

Sediment-water nutrient fluxes: Preliminary results of *in situ* measurements in Alfaques Bay, Ebro River Delta

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SUMMARY: Sediment-water exchanges of oxygen, ammonium, nitrate, total dissolved nitrogen, phosphate and total dissolved phosphorus were measured by means of an *in situ* incubator of 7 l volume and 700 cm² base area. The incubations lasted for three hours and were done over a whole season on different kinds of sediments in Alfaques Bay. We present some preliminary results on: i) methodological aspects, ii) spatial and temporal variability of fluxes, and iii) estimates of contribution of benthic nutrient regeneration relative to total nutrient loading of the Bay. Oxygen uptake averaged 1700 $\mu\text{mol m}^{-2} \text{h}^{-1}$ (range 200-3500); no differences were found between sandy and muddy sediments. The release of ammonia from the sediment averaged 70 $\mu\text{mol m}^{-2} \text{h}^{-1}$ and was higher in muddy sediments than in sandy ones. Very low to null nitrate and nitrite fluxes and only small fluxes of organic nitrogen were detected. We conclude that ammonium release from sediment is the major path of nitrogen regeneration. Some sediments removed dissolved reactive phosphorus (DRP) from the water and released dissolved organic phosphorus (DOP). Additional manipulative experiments revealed DRP release under particular conditions (turbulence, anoxia). From these data, we estimate that at least 50 % of the nitrogen requirements of phytoplankton in the area may be supplied by benthic remineralization.

Key words: Ebro delta, nutrient fluxes, sediment-water interactions.

INTRODUCTION AND OBJECTIVES

The Ebro Delta is a clear example of interactions between various systems: the river, crops grown in the area, irrigation channels, coastal lagoons and the sea. On both sides of the delta, two semi-enclosed areas (Fangar Bay and Alfaques Bay) are fed, and are deeply influenced, by the freshwater from the irrigation channels which cross rice fields and lagoons in the delta from March/April to October/November, depending on the needs of the rice culture (Fig. 1).

The bays are delta subsystems of special interest, since: i) they are ecosystems forced by external inputs, i.e. irrigation channels that carry large amounts of both dissolved and particulate materials to the bays; ii) they constitute a highly dynamic ecosystem that could potentially be used in aquaculture programmes.

A series of investigations was initiated in 1982,

focussing on primary production of plankton and microphytobenthos, and of the hydrographic processes which allow it to work (CAMP & DELGADO, 1987; DELGADO & CAMP, 1987). Primary production is, on average, about 80 g C m⁻² y⁻¹ for phytoplankton and 30 g C m⁻² y⁻¹ for microphytobenthos (DELGADO, 1987). These values are high relative to other coastal waters (KORLENTZ-MISHKE *et al.*, 1970; FALKOWSKI, 1980; etc.) Hydrographic studies (CAMP & DELGADO, 1987; PRAT *et al.*, 1988a, b), show that the amount of dissolved nutrients brought in by irrigation channels is not enough to explain such high primary production. This finding supports the idea that intense benthic nutrient regeneration is taking place, and the question arises to what extent this regeneration contributes to primary production. In shallow areas, the volume of water over the sediment is small enough for its chemical composition to be influenced, by fluxes from the sediment (DAVIES,

