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Spatial and Temporal Patterns of Water Quality in Cullera Bay

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ABSTRACT

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The Júcar River, characterized by a very irregular freshwater flow, discharges into the Spanish Mediterranean coastal waters. However, the flow at its mouth is usually insignificant due to the overexploitation of upstream water. Under normal conditions, the final stretch of the river (downstream from the Cullera weir) is nurtured only by water released from the weir and small discharges from lateral irrigation channels. During periods of heavy rain, however, a significant amount of water flows through the Cullera weir. An analysis of data acquired during several field campaigns in Cullera Bay clearly reveals a zonal distribution of nutrients and chlorophyll-*a* within the bay: a southern area of continental influence, located near the mouth of the Júcar River; a region affected by karst filtrations and minor freshwater inputs, located to the north of the bay around Cullera Cape; and a third zone in between, characterized by higher salinities. Spatial salinity distribution is indicative of the spatial distribution of some of the nutrients discharged by the river, particularly nitrite, nitrate, orthosilicic acid and total phosphorus (TP), since it has been shown that their behavior is inverse to that of salinity. However, neither soluble reactive phosphorus (SRP) nor ammonium, which are mainly affected by biological activity, show this type of behavior. Five different conditions/scenarios were identified during the overall sampling period based on the time-series analysis of wind parameters, rainfall, freshwater flow, salt-wedge thickness at the measuring station on the river, and by comparing the average surface salinity at the sea stations with the values obtained at the coastal stations.

ADDITIONAL INDEX WORDS: *Nutrient, stratified estuary, Mediterranean Sea.*

INTRODUCTION

The input of continental nutrients tends to be the factor that determines the trophic state of coastal ecosystems. Such inputs are mainly due to freshwater river discharges, runoff and the upwelling of phreatic waters at the seabed.

Before current levels of development were reached, rivers were the main source of continental nutrient inputs. However, the ever-growing use of chemicals for different anthropic activities has led to an increase in direct nutrient dumping in coastal waters—in many cases, this input has become quantitatively more important than the riverine input (PÉRÈS, 1980)—and to an increase in nutrient concentrations in rivers and streams (BALLS, 1994; COOPER, 1995; MÉNESGUEN *et al.*, 1995).

The increase in nutrient inputs in coastal ecosystems is assumed to bring harmful effects, leading to eutrophication episodes (MURRAY and LITTLER, 1978; SOLER *et al.*, 1988). However, the opposite situation—a reduction in nutrient loads due to human activities commonly related to freshwater extractions—is also problematic. Examples include reduced biomass and productivity in coastal ecosystems that depend on nutrient input from rivers, as in the case of the collapse of sardine fishery in the eastern Mediterranean Sea after the Aswan Dam was built (BEN-TUVIA, 1973; HALIM *et al.*, 1967; OREN, 1970) and the bivalve community in the Gulf of California (KOWALEWSKI *et al.*, 2000).

Additionally, the concentration of different nutrients in coastal waters varies throughout the year because of seasonal climate changes, which affect circulation and biological activity and processes. Usually, the continued presence of relatively high-nutrient concentrations in the unstratified water column in spring and the increase in light intensity after the winter restriction causes the largest of the seasonal plankton proliferations. The growth of plankton causes nutrients to be absorbed and causes nutrient levels to drop in the euphotic layer, occasionally reaching nutrient exhaustion by the beginning of summer, when thermal water-body stratification begins (RILEY and CHESTER, 1971). However, this pattern is not always observed in coastal waters because various oceanic phenomena (e.g., waves, tidal action, currents and coastal upwelling of bottom waters) strongly influence the movement of water and materials (KENNISH, 1997).

This study analyzes the spatial and temporal distributions of salinity, nutrients and chlorophyll in Cullera Bay during a one-year period.

