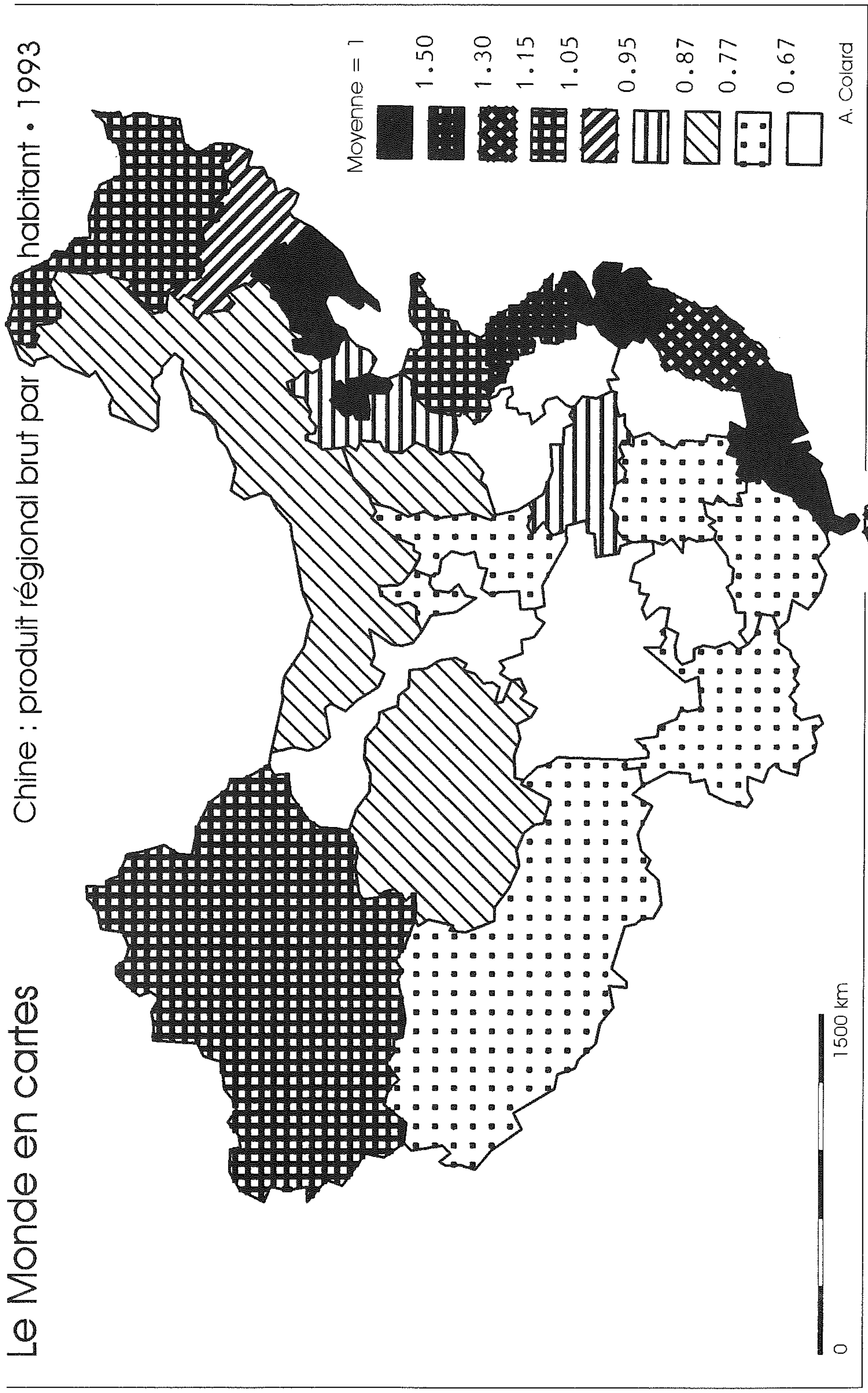
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