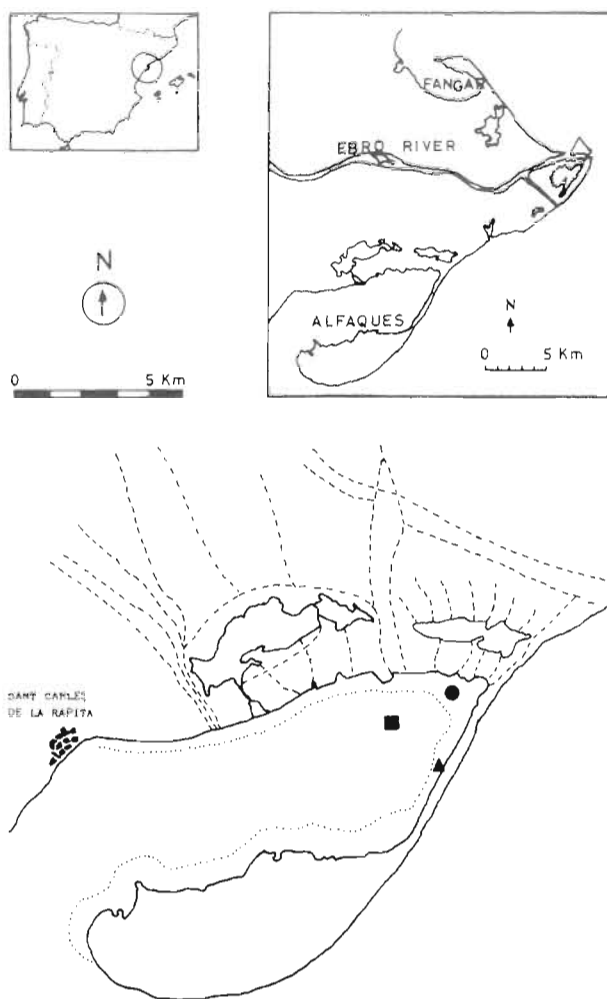


FIG. 1. — Alfaques Bay, in the southern part of the Ebro Delta (NE of Spain). The dotted line represents the limit between the shallow (1-2 m) and the deep (5-6 m) part of the bay. The irrigation channels as well as the coastal lagoons are shown. The positions of the sampling stations are also indicated. Triangle, station 1; dot, station 2; square, station 3.

1975; NIXON *et al.*, 1976; ROWE *et al.*, 1977; HARRISON, 1978; NIXON, 1981).

The present study deals with regeneration in sediments. The first objective was to estimate the magnitude and direction of nutrient exchanges between sediments and water. The second, to detail seasonal and spatial variation. The third objective was to examine the influence of the type of sediments. The experimental approach was done mainly using *in situ* incubations. The future goal of the work, not included in this paper, will be to determine which mechanisms control and define these exchanges, mainly through laboratory experiments.

METHODOLOGY

Measurements were made in Alfaques Bay. Various types of sediment and environmental condi-

tions exist here, influenced to a greater or lesser degree by the influx of freshwater. Three stations were chosen due to their distinctive characteristics (Fig. 1): station 1 was on a shallow sandy bottom, far from the influence of the channels and with low to null inputs of allochthonous organic matter; station 2 was on a shallow muddy sediment near the opening of a discharge channel; and station 3, on muddy sediment, was located in the deepest part (5 m) of the Bay. Incubations of sediments were performed seasonally using 7 l hemispherical PVC domes, each with a 700 cm² circular base, placed on the sediment surface (Fig. 2). Opaque (black) domes were used throughout this work. Control domes in the same conditions as the experimental ones except that they were isolated from the sediment by circular PVC plates, were also incubated. In very fine sediments such as those studied, the placement of an incubation chamber on the sediment is critical, since the surface layer can be easily disturbed. To avoid this, a ring with a sharpened, lower edge was gently pushed into the sediment and left there for some time (Fig. 2). Then, the dome was attached to the ring. Once placed, water samples were taken from the dome using 50 ml syringes. Three hours later, more samples were taken (The reason for this time interval is given in 3.1.) To replace the volume of water removed by extraction of samples, an empty polyethylene bag was placed in

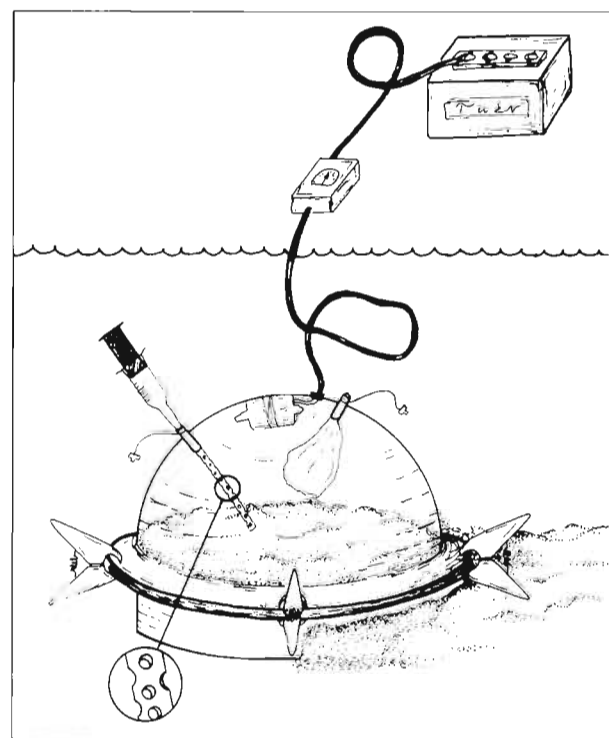


FIG. 2. — Diagram of the experimental apparatus showing the ring half embedded in the sediment, the dome, the sampling syringe, the stirring device controlled from the surface, and the compensation volume bag.

the dome, with an opening to the outside. This bag filled as samples were removed (Fig. 2) A small electric pump, working at low speed, was placed in each dome to induce a slow circulation of the water inside and to prevent stratification in the head space (PATCHING & RAINE, 1983). To assess whether stagnation interferes significantly with the results or not, an experiment was performed using 6 domes, three unstirred as controls and three stirred as described.

