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Abstract: The Ebro river flows to the Mediterranean coast of Spain. During its final stretch, the Ebro behaves in a similar way to a highly stratified estuary. This paper describes the transport of nutrients to the Ebro estuary, evaluates the general movement of nutrients in the estuarine region, using a mass balance approach, and estimates the amounts of nutrients discharged to the coastal environment. Given the strong saline stratification, this study only includes the surface layer that contains the continental freshwater. The annual nutrient budget for the Ebro estuary shows a net excess for nitrogen and phosphorus, while silicate almost attains equilibrium between addition and removal. There are several reasons for gains in nitrogen and phosphorous: a contribution of dissolved and particulate compounds in the freshwater (some of which are mineralized); a lower uptake of phytoplankton indicated by chlorophyll reduction in the estuary; an entrainment of the nutrient-rich upper part of the salt wedge; and, to a lesser extent, the impact of wastewater and agricultural water use. The biggest load discharged into the Mediterranean Sea by the Ebro is nitrogen, followed by silicate with over 10 000 tons of each deposited annually. Phosphorus is discharged at relatively low concentrations and with an annual load of about 200 t yr-1.

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NUTRIENT FLUX AND BUDGET IN THE EBRO ESTUARY

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ABSTRACT

The Ebro river flows to the Mediterranean coast of Spain. During its final stretch, the Ebro behaves in a similar way to a highly stratified estuary. This paper describes the transport of nutrients to the Ebro estuary, evaluates the general movement of nutrients in the estuarine region, using a mass balance approach, and estimates the amounts of nutrients discharged to the coastal environment. Given the strong saline stratification, this study only includes the surface layer that contains the continental freshwater. The annual nutrient budget for the Ebro estuary shows a net excess for nitrogen and phosphorus, while silicate almost attains equilibrium between addition and removal. There are several reasons for gains in nitrogen and phosphorous: a contribution of dissolved and particulate compounds in the freshwater (some of which are mineralized); a lower uptake of phytoplankton indicated by chlorophyll reduction in the estuary; an entrainment of the nutrient-rich upper part of the salt wedge; and, to a lesser extent, the impact of wastewater and agricultural water use. The biggest load discharged into the Mediterranean Sea by the Ebro is nitrogen, followed by silicate with over 10 000 tons of each deposited annually. Phosphorus is discharged at relatively low concentrations and with an annual load of about 200 t yr^{-1}.

Key words: Salt-wedge estuaries, nitrogen, phosphorus, silicates

1. INTRODUCTION

Estuaries are ecosystems of transition between continental freshwater and marine waters. The load of nutrients in rivers (primarily nitrogen and phosphorus) has been increasing as a result of an expanding human population in the river catchment area. This increase is a result of urban wastewater, as well as the increased use of farmland fertilizer and animal manure – with consequent leaching into the river course (Downing et al., 1999; Bricker et al., 2008). However, the load of silicate has not followed this trend because it is less influenced by human activities. Silicate is deposited behind dams built on rivers and this reduces the load of silicate flowing downstream (Humborg et al., 1997; Sferratore et al., 2008). However, these trends cannot be extended to coastal waters because of the role estuaries play in the biogeochemical cycle of nutrients. This cycle may cause gains or losses in various elements as they flow towards the sea (Nedwell et al., 1999; Tappin, 2002).

The Ebro flows into the Mediterranean Sea and forms a highly stratified estuary – where superficial freshwater flows into the sea, while another deeper body of seawater penetrates towards the land. Between these two layers there is a transitional zone (halocline), where salinity changes sharply in just 40-50 cm. The estuary of the Ebro is located in a microtidal sea, so advective circulation prevails over tidal flow, and the advance or retreat of the salt wedge mainly depends on river discharge (Ibáñez et al., 1997). Because the river and its tributaries are heavily regulated by 187 dams along its basin (Batalla et al., 2004) the presence of a salt wedge in the final kilometres of the Ebro is normal for most of the year (Dolz et al., 1997). The salt wedge disappears only when the flow of the river rises above 400 $m^3 s^{-1}$ (Guillen and Palanques, 1997; Dolz et al., 1997; Falco, 2003). Historical records for water flow in the Ebro show a decrease of nearly 40% in mean annual flow over the last fifty years (Sabater et al., 2008). This negative trend is one of the highest among the rivers flowing into the Mediterranean Sea, and is a consequence of the construction of dams on the one hand, and precipitation decrease in the basin, on the other (Ludwig et al., 2003).

The Ebro estuary is currently subject to various pressures. It is known that the nutrients reaching the waters surrounding the continental shelf at the mouth of the Ebro are vital for sustaining fish species such as sardines (*Sardina pilchardus*) and anchovy (*Engraulis encrasicolus*). These nutrients are essential for increasing the fertilization and production of local plankton, which is crucial for the survival of fish larvae. In the 1970s, these two species accounted for two-thirds of the catches made in the area of the continental shelf influenced by the Ebro (Bas et al., 1989). Evidence has been found of the influence of river inputs and the mixing of wind currents on the productivity of sardines and anchovy in the north-western Mediterranean Sea (Lloret et al., 2004). In the last 40 years, landings of anchovy have declined while those of sardine have not (Lloret et al., 2004).

The Ebro is one of Spain's largest rivers and the level of water utilization with dams and irrigation systems is very high (Dolz et al., 1997 and Batalla et al., 2004). Spain has one of the highest dam/inhabitant and dam/surface ratios in the world (Jimenez Torrecilla and Martinez-Gil, 2005), and a new national water plan was approved in 2001. This plan included the construction of more than 100 new reservoirs, as well as the transfer of 1050 hm^3 per year from the lower Ebro to the northern and southern Mediterranean regions (Day et al., 2006). This plan was halted by a change of government in 2004. The decision to stop the plan continues to cause severe protests from potential water users – who consider the transfer of these waters as crucial for the socioeconomic development of regions to the south of the Ebro.

In addition, the implementation of the EU Water Framework Directive 2000/60/EC required a study of the processes that determine the quality of freshwater, transitional, and marine waters; as well as a definition of the strategies and plans for improving the ecological quality of the water mass. For this reason, understanding the net flow of nutrients from the Ebro to the sea became essential for an interpretation of the current situation and a prediction of future trends (ACA, 2005).

The objectives of this study are to describe the transport of nutrients to the Ebro estuary and to evaluate the general movement (including transport, removal and addition) of nutrients in the estuarine region, using a mass balance approach. This approach employs a simple box model for evaluating net movement of water and nutrients through the estuary, based on data collected during nine cruises made under different environmental conditions. This approach is simple in concept, rapid to develop, and practical for establishing future specific data collection objectives.

2. STUDY AREA

The Ebro is the longest European river (928 km) that empties into the Mediterranean Sea. It also has the second largest basin (88 835 km^2), and the third largest flow (mean annual discharge over the last 20 years of the 20th century was 384 m^3 s^{-1}(Guillen and Palanques, 1997)). High discharge occurs on average from October to March, because of the oceanic climate, characterised by abundant rainfall, which reaches a peak in the winter months, and in May because of snowmelt from the Pyrenees. Low discharge occurs from July to October. Many dams in the basin regulate the annual flow. Regulation of the Ebro in the 1960's caused a major change in discharge pattern by altering flow timing and particularly, flood peaks (Lopez-Moreno et al., 2002). The Mequinenza and Ribarroja reservoirs (located on the main river and about 100 km from the mouth) have a notable regulatory effect on flows in the delta (Dolz et al., 1997). The main activity in the basin is agriculture (50% of the surface area of the basin). With the construction of reservoirs, dry farming gave way to irrigation farming.

Currently, irrigation farming in the Ebro basin covers 783 900 ha or 9.2% of the total surface area of the basin (CHE, 2008). The main crops are vineyards, orchards and corn (Sabater et al., 2009). Density of population in the area is 33 inhab. km^{-2}, which is well below the national average of 78 inhab. km^{-2}.

This paper focuses on the river estuary, which is located inside the delta formed by the river on the Mediterranean coast (Figure 1). The Ebro delta covers 320 km^2 and is divided in the middle by the river. Of its surface area, rice fields account for 66.5%, fruit and orchards 6.3%, urban areas make up 3.1 %, and the remainder is a natural park with beaches, marshes, lagoons, etc. Rice farming in the delta involves continuous flooding between May and September, with water from the Ebro entering the rice fields, and moving through them slowly before discharging into coastal lagoons and bays of the delta, or the sea itself. The Ebro delta has a population of 16 700 inhabitants, approximately 13 000 of whom live in Deltebre and Sant Jaume d'Enveja. The wastewater from these two towns on the banks of the Ebro is dumped into the river. The Ebro estuary is a 'salt wedge estuary' or type 4 in the Hansen-Rattray classification (Ibañez et al., 1997). As the estuary is located in a micro tidal area (with a maximum range for astronomical tide of 0.25 m) it has a strong and clearly marked halocline with dynamics driven mainly by river discharge. Ibañez et al. (1997) found a high correlation between river discharge and the depth of the salt wedge in the estuary.

