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Salinity, Nutrient and Chlorophyll *a* Vertical Variations in the Ebro River Plume

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ABSTRACT

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Four water sampling campaigns in the Ebro River Plume were carried out, in spring, summer and autumn of 1999 and winter of 2000. In these campaigns salinity, nutrient and chlorophyll *a* spatial distributions in the water column of river plume area were studied (where salinity values increase with depth). The sampling within the first meter of water column was carried out with a specifically designed device (SWAS). This device was designed by Dr. Jean Jacques Naudin to sample in the Rhone River Plume, although some modifications were introduced in the equipment to adapt it to Ebro River Plume conditions in order to obtain a very high vertical resolution in the sampling of the upper water column. Water samples could be acquired simultaneously at eight different depths (0.00, 0.05, 0.10, 0.20, 0.30, 0.50, 0.75 and 1.00 m) plus another additional at 5.0 meters. Salinity, concentration of ammonium, nitrite, nitrate, reactive soluble phosphorus (RSP), total dissolved phosphorus (TDP), total phosphorus (TP), ortosilicic acid and chlorophyll *a* were measured in each water sample. The results of sample analysis allowed to obtain salinity profiles of this surface layer, clearly showing the reduced thickness of river plume when the sea is under low energetic conditions, with a sharp rise of salinity in the first centimeters of water column. Some discontinuities in this pattern were identified, specially when wind blew from the sea, introducing waters of higher salinity and temperature in the upper part of the water column. In most of the sampling stations, nutrient profiles showed a generally decreasing trend of their concentrations with the water depth, although several deviations of this pattern could be observed. These deviations were not due to freshwater load variations and many of them took place in the first 20 centimeters of water column. Since these variations in nutrient concentrations are not apparently related to freshwater loads and/or chlorophyll *a* level changes, the origin of these variations could be planktonic organisms motions in this thin layer and activity changes due to these movements.

ADDITIONAL INDEX WORDS: *Nitrogen, phosphorous, sampling system, coastal.*

INTRODUCTION

When reaches the sea, freshwater from rivers flows over the more dense marine water, progressively mixing with it. Due to this density gradient, a plume is formed, whose extension and morphology depend on hydrodynamic conditions, river discharge, tidal conditions, waves and wind-induced sea currents (Broche *et al*., 1998; Marsaleix *et al*., 1998).

Continental waters have less salinity and higher nutrient concentration than marine waters. Due to their lower density, continental waters buoy up over the denser marine waters, so the plume structure is usually composed by a surface layer with depth increasing salinity values.

As a consequence of the difference in nutrient concentration between continental and marine waters, a nutrient mixing and diffusion process is generated following, in principle, an inverse relationship with salinity (Davies & Xing, 1999).

As pointed out by Broche *et al*. (1998) and Morris *et al.* (1995), the spatial and temporal distribution of nutrients, in both, the estuary and plume, is not only dependent on the physical mixing (between freshwater and saline water) itself, but also on different physical, chemical and biological processes that may occur, such as advection-settling, flocculation-disaggregation, adsorption-desorption, production-grazing or uptake-excretion. Naudin *et al.* (1997) found that salinity reduction induced by the freshwater output to marine environment interrupts primary production during the fluvial influence. That process may be due to the salinity inhibitor effect over freshwater phytoplanktonic populations before brackish/marine species can compensate the losses due to this cause.

The objective of this study is to analyze the nutrient distribution patterns in the estuarine mixture of Ebro River plume, using a new high precision sampling method in the surface layer, where fresh/brackish waters are located.

STUDY AREA

The Ebro River flows into the Mediterranean Sea, on the eastern coast of Spain. It has an estimated length of 928 km and its drainage basin area is about 85,550 km^2.

The Ebro delta is located 40º 40' N and 0º 40' E (figure 1) and has an extension of 330 km^2 being the deltaic part of the river 29 km long. The mean depth is 6.8 m and its average width is 237 m. There is only one "operating" mouth, although during extreme floods an extra mouth could appear. 75% of the Ebro delta area is used in agriculture mainly rice crops.