The concentrations of oxygen, inorganic dissolved nitrogen (nitrates, nitrites, ammonium), reactive soluble phosphorus, total dissolved nitrogen and total dissolved phosphorus were measured using the standard methods described in GRASSHOF (1983).

RESULTS AND DISCUSSION

Methodological results

An adequate incubation period has to satisfy two basic conditions: a) to be long enough to permit noticeable, significant changes in nutrient concentrations, b) not to modify dramatically the experimental conditions.

To demonstrate that these conditions are met with a 3 hr incubation time, a series of experiments in which nutrient concentrations were recorded every 10 min and oxygen concentration was measured continuously using an oxygen sensor were carried out. The linearity of ammonium and oxygen vs. time was maintained during the 3 hr period, while the global oxygen concentration changes do not amount to more than 20 % of the initial concentration (Fig. 3). The fluxes of both nitrites and phosphates were erratic or non-existent (Fig. 3). This has been confirmed in the majority of later experiments, while the flux of nitrates, although weak or null shows a trend which will be discussed later.

Results of the experiment on stirring effect are shown in Table I. The stagnation induced by the dome seriously interfered with the processes of nutrient exchange between water and sediment and it thus appears unavoidable, from a methodological point of view, to provide the domes with some kind of mixing.

The variability of the data was studied by replicating the experiments under identical conditions.

TABLE I. — Results of the experiment comparing stirred with nonstirred domes. Data are fluxes in $\mu\text{mol m}^{-2} \text{h}^{-1}$; SEM are given in each case ($n = 3$).

	Non stirred	Stirred
Oxygen	-327 ± 43	-764 ± 68
Ammonium	0 ± 0	37 ± 1.5
Nitrate	4 ± 1.8	-5 ± 4.3

Coefficients of variation were high (Table II), as stated by other authors (NIXON *et al.*, 1980; FLOREK & ROWE, 1983; FISHER *et al.*, 1982; ULLMAN & SANDSTROM, 1987). Oxygen consumption variability is, in general, lower than variability of nutrient release. This difference probably reflects the scale at which control mechanisms take place. According to