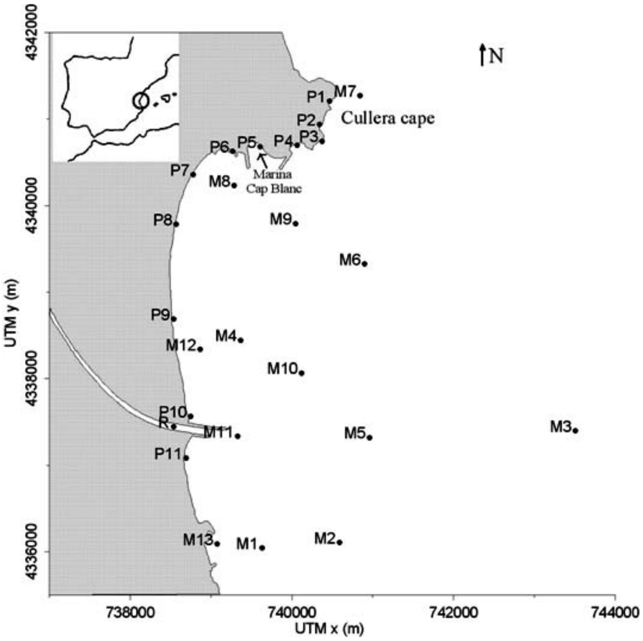


Figure 1. Cullera Bay, on the Spanish Mediterranean coast. Location of sampling stations (M: sea stations, P: nearshore stations and R: fluvial station).

STUDY AREA

Cullera Bay is located on the east coast of Spain (Figure 1). In this area, the Júcar River flows into the Mediterranean Sea, creating a stratified estuary system. The main features of this system are the microtidal character of the Mediterranean Sea and the major upriver agrarian exploitation experienced by the Júcar River. This reduces the freshwater flow in the lower stretch of the river, which reaches minimum levels (under detection limits) at the estuary mouth during most of the year (Figure 2). Only during the heavy-rainfall season can the river discharge rate be detected at the mouth. Circulation and water quality in Cullera Bay are also affected by man-made structures such as the Júcar channeling dikes, the Cap Blanc marina in the northern area of the bay, traditional bivalve farming facilities and the marine outfall located in front of the river mouth. The effects of the outfall are particularly harmful in summer, when the population of Cullera increases from 21,372 (INE, 2004) to more than 100,000 inhabitants.

MATERIAL AND METHODS

Nine field campaigns were carried out in Cullera Bay between June 2002 and July 2003 (Table 1) as a part of the European project ECOSUD (Estuaries and Coastal Areas. Basis and Tools for a More Sustainable Development). The experiment involved near-surface water sampling at 13 sea locations, 11 nearshore stations and 1 river station near the river mouth (Figure 1). At each station, samples were taken at three depths (0.0, 0.10 and 1.00 m) using a device called Surface Water Sampler (SWAS) (NAUDIN *et al.*, 1997). Additional samples were collected at a depth of 5.0 m and near the bottom using a pipe connected to a vacuum pump. At Station M11, near the river mouth, water samples were also taken at 0.05 m, 0.20 m, 0.30 m and 0.50 m. All of the samples were collected in two-liter plastic bottles and kept at 4°C until their arrival at the laboratory (always within 10 hours of the sampling time).

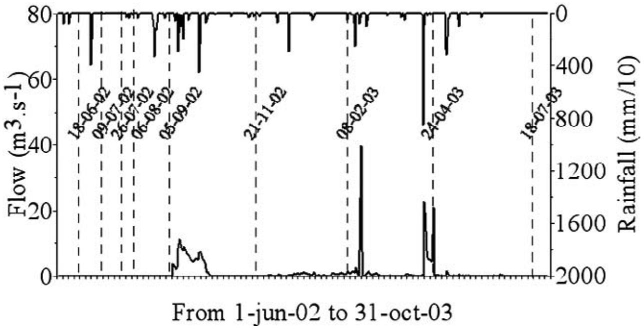


Figure 2. Daily average Júcar flow levels and precipitation (lower line: flow; upper line: rainfall).

At the river mouth, a Turo T-611 multiparameter probe was used to establish the depth of the freshwater-saltwater interface, located where the observed conductivity gradients were largest.

At the laboratory, the water samples were analyzed using different methods. For the analysis of nutrients—ammonium, nitrite, nitrate, SRP (soluble reactive phosphorus), TDP (total dissolved phosphorus), TP (total phosphorus) and orthosilicic acid—an Alliance Instruments Evolution II air-segmented continuous-flow auto-analyzer was used. The methodology described by TREGUER and LE CORRE (1975) was followed, considering the remarks by PARSONS *et al.* (1984) and KIRKWOOD *et al.* (1991).

Salinity was measured using an inductive conductimeter gauged with the appropriate patterns (I.A.P.S.O Standard Seawater, Ocean Scientific International Ltd., K15 = 0.99986, S = 34.995%). Chlorophyll-*a* content was determined with the three-color method based on visible spectroscopy, using JEFFREY and HUMPREY's (1975) equations to obtain the concentration.