The Ebro water flow rates are highly variable, because the river is regulated by 138 dams located all along its length, which have a total capacity of about 6.51 Km^3. The river total flow is around 10,000 Hm^{3}yr^{-1} (varying between 5,000 and 14,000 Hm^3), carrying 21,000 T of nitrogen and 1,200 T of phosphorus (Dolz *et al*., 1997). The last stretch of the river behaves most of the time as a stratified estuary with a salt wedge, usually reaching the vicinities of Gracia Island (18 km upstream the mouth), although the position depends mainly on flow rates and secondarily on sea level oscillations (Ibañez *et al.*, 1997). Astronomic tides are negligible in this Mediterranean region, with amplitudes not higher than 30 cm with half-day periodicity (Rodríguez, 1982).

MATERIAL AND METHODS

Within the frame of the research project PIONEER funded by European Union, four water sampling campaigns were carried out at the Ebro River estuary and plume during 1999 and 2000, in spring, summer, autumn and winter. This work focuses on the analysis of data acquired in the river plume. At each station, water samples were collected at 0.00, 0.05, 0.10, 0.20, 0.30, 0.50, 0.75 and 1.00 m water depths, using an "ad-hoc" device that allows a water sampling of the surface layer with high vertical resolution. This device, called SWAS (Surface Water Sampler), previously developed by Dr. J.J. Naudin for sampling at the Rhone River (NAUDIN *et al*., 1997, 2001), has been adapted to be used in this project. This device is a floating rigid platform (placed in the water surface) with 8 polytetrafluoroethylene (PTFE) tubes, each one of them with the specified length to take samples at those predefined water depths by means of a vacuum system. The ends of the submerged tubes were closed with corks, and the admission orifices were lateral-placed in order to avoid whirlpools and other not-desired currents. An additional sample was collected at 5 m depth through a hose connected to a vacuum pump. At each sampling station, the water was collected in plastic bottles, refrigerated and carried to the laboratory (always within the first 12 hours after collected). When the samples arrived to the laboratory, they were divided in several proportional parts, due to different conservation procedures (APHA, 1998). Nutrient analyses were performed with an Alliance Instruments Evolution II continuous flux air segmented autoanalyzer. The employed methods are described by TREGUER & LE CORRE (1975). Salinity was determined by means of an induction conductivity-meter (Grundy Environmental Systems Corporation, 6230 N), calibrated with the suitable standards (I.A.P.S.O. Standard Seawater, Ocean Scientific International, Ltd, K15= 0.99986, S= 34.995‰). Chlorinity values were computed from salinity ones through Wooster's linear equation (RILEY & CHESTER, 1971). Chlorophyll *a* concentration was determined using the trichromatic method based on visible spectroscopy (APHA, 1998) and using JEFFREY & HUMPHREY (1975) equations.

RESULTS AND DISCUSSIONS

Salinity/Chlorinity

As was previously stated, the Ebro River is a stratified estuary, where freshwater only partially mixes with seawater. Hence, the surface water in the vicinities of the river mouth has quite low salinity values. Once the freshwater passes the mouth and arrives to the sea, vertical and horizontal diffusion processes take place. Freshwater (lower density) “buoys up” on seawater (higher density) forming the so called “buoyant plume” which is moved by dominant winds and mixed by swell waves (DURAND *et al*., 2002; MAIDANA *et al*., 2002; SIERRA *et al*., 2002).

In all the field campaigns, salinity/chlorinity profiles presented a strong gradient in the surface layer of the water column, decreasing with the distance to the mouth due to mixing processes (ROMERO, 2003). This can be observed in figure 1 where chlorinity profiles (9th October 1999) are presented. Chlorinity increases with water depth although the most significant changes are observed in the first meter of the water column. Nevertheless, this general pattern is not always observed. For example, at 5M1 sampling station, the wind field (coming from SSW) introduced saltwater heated by solar radiation through the surface, leading to a higher chlorinity value at 0.00 m than that corresponding to 0.05 m depth. At stations 5M6 and 5M7 several variations in chlorinity along the first meter of water column can be observed, probably due to the increase of wind velocity and changes in its direction, leading to more intense currents and turbulence in this layer. Moreover, at these stations, the smaller variation range of chlorinity facilitates the formation of these atypical profiles, since any minimal change leads to significant variations.

In figure 1 the high vertical sampling resolution obtained with SWAS in the surface layer can be observed, in fact where the fresh/ brackish water is located.

Nutrients

A large nutrient load can be found in the lower course of Ebro River. Obviously, the different vertical profiles of the analyzed nutrients follow an inverse pattern to those of chlorinity, as can be observed in figure 2. There nutrient and chlorophyll *a* profiles are presented, corresponding to two stations of similar chlorinity and therefore similar fluvial influence, on two consecutive days (9th and 10th October 1999).