3. MATERIAL AND METHODS

Nine sampling campaigns in the Ebro estuary were carried out during a year-long period (from April 1999 to February 2000). The cruise dates were: (1) April 3, 1999, (2) April 5, 1999, (3) April 7, 1999, (4) July 7, 1999, (5) July 8, 1999, (6) July 12, 1999, (7) October 6, 1999, (8) February 3, 2000, and (9) February 5, 2000. In addition, a detailed bathymetric map was made of the last 18 km of the river between 18 and 22 July, 1999.

Water samples were taken at six river stations shown in Figure 1. Samples were collected at different depths of the water column. Because very steep gradients occur in the area of the interface, more intense and accurate samplings were made in this area. Details of the sampling techniques are described in Mosso et al. (2008). In addition, a Hydrolab Surveyor 3 multiparametric probe was used to make vertical conductivity profiles.

It is important to emphasize that only data from samples collected in the layer of freshwater above the start of the halocline was used for determining the flows. The remaining data was used in the interpretation of biogeochemical processes. The depth of the freshwater-saltwater interface varied at each sampling station (becoming deeper as distance from the sea increased) and for each flow of the Ebro. This depth was obtained from the conductivity profiles, using the first inflection point in the conductivity function plotted against depth (Legovic, 1991).

The following parameters were analysed in all the samples: salinity, chlorinity, ammonium, nitrate, nitrite, dissolved inorganic phosphorus (DIP), total phosphorus (TP), silicate, and chlorophyll a. Dissolved inorganic nitrogen (DIN) was calculated as the sum of: NO_3^-, NO_2^- and NH_4^+. Nutrient analysis was performed with an Alliance Instruments Evolution II Autoanalyzer. The methods employed are described by Treguer and Le Corre (1975), when considering Parsons et al. (1984) and Kirkwood et al. (1991). A persulphate digestion (Valderrama, 1981) was made for TP and the phosphate was subsequently analyzed. Salinity

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was determined by means of an induction conductivity-meter (Grundy Environmental Systems Corporation, 6230 N), calibrated with suitable standards (IAPSO Standard Seawater, Ocean Scientific International Ltd, K15=0.99986, S=34.995‰). Chlorinity values were computed from salinity values using Wooster's linear equation (Riley and Chester, 1971). Chlorophyll *a* was measured using the trichromatic method, based on spectrophotometry (APHA, 2005).

Data regarding the river flow was provided by the Ebro Hydrographic Confederation and taken from the Tortosa gauging station.

Approach for estimating the annual nutrient flux arriving at the Ebro estuary

The flux or load of a chemical substance transported by a river is the simple product of the chemical concentration (*C*) and water discharge (*Q*). But for most substances *C* is not constant over time. Calculating the load values for a station at a given point is relatively straightforward using the concentrations of analyzed samples and the flow volume at a specific point. It is much more complex to calculate fluxes for longer periods of time to any degree of certainty because this requires long-term concentration and discharge measuring.

Niencheski and Windom (1994) recommended the following method for estimating the annual flow of nutrients reaching an estuary:

$$Total\ load\ (t\ yr^{-1}) = K \sum_{i=1}^{n} C_i Q_i / n \qquad\qquad Eq\ (1)$$

Where *K* is the conversion factor to take account of the record period (*K*= 12 months/number of sampling months); C_i is the instantaneous concentration as determined by discrete samples (t m^{-3}); Q_i is the instantaneous discharge at the time of sampling (i.e. daily average) (m^3 yr^{-1}); and *n* is the number of sampling campaigns.

Approach for calculating nutrient mass balance

We assessed the general movement of nutrients in the estuarine region using a mass balance approach. To this end, the study area was divided into five boxes (Figure 1). Box A represents the highest part of the estuary and contains two urban areas (Deltebre and Sant Jaume d'Enveja); boxes B, C and D represent the middle of the estuary; while zone E shows the area nearest the sea. This division was made on the basis of physiographic features, a bathymetric survey of the final section of the river, the location of the sampling stations, and the depth of the halocline. The position of the halocline depends on the flow and it alters the volume of freshwater flowing into the Mediterranean Sea. So, the depth of the halocline varies for each box and sampling day.

The mass balance of nutrients in the estuary of the Ebro delta was obtained from the difference between the measured mass values of nutrients (M_m) taken from samples collected in the field, and estimated mass values of nutrients (M_e) from conservation equations (Eq 2). If the difference is positive (balance > 0), there is an addition (excess) of the nutrient, while a negative balance would indicate a reduction (loss) of nutrients in the system.

The measured nutrient values (M_m) in the freshwater layer taken from each of the sampling stations were averaged to calculate the mass in each box (t). The estimated mass values of the

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nutrients (M_e) are a function of the measured concentrations in each of the samples, as well as the length of residence time (flushing time), and the current flow. They can be expressed as:

$$M_e(t) = T_i \cdot C_{(box-1)} \cdot Q_i \qquad\qquad \text{Eq (2)}$$

where $C_{(box-1)}$ is the measured concentration of the nutrient in the previous box (t m^{-3}). For box A, $C_{(box-1)}$ is the concentration of the nutrient in the freshwater input from the Ebro during sampling period i as measured at station R; Q_i is the instantaneous discharge at the time of sampling (m^3 h^{-1}); and T_i is the residence time (h).

Residence time is the time required to replace an equivalent volume of freshwater in an estuary at the river discharge rate. The formula below is applied to obtain the residence times for each box and sampling day. It takes into account that the water in the upper layer sometimes has a low level of salinity (Dyer, 1997).

$$T_i(h) = V_i/Q_i \left(1 - S_{box}/S_{ref}\right) \qquad\qquad \text{Eq (3)}$$

Where V_i is the volume of each box for a particular sampling day (m^3); Q_i is the instantaneous discharge at the time of sampling (m^3 h^{-1}); S_{box} is the average salinity measured in the freshwater layer for each box; and S_{ref} is the level of salinity in the Mediterranean Sea.

Finally, the previously mentioned bathymetric profile cross sections were used to calculate the volume of each box. The locations where these profiles were made are indicated with lines in Figure 1 and the limits of each box are also defined. For each of these profiles a cross sectional value (m^2) and the distance to the previous profile (m) is available. Because we are only interested in calculating the volume of freshwater, it was necessary to estimate the position of the interface for each box for each sampling day (as this varied depending on the flow). The interface position was calculated for each profile and sampling day as the mean depth from the start of the halocline between the two closest sampling stations up and downstream of each profile.

The calculations assume that the system is in steady state (averaged over the year) and that the only significant inputs of nutrients and freshwater are from the Ebro as it empties into the upper estuarine region (i.e. at station R).

As mentioned before, the Ebro estuary is highly stratified, a salt wedge is present most of the year, and the deeper salt water mixes only weakly, or scarcely mixes at all, with the fresh surface water (Falco et al., 2006). For the purposes of this study, we worked only with the freshwater layer.

4. RESULTS AND DISCUSSION

Table 1 shows the flow data, depth of the interface, volume and residence time for each box in each of the four seasons of the year, taken from the data measured in the nine sampling campaigns. The Ebro had the lowest river discharge during summer because of the strongly reduced precipitation during this season and increase in water consumption for irrigation (Sabater et al., 2009). Maximum values were observed in winter; the February maximum is

typical for the rivers that are rainfall dominated (such as the Ebro). This pattern of seasonal variation is typical of most of the Mediterranean rivers, although in the Ebro's case it is tempered by the numerous dams along it. In the salt wedge estuary, the depth of the salt wedge is mainly influenced by the circulating flow (Ibañez et al., 1997). Hence, in the summer the interface was shallower in all the sampling stations. Figure 2 shows how the depth of the freshwater-saltwater interface decreased with decreased distance to the mouth of the estuary, illustrating the characteristic horizontal distribution of a salt wedge estuary.

Table 2 shows the means of chlorinity, nutrients and chlorophyll *a* recorded at each of the sampling stations for each season. It also gives information on R (river end member) station and S (sea end member). All raw data are presented in Falco (2003). As can be seen, the maximum concentrations of chlorophyll occurred in spring both in R and the stations located within the estuary, whereas the maximums for nitrates occurred in winter and autumn for DIP and silicate. Maximums for nitrate in station R occurred in winter, coinciding with the winter rains flushing nitrate from the catchment. However, the minimum concentrations did not occur in summer, as might be expected, because the practice of irrigation farming in the basin generates returns from irrigation full of nitrate. DIP input is generally influenced by point sources, such as wastewater. Consequently, the lowest concentrations occurred in winter because there was an increase in flow but the discharges did not vary. As regards silicate, the changes in concentration during the year are more a product of changes in biological activity in the dams upstream than seasonal changes in the silicate load. The same is true of the maximum of chlorophyll in spring, which is a result of the seasonal cycle of the phytoplankton stored in the reservoirs located 100 km upstream. If 5 µg l^{-1} of plankton chlorophyll concentration is taken as the limit which defines waters as either oligotrophic or eutrophic (Margalef, 1983), then the Ebro is eutrophic. The table also includes the standard deviation for each parameter, which was high in the case of ammonium and DIP, probably because these are the parameters most influenced by point sources.

