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Statistical analysis of nutrient data quality (nitrate and phosphate), applied to useful predictor models in the northwestern Mediterranean Sea

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ABSTRACT

A dataset comprising 12 oceanographic cruises (from 1979 to 1983), covering two regions in the Northwestern Mediterranean Sea (Gulf of Lyon and Catalan Sea), was statistically analysed for nitrate and phosphate relationships with silicate, salinity and depth. This analysis provided a preliminary assessment of the data's quality, as well as a predictor model of these nutrients below the surface layer. Results from the statistical analysis showed no significant difference ($P = 0.05$), between the regression equations (nitrate-depth and phosphate-salinity) of most cruises in the Gulf of Lyon, indicating that these relationships do not change in this area, particularly in summer and autumn. A significant relationship between nitrate and phosphate with salinity and depth (multiple regression) was observed, suggesting that nitrate and phosphate distribution in the intermediate level are significantly related to the mixture of the water masses and the degradation of organic matter. The phosphate data showed a wide variance and a bias, probably due to procedural problems in the chemical analysis. Below the Intermediate Levantine Water, results from the ANOVA showed no significant variation of the phosphate and nitrate concentrations in the water column. However, a spatial and temporal variation was observed in this level.

Key words: Nitrate, phosphate, statistical analysis, northwestern Mediterranean Sea, nutrients.

RESUMEN

Análisis estadístico de la calidad de los datos de nutrientes (nitrato y fosfato) y obtención de un modelo objetivo de predicción en el Mediterráneo noroccidental

Se ha analizado estadísticamente un conjunto de datos de 12 campañas oceanográficas (realizadas de 1979 a 1983), abarcando dos regiones en el mar Mediterráneo noroccidental (golfo de León y mar Catalán), relacionando el nitrato y el fosfato con el silicato, la salinidad y la profundidad. El análisis ha proporcionado una visión de la calidad de los datos y un modelo de predicción para estos nutrientes por debajo de la capa superficial. Los resultados del análisis estadístico han mostrado que las ecuaciones de regresión (nitrato-profundidad y fosfato-salinidad) de algunas campañas del golfo de León no presentaron diferencias significativas (P = 0,05), indicando que estas relaciones no cambian en esta área, principalmente en verano y otoño. Se puede observar una relación significativa entre nitrato y fosfato con salinidad y profundidad (regresión múltiple), sugiriendo que las distribuciones del nitrato y del fosfato en la capa intermedia están relacionadas con la mezcla de las masas de agua y la degradación de la materia orgánica. Los datos de fosfato mostraron una variancia elevada y errores, probablemente debido a cuestiones de metodología y análisis químico. Por debajo de la masa de Agua Levantina Intermedia, los resultados del ANOVA han mostrado que no hay una variación significativa de las concentraciones de nitrato y fosfato en la columna de agua. Por otro lado, se puede observar una variación espacial y temporal en esta capa.

Palabras clave: *Nitrato, fosfato, análisis estadístico, Mediterráneo noroccidental, nutrientes.*

INTRODUCTION

Nutrients are essential elements for the growth and functioning of photosynthetic marine organisms, especially when light is not limited. Nitrogen and phosphorus are incorporated into the soft tissues of plankton, whereas silicon is only involved in the hard skeletal parts of some organisms (Chester, 1990).

The data on the concentration of nutrients in water are often used in the study of physical, chemical and biological processes that govern the distribution of plankton in the ocean, as well as in tracing oceanic water masses and their evolution.

Vertical profiles of nitrate and phosphate in the major oceans are similar. In the intermediate layer, the concentrations increase rapidly with depth for both nutrients (N and P), reaching a maximum concentration between 500 and 1 500 m, depending on the area under study. The concentrations in the bottom layer vary little with depth. These profiles, however, differ between the various oceans, and values can decrease under 1 000 m.

Since the International Decade of Ocean Exploration (IDOE), oceanographic programmes (e.g., GEOSECS, NORPAC, and TTOY) have committed themselves to providing the highest quality data on as many measurable components of seawater as possible.

Maps were produced of geochemical tracer distribution, which were used to elaborate physical models of the deep circulation of the ocean.

International intercalibration exercises were carried out periodically, led by the Marine Chemistry Working Group, showing that the accurate determination of nutrients had some problems. Experimental errors, such as inaccuracy in the calibration method and even environmental factors can affect the results, presenting bias and a great dispersion in the data frequency histogram from a single sample.

The results obtained from oceanographic cruises made it possible to relate nutrients to physical factors, which assisted in identifying water masses and predicting nutrient concentrations (Carmack, 1963; Stefansson and Atkinson, 1971; Broecker and Takahasi, 1980; Chung, 1980; Zentara and Kamykowski, 1977; Kamykowski and Zentara, 1986). Some of these studies were adopted as examples of accurate data, which led to the definition of confidence limits.

In oceanography, the regression relation between nutrients and physical variables, depth and salinity, can present a similar trend (in the intermediate layer), because the factors (degradation of organic material and nutrient content of water mass) that influence the vertical distribution of nutrients are also connected with physical variables, regardless of the season of the year (Zentara and Kamykowski, 1977).

Coste, Jacques and Minas (1971) studied the distribution of nutrients between Sicily/Sardinia and Tunisia, and found a linear correlation between nitrate and salinity in the intermediate layer, with an R^2 of approximately 0.8. This study concluded that this nutrient's variation inside the transition layer was due to the mixture of two water types (Atlantic Water and Levantine Water); therefore, this variation was not biological in origin.