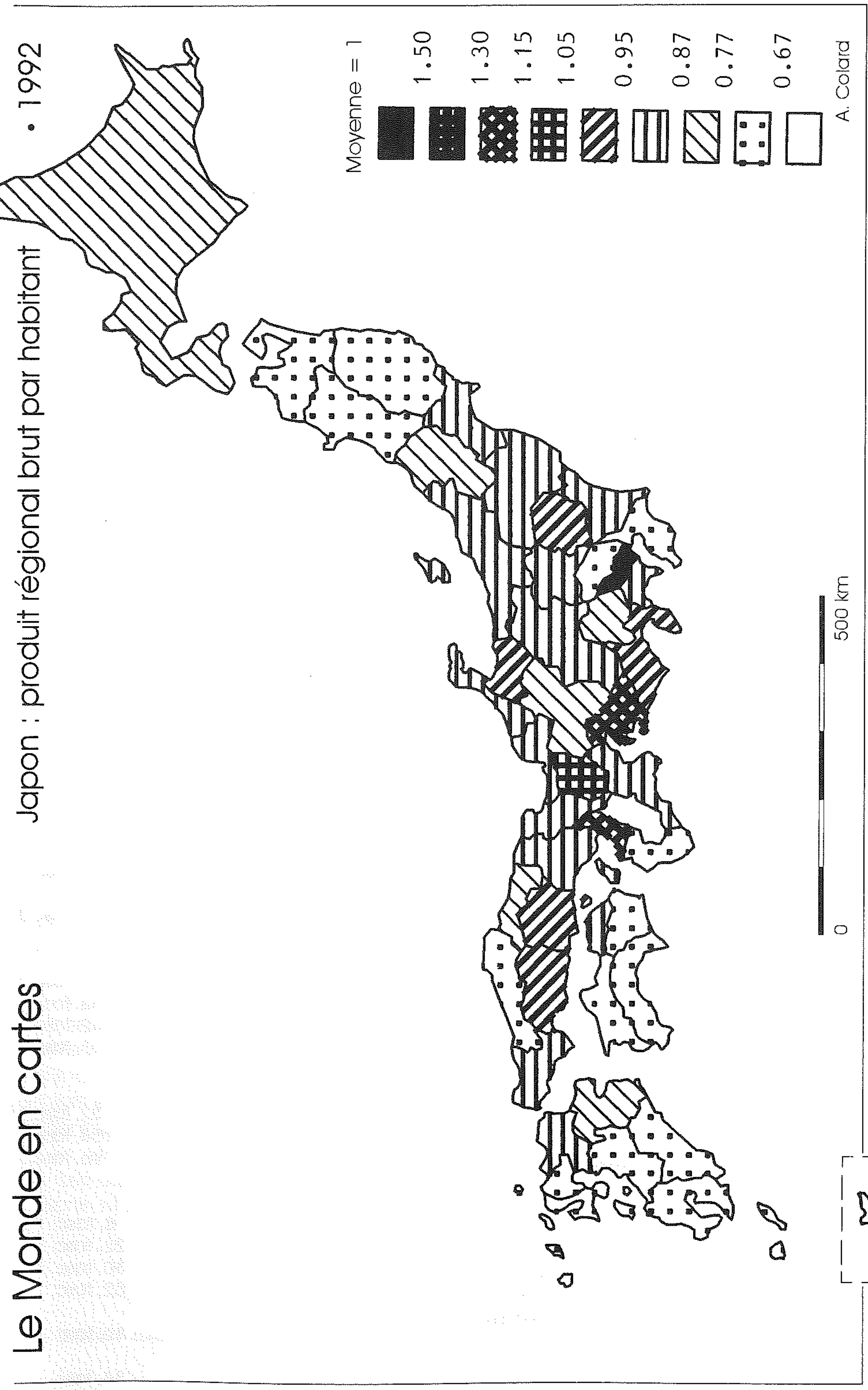
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