Figure 2 also shows how chlorinity increased the nearer the stations are to the mouth. In stratified estuaries there is a net flux of surface water to the sea and another of deep water to the headwaters of the estuary. Mixing occurs through the interface between surface and deep waters all along the estuary, which means that the water flowing on the surface layer downstream of the estuary increases in chlorinity as a result of contact with saline water (Dyer, 1997). With the exception of the autumn sampling, figure 2 shows that certain nutrients, such as ammonium and DIP, had higher values at stations D and E (those closest to the mouth). This is probably due to the mineralization that occurs in stations with a greater saline influence because of contact with seawater.

4.1 Chemical transport to Ebro Estuary

Because we did not have instantaneous discharge values at Station R (where the Ebro empties into the estuary), we assumed that the discharge was the same as in Tortosa – the last gauging station in the direction of flow and about 45 km from the mouth of the river. The transit time from Tortosa to the river mouth is about one day for flows smaller than 500 m^3 s^{-1} (Maidana et al., 2002). Thus, discharges at the upper estuary were calculated using daily mean discharge values for the river flow at Tortosa – as recorded the day before sampling. The Ebro is heavily regulated and so the variations of rainfall are softened. This means that the variation in the flow at the end of the river is directly related to agricultural and hydroelectric usage, and varies less than it would under a natural regime. As a result, the salt wedge is present for most of the year, and station R may considered as representing freshwater. During the twelve-

month period in which the samples were taken (between April 1999, and March 2000), the $400 \text{ m}^3 \text{ s}^{-1}$ level was only exceeded 2.7 % of the time. This is the limit that various authors (Guillen and Palanques, 1997; Dolz et al., 1997; Falco, 2003) have proposed as the flow rate above which the salt wedge disappears from the final stretch of the river.

The annual load of ammonium, nitrite, nitrate, DIN, DIP, TP, and silicate brought by the Ebro to the estuarine region has been calculated using Equation 1. Table 3 shows the annual flow of materials associated with the freshwater input, and it can be seen that the most significant input corresponded to DIN and silicate, with 13 560 and 12 416 t yr^{-1} respectively, while the DIP input was only 180 t yr^{-1}. In the DIN, nitrate represented the 96% of the total. The Ebro river presents such amounts of nutrients because Spain is a country with a strong tradition of farming and livestock, and water resources contain increasing levels of nitrate. This is mainly due to the abuse of fertilizers, poor management of livestock waste, and to a lesser extent, domestic wastewater (Pinilla, 1997).

Table 3 also compares the nutrient input to the Ebro estuary with four other systems, one of which is a regional river with similar characteristics to the Ebro; the others being basins with similarities and varying land uses. The systems are: the Rhone in France (Ludwig et al., 2003), Patos Lagoon estuarine zone (Brazil) (Niencheski and Windom, 1994); the total input from the nine rivers on the South-Eastern coast of the USA (Windom et al., 1975); and the estimated fluvial fluxes (mainly from the Tama River) in Tokyo Bay (Maeda, 1991). The Rhone is a Mediterranean river with similar seasonal flow rate variations to the Ebro although it has not followed the same trend of reduction in water discharge that the Ebro has shown in the last 40 years. This is important because also in this basin, impoundments and dams are frequent. Apparently, human activities have less impact on the amount of annual water flow out of this basin, or this impact is compensated by more humid conditions (Ludwig et al., 2003). The basin is predominantly agricultural, with 53.7% of the soil given over to crop farming. In Patos Lagoon, as with the Ebro, the waters are used for irrigating shore croplands (especially rice), and the dumping of untreated domestic urban effluents occurs in the salinity gradient (Niencheski et al., 2006). Ebro input was also compared with the total input from nine rivers which account for 95% of the total discharge of freshwater in the southeastern coast of the USA (between Georgetown, South Carolina, and Jacksonville in Florida) (Windom et al., 1975). The Ebro River, Patos Lagoon and the southeastern coast of USA have a similar geomorphology. Tokyo bay was chosen, because it is one of the most euthrophied semi-enclosed bays in Japan (Maeda, 1991). In the Tama basin, the upper reaches of the river are primarily surrounded by woodland, whereas the middle and lower reaches are home to business and residential districts, with the consequent dumping of metropolitan wastewaters in the river (Hashiba et al., 2000).

It can also be seen that the values of nitrate (in t yr^{-1} and in t km^{-2}) for the Rhone and Ebro were higher than those in the USA, as well as Patos Lagoon in Brazil. Flows calculated per unit area were higher for nitrite than in Patos Lagoon; while the level of ammonium was slightly lower than in Patos Lagoon and the USA. After Tokyo Bay, the Rhone and the Ebro were the systems with the highest DIN contribution (in t km^{-2}), mainly because of its high nitrate concentrations. Nitrate is usually dominated by diffuse sources, in particular agriculture, which is characterized in southern Europe by intensive cultivation practices, with an estimated nutrient application to agricultural land (inorganic fertilizer and manure) of between 30-70 kg N ha^{-1} (Ludwig et al 2009). The DIN flows of the Ebro and the Rhone were moderate, however, when compared to Tokyo Bay. The Tama River is highly polluted by the waste waters of Tokyo City (Takii and Fukui, 1991), where, in addition to the nitrate, the

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other types of DIN (ammonium and nitrite) could also be present due to the high levels of organic pollution.

The flow of phosphorus in the Ebro (t km^{-2}) was similar to Patos Lagoon and Rhone and substantially lower than Tokyo Bay. As already mentioned, Tokyo Bay is very eutrophied – much more so than the Ebro. Phosphorus pollution is normally dominated by point sources, such as urban waste waters, as in the case of the Tama.

The level of silicate (t km^{-2}) in the Ebro, was lower than in Patos Lagoon, but was still in the same order of magnitude; while data from the other areas was unavailable since silicate is not often measured by programs monitoring the water quality of rivers. In contrast to nitrate and phosphate, dissolved silicate is almost exclusively derived from chemical weathering of rocks and soils. Anthropogenic factors that can modify the natural riverine silicate loads are the construction of major dams and the subsequent sequestration of silicate in the reservoir. When eutrofication conditions are favourable for diatom growth, silicate retention can also occur in large rivers.

4.2 Nutrient mass balance for the Ebro Estuary

In Figure 3, the excess (values > 0), or deficit (values < 0) for ammonium for each of the five boxes is plotted against time and using data collected during the nine cruises. The lines connecting the results from each sampling period clearly assume that the content of the box changes linearly with the time between sampling periods. Similar plots were constructed for the other nutrients. This figure primarily shows an excess of ammonium in the box A that receives ammonium from the river, as well as from the sewage discharged by the two urban areas (Deltebre and Sant Jaume d'Enveja) with a combined population of some 13 000 inhabitants. However, in boxes B and C there are losses; while in the boxes nearest to the mouth (D and E) gains are recorded.

The excess or deficit was integrated for each nutrient and each box over the period of the study in order to estimate the net nutrient excess or deficit in the estuary. The final value is simply the area under the polygonal function, obtained geometrically by calculating the area of the trapezoids, which are limited by the segments of the polygonal function and the axis of the abscissas. Results were then adjusted for an annual cycle using a conversion factor which takes into account the period of the study (K= 12 months/number of sampling months). Figure 4 shows the net budgets for nutrients for the entire estuary (i.e. excess or deficit) for all five boxes together. The results shown in figure 4 indicate that there was a net excess of ammonium, nitrate, DIN, and DIP; while there was a deficit of TP, nitrite and silicate in the Ebro estuary over the annual cycle.

A possible direct anthropogenic source of DIN and DIP arrives in the estuary from the two towns, Deltebre and Sant Jaume d'Enveja. Although it is difficult to estimate the input of nutrients associated with sewage, the estimated discharge per capita is 7 kg N yr^{-1} and 0.2 kg P yr^{-1} (Niencheski and Windom, 1994). By applying these values to the estimated population, it may be possible from the total observed excess, to explain a level of 22% for nitrogen and 12% for phosphorus.

An additional anthropogenic source could be the ricefields located alongside the estuary (more than 200 km^2). It would be reasonable to believe that some of the gains are from these

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systems, but studies conducted by Forés (1989) in the Ebro delta, showed the ricefields acting as a natural filter on dissolved nutrient content since ricefields can retain nutrients in their inorganic form and release them at lower concentrations than at which they entered, and in different forms - organic and particulate (i.e. as detritus). One of the main characteristics of ricefields is that they are subject to continuous flooding: the freshwater from the Ebro continuously enters and exits the ricefields. Drainage channels collect water from the ricefields and, with some chemical transformations in their nutrient content, transport it to the coastal lagoons (mainly La Encañizada) and the bays of Fangar and Alfacs (Forés, 2001). However, it was found that some ricefields in the area drain directly into the Ebro, and this certainly represents a contribution of inorganic nitrogen forms. These contributions are difficult to quantify because of variations in the process of fertilization and assimilation.

Another additional anthropogenic source could be some of rice processing industry in the Ebro delta that deliver wastewater into the estuary. These contributions close to the urban areas have not yet been quantified.