The present paper analyses the distribution of nitrate and phosphate in relation to other oceanographic parameters, over 12 oceanographic cruises covering two regions in the Northwestern Mediterranean Sea (Gulf of Lyon and Catalan Sea), between 1979 and 1993. A selection of the most precise datasets was made in accordance with various statistical criteria. Finally, mathematical models were formulated to evaluate the data's predictive capacity. These models aim to offer a more efficient mathematical relationship, and to explain the variation of each nutrient with the other parameters and their consistency over time and space.

METHODOLOGY

Nitrate and phosphate data from 12 oceanographic cruises (table I), covering parts of the northwestern Mediterranean Sea (figure 1), were statistically analysed and relationships with silicate, salinity and depth were examined.

The statistical analysis conducted in this study had two objectives: 1) to establish a predictive model by observing which of all the regression relations from all cruises did not vary throughout the year in the regional areas of the Gulf of Lyon and the Catalan Sea; 2) to detect the cruises with analytical bias which jeopardized the data's viability.

Samples were collected at each oceanographic station with Niskin bottles mounted on a General Oceanic Rosette attached to CTD systems. Nutrient analyses were performed on untreated samples im-

Table I. Oceanographic campaigns

Regions	No.	Campaigns	Longitude		Latitude		Date
			Min.	Max.	Min.	Max.	
Gulf of Lyon	G_1	Pelagolion I	3.08	5.88	42.05	43.46	09-86
	G_2	Pelagolion II	3.12	5.85	42.05	43.45	12-86
	G_3	Discovery/88	3.61	6.00	40.95	43.38	12-88
	G_4	Bannock	3.40	6.23	41.45	43.24	07-89
	G_5	Rhodiber	3.38	6.71	40.95	43.38	09-88
	G_6	Discovery/93	3.70	6.13	40.76	43.36	08-93
Catalan Sea	M_1	Tanit	1.79	4.00	39.08	42.84	08-79
	M_2	Fronts 89	0.56	3.02	40.20	41.33	06-89
	M_3	Fronts 90	2.13	3.17	40.14	41.30	02-90
	M_4	Fronts 91	2.15	3.07	40.51	41.31	04-91
	M_5	Fronts 92	2.13	3.10	40.20	41.15	11-92
	M_6	Fronts 93	0.03	3.43	38.80	41.61	06-93

mediately after sampling, with a SKALAR autoanalysis system. The methods used were those of Whitledge *et al.* (1981): for phosphate, giving a precision of better than 1 % , with a range of 0.05 to 0.50 µmol/l; and for nitrate, better than 0.1 %, in the range 0.03 to 10.00 µmol/l.

In this analysis, the data were divided into three different water layers:

1) Upper Layer - from the surface to the nutricline (mean depth = 84 m Gulf of Lyon and 71 m in the Catalan Sea);

2) Intermediate Layer - from the nutricline to the depth of maximum salinity, which defines the Levantine Intermediate Water (varies from 450 m to 989 m in the Gulf of Lyon and from 71 m to 618 m in the Catalan Sea);

3) Bottom Layer - from the depth of maximum salinity to the last sampling depth.

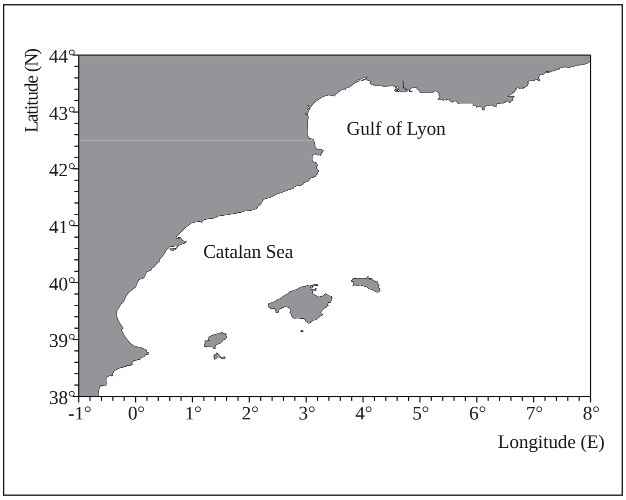

Figure 1. Map of the area

The first layer was not studied, due to complexities stemming from biological activity.

Following the methods of Montgomery and Peck (1982), the statistical analyses were performed using the Biomedical Statistical Package (BMDP) procedure (Anon., 1990). It includes a simple, multiple linear regression calculation (dependent variables were nitrate and phosphate, and independent variables were salinity, depth, and silicate), with associated statistics, including variance-covariance tables. If there were linear dependencies between the regressors (independent variables), the usual least-squares analysis of the regression model would become inadequate. In these cases, we used methods for detecting the presence of collinearity. Variance Inflation Factors (VIFS) and the Condition Number were also analysed. When these are less than 10 and less than 100, respectively, there is no serious problem with collinearity (Montgomery and Peck, 1982).

Comparisons among the set of regression equations for all cruises were made to test differences between the slopes and intercepts. The assumption of the homogeneity of slopes enabled us to group all the cruises that were not significantly different (5 % significance level). From these linear regression equations, a predictor was defined for each nutrient based on three criteria: adjusted R^2 (the highest); root mean square error (sqrtMS) (the lowest); and the group of cruises having highest number of linear regression equations that were not significantly different. Those three criteria were used to choose the predictive model. From them, and because this resulting regression best illustrated the distribution of the nutrients in the water column (> R^2), we were able to select a regression relation that was constant in time and space. To downplay the importance of cruises with more methodological errors, we gave more credence to data showing higher variance in all the regression relations, considering seasonal differences, interannual differences, and so on. Even though the regression relations with nutrients and physical factors can vary according to seasonal differences, they should show, to a large extent, a constant pattern in the nutrient distribution. If the data of some cruises showed insignificant results in all their relationships, we considered this attributable to a variance not necessarily only due to space and time, but also due to possibly significant errors in the research methodology.