For each sampling station, the average values of each parameter analyzed and the respective variation coefficients were obtained for the entire sampling period. These values

Table 1. *Dates of the nine sampling campaigns.*

Sampling campaign	Date
Campaign 1	18 June 2002
Campaign 2	9 July 2002
Campaign 3	26 July 2002
Campaign 4	6 August 2002
Campaign 5	5 September 2002
Campaign 6	21 November 2002
Campaign 7	8 February 2003
Campaign 8	24 April 2003
Campaign 9	18 July 2003

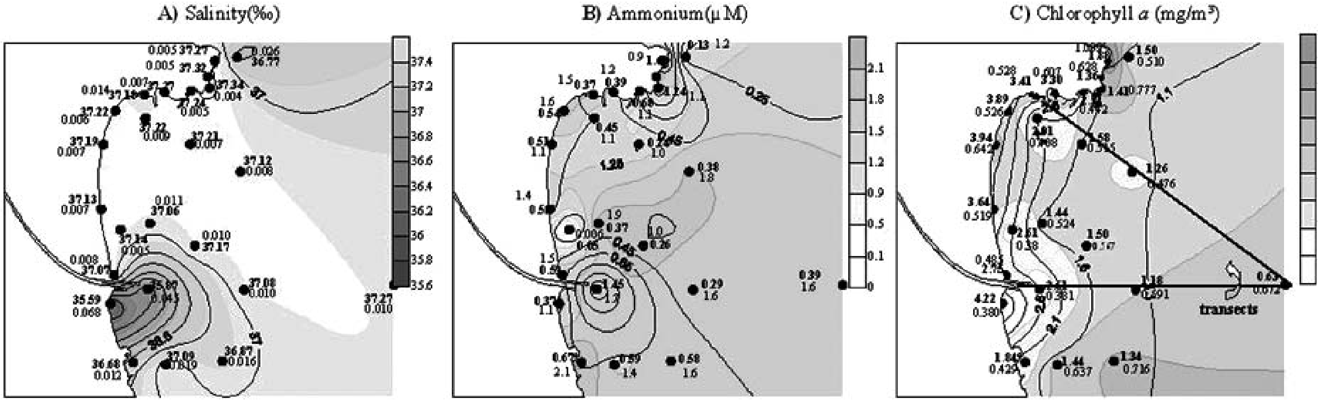


Figure 3. Distribution of surface averages (black curves and values) and their variation coefficients (grayscale contours and values) for (A) salinity, (B) ammonium and (C) chlorophyll-*a*. The values at each station were obtained by averaging the measurements obtained in the nine field campaigns.

are used indicatively in this paper. They do not attempt to reflect the real average values in the bay.

RESULTS AND DISCUSSION

Spatial Distribution

The distribution of the surface-salinity averages and their variation coefficients showed three clearly differentiated zones in all of the sampling campaigns (Figure 3A). The first is found to the south of the bay, near the mouth of the Júcar River. This is a zone of continental influence, where the stations with the smallest salinity averages and largest variation rates are found (P11, M11, M13, M2, P10, M5, M12 and M1). The latter is caused not only by the major variations in the Júcar River inflow throughout the sampling year (Figure 2) but also by changes in the behavior of the freshwater plume due to variations in the local wind direction. The second zone is located to the north of the bay, near Cullera Cape, and includes Stations M7, P1, P2, P3, P4, P5 and P6. In this area, karst filtrations and sporadic freshwater inputs from an irrigation ditch on the northern side of the cape are detected. These phenomena may significantly affect the salinity values measured at M7, P1 and P3 (although not P2, since it is a confined cove). This effect is particularly enhanced when significative irrigation flows in the ditch concur with north-northeast winds, as occurs in Campaign 9. Salinity values obtained at Stations P1 to P6 are affected by karst filtrations, which carry runoff and wastewater leaked from the sewage system. At P1 and P3, located in the surf zone, the salinity decrease is not as clear because mixing is enhanced. Finally, a third zone with higher salinity averages and low variation rates is apparent to the north and east of the bay, including the station that is the furthest offshore (M3) and those located to the north of the river mouth (P7, P8, P9, M8, M9, M6, M4 and M10). In this area, surface salinity is strongly influenced by higher-salinity open-sea waters due to local hydrodynamic characteristics. The two exceptions to this were Campaign 6, because of major continental influence due to local rainfall, and Campaign 9, in which the freshwater input from the irrigation ditch north of Cullera Cape was dragged towards the area by northeast winds.