The spatial distributions observed on the different samples show that nutrients decrease as the water depth and the distance to the mouth increase, as could be expected (RAGUENEAU *et al*., 2002). However, in some nutrient profiles, peak values at different depths or “zigzag profiles” have been observed (ROMERO, 2003).

Ammonium

At most of the stations and during almost all the field observations, the ammonium concentration decreases as depth and salinity increase (ROMERO, 2003). But as it can be observed in figure 2, ammonium profiles show many deviations along water column. The reasons for this behaviour seem to be:

-There are not significant differences between fluvial and marine concentrations (as for other nutrients), so the variation range is small and any minimal change can lead to significant repercussions.

-This nitrogen form has important inputs and outputs from other nitrogen forms. Thus, its preferable absorption over other nitrogen forms must be pointed out (ESTRUM-YOUSEF & SCHOOR, 2001), as well as its thermodynamic instability (Jaffe, 1994), nitrification (HERBERT, 1999) and zooplankton excretions and exudations (WRIGHT, 1995).

It is interesting to note the existing differences between both profiles at different depths, with higher observed concentrations on 10th October. Nutrient distributions at all the sampled stations during this campaign suggest that a significant growth of phytoplanktonic communities could be expected on 10th October (since there is a significant decrease of nitrate and SRP concentrations). Nevertheless this increase was not accompanied by a significative increase of chlorophyll *a* concentrations, indicating that a simultaneous zooplankton growing took place. Probably, zooplankton exudations along the water column were the responsible for this ammonium increase in the more saline area.

Nitrite

During all the field campaigns, at all the sampling stations, the nitrite concentration decreases as salinity and water depth increase. As in the case of other nutrients, although not significantly important, small subsurface peak values have been observed at some stations (not shown). These slight deviations can be related to motion and activity of planktonic communities and to the small concentration values, allowing a larger influence of biological activity on this pattern.

Nitrate

As in other nitrogen forms, nitrate concentrations decrease as water depth increases, as shown in figure 2. Nevertheless there are small magnitude deviations to this general pattern at some of the stations, especially in subsurface layers, that can be related to movement and activity of planktonic communities.

Soluble Reactive Phosphorus (SRP)

As shown in figure 2, RSP concentrations decrease as water depth increase, but similarly to other parameters, small subsurface peak values have been observed, probably due to the movement and activity of planktonic communities in this layer. At the stations located close to the river mouth (not shown) there are concentration increases apparently due to the mortality and mineralization of fluvial phytoplankton by saline shock produced by the mixing process (UNCLES *et al*., 1998). As it is pointed out in NAUDIN *et al*. (1997, 2001) and RAGUENEAU *et al*. (2002) it seems that this saline shock inhibition prevails over the positive effect of nutrient contribution to phytoplankton. At some stations (out of the plume limit) RSP values are under the detection limit of the analysis method in the whole water column. Even at stations presented in figure 2 (close to river