Prior to testing for equality of slopes and intercepts, the outliers were extracted in accordance with Draper and Smith (1966).

In the bottom layer, nutrient concentrations presented slight variation, and the regression relations were not significant. An ANOVA was carried out to compare the nutrient distribution below the hook shown by the Levantine Intermediate Water, considering seven oceanographic cruises for nitrate (Pelagolion II, Discovery/88, Rhodiber, Discovery/93, Fronts 89, Fronts 90 y Fronts 93) and six for phosphate (Pelagolion II, Discovery/88, Rhodiber, Discovery/93, Fronts 89 and Fronts 90). Two depth ranges were defined: range 1 for depths ≤ 1 000 m; and range 2 for depths ≥ 1 000 m. The result was a nested ANOVA with three effects: two main effects (depth ranges and cruises), and one nested effect (stations, nested within cruises). Results were obtained using ANOVA with unbalanced data, with the GLM procedure from the SAS Institute Inc (Anon., 1982).

RESULTS AND DISCUSSION

The simple and multiple linear regression equations were determined for all oceanographic cruises, between the variables nitrate (dependent) and silicate, salinity and depth (independent) (tables II and III). The multiple regression models present, in general, high determination coefficients (R^2) and low root mean square errors (sqrtMS), with the exception of the Fronts 91 cruise (M_4), with a non-significant R^2 and a high value of the sqrtMS (table III). There was no linear dependency between the regressor variables (salinity and depth), because the factors that serve as index to measure this multicollinearity, the VIF and K, were less than 10 and 100, respectively (Montgomery and Peck, 1982).

The results obtained showed a variation of nitrate in relation to depth, and the degradation of organic material, one of the most important factors in the distribution of nitrate in the water column.

The regression equations were compared among themselves and in almost all the relationships (except the relationship between nitrate and silicate), showed groups of cruises which were not significantly different at the 5 % level. The miner-

Table II. Models of simple regression (nitrate vs silicate, nitrate vs salinity), determination coefficient (R^2) and root mean square error (sqrtMS)

Campaigns	Nitrate-Silicate			Nitrate-Salinity		
No.	Equation	sqrtMS	R^2	Equation	sqrtMS	R^2
G_1	$y = 0.76 x + 3.34$	2.069	0.26	$y = 13.67 x - 518.78$	1.632	0.57
G_2	$y = 2.03 x - 1.81$	1.449	0.85	$y = 23.86 x - 905.93$	1.868	0.80
G_3	$y = 1.23 x + 0.38$	0.992	0.79	$y = 14.23 x - 540.09$	1.034	0.78
G_4	$y = 0.35 x + 3.79$	1.530	0.15	$y = 15.34 x - 583.94$	0.776	0.74
G_5	$y = 1.08 x + 0.67$	1.428	0.63	$y = 13.51 x - 512.57$	1.172	0.78
G_6	$y = 1.14 x + 0.95$	1.089	0.77	$y = 14.85 x - 563.57$	0.696	0.93
M_1	$y = 0.40 x + 3.57$	1.806	0.06	$y = 10.23 x - 387.68$	0.943	0.75
M_2	$y = 1.08 x + 0.36$	0.796	0.84	$y = 14.35 x - 543.38$	1.227	0.61
M_3	$y = 0.73 x + 1.91$	1.401	0.59	$y = 5.53 x - 206.08$	2.026	0.13
M_4	$y = 2.50 x + 0.57$	2.811	0.42	$y = 2.83 x - 103.40$	4.100	0.004
M_5	$y = 1.05 x + 2.01$	1.270	0.62	$y = 14.79 x - 561.69$	1.282	0.53
M_6	$y = 1.11 x + 1.65$	0.933	0.78	$y = 7.66 x + 281.84$	1.372	0.54

Table III. Models of simple regression (nitrate vs depth) and multiple regression (nitrate vs salinity (S) and depth (Z)), determination coefficient (R^2) and root mean square error (sqrtMS)

Campaigns	Nitrate-Depth			Nitrate-Salinity and Depth		
No.	Equation	sqrtMS	R^2	Equation	sqrtMS	R^2
G_1	$y = 0.02x + 2.98$	1.923	0.36	$y = 11.06 S + 0.002 Z - 489.21$	1.569	0.61
G_2	$y = 0.03x + 2.23$	2.608	0.51	$y = 27.14 S - 0.007 Z - 1030.8$	1.900	0.81
G_3	$y = 0.01x + 3.40$	1.521	0.50	$y = 12.88 S + 0.02 Z - 489.21$	1.020	0.79
G_4	$y = 0.01x + 2.84$	0.803	0.77	$y = 7.69 S + 0.009 Z - 291.48$	0.649	0.82
G_5	$y = 0.01x + 2.93$	1.748	0.45	$y = 14.04 S - 0.001 Z - 532.79$	1.175	0.75
G_6	$y = 0.02x + 2.95$	1.412	0.61	$y = 14.34 S + 0.001 Z - 544.19$	0.679	0.94
M_1	$y = 0.01x + 1.58$	1.222	0.56	$y = 7.94 S + 0.005 Z - 300.81$	0.882	0.78
M_2	$y = 0.01x + 3.91$	1.304	0.61	$y = 9.29 S + 0.005 Z - 347.24$	1.085	0.70
M_3	$y = 0.01x + 4.32$	1.723	0.61	$y = 2.26 S + 0.009 Z - 81.91$	1.789	0.34
M_4	$y = 0.005x + 4.2$	3.676	0.01	$y = 2.72 S + 0.000 Z - 99.54$	4.129	0.00
M_5	$y = 0.01x + 3.34$	1.290	0.62	$y = 6.38 S + 0.009 Z - 240.34$	0.970	0.74
M_6	$y = 0.01x + 3.54$	1.415	0.49	$y = 5.02 S + 0.0072 Z - 193.97$	1.196	0.64