Nutrients associated with the total suspended matter (TSM) input from the Ebro River may be an additional source, and thus explain the observed excesses if it is assumed that all particulate nitrogen and phosphorus in the TSM is transformed into inorganic forms. Figure 4 shows TP losses (-8.6 t yr^{-1}), while gains are shown for dissolved inorganic forms (22.4 t yr^{-1}). TP includes dissolved phosphorus (inorganic (DIP) and organic) as well as particulate phosphorus. TP losses within the estuary can only be due to a loss of particulate phosphorus, as well as dissolved organic forms, some of which mineralize into dissolved inorganic forms, and some of which fall towards the salt wedge and, consequently, to deeper layers. There was no data for total nitrogen (TN). However, we can estimate the flow of particulate nitrogen plus dissolved organic nitrogen (PN + DON) by using the following approach: calculate the difference between TP and DIP and assume that all particulate phosphorus (PP) is organic, and that PP plus dissolved organic phosphorus (DOP) maintain the Redfield relationship (Redfield et al., 1963). This enables an estimation of the flows of particulate and dissolved organic nitrogen entering the estuary. Using this approach, we estimate that around 2 557 tons per year of PN + DON enter the estuary. These estimates coincide with PN data for the last 50 km of the Ebro presented by Muñoz and Prats (1989), which indicate that particulate nitrogen (PN) is between 0.1 and 0.5 mg l^{-1}. This means that between 576 and 2 878 PN t yr^{-1} should enter the estuary. Some of this fraction may be mineralized and oxidized into dissolved forms, while some may have settled to deeper layers.

To explain the gains in DIN and DIP it is necessary to consider that within the estuary there was a reduction of 2.3 t yr^{-1} of chlorophyll *a* (Fig. 4). A decrease in the amount of chlorophyll implies a decrease in nutrient uptake by phytoplankton.

Also, to justify the excess of DIN and DIP within the estuary it is necessary to consider the contributions coming from the salt wedge. For the purposes of this study, we worked with the surface water layer alone, but in estuaries with a distinct saline stratification there is an increased level of salinity from the beginning to the end of the estuary in the freshwater layer. This is because of the entrainment of the upper part of the salt wedge to the layer of freshwater that lies immediately above (Dyer, 1997). This mixing process provides salts, as well as nutrients. Figure 5 shows the absolute maximum levels of nutrients in the halocline. These high levels in the halocline are a consequence of mineralized organic matter settling from the surface layer, which can be temporarily retained at the interface. This is probably due to the sudden increase of fluid density acting as a filter, leading to a decrease of particle

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settling velocity and its temporal retention. This phenomenon has also been observed in other estuaries such as the stratified Krka (Sempere and Cauwet, 1995).

Inputs from the air could only be significant for nitrogen. Gaseous forms of phosphorus and silicate compounds have an almost negligible role because significant quantities have not been found in the natural environment. Nedwell et al. (1999) have demonstrated that the nitrogen fixation in estuarine zones represents a maximum of 1% of the total nitrogen input to an estuary, and therefore this process has little influence on the balance of nitrogen in an estuary.

The box model approach indicates that less than 1% of the silicate flux to the Ebro was removed within the Estuary. The level of dissolved silicate in the water varied greatly throughout the year (from 55.2 μM for July, 1999, to 108.3 μM in October, 1999) and the percentage of diatoms within the whole phytoplankton community also varied (50% in July, 1999, and 4% in October). As a result of these variations, the system attains equilibrium in between silicate addition and removal. These significant changes in the levels of silicate and diatoms in the Ebro are probably influenced by the phytoplankton content of water stored in reservoirs located 100 km upstream. It must be remembered that wastewater does not supply silicate, and that the only other possible source is the mineralization of those phytoplankton species that contain the nutrient – such as diatoms. The regeneration of silicate is not organic degradation, but the result of chemical processes which are much slower than those of nitrogen and phosphorus (Dugdale and Wilkerson, 2001). We therefore assume that the main cause of the deficit is the uptake of silicate from those species that use silicate as a nutrient. To check whether this supposition is feasible, an estimate was made of the amount of silicate that could be absorbed by the diatoms. The estimation was based on the available percentage of diatoms and the amount of chlorophyll. Estimates of carbon content were made with reference to the relationship between carbon and chlorophyll (Ciotti et al., 1995, Faugeras et al., 2003). The average amount of silicate that the diatoms could absorb daily was calculated using the Redfield ratio, integrated and adjusted to an annual cycle, as 272 t yr^{-1}. These calculations support the supposition that losses of 102 t yr^{-1} of silicate may result from uptake by diatoms. It must also be remembered to take into account the entrainment of deeper waters that contain less silicate (see Fig. 6), unlike the phosphorous and nitrogen, and this will further explain the losses occurring in the estuary.

Nitrogen followed by silicate were the main products poured into the Mediterranean Sea by the Ebro (more than 10 000 tons of each annually). This data is consistent with information obtained for the Ebro by Cruzado et al. (2002) for the period 1996-1997. Deposited in smaller quantities (around 200 t yr^{-1}), it is noteworthy that phosphorus is the limiting nutrient for phytoplankton growth in the Mediterranean Sea (Krom et al., 2004). These contributions are important because they increase the local fertilization and production of plankton, which is crucial for the survival of fish larvae. It has been demonstrated by authors such as Palomera et al. (2003) and Lloret et al. (2004) that the Ebro runoff on the continental marine shelf affects the productivity of two of the most abundant species of small pelagic fish: sardines and anchovies.

5. CONCLUSIONS

The annual load of DIN provided by the Ebro to the estuary region was 13.5 10^3 t yr^{-1}. Nitrate represented 96% of the total – whose origin was mostly leaching from farmland and livestock. The load of silicate was at the same level as DIN, and the level of DIP was 180 t yr^{-1}.

The annual nutrient budget for the Ebro estuary showed an excess for nitrogen and phosphorous. Nevertheless, phosphorous was discharged at relatively low concentrations and it is the limiting nutrient. The excess can be explained by several factors: contributions of dissolved and particulate compounds (some of which are mineralized and oxidized in a dissolved form); a reduced uptake by phytoplankton because of a decrease of chlorophyll in the estuary; the entrainment of the upper and nutrient-rich part of the salt wedge; and to a lesser extent, the effects of wastewater. Nevertheless, the estuary showed equilibrium between addition and removal for silicate.

The implementation of the EU Water Framework Directive will require complementary studies of the Ebro to establish trends in transport of dissolved and particulate elements from continental waters to the estuary and to understand the effect of changes in the supplied nutrients on the coastal ecosystem.

ACKNOWLEDGEMENTS

6- REFERENCES

Agència Catalana de l'Aigua (ACA), 2005. Caracterització de masses d'aigua i anàlisi del risc d'incompliment dels objectius de la Directiva Marc de l'Aigua (2000/60/CE) a Catalunya (conques intra i intercomunitàries). Document de síntesi. En compliment als articles 5, 6 i 7 de la Directiva. Departament de Medi Ambient i Habitatge, Generalitat de Catalunya, Barcelona, 79 pp.

APHA, 2005. Standard methods for the examination of water and wastewater, 21th edition. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, 1368 pp.

Bas, C., Macpherson, E., Sardà, F., 1989. Peces y pescadores. Los niveles tróficos explotables. In: R. Margalef (Editor), El Mediterráneo occidental. Omega, Barcelona, pp. 298-319.

Batalla, R.J., Gómez, C.M., Kondolf, G.M., 2004. Reservoir-induced hydrological changes in the Ebro River basin (NE Spain). Journal of Hydrology 290, 117–136.

Bricker, S.B., Longstaff, B., Dennison, W., Jones, A., Boicourt, K., Wicks, C., Woerner, J., 2008. Effects of nutrient enrichment in the nation's estuaries: A decade of change. Harmful Algae 8, 21–32.

Ciotti, A.M., Odebrecht, C., Fillmann, G., Möller, O.O. Jr., 1995. Freshwater outflow and Subtropical Convergence influence on phytoplankton biomass on the southern Brazilian continental shelf. Continental Shelf Research 15, 1737-1756.

Confederación Hidrográfica del Ebro (CHE), 2008. Regadío y usos agrarios. Confederación Hidrográfica del Ebro, Zaragoza, Spain. Available from: <http://www.chebro.es/usosRegadios.htm> (verified 9 oct. 2009)

Cruzado, A., Velásquez, Z., Pérez, M.C., Bahamón, N., Grimaldo, N.S., Ridolfi, F., 2002. Nutrient fluxes from the Ebro River and subsequent across-shelf dispersion. Continental Shelf Research 22, 349-360.

Day, J.W. Jr., Maltby, E., Ibáñez, C., 2006. River basin management and delta sustainability: A commentary on the Ebro Delta and the Spanish National Hydrological Plan. Ecological Engineering 26, 85–99.

Dolz Ripollés, J., Gómez Valentín, M., Nieto Romeral, J., 1997. El Ebro en el delta. Revista de Obras Públicas 3368, 7-14.

Downing, J.A., McClain, M., Twilley, R., Melack, J.M., Elser, J., Rabalais, N.N., Lewis, W.M.Jr., Turner, R.E., Corredor, J., Soto, D., Yanez-Arancibia, A., Kopaska, J.A., Howarth, R.W., 1999. The impact of accelerating land-use change on the N-Cycle of tropical aquatic ecosystems: Current condictions and projected changes. Biogeochemistry 46, 109-148.

Dugdale, R.C., Wilkerson, F.P., 2001. Sources and fates of silicon in the ocean: the role of diatoms in the climate and glacial cycles. Science Marina 65, 141-152.