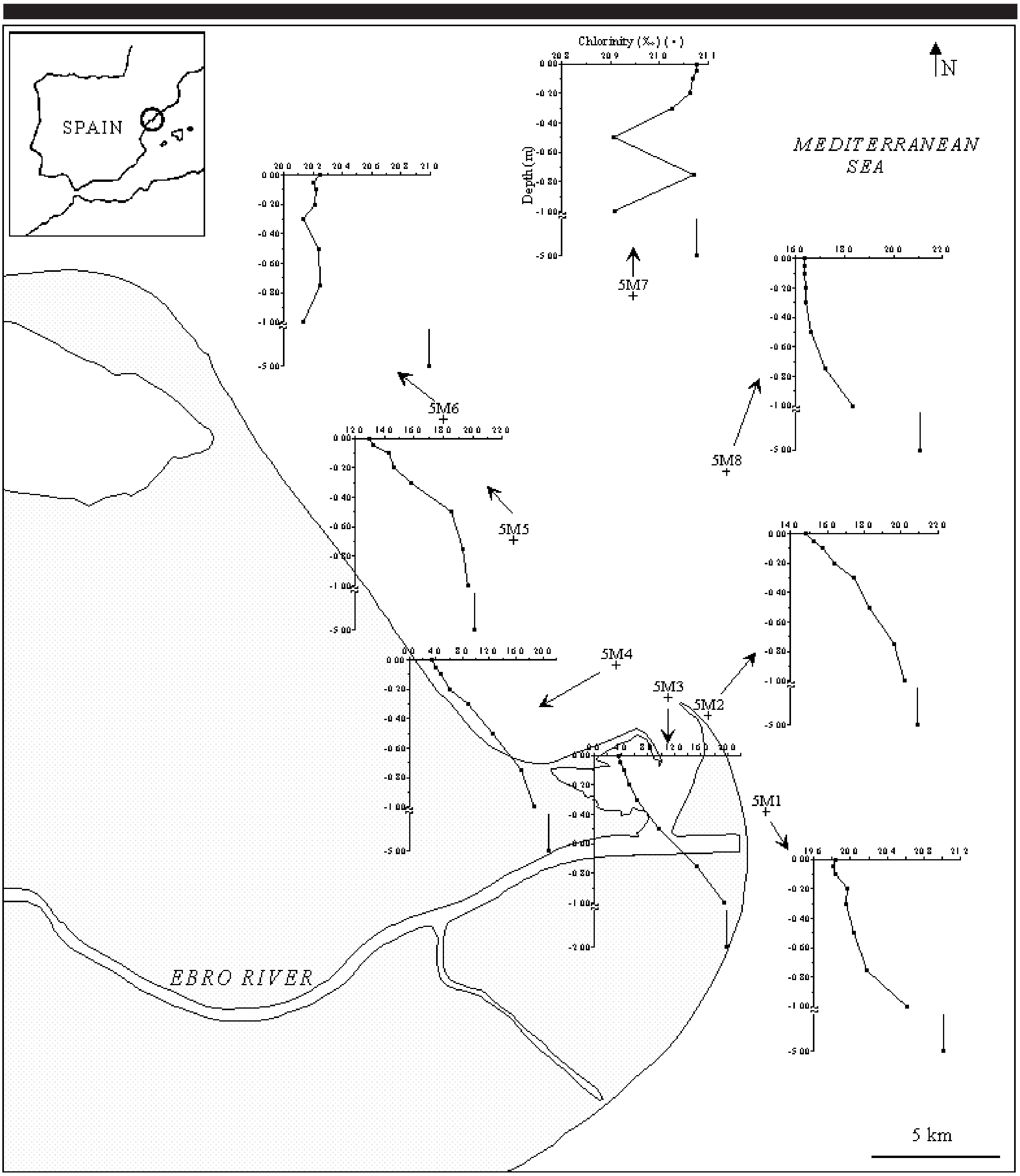


Figure 1. Study area and chlorinity profiles on 9th October 1999.

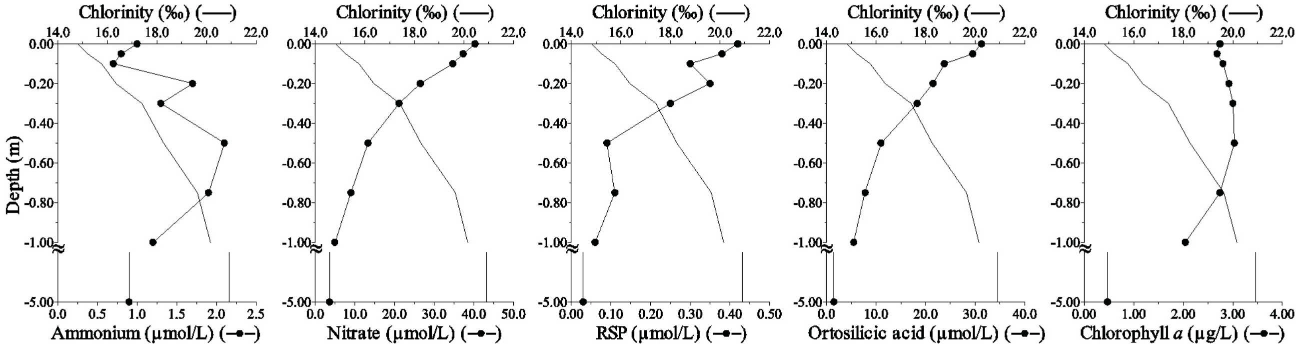
mouth) RSP reaches values close to depletion at relatively shallow depths. As it was previously pointed out, it seemed to be a larger phytoplanktonic growing on 10th October, with RSP reaching depletion since 30 cm of water depth.