alization processes are different for both nutrients (nitrate and silicate), and although they are correlated, there are different interferences for both processes. For example, the nutricline was observed at different depths for both nutrients. According to Chester (1990), organic nitrate is associated with the soft tissue of organisms, and mineralizes mainly through bacteria. Furthermore, it has a rapid regeneration in the water column, showing a maximum concentration in intermediate water. On the contrary, silicate, as a refractory nutrient, is incorporated into the shells of organisms, thus presenting a slow mineralization in the water column, exhibiting a distinct maximum in the bottom layer. In table II, the values of R^2 for this relationship showed high correlation for some cruises and insignificant correlation for others. Some examples in the literature show that this relationship can be constant in special situations. Friederich and Codispoti (1979) studied the factors that influence the distribution of dissolved silicon on the African shelf, and observed that the relationship of nitrate and silicon near the coast, in the upwelling source waters, appears to be quite constant, due to the presence of a shallow bottom, which tends to retain silicon losses from the system.

The comparative study among other regression equations showed that the cruises in which the regression equations do not significantly differ (5 % confidence level) are in the same area of study (Gulf of Lyon or Catalan Sea). That is, the variation of the local effects that determine the stratification of the water column, and the in situ phytoplankton or bacteria dynamics, do not affect the relationship among these variables. However, the large- and mesoscale oceanographic processes -such as the currents associated with superficial and deeper circulations, the fluvial influence, and the variations in the transition states of the physical and biological processes- do indeed alter the local expression of these relationships.

The two groups of cruises for which the regression equations do not differ significantly in the relationship between nitrate and salinity are: in the Gulf of Lyon, cruises Pelagolion 1, Discovery/88, and Rhodiber; and in the Catalan Sea, cruises Fronts 90, Fronts 91, and Fronts 93. In the relationship between nitrate and depth in the Gulf of Lyon, there is a higher number of cruises that do not differ significantly in their regression equations: Pelagolion I, Bannock, Discovery/88, Rhodiber, and Discovery/93. In the Catalan Sea, there are more cruises with similar equations in the multiple regression of nitrate vs salinity and depth: Fronts 90, Fronts 91, Fronts 92, and Fronts 93. We can therefore, conclude that in the area of the Gulf of Lyon, because the cruises were carried out in summer and autumn, seasons of the year that do not present pronounced local differences (e.g. turbulence, winds, or incidence of light), the gradient of nitrate was found at the same depth; i.e., the relationship between nitrate and depth was constant in this specific area. In the Catalan Sea, it was necessary to incorporate salinity into the model, in order to obtain a higher number of cruises that did not differ significantly (5 % confidence level). In the Catalan Sea, the cruises were carried out during every season of the year, adding to local variations.

According to Chester (1990), the distribution of dissolved constituents in the sea is controlled by the combination of the circulation and the effect of internal biochemical processes. The distribution of these constituents is connected to the advection and mixing of different water masses.

The relationship between nitrate and depth, which did not differ significantly (Gulf of Lyon cruises), is shown in figure 2. It can be observed that the Gulf of Lyon cruises showed a strong relationship among themselves.

Since the multiple regression equations were the models that best explained the variation of nitrate in the water column for the Catalan Sea, these were selected to determine the predictive equation for this area. The results showed an equilibrium between the physical and chemical processes that control the vertical distribution of nitrate in the water column, throughout the year (mixing of the water column and degradation of organic material). However, this does not imply that processes such as denitrification or other phases of the nitrogen cycle do not occur on a smaller scale. Friederich and Codispoti (1979) have found nutrient variation in relation to salinity and depth, on the Peruvian coast, due to the strong influence of denitrification and the intense mixture of water masses.

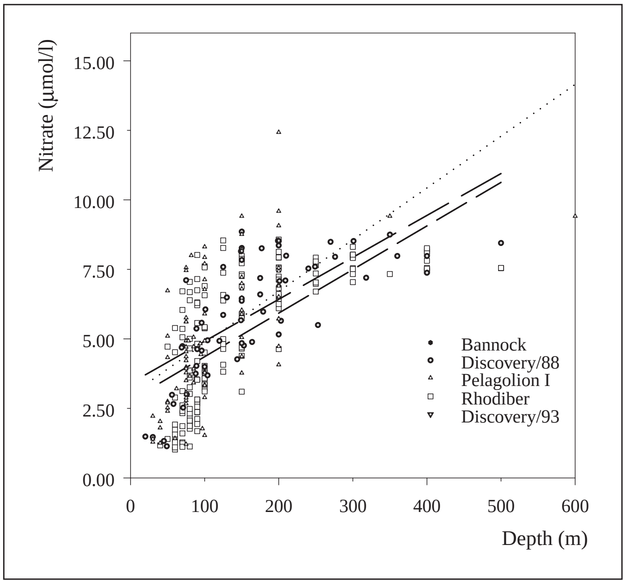

Figure 2. Nitrate vs depth for the Gulf of Lyon cruises, which do not differ significantly (5 % confidence level)

To adjust our general equation for the Catalan Sea, we included the slope and the intercept of the cruises Fronts 90, Fronts 92, and Fronts 93.