Salinity distribution is indicative of the spatial pattern of some nutrients, such as nitrite, nitrate, orthosilicic acid and TP, since it has been shown that their behavior is inverse to that of salinity. This is because continental inputs have larger nutrient concentrations than seawater and their behavior is not affected by water mixing. Thus, the greatest nutrient concentrations are observed in the areas of greatest continental influence (P11, M11, M13, M2, M4, M5 and M1). However, the distribution of orthosilicic acid does not follow the expected inverse pattern because it is affected by significant proliferations of diatoms.

This inverse behavior, followed by orthosilicic acid in the absence of diatom proliferation, is not observed at all in Cullera Bay (except at M11, due to the strong continental influence). Nor is it found in the fundamental source of the limiting nutrient, SRP (KROM *et al.*, 2004; ROMERO, 2004), or in the type of nitrogen most affected by biological activity, ammonium, which is the preferred source of nitrogen for phytoplankton and the first form of organic nitrogen to be remineralized (ESTRUM-YOUSEF and SCHOOR, 2001; GONZÁLEZ, 1989; KUDO and HARRISON, 1997). The maximum ammonium values were measured at P1 and P3 (Figure 3B), but they were not accompanied by decreases in salinity. This is mainly because these stations are located in a surf zone that favors water mixing and the continental ammonium inputs originated from karst runoff and sewage-system leaks. Furthermore, ammonium concentration at M8 is higher than that of the surrounding waters (considered open-sea waters) because the dynamics encourage nutrients to be stored in the benthos because the sea bottom is shallow and flat (GONZÁLEZ DEL RÍO, 1986).

Figure 3C shows the chlorophyll-*a* distribution in the bay. The maximum levels are found along the coastline (P11, P8, P7, P9 and P6). The cross-shore distribution was analyzed by defining two transects with clearly defined spatial variations. The first transect (starting near the cape), which includes Stations M8, M9, M6 and M3, reveals a decrease in chloro-

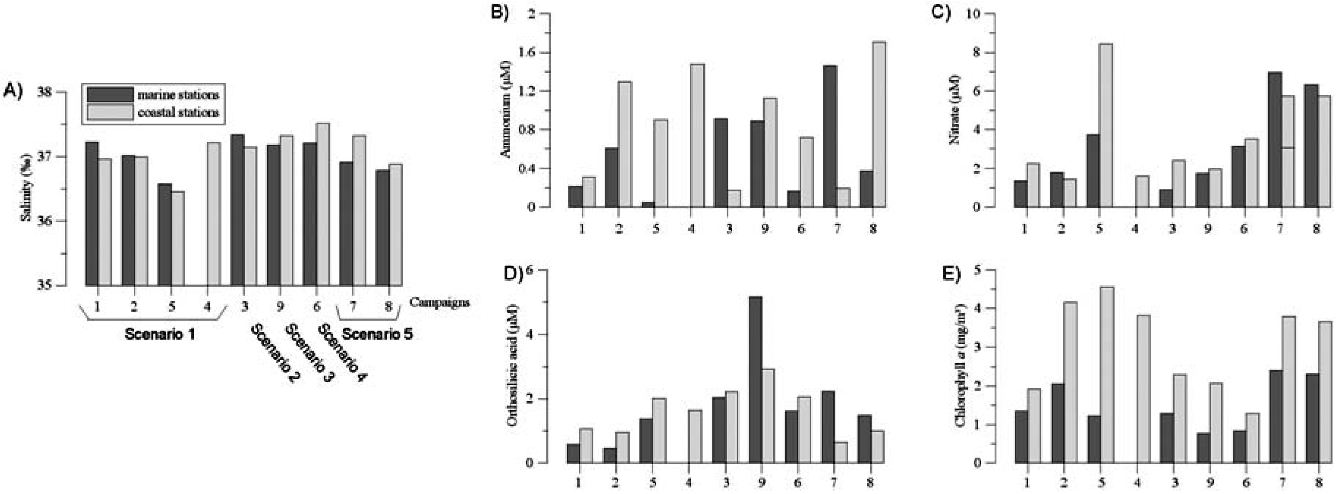


Figure 4. Bar chart for A) salinity, B) ammonium, C) nitrate, D) orthosilicic acid and E) chlorophyll-*a* averages at sea and coastal stations.

phyll-*a* concentrations as the distance from the coast increases. Larger values are found near the cape because, despite the minor continental influence, the hydrodynamic behavior in this area promotes the benthic accumulation of nutrients (sediment trap), which therefore favors high concentrations of chlorophyll-*a*. The second transect, which includes Stations M11, M5 and M3, shows concentration gradients governed by the continental input from the river's freshwater discharge. At Station M7, however, the large chlorophyll-*a* concentration is not significant, since the main continental inputs are due to sporadic freshwater discharges from agriculture. This input is rich in nitrogen but poor in phosphorus and thus limits phytoplankton growth at this point.