Dyer, K.R., 1997. Estuaries: a physical introduction, 2nd edition. John Wiley & Sons Ltd, West Sussex, 195 pp.

EC Parliament and Council, 2000. Directive of the European Parliament and of the Council 2000/60/EC Establishing a Framework for Community Action in the Field of Water Policy. European Comission, Luxembourg. PE-CONS 3639/1/100 Rev 1.

Falco, S., 2003. Nutrients behaviour in a stratified estuary: Ebro delta case. Ph.D. Thesis, Universidad Politécnica de Valencia, Spain, 481 pp.

Falco, S., Romero, I., Rodilla, M., Sierra, J.P., González del Río, J., Mösso, C., Perez, M.C., 2006. Chlorophyll and phytoplankton maximum at the halocline of the Ebro River Estuary. Journal of Coastal Research SI 39, 526-530.

Faugeras, B., Lévy, M., Mémery, L., Verron, J., Blum, J., Charpentier, I., 2003. Can biogeochemical fluxes be recovered from nitrate and chlorophyll data? A case study assimilating data in the Northwestern Mediterranean Sea at the JGOFS-DYFAMED station. Journal of Marine Systems 40–41, 99–125.

Forés, E., 1989. Ricefields as filters. Arch. Hydrobiol. 116, 517-527.

Forés, E., 2001. Importancia ecológica de los arrozales en el Delta del Ebro y efectos del PHN. In: N. Prats, C. Ibañez (Editors), El curso inferior del Ebro y su Delta. Situación Actual. Impacto Ambiental del Plan Hidrológico. U. Cantabria-U. Barcelona, Barcelona, pp. 149-167.

Guillen, J., Palanques, A., 1997. A historical perspective of the morphological evolution in the lower Ebro river. Environmental Geology 30, 174–180.

Hashiba, H., Kameda, K., Uesugi, S., Tanaka, S. 2000. Land use change analysis of Tama River Basin with different spatial resolution sensor data by landsat/MSS and TM. Adv. Space Res. 26, 1069-1073.

Humborg, C., Ittekott, V., Cosiasu, A., Bodungen, B., 1997. Effects of Danube river dam on Black Sea biogeochemistry and ecosystem structure. Nature 386, 385-388.

Ibañez, C., Pont, D., Prat, N., 1997. Characterization of the Ebre and Rhone Estuaries. A basis for defining and classifying salt-wedge estuaries. Limnology and Oceanography 42, 89-101.

Jimenez Torrecilla, N., Martinez-Gil, J., 2005. The new culture of water in Spain: a philosophy towards a sustainable development. E-Water 2005-07. European Water Association, http://www.ewaonline.de/journal/2005_07.pdf. Accessed 31 Jan 2009.

Kirkwood, D., Aminot, A., Pertillä, M., 1991. Report on the Results of the ICES Fourth Intercomparison Exercise for Nutrients in Sea Water. Cooperative Research Report No. 174. International Council for the Exploration of the Sea, Copenhagen, 83 pp.

Krom, M.D., Herut, B., Mantoura, R.F.C., 2004. Nutrient budget for the Eastern Mediterranean: Implications for phosphorus limitation. Limnology and Oceanography 49, 1582-1592.

Legovic, T., 1991. Exchange of water in a stratified estuary with an application to Krka (Adriatic Sea). Marine Chemistry 32, 121-135.

Lloret, J., Palomera, I., Salat, J., Solé, I., 2004. Impact of freshwater input and wind on landings of anchovy (*Engraulis encrasicolus*) and sardine (*Sardina pilchardus*) in shelf waters surrounding the Ebre (Ebro) River delta (north-western Mediterranean). Fisheries Oceanogr. 13, 102–110.

López Moreno, J.I., Beguería, S., García Ruiz, J.M., 2002. Influence of the Yesa reservoir on floods of Aragon River, Central Spanish Pyrenees. Hydrology and Earth System Sciences 6(4), 753-762.

Ludwig, W., Meybeck, M., Abousamra, F., 2003. Riverine transport of water, sediments, and pollutants to the Mediterranean Sea. UNEP MAP Technical report Series 141, UNEP/MAP Athens, 111 pp. Available from: http://www.unepmap.org/ (verified 17 sep. 2009).

Ludwig, W., Dumont, E., Meybeck, M., Heussner, S., 2009. River discharges of water and nutrients to the Mediterranean and Black Sea: Major drivers for ecosystem changes during past and future decades?. Progress in Oceanography 80, 199–217.

Maeda, M., 1991. Characteristics of the Tama River System. In: IOC/WESTPAC Workshop on River Input of Nutrients to the Marine Environment in the Western Pacific. IOC Workshop Report nº 79, pp. 1-33.

Maidana, M.A., Naudin, J.J., Espino, M., García, M.A., Sánchez-Arcilla, A., 2002. Feasibility and usefulness of steady-state calculations of the mean circulation in the vicinity of the Ebro mouth. Model tests against field data. Continental Shelf Research 22, 229–245.

14

Margalef, R., 1983. Limnologia. Omega, D.L., Barcelona, 1010 pp.

Mösso C., Sierra, J.P., Rodilla, M., Romero, I., Falco, S., González del Río, J., Sánchez-Arcilla, A., 2008. High vertical resolution sampling in density interfaces of estuaries and river plumes. Estuaries and Coasts 31, 258-268.

Muñoz, I., Prats, N., 1989. Effects of river regulation on the lower Ebro river (NE Spain). Regulated Rivers: Research & Management 3, 345-354.

Nedwell, D.B., Jickells, T.D., Trimmer, M., Sanders, R., 1999. Nutrients in Estuaries. Advances in Ecological Research 29, 43-92.

Niencheski, L.F., Windom, H.L., 1994. Nutrient flux and budget in Patos Lagoon estuary. The Science of the Total Environment 149, 53-60.

Niencheski, L.F.H., Baumgarten, M.G.Z., Cabrera, L., Juliano, S.K., 2006. Patos Lagoon: indicators of organic pollution. Journal of Coastal Research SI 39, 1357-1359.

Palomera, I., Salat, J., Lloret, J., 2003. Impacto de los caudales fluviales sobre los ecosistemas pelágicos. In: P. Arrojo, L. Moral (Editors), La Directiva Marco del Agua. Realidades y Futuros. III Congreso Ibérico sobre Gestión y Planificación del Agua. Institución Fernando el Católico, Sevilla, pp.273-288

Parsons, T.R., Maita, Y., Lalli, C.M., 1984. A manual of chemical and biological methods for seawater analysis. Pergamon Press, London, 173 pp.

Pinilla, L., 1997. Evolución de la calidad del agua en el tramo inferior del Ebro. Revista de Obras Públicas 3368, 101-112.

Redfield, A.C., Ketchum, B.H., Richards, FA., 1963. The influence of organisms on the composition of sea-water. In: M.N. Hill (Editor), The Sea Vol.2. Wiley Interscience, New York, pp. 26-77.

Riley, J.P., Chester, R., 1971. Introduction to marine chemistry. Academic Press, London, 465 pp.

Sabater, S., Feio, M.J., Graça, M.A.S., Muñoz, I., Romaní, A.M., 2009. The Iberian rivers. In: K. Tockner, U. Uehlinger, C.T. Robinson (Editors), Rivers of Europe. Academic Press, pp. 113-150.

Sabater S., Artigas, J., Durán, C., Pardos, M., Romaní, A.M., Tornés, E., Ylla, I., 2008. Longitudinal development of chlorophyll and phytoplankton assemblages in a regulated large river (the Ebro River). Science of the Total Environment 404, 196– 206.

Sferratore A., Billen, G., Garnier, J., Smedberg, E., Humborg, C., Rahm, L., 2008. Modelling nutrient fluxes from sub-arctic basins: Comparison of pristine vs. dammed rivers. Journal of Marine Systems 73, 236–249.

Sempere, R., Cauwet, G., 1995. Occurrence of organic colloids in the stratified estuary of the Krka River (Croatia). Estuar. coast. Shelf Sci. 40, 105-114.

15

Takii, S., Fukui, M., 1991. Relative Importance of Methanogenesis, sulfate reduction and denitrification in sediments of the lower Tama River. Bulletin of Japanese Society of Microbial Ecology 6 N°1, 9-17.

Tappin, A. D., 2002. An Examination of the Fluxes of Nitrogen and Phosphorus in Temperate and Tropical Estuaries: Current Estimates and Uncertainties. Estuarine, Coastal and Shelf Science 55, 885–901.

Tréguer, P., Le Corre, P., 1975. Manuel d'analyse des sels nutritifs dans l'eau de mer. Utilisation de l'AutoAnalyser II Technicon, 2nd ed. Université de Bretagne Occidentale, Brest, 110 pp.

Valderrama, J. C., 1981 The simultaneous analysis of total phosphorus and total nitrogen in natural waters. Marine Chemistry 10, 109–122.

Windom, H.L., Dunstan, W.M., Gardner, W., 1975. River input of inorganic phosphorus and nitrogen to the Southeastern salt-marsh estuarine environment. In: F.G. Howell, J.B. Gentry, M.H. Smith (Editors), Mineral Cycling in Southeastern Ecosystems. ERDA symposium Series, U.S. Energy Research and Development Administration, Oak Ridge, Tenn, pp. 309-313.