For the Gulf of Lyon, the relationship between nitrate vs salinity and depth (multiple regression) was the most efficient relationship to explain this nutrient variation (smaller sqrtMS and greater R^2) (table III). However, to determine the general predictive equation, the relationship between nitrate and depth was selected, because it appears to be constant in this particular area (a higher number of cruises showed no significant difference). The cruises included in this predictive equation are: Pelagolion I, Discovery/88, Rhodiber, Bannock, and Discovery/93.

The general predictive equations are:

Gulf of Lyon
$y = 3.05 + 0.016\ Z$ (y = nitrate and Z = depth)
Catalan Sea
$y = -187.86 + 0.0072\ Z + 5.02\ S$ (y = nitrate, Z = = depth and S = salinity)

For a better evaluation of the general equation for the Catalan Sea, the predicted data were compared with real data from the cruise Fronts/86 (provided by the Instituto de Ciencias del Mar, CSIC, Spain). The probabilities of the slope and intercept between the general predictive equation and the multiple regression equation for this specific cruise ($-218.178 + 0.005\ Z + 5.77\ S$; Z = depth and S = salinity) showed that they did not differ significantly at the 5 % confidence level (slope probabilities: Z = 0.32, S = 0.79 and intercept = 0.78). The data profiles from this cruise (predicted and real) were equivalent (figure 3).

In the Gulf of Lyon, the nitrate data for all cruises were within the established statistical criteria. Considering the seasonal and inter-annual differences, the relationships' variance did not show evidence of significant errors in the study's methodology. On the other hand, the data from the cruise Fronts 91 (M_4), in the Catalan Sea, showed a higher dispersion in their relationships, with insignificant correlating values between the variables. In this case, the apparent methodological errors are substantial, ruling out the data's viability.

Following a different methodology for the bottom layer, a statistical study using a nested ANOVA was carried out, considering nitrate concentration as a variable, the range of the depth and the cruis-

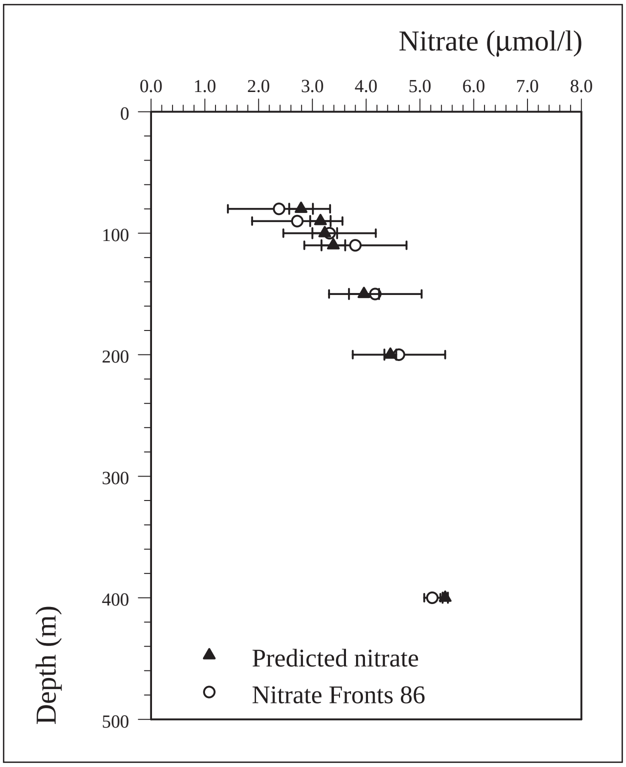

Figure 3. Vertical profile of nitrate from the Fronts 86 campaign (the predicted profile was calculated from a general predictive equation for the Catalan Sea)

es as main factors, and the stations as a nested factor. From this analysis, it can be observed that significant differences exist between the datasets (table IV). The nitrate concentration in the bottom layer was not constant in the water column of each cruise; i.e., there was a significant difference between the ranges 1 and 2 (P = 0.041). However, these results depend on the cruises and the range, because the interaction between cruise and range was significant. For example, the cruises Discovery/93 and Fronts 93 showed no significant difference between the values of range 1 (under 1 000 m, the nitrate concentration was similar for the two cruises), but the values of range 2 were significantly different (table V).

Table IV. Analysis of variance (ANOVA) for the nitrate means from the bottom layer. (St): station; (DF): degree of freedom; (SS): sum of squares; (MS): mean square; (F): T test; (P): probability

Sources of variation	DF	SS	MS	F	P
Campaigns	7	102.65	14.66	160.25	0.000
Range	1	0.38	0.38	4.21	0.041
Campaign*Range	5	1.25	0.25	2.73	0.019
St (Campaign*Range)	145	82.27	0.57	6.20	0.000

Table V. Nitrate means (M) and standard error of the mean (E) from the bottom layer (the means were computed using least-square statement for unbalanced designs)

Campaigns	M	E
G_2 r = 1	10.53	0.09
G_2 r = 2	10.19	0.17
G_3 r = 1	8.43	0.06
G_3 r = 2	8.14	0.08
G_5 r = 1	8.06	0.05
G_5 r = 2	7.77	0.10
G_6 r = 1	8.79	0.07
G_6 r = 2	8.49	0.07
M_1 r = 1	6.99	0.10
M_1 r = 2	7.24	0.12
M_2 r = 1	8.39	0.09
M_3 r = 1	8.29	0.09
M_6 r = 1	8.85	0.03
M_6 r = 2	8.74	0.04