Temporal Distribution

As mentioned above, physicochemical and biological parameters are generally determined by three factors:

- The continental inputs.
- The influence of local winds on the continental inputs.
- The internal processes of the system (vertical/horizontal water circulation, processes resulting in mixing/dilution and accumulation processes).

Therefore, in addition to the seasonal patterns that are usually expected in a littoral system, the pattern disruptions caused by continental inputs must also be considered. For example, there is a high correlation between the freshwater discharge rate and the position of the freshwater-seawater interface in stratified estuaries (FALCO, 2003; IBAÑEZ, 1993).

In the particular case of Cullera Bay, the river's freshwater flow measured at the Cullera gauging station is negligible in some sampling campaigns. However, conductivity data obtained at the sampling station close to the mouth of the Júcar River (Station R in Figure 1) shows a marked halocline, suggesting the existence of freshwater inputs downstream from the gauging station originating either from agriculture or the wastewater treatment plant.

Furthermore, the data from the sampling stations inside the bay show only minor vertical temperature variations, mainly close to the bottom. This temperature uniformity is explained partly by the shallowness of the bay, which impedes the development of a real thermocline, and partly by the storms that occurred repeatedly throughout the sampling period, which enhanced the mixing processes and prevented the establishment of typical conditions. Moreover, the absence of a long period of calm prevented the exhaustion of the limiting nutrient in the water column and the collapse of phytoplankton proliferations. The only decreases in chlorophyll-*a* concentration and SRP content were detected during Campaign 5, but neither case approached the typical conditions for the season.

Five different conditions/scenarios were identified from the analysis of each campaign. These scenarios took into account local wind direction, rainfall (registered at the Mareny de San Lorenzo weather station located 2 km north of Cullera Cape), river flow distribution (measured at the Cullera gauging station—see Figure 2) and freshwater-saltwater interface position (obtained at the river sampling station). They also compare the surface-salinity averages at the coastal and sea stations (Figure 4). Three of these scenarios take place in the summer and are characterized by river-flow rates close to zero at the gauging station. Two of the summer scenarios involve breezes from the E-SE and lower salinities at the beach stations than at the sea stations (Figure 4). The first one (Scenario 1) involves sporadic rainfall just before the sampling period and the presence of a halocline at Station R and was detected during Campaigns 1, 2, 4 and 5 (Figure 5A). The second one (Scenario 2) involves a dry period before the sampling campaign and does not present the halocline. It was observed during Campaign 3 (Figure 6A). In Scenario 1, the rain runoff and reduced river-flow rate led to lower average salinities near the coast than at sea, as was seen at practically all of the beach stations north of the river mouth (from P10 to P4). In the second scenario, the salinity decrease near