Phosphorus presented a typical behaviour of a nutrient-limited system receiving an input of this nutrient from the river. In fact, in the Mediterranean Sea the growth of phytoplankton is limited by phosphorus (KROM *et al.*, 1991; ESTRADA, 1996; THINGSTAD *et al.*, 1998) and not by nitrogen as in most of the oceans (RYTHER & DUNSTAN, 1971; VOLLENWEIDER *et al.*, 1996). In these conditions an active absorption by phytoplankton took place, leading to generalised decreases during the mixing process (SOUCHU *et al.*, 1997). This has been observed in the four field campaigns, where RSP shows clear losses in the mixing process between freshwater and marine water, reaching limits close to depletion in all the seasons at most of the stations (ROMERO, 2003).

Ortosilicic Acid

A similar trend can also be observed for this nutrient, since concentrations decrease as water depth increases, as it can be observed in figure 2. Similarly to nitrite, this nutrient shows some small magnitude deviations in the first centimetres of the water column at some of the stations, probably due to absorption and movement of planktonic communities.

A) 9th octuber 1999



B) 10th octuber 1999

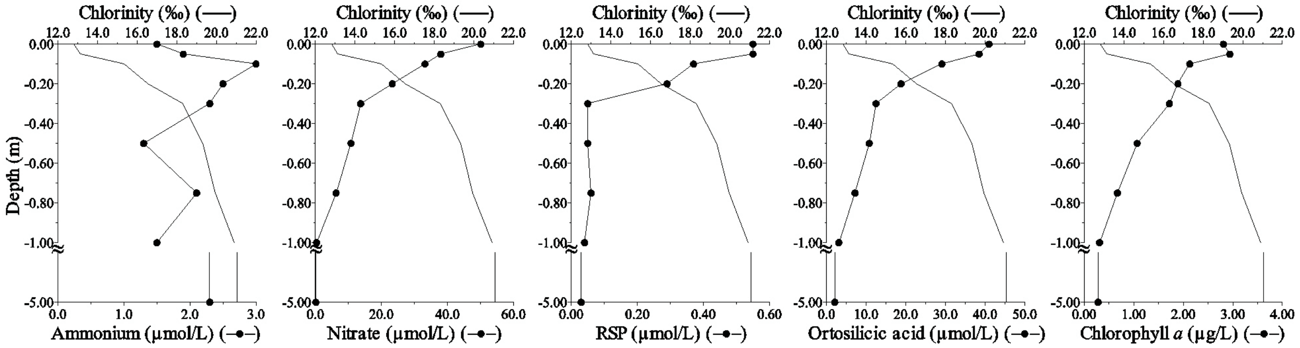


Figure 2. Vertical profiles of chlorinity, nutrients and chlorophyll *a* in 9th and 10th October 1999.

Chlorophyll a

As shown in figure 2, concentrations decrease as water depth increase, but at some stations (as the two presented in figure 2) larger subsurface (0.05 to 0.20 m) values are found, probably due to inhibition caused by UV radiation in the first centimetres of water column (MACINTYRE *et al.*, 2002) and for the influence of planktonic community movements (MACINTYRE *et al.*, 2000; SERRA *et al.*, 2003).

CONCLUSIONS

With this device (SWAS) a high vertical sampling resolution has been obtained, achieving water sample collection at depths of 0.00, 0.05, 0.10, 0.20, 0.30, 0.50, 0.75 and 1.00 m, allowing the observation of different chlorinity values within the layer of the river plume. In fact, although the information provided by this system about chlorinity was previously known, it allowed obtaining additional information about nutrients.

River discharge is one of the main factors controlling river plume spreading and nutrient contributions to region of freshwater influence (ROFI), where all studied parameters are clearly related to chlorinity. It has been shown that spatial chlorinity distribution (both vertical and horizontal) is highly dependent on hydrodynamic conditions, which play a fundamental role moving and mixing freshwater/brackish river water with marine saltwater.

Nutrient and chlorophyll *a* profiles show, in general, an inverse distribution to that of chlorinity. However, regarding the irregular vertical distribution at some sampling stations and for all nutrient forms analyzed as well as for chlorophyll *a*, planktonic biocenosis movements in the water column are partially responsible of this behaviour.

Differences existing between two consecutive sampling campaigns (9th and 10th October) have been verified. Although fluvial concentrations of chlorophyll *a* and nutrients were similar in both campaigns, some parameter distributions were rather different. The largest differences were found in ammonium and RSP, which are respectively preferential nitrogen and phosphorus forms for consumption of planktonic communities.

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