Table V and figure 4 show the mean nitrate concentrations for both ranges in all the cruises as well as the standard error of the mean. The means were computed using least-square statement for unbalanced designs. Because the nitrate concentration was different for most of the cruises and it was not constant in time and space, a general mean was not determined for all the cruises. The nitrate range presented by Seritti *et al.* (1986) in the deep waters (200 m or more) on the Alborán Sea (8.5-9.8 µmol/l) is not as wide as the ones we found in the

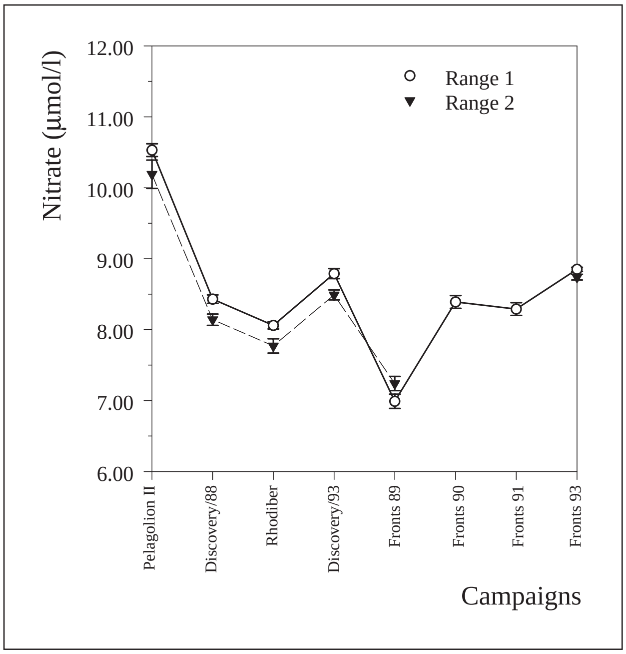

Figure 4. Nitrate vs campaigns for the two depth ranges from the bottom layer

Gulf of Lyon (7.77-10.53 µmol/l) or the Catalan Sea (6.99-8.85 µmol/l). The mean values of range 1 are higher than those of range 2, and the variation between the ranges was similar in almost all of the cruises (table V and figure 4).

In the present study, all the correlations determined for nitrate, were also calculated for phosphate. Most of them presented non-significant determination coefficients. These results could indicate the existence of bias and possible systematic errors in the phosphate determination. However, in the cruise Discovery/93, the most recent one carried out in the Gulf of Lyon, the data shows high R^2 values, always ≥ 0.60 (table VI to VIII). In this cruise, the possible random errors seem to have been eliminated.

The highest values of R^2 were determined in the relationship between phosphate vs salinity and depth, as in the case of nitrate. The variation of phosphate in the intermediate layer is also explained to a large extent by salinity (water mass) and depth (related to the degradation of organic material).

In the relationship between phosphate and salinity, four cruises carried out in Gulf of Lyon did not differ significantly. However, if only the slopes are compared, the similarities comprise a higher number of cruises in all the relationships. With a high probability, it can be said that the grade of variation of the phosphate relationships was constant in the two areas, independently of the season. The cruises in the Gulf of Lyon and the Catalan Sea were found in the same group, and did not differ significantly.

The relationship selected to determine the predictive equation was phosphate vs salinity and

Table VI. Simple regression models (phosphate vs nitrate, phosphate vs silicate), determination coefficient (R^2) and root mean square error (sqrtMS)

Campaigns	Phosphate-Nitrate			Phosphate-Silicate		
No.	Equation	sqrtMS	R^2	Equation	sqrtMS	R^2
G_1	y = 0.03 x + 0.28	0.172	0.11	y = 0.09 x + 0.19 0	0.147	0.32
G_2	y = 0.03 x + 0.09	0.158	0.44	y = 0.05 x + 0.10	0.175	0.32
G_3	y = 0.03 x + 0.18	0.161	0.16	y = 0.05 x + 0.13	0.155	0.22
G_4	y = 0.08 x + 0.27	0.238	0.35	y = 0.03 x + 0.53	0.291	0.03
G_5	y = 0.03 x + 0.14	0.071	0.48	y = 0.03 x + 0.16	0.078	0.36
G_6	y = 0.05 x + 0.08	0.065	0.76	y = 0.06 x + 0.11	0.074	0.69
M_2	y = 0.04 x + 0.22	0.127	0.31	y = 0.05 x + 0.20	0.127	0.31
M_3	y = 0.02 x + 0.07	0.068	0.37	y = 0.01 x + 0.16	0.099	0.08
M_4	y = 0.003 x + 0.42	0.193	0.00	y = 0.0007 x + 0.44	0.194	0.00
M_5	y = 0.04 x + 0.12	0.067	0.56	y = 0.04 x + 0.18	0.076	0.44

Table VII. Simple regression models (phosphate vs salinity, phosphate vs depth), determination coefficient (R^2) and root mean square error (sqrtMS)