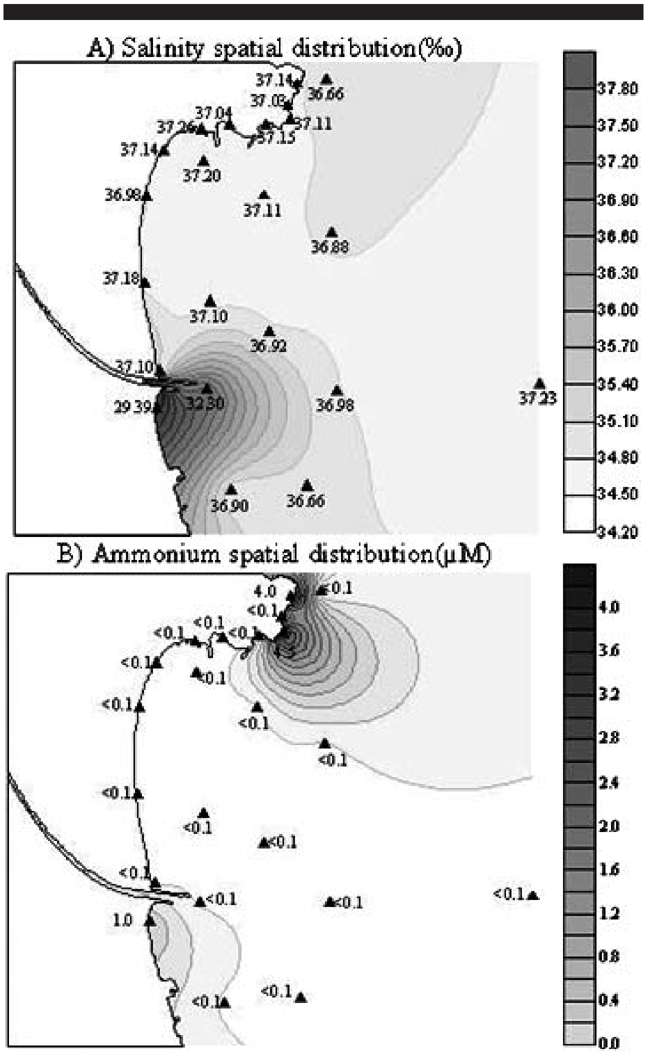


Figure 5. Surface distribution of (A) salinity and (B) ammonium. Scenario 1, Campaign 5 (September 5, 2002).

the coast affects only the four beach sampling stations closest to the river mouth (P10, P9, P8 and P7). In both cases, the lowest salinities are obtained at P11. This is due to the asymmetry in the length of the river-mouth jetties, which tends to direct the weak freshwater plume towards the south. The third summer scenario (Scenario 3) appears in Campaign 9 (Figure 6B), when there is no rainfall prior to the sampling campaign and the river flow rate appears to be zero at the gauging station. Nevertheless, there is a vertical salinity gradient at the river sampling station, suggesting the presence of freshwater inputs into the river downstream from the gauging station, probably due to irrigation water return. The most significant characteristic of this scenario is a freshwater input from the ditch north of Cullera Cape, which is dragged into the bay by NE winds, causing surface salinities at the sea stations to drop with respect to the coastal values.

Scenario 4, registered for Campaign 6 (Figure 7A), is completely different. It is characterized by the absence of rain and river flow in the days prior to the sampling. Nevertheless, the surface salinities at sea stations such as M3, M6 and M4 are very low. Since the salinity at M11 is higher, the low values at the sea stations cannot be explained by the riverine input. Because the prevailing winds during this campaign blew from the W-NW, the irrigation ditch north of the cape can also be ruled out as the source of the fresh water. By comparing the salinity distribution with the nitrate spatial pattern (Figures 7A and 7B) and by verifying that the main source of nitrates in the south is the Júcar output (whereas in the north the high concentration is due to the degradation of the benthic inputs), it was determined that the surface salinity anomalies observed during this campaign were due to local rainfall in the bay. These conditions are not expected to be very common, so this scenario is presumed to occur very sporadically.

Finally, Campaigns 7 (Figure 6C) and 8 present a totally different scenario (Scenario 5). These were the only cases in which the Júcar flow at the gauging station was not zero. They show precipitation in the days prior to the sampling campaign—in the case of Campaign 8, rainfall was very significant (Figure 2). Despite these high rainfall values, observations showed higher surface salinity averages at the beach than at the sea stations, mainly due to the continental influence exerted by the Júcar River in the bay. For Campaign 8, observations show a very marked interface at a depth of 1 m at the river station.

Changes over time for the various nutrients are presented in Figure 4, which shows the surface averages of salinity, nitrate, ammonium, silica and chlorophyll-*a* for each campaign at the sea and coastal stations. This figure shows inverse nitrate and salinity distributions in four of the five scenarios. The exception is Scenario 4 (Campaign 6), in which the freshwater input was due to direct rainfall in the bay; therefore, the nitrate input is insignificant (Figures 4 and 7). However, the "inverse-behavior rule" does not apply to ammonium, as its distribution is governed not only by the salinity structure but also by the origin of the continental inputs, the system's internal dynamics and the presence of benthic inputs in the north of the bay. As a result, depending on which process is predominant, the temporal distribution of ammonium varies. For example, in the first scenario, Campaigns 2 and 4 show higher ammonium and chlorophyll-*a* concentrations than the rest of the Scenario 1 campaigns, suggesting that these high levels can be attributed to the activity of the biological community.

Campaign 5 also stands out in this scenario (Figure 5B), because significant concentrations of ammonium are detected only at the beach stations in the north of the bay, due to freshwater inputs from karst filtrations with water runoff and/or sewage-system leaks. Scenario 1 also includes the campaigns in which the maximum concentrations of chlorophyll-*a* were obtained for all of the beach stations. This suggests that there is a system feedback process that forces the ammonium generated to be reused immediately.