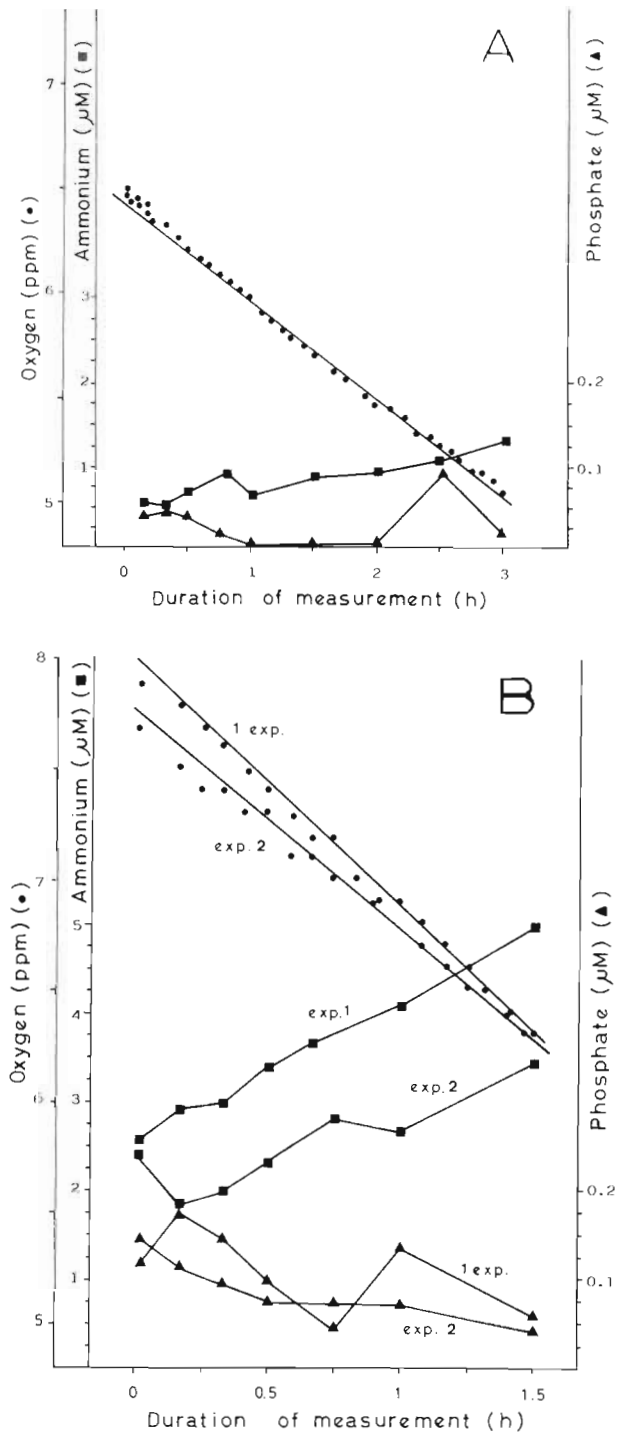


FIG. 3. — Evolution of some parameters recorded continuously during incubations of three hours (A) and 1.5 hours (B, two independent experiments).

TABLE II. — Variability of the data presented. Coefficient of variation (SEM/mean \times 100) is given for our data compared with data from the literature.

	Oxygen	Ammonium	Nitrate
Range	3 to 20	24 to 84	13 to 98
Average	12	56	44
Literature	15	0 to 38	2 to 140

FALLON *et al.* (1983) and HOPKINSON (1987), a major part of oxygen consumption must be attributed to bacteria (up to 75 %), while macrofauna affects nutrient release much more decisively through mechanisms such as excretion, bioturbation, interstitial water flow, etc. (ALLER, 1980; CALLENDER & HAMMOND, 1982; EMERSON *et al.*, 1984; MCCAFFREY *et al.*, 1980; CHRISTENSEN *et al.*, 1984; YAMADA & KAYAMA, 1987). In areas of 700 cm², it can be assumed that bacteria are much more evenly distributed than macrofauna, so that our data are in agreement with the hypothesis referred to. Nevertheless, the precise study of the causes of variability would require much more experimental work, beyond the objectives of our research; but for practical purposes, we have considered that three replicates for each one of the experimental conditions (dark and control) are enough to lower the variance to acceptable levels.

Experimental results

The results obtained are summarized in table III. The ammonium release is similar to the values usually found in shallow coastal waters (ROWE *et al.*, 1975; HOPKINSON & WETZEL, 1982; LYONS *et al.*, 1982; FISHER *et al.*, 1982; NOWICKI & NIXON, 1985; etc.). The low values of nitrate fluxes are a fairly well known fact that probably arises from the equilibrium of the various processes which affect the dynamics of nitrogen in sediments (JENKINS & KEMP, 1984; GRUNDMANIS & MURRAY, 1977), which depends upon environmental conditions. In station 1 (sand), flux is low (of the order of 25 % in relation to ammonium), but it is even lower in station 2 (shallow mud) and becomes negative (up to 25 % of ammonium release) in station 3 (deep mud). The release of phos-

TABLE III. — Summary of the data obtained. Fluxes are in $\mu\text{mol m}^{-2} \text{h}^{-1}$.

Station	n	Oxygen	Ammonium	Nitrate	O/N
Sandy shallow	18	-1196 \pm 125	44 \pm 8	8 \pm 3	23
Muddy shallow	8	-2708 \pm 209	68 \pm 17	0	40
Muddy deep	8	-1492 \pm 268	100 \pm 35	-22 \pm 2	19

phorus is virtually nonexistent, a point which will be discussed later.

In general, the differences between the three stations are due to the vicinity of the freshwater inputs; the stations closer to the discharge channels (2 and 3) are more active than the third one (station 1). If the values presented are extrapolated (taking into account the distribution of sediment types: 18 % sandy; 5 % shallow muddy; 77 % deep muddy) for the whole bay, it can be concluded that the ammonium fluxes can meet almost half of the nitrogen requirements of phytoplankton, according to recent production estimates (DELGADO, 1987). The data presented here are insufficient to establish an accurate balance, but they point out the key-role of benthic remineralization in the nutrient dynamics of the system.

Nutrient-exchange is seasonal (Fig. 4). Station 1 shows maximum activity in summer, while in stations 2 and 3 maximum activity occurs earlier, shortly after the opening of the irrigation channels in the spring. It seems logical to suppose that nutrient release is determined by temperature in Station 1 (Fig. 5), while the other two stations are influenced to a greater extent by the amount of the influxes. The ratio nitrogen