Campaigns	Phosphate-Salinity			Phosphate-Depth		
No.	Equation	sqrtMS	R^2	Equation	sqrtMS	R^2
G_1	y = 0.77 x – 29.10	0.153	0.32	y = 0.002 x + 0.19	0.150	0.32
G_2	y = 1.00 x – 36.66	0.157	0.43	y = 0.001 x + 0.19	0.189	0.21
G_3	y = 0.49 x – 18.23	0.156	0.20	y = 0.0007 x + 0.26	0.160	0.18
G_4	y = 1.51 x – 57.31	0.199	0.55	y = 0.002 x + 0.38	0.243	0.32
G_5	y = 0.38 x – 14.38	0.078	0.40	y = 0.0004 x + 0.22	0.088	0.22
G_6	y = 0.77 x – 29.18	0.073	0.70	y = 0.001 x + 0.22	0.084	0.60
M_2	y = 0.66 x – 24.77	0.129	0.21	y = 0.0005 x + 0.36	0.131	0.26
M_3	y = 0.01 x + 0.24	0.091	0.01	y = 0.0002 x + 0.22	0.160	0.05
M_4	y = 0.24 x – 8.68	0.196	0.01	y = 0.0001 x + 0.43	0.194	0.00
M_5	y = 0.29 x – 10.98	0.092	0.08	y = 0.0005 x + 0.24	0.077	0.43

Table VIII. Multiple regression models (phosphate vs salinity (S) and depth (Z)), determination coefficient (R^2) and root mean square error (sqrtMS)

Campaigns	Equation	sqrtMS	R^2
G_1	$y = 0.41 S + 0.001 Z - 15.43$	0.151	0.35
G_2	$y = 1.24 S - 0.0005 Z - 47.02$	0.159	0.45
G_3	$y = 0.38 S + 0.0002 Z - 14.21$	0.157	0.21
G_4	$y = 1.68 S - 0.0003 Z - 63.72$	0.214	0.55
G_5	$y = 0.46 S - 0.0002 Z - 17.34$	0.077	0.40
G_6	$y = 0.54 S + 0.0004 Z - 20.54$	0.069	0.73
M_2	$y = 0.30 S + 0.0004 Z - 10.68$	0.123	0.30
M_3	$y = 0.40 S + 0.0003 Z - 15.27$	0.098	0.23
M_4	$y = 0.25 S - 0.0003 Z - 8.68$	0.197	0.02
M_5	$y = -0.19 S + 0.001 Z + 7.49$	0.078	0.34

depth for both areas, due to the higher R^2 values, lower sqrtMS values, and higher number of cruises with similar slopes. A mean slope was calculated from the regression equations of the cruises: Pelagolion I, Discovery/88, Discovery/93, Fronts 89 and Fronts 90. Because the intercepts of these equations were different, the mean of every variable was taken from the data in each cruise. The objective was to determine a predictive equation with the regression line crossing through the origin.

Therefore, the general predictive equation for both areas was determined as:

$y = 0.74 S + 0.0002 Z$ (y = phosphate, S = salinity and Z = depth).

Although the selected relationship for the predictive equation was phosphate vs salinity and depth, the relationship between phosphate and nitrate is important within the oceanic processes, because these nutrients have similar remineralization within the biogeochemical cycle. Chester (1990) showed a linear relationship between nitrate and phosphate in seawater with an $R^2 = 0.93$ (data taken from water column profiles in the Pacific Ocean). Organisms control the distribution of these nutrients and they are classified as labile nutrients; although phosphate's biochemical cycle differs somewhat from that of nitrate (Valiela, 1984), the processes that regenerate these nutrients in oxygenated waters are similar. In the present study, the value of R^2 in this relationship is relatively low, but the systematic errors from the methodology of phosphate need to be taken into account.

For studying phosphate distribution in the bottom layer, the method used for nitrate was applied, although with a lower number of cruises (ANOVA, table IX). The concentrations of phosphate differed significantly (at the 5 % level) between cruises, but the depth ranges did not ($P = 0.47$); therefore, phosphate concentration does not vary with depth, because the interaction between cruise and range was not significant ($P = 0.25$) (figure 5), concluding that the phosphate distribution was constant under 1 000 m.

Table IX. Analysis of variance (ANOVA) for the phosphate means from the bottom layer. (St): station; (DF): degree of freedom; (SS): sum of squares; (MS): mean square; (F): T test; (P): probability

Sources of variation	DF	SS	MS	F	P
Campaigns	5	0.58	0.116	28.32	0.000
Range	1	0.00	0.002	0.53	0.467
Campaign*Range	3	0.02	0.057	1.39	0.249
St (Campaign*Range)	69	1.50	0.022	5.31	0.000

Table X shows the phosphate mean for all cruises and their respective standard errors. The means were computed using least-square statements for unbalanced designs. The cruise Discovery/93 presented the smallest standard error (0.009), which indicates a higher accuracy in the data.

Table X. Phosphate means (M) and standard error of the mean (E) from the bottom layer

Campaigns	M	E
Pelagolion II	0.41	0.020
Discovery/88	0.54	0.011
Rhodiber	0.39	0.012
Discovery/93	0.56	0.009
Fronts 89	0.60	0.020
Fronts 90	0.31	0.020

Bethoux *et al.* (1992) have presented a temporal study of phosphate in the bottom layer of the Mediterranean Sea. Their results showed an evolution of this nutrient from 1960 to 1990, with a concentration increase of 0.34 to 0.40 µmol/l. The present study (period from 1979 to 1993) showed much variation in that period, but no trend (figure 5).