The comparison of Campaigns 7 and 8, both belonging to Scenario 5, shows that the average concentrations of chlorophyll-*a* and orthosilicic acid were very similar but that ammonium values increased sharply at the sea stations during Campaign 7 and at the beach stations during Campaign 8.

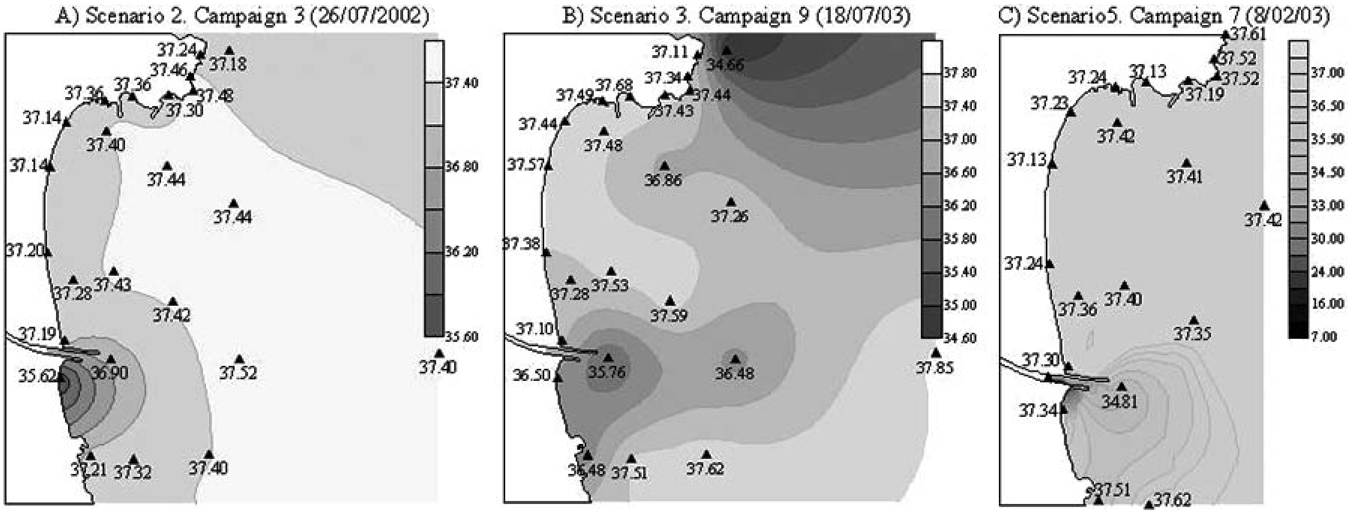
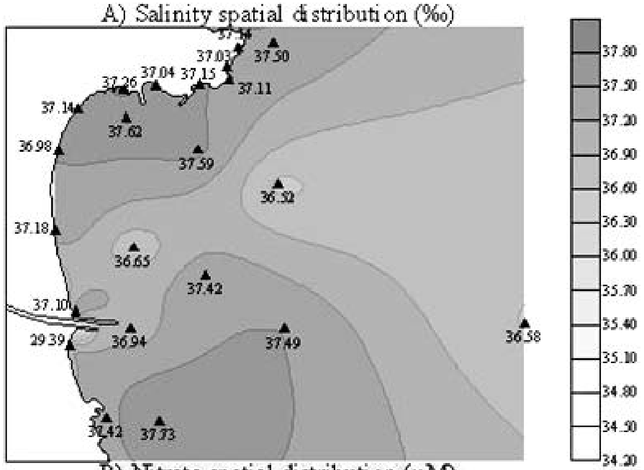


Figure 6. Surface distribution of salinity (‰). (A) Scenario 2 (Campaign 3), (B) Scenario 3 (Campaign 9) and (C) Scenario 5 (Campaign 7).

A) Salinity spatial distribution (‰)



B) Nitrate spatial distribution (µM)

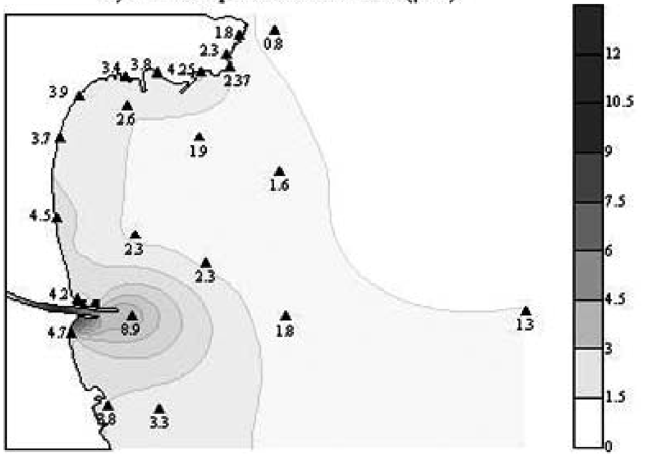


Figure 7. Surface distribution of (A) salinity (‰) and (B) nitrate (µM). Scenario 4, Campaign 6 (November 21, 2003).

This may have been due to the fact that the rainfall prior to the Campaign 7 sampling period was not very significant; therefore, the runoff input was not significant and the main source of ammonium was the river, which easily affects the measurements at the sea stations. In Campaign 8, the spatial distribution of this parameter implies that, in addition to the riverine input, a significant source of ammonium affects the beach stations in the north of the bay, with concentrations even higher than those found in front of the river mouth (M11). This source is probably related to runoff and the removal of the benthic store in the northern area (GONZÁLEZ DEL RÍO, 1986).

Orthosilicic acid behaves differently than expected due to diatom proliferations. Sometimes, in the absence of diatoms, it behaves like nitrate, whose distribution is more closely related to that of salinity, considering that the inputs from different continental sources occasionally show significant differences in silicon content. For example, in Campaign 9, the absolute maximum for silicon is reached at both the sea and coastal stations because the main freshwater source is the ditch north of the cape. Other times, when diatoms proliferate in the bay, the concentration of orthosilicic acid is more similar to SRP concentration, since it becomes the limiting nutrient for these organisms. A clear example of this takes place during Campaign 5, when the silicon concentration decreases considerably.

CONCLUSIONS

The salinity distribution in Cullera Bay shows three differentiated areas:

- A south zone of continental influence, located near the mouth of the Júcar River.
- A north zone, near Cullera Cape, where the existence of karst filtrations and freshwater inputs from an irrigation ditch north of the cape was established.
- A central zone with higher salinity averages, which in-

cludes most of the offshore sampling stations and those located north of the river mouth.

Spatial salinity distribution is indicative of the spatial distribution of some nutrients, especially nitrite, nitrate, orthosilicic acid and TP, since their behavior is inverse to that of salinity. This opposite behavior does not apply to SRP or ammonium because the biological activity in the water body acts as a sink (for SRP and ammonium) and as a source (for ammonium). Orthosilicic acid has intermediate behavior depending on the proliferation of diatoms.

The distribution of chlorophyll-*a* presents its maximum values along the coastline. Its concentration decreases with the distance from the coast along two transects. One of the transects goes from the mouth of the Júcar River to the station that is the furthest offshore (M3). The other runs from the north of the bay to M3 and shows the existence of an accumulation zone in the north of the bay.

Storms during the summer of 2002 prevented the process of limiting nutrient exhaustion that normally occurs in this calm period.

From the analysis of the different sampling campaigns, five conditions/scenarios were detected:

- Scenario 1 (Campaigns 1, 2, 4 and 5) occurs in the summer, with local breezes and sporadic rainfall prior to the sampling days.
- Scenario 2 (Campaign 3) occurs in the summer, with local breezes but with no prior rainfall.
- Scenario 3 (Campaign 9) occurs in the summer, with NW winds that bring water from the ditch north of the cape into the bay.
- Scenario 4 (Campaign 6) presents salinity and nitrate distributions that suggest the presence of rainfall in the bay.
- Scenario 5 (Campaigns 7 and 8) presents significant river flow, so the continental influence is more intense in the bay.

Generally, nitrate behavior is inverse to that of salinity in all of the scenarios except Scenario 4, because the most probable freshwater source in this case is direct rainfall in the bay.

However, the temporal distribution of ammonium varies depending on the dominant process in each scenario because its distribution is governed not only by salinity distribution but also by the origin of the continental inputs, the internal dynamics of the system and the presence of benthic inputs in the northern area.

Because of the effects of the diatom proliferations, orthosilicic acid behaves differently than expected. In the absence of diatoms, orthosilicic acid behaves like nitrate, whereas in the presence of diatoms, it behaves similarly to the limiting nutrient (SRP).

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