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FIGURE CAPTIONS

Figure 1: Delta of the Ebro river, on the north-western Mediterranean coast. Locations of sampling stations and boundaries of boxes used in the mass balance calculations.

Figure 2: Depth of the interface in each of the boxes. Chlorinity, ammonium and DIP in the surface layer along the estuary.

Figure 3: Difference between the total content observed and the total content calculated (excess or deficit) for N-ammonium in each of the five estuarine boxes during the period of study.

Figure 4: Estimate of the net budgets of nutrients integrated over the annual cycle in the Ebro estuary.

Figure 5: Vertical profiles of DIP and ammonium at stations R, A, B, C, D and E on 12 July 1999. Salinity is presented as a dotted line to denote the interface.

Figure 6: Vertical profiles of Si at stations R, A, B, C, D and E on 6 October 1999. Salinity is presented as a dotted line to denote the interface.

TABLES

Table 1: Flow rate, depth of interface, volume and residence time of freshwater in each of the boxes during the different seasons of the year (M: Means and SD: standard deviation).

Table 2: Means (M) and standard deviation (SD) for chlorinity, nutrients and chlorophyll *a* in each of the boxes and end members R (river) and S (sea) for each season of the year.

Table 3: Annual material fluxes to Ebro estuary, associated with freshwater input, and compared with other systems.

Figure 1
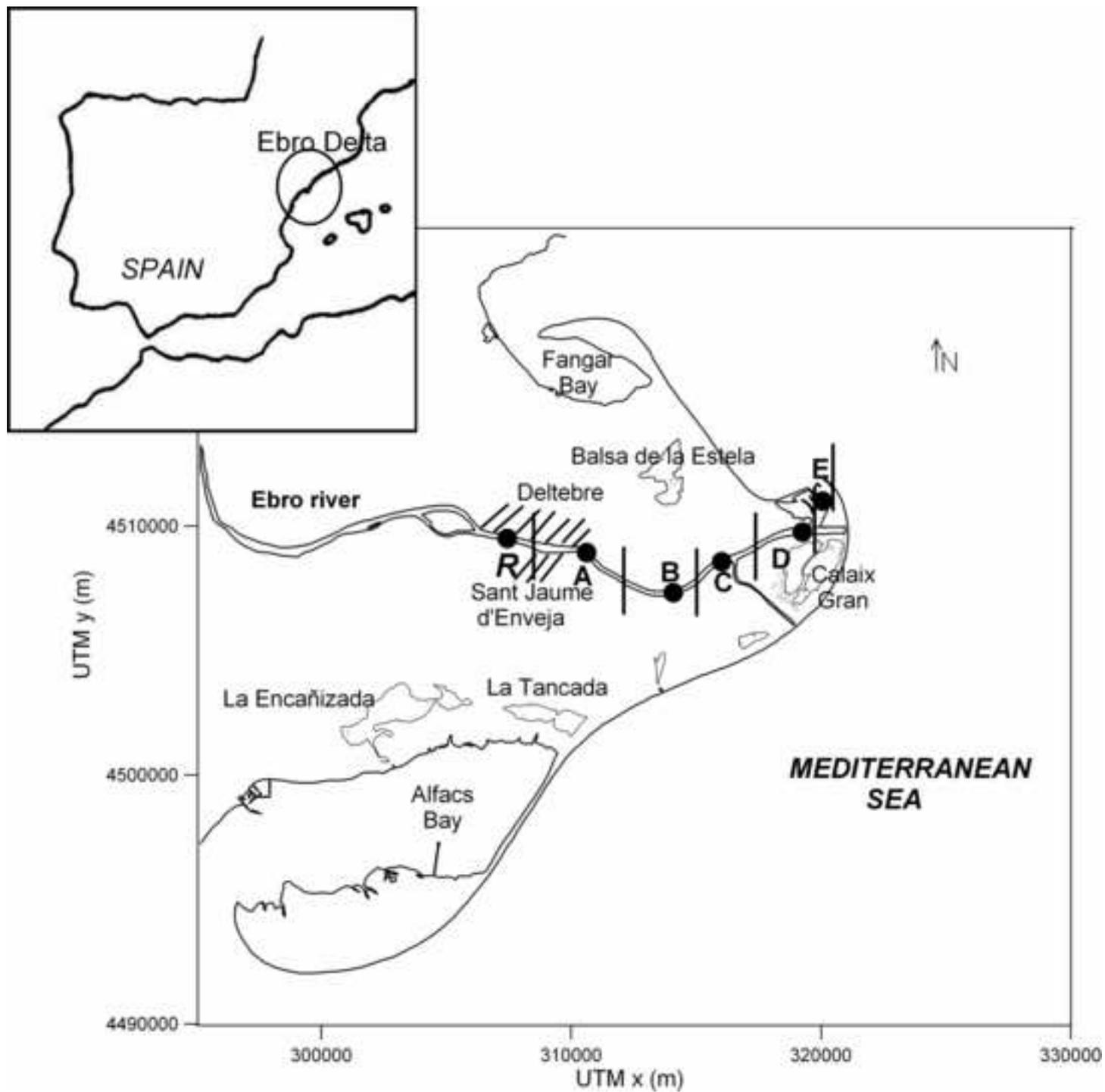**Click here to download high resolution image**