Due to biases found in the phosphate data, it cannot be affirmed that the variance in the deep layer is due only to inter-annual differences, con-

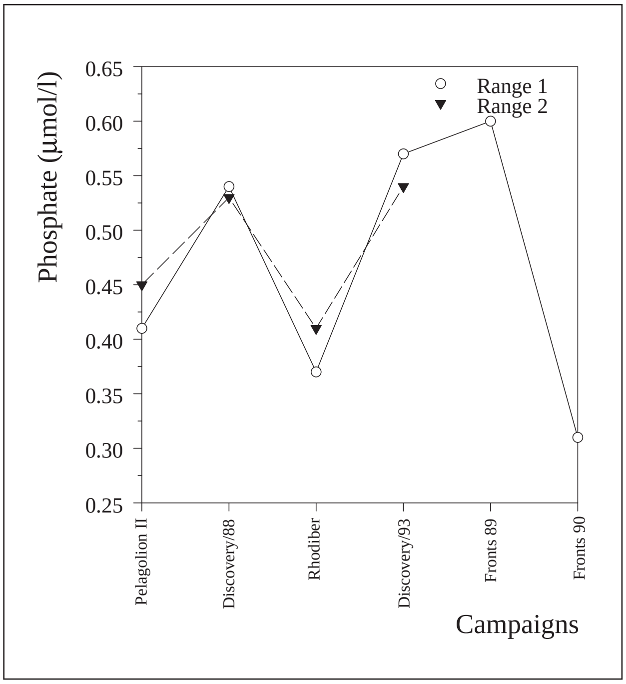

Figure 5. Phosphate vs campaigns for the two depth ranges from the bottom layer

vection, and so on. In figure 6, the variance coefficient (CV) for the nitrate and phosphate data can be observed in the three water-column layers (surface, intermediate and deep) of the various oceanographic cruises. The surface layer presented higher CV values; there are atmospheric continental influences that cause local variation in this layer. The absence of these influences on the intermediate and deep layers decreases their average total variance respectively. Although the variation of nitrate values (CV), is lower in the intermediate and deep layers, a higher local variance of phosphate data can be observed in the deep layer (comparing the CV values between both nutrients). This confirms the biases found in the concentration of phosphate in the intermediate layer.

CONCLUSION

The statistical methodology used in the present study proved to be simple and efficient, because it made it possible for us to detect errors in the data of some oceanographic campaigns (mainly in the phosphate data), as well to elaborate predictive models which aided the understanding of the specific factors that altered nutrient variation in the two study areas (Gulf of Lyon and Catalan Sea).

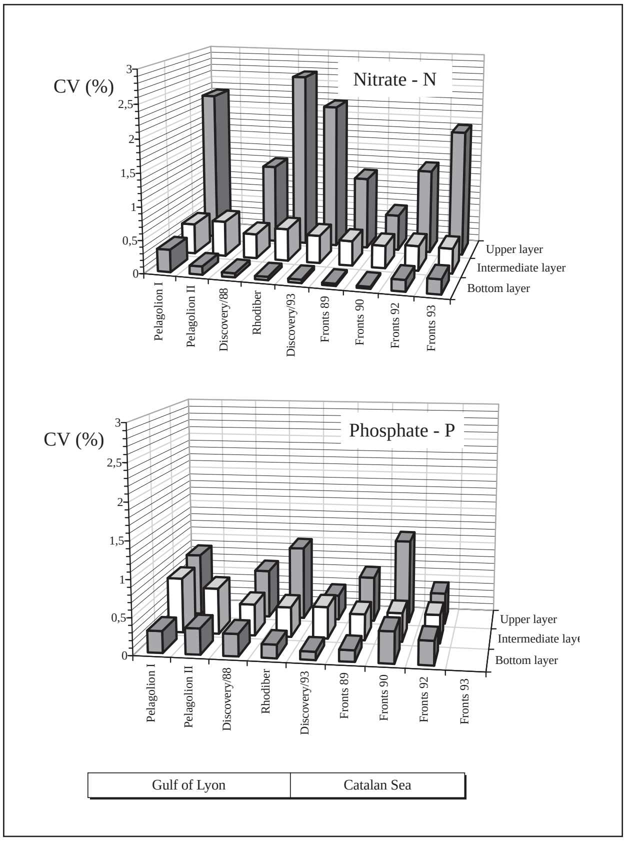

Figure 6. Coefficient of variation (CV) of nitrate and phosphate in the Catalan Sea and Gulf of Lyon for the three layers in the water column

The results of the statistical study for both nutrients (nitrate and phosphate) showed that the variations were different in time and space. Starting from the hypothesis that the mathematical model explains the nutrient variation in these areas (in the intermediate layer), and especially that this variation is constant in time and space, the differences between the nutrients were as follows. 1) The main factor in the variation of nitrate in the Gulf of Lyon was depth (or pressure). The gradient of nitrate in this area was found at the same depth, in autumn and summer. In the Catalan Sea, it was necessary to incorporate the parameter of salinity to the model, to obtain a constant mathematical relationship between nitrate and the area's other parameters. This relationship was valid for the entire year, not only for autumn and summer. Therefore, in the Gulf of Lyon the biochemical processes (such as degradation of organic material) were most responsible for nitrate variation in the intermediate layer, whereas in the Catalan Sea other factors -such as the vertical circulation and mixing of different water masses- need to be considered to explain this variation throughout the year. 2) In contrast with nitrate, the phosphate variation was constant in the two areas (Gulf of Lyon and Catalan Sea), independently of the season. Another difference between phosphate and nitrate models is that the first passes through the origin, i.e., gradient of phosphate; even though it was the same in the two areas, it was detected at different depths.

In the deep layer, variations in the concentrations of nitrate and phosphate were detected in the two study areas and between the oceanographic cruises. Only the phosphate values were constant in the water column under 1000 m.

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