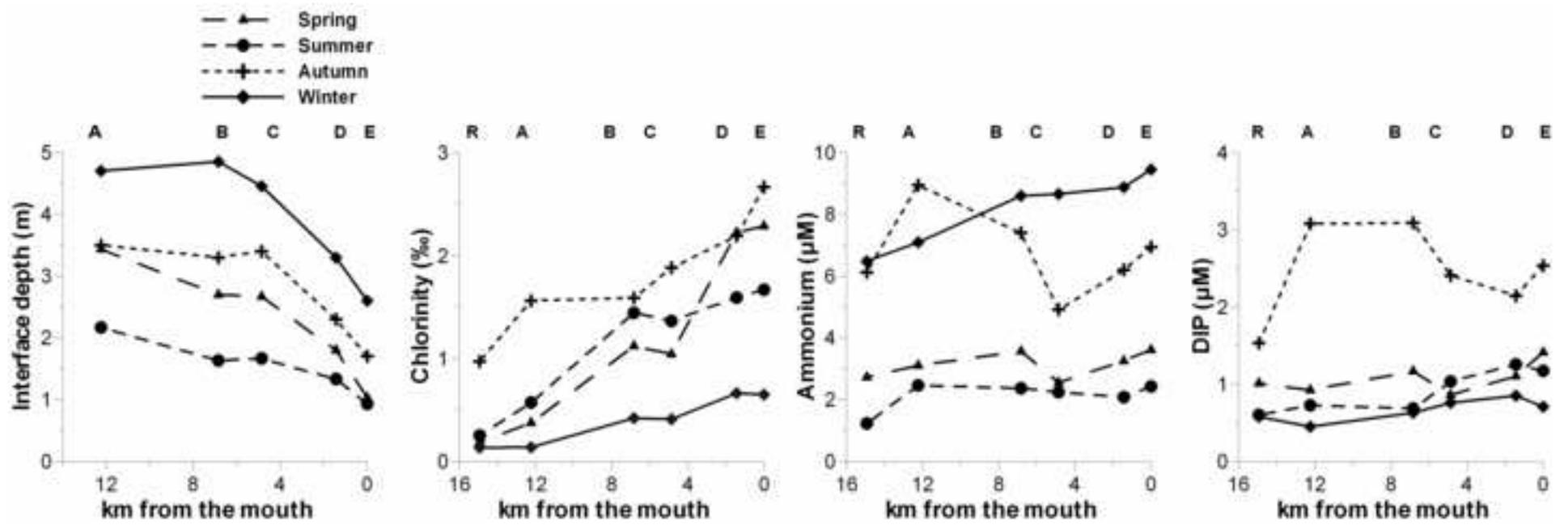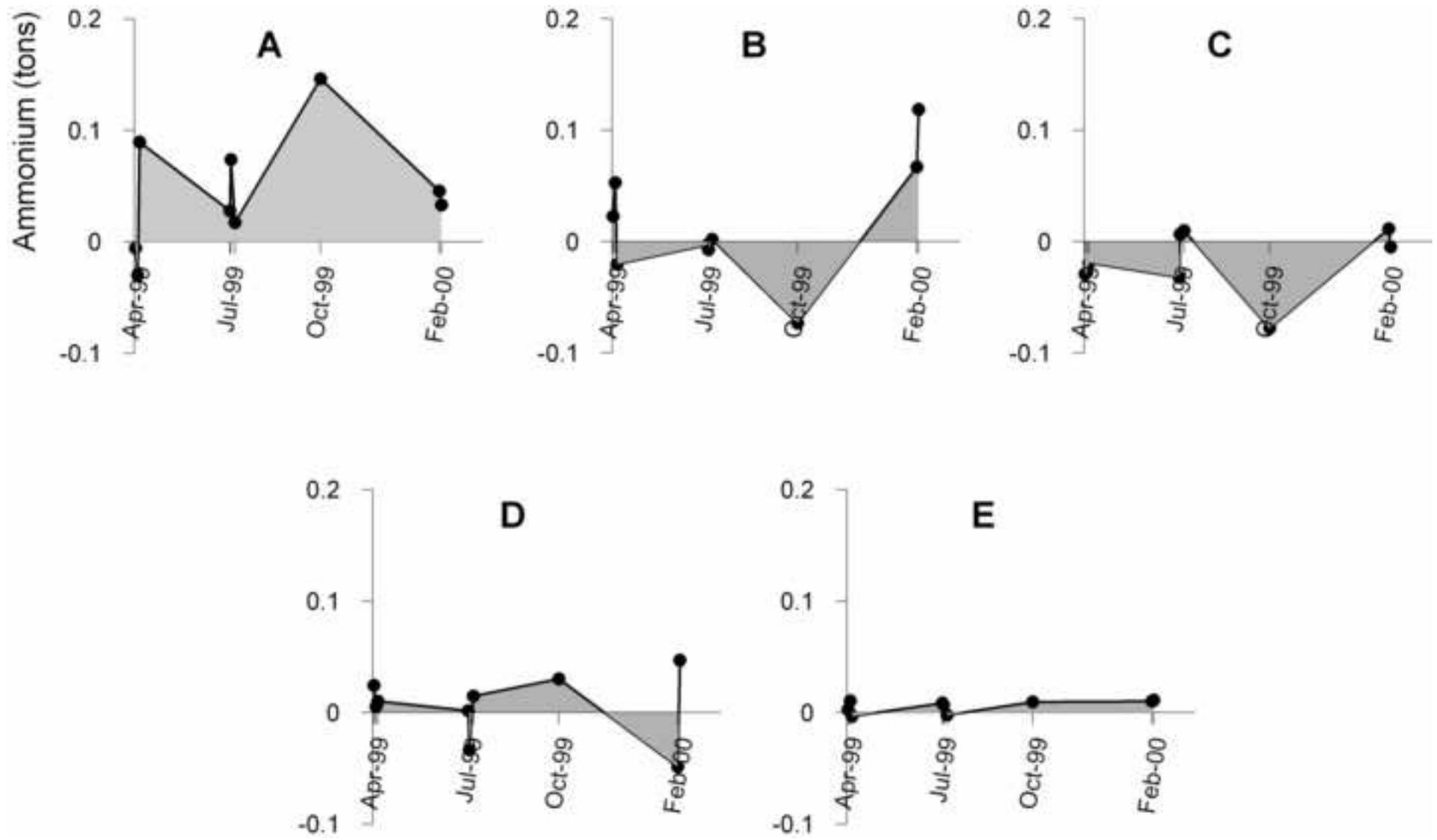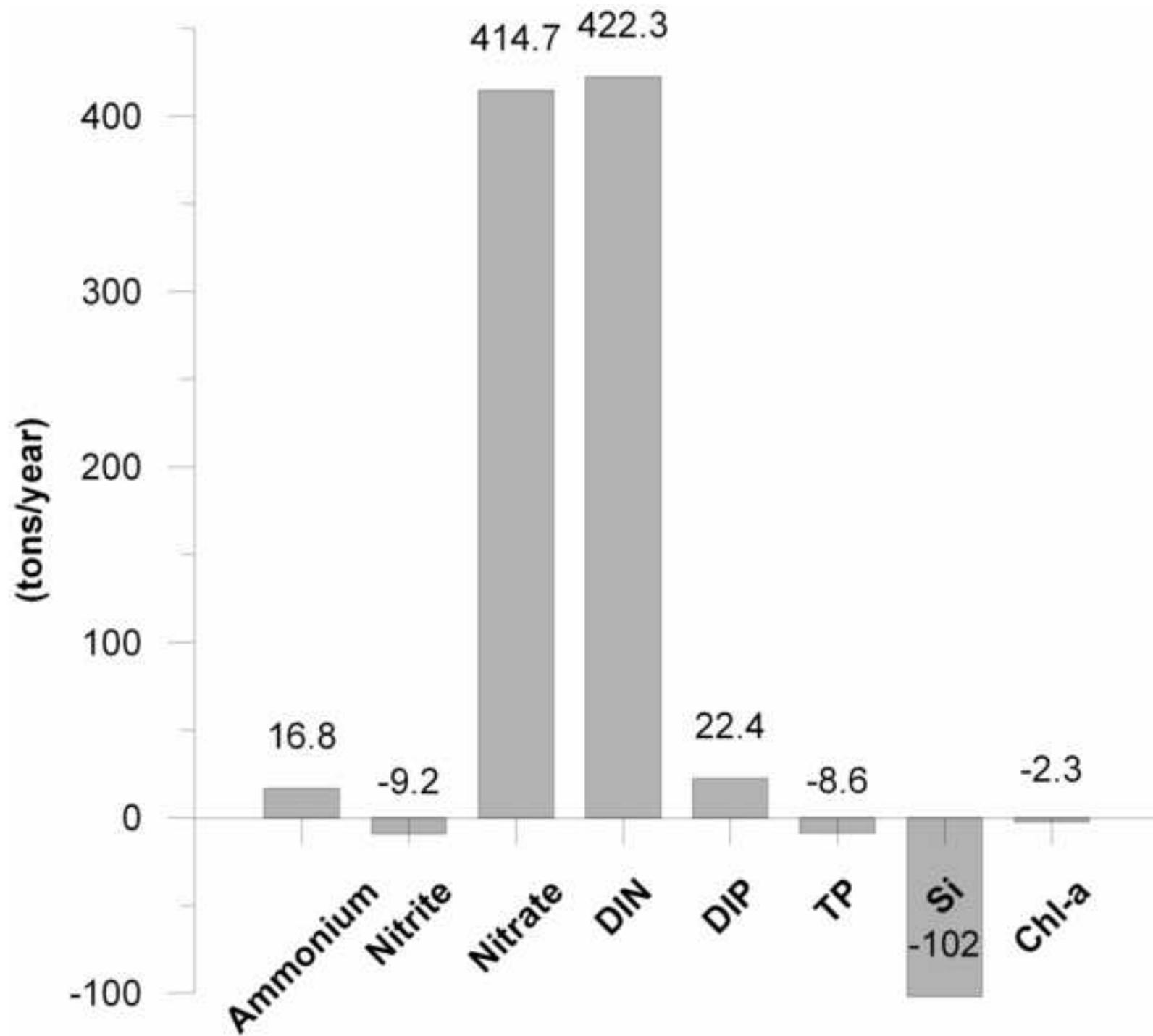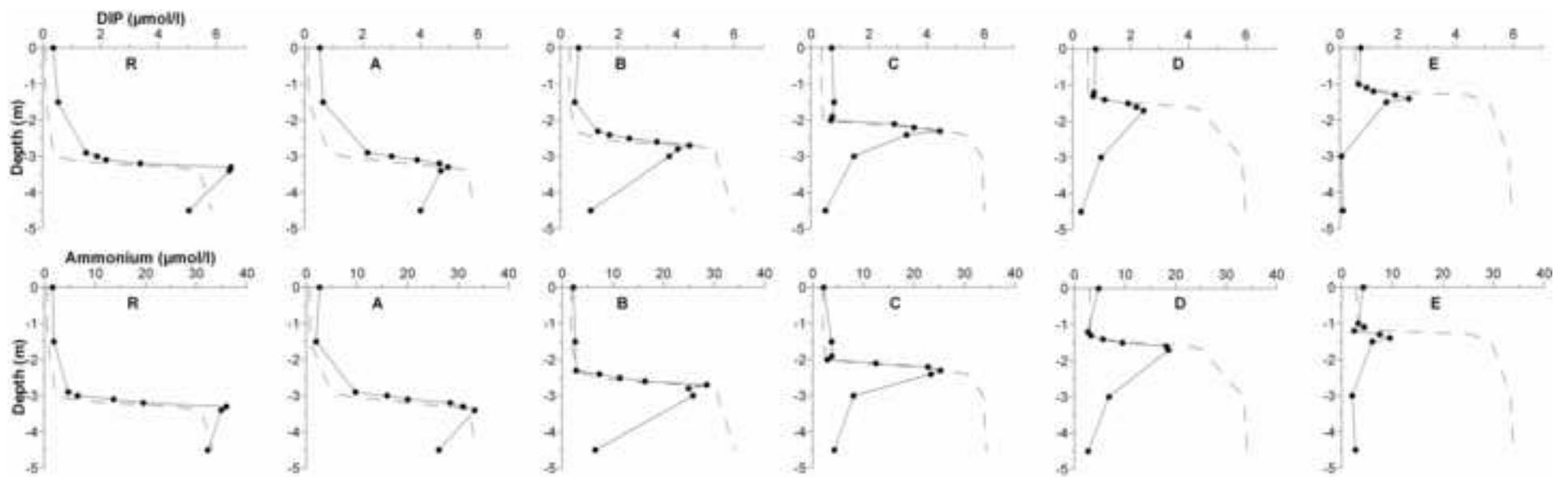**Figure 2**
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Figure 4
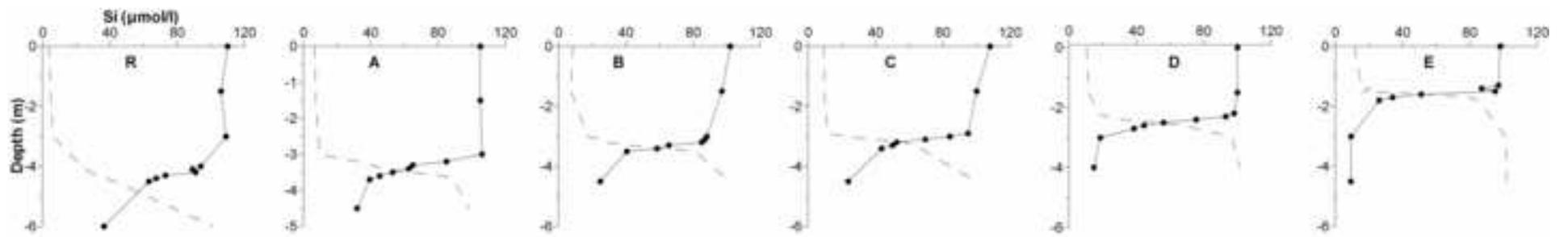
TABLES

Table 1: Flow rate, depth of interface, volume and residence time of freshwater in each of the boxes during the different seasons of the year (M: Means and SD: standard deviation).

Season	Station	Depth of the interface (m)		Volume of freshwater (m^3)		Residence time (h)		River flow ($m^3 s^{-1}$)	
		M	SD	M	SD	M	SD	M	SD
Spring	A	3.4	0.5	3 459 731	354 200	5.26	0.11	179.9	22.2
	B	2.7	0.3	2 919 808	344 175	4.27	0.19		
	C	2.7	0.3	1 788 757	196 619	2.63	0.11		
	D	1.8	0.3	1 309 610	111 890	1.81	0.13		
	E	1.0	0.1	672 864	27 559	0.93	0.07		
Summer	A	2.2	0.2	2 241 112	129 666	4.75	0.35	128.2	15.1
	B	1.6	0.2	1 851 846	196 262	3.75	0.25		
	C	1.7	0.4	1 191 939	260 377	2.40	0.24		
	D	1.3	0.5	997 792	337 084	1.97	0.49		
	E	0.9	0.5	568 521	241 878	1.11	0.39		
Autumn	A	3.5		3 708 615		5.10		187.0	
	B	3.3		3 395 395		4.66			
	C	3.4		2 224 452		3.01			
	D	2.3		1 678 074		2.23			
	E	1.7		919 147		1.19			
Winter	A	4.7	0.7	4 588 317	165 753	5.04	1.59	266.0	93.0
	B	4.9	0.6	4 529 711	523 783	4.84	1.13		
	C	4.5	0.9	3 186 412	738 130	3.34	0.43		
	D	3.3	0.6	2 690 432	742 884	2.76	0.22		
	E	2.6	0.6	1 368 539	234 436	1.43	0.27		

Table 2: Means (M) and standard deviation (SD) for chlorinity, nutrients and chlorophyll *a* in each of the boxes and end members R (river) and S (sea) for each season of the year.

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Season	Station	Chlorinity (‰)		Ammonium (µM)		Nitrite (µM)		Nitrate (µM)		DIN (µM)		DIP (µM)		TP (µM)		Silicate (µM)		Chlorophyll a (µg l^{-1})	
		M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD	M	SD
Spring	R	0.184	0.030	2.7	2.4	1.75	0.33	96.4	22.1	100.9	19.5	1.01	0.75	2.44	0.17	49.1	29.6	25.27	7.27
	A	0.374	0.228	3.1	2.5	1.75	0.34	158.6	44.0	163.5	42.0	0.93	0.58	2.49	0.68	46.7	29.4	26.35	9.49
	B	1.121	0.465	3.6	2.1	1.80	0.32	133.1	3.6	138.4	3.1	1.17	0.76	1.65	0.17	44.3	26.8	21.47	5.40
	C	1.043	0.226	2.6	2.1	1.80	0.32	161.2	15.7	165.6	17.8	0.86	0.38	2.35	1.03	40.3	17.3	22.83	5.72
	D	2.221	1.041	3.3	2.6	1.71	0.37	140.2	49.3	145.2	50.3	1.10	0.49	1.97	0.20	42.3	26.9	18.49	4.49
	E	2.286	0.468	3.6	2.4	1.72	0.35	168.6	7.3	174.0	8.8	1.41	0.29	2.40	0.71	41.9	15.3	17.59	5.26
	S	20.377	0.183	1.2	0.5	0.01	0.00	14.0	17.8	15.2	18.2	0.11	0.14	0.92	1.06	1.4	1.6	10.38	10.16
Summer	R	0.253	0.079	1.2	0.8	0.83	0.13	146.7	22.7	148.7	22.0	0.60	0.14	2.14	0.26	55.2	1.6	12.91	6.92
	A	0.571	0.200	2.5	0.2	0.89	0.12	151.6	14.0	155.0	14.0	0.73	0.13	2.15	0.15	56.8	1.8	12.38	5.02
	B	1.443	0.587	2.4	0.1	0.94	0.15	150.5	23.1	153.8	23.0	0.69	0.27	2.19	0.28	55.0	1.5	12.90	6.58
	C	1.365	0.033	2.2	1.2	0.84	0.16	142.4	14.4	145.5	14.9	1.04	0.34	2.00	0.23	54.6	1.2	12.75	4.57
	D	1.589	0.184	2.1	2.4	0.76	0.27	136.0	15.8	138.9	13.7	1.26	0.41	2.15	0.32	53.6	0.5	14.28	2.84
	E	1.666	0.079	2.4	1.6	0.76	0.21	135.1	13.6	138.3	12.0	1.17	0.42	2.09	0.44	53.0	3.3	13.08	3.87
	S	19.965	0.387	5.5	4.9	0.03	0.02	4.2	4.2	9.7	9.0	0.23	0.24	0.83	0.25	11.9	9.6	4.51	3.39
Autumn	R	0.972		6.12		3.61		113.59		123.3		1.53		3.58		108.3		10.59	
	A	1.561		8.94		3.22		126.75		138.9		3.08		3.93		105.3		10.83	
	B	1.588		7.40		2.74		117.31		127.4		3.09		2.80		99.5		9.98	
	C	1.880		4.91		2.08		119.73		126.7		2.41		3.27		104.0		11.03	
	D	2.188		6.20		1.53		111.92		119.6		2.15		3.16		100.0		9.12	
	E	2.664		6.95		1.32		104.48		112.7		2.54		2.89		97.5		7.98	
	S	20.358		7.10		0.10		1.80		9.0		0.38		0.91		9.2		5.35	
Winter	R	0.133	0.005	6.5	1.8	2.88	0.34	151.1	50.6	160.4	48.5	0.58	0.02	2.23	0.03	69.4	1.2	8.42	3.05
	A	0.137	0.014	7.1	1.9	2.96	0.39	173.3	19.8	183.3	17.6	0.45	0.02	2.23	0.07	72.6	5.4	7.65	2.63
	B	0.420	0.134	8.6	1.1	2.98	0.43	188.9	5.5	200.5	4.0	0.63	0.11	2.28	0.24	71.4	5.8	6.59	1.46
	C	0.412	0.147	8.6	1.4	2.91	0.19	179.5	5.9	191.0	4.3	0.76	0.16	2.22	0.34	72.0	4.5	6.47	1.64
	D	0.662	0.065	8.9	0.5	3.01	0.18	185.9	8.6	197.8	8.9	0.85	0.25	2.27	0.14	71.9	1.5	6.28	0.74
	E	0.650	0.162	9.4	0.6	3.13	0.19	178.4	20.1	191.0	20.5	0.71	0.13	2.23	0.27	70.1	1.6	6.22	1.39
	S	19.978	0.346	1.8	0.8	0.36	0.25	13.5	8.0	15.6	9.1	0.03	0.01	0.21	0.04	6.2	4.3	1.92	0.64

Table 3: Annual material fluxes to Ebro estuary, associated with freshwater input, and compared with other systems.

	Ebro	Rhone	Patos Lagoon	South-eastern USA	Tokyo Bay	Ebro	Rhone	Patos Lagoon	South-eastern USA	Tokyo Bay
	Total Flux (t yr^{-1})					Watershed (km^2)				
						88 835	95 600	150 432	150 343	1 240
						Total Flux (t km^{-2})				
N_Ammonium	395		1 274	2 478		$4.4.10^{-3}$		$8.46.10^{-3}$	$1.64.10^{-2}$	
N_Nitrite	207		51			$2.3.10^{-3}$		$3.39.10^{-4}$		
N_Nitrate	12 959	77 500	4 999	10 262		0.146	0.811	$3.32.10^{-2}$	$6.82.10^{-2}$	
DIN	13 560	*84 056	6 324	12 740	110 000	0.152	0.879*	$4.20.10^{-2}$	$8.47.10^{-2}$	88.71
DIP	180	2 500	563	1 588	10 000	$2.0.10^{-3}$	$5.2.10^{-3}$	$3.74.10^{-3}$	$1.06.10^{-2}$	8.06
TP	534									
Silicate	12 416		133 779			0.140		0.89		

*estimated using data on the % of the different nitrogen species in the Rhone river (Ludwig et al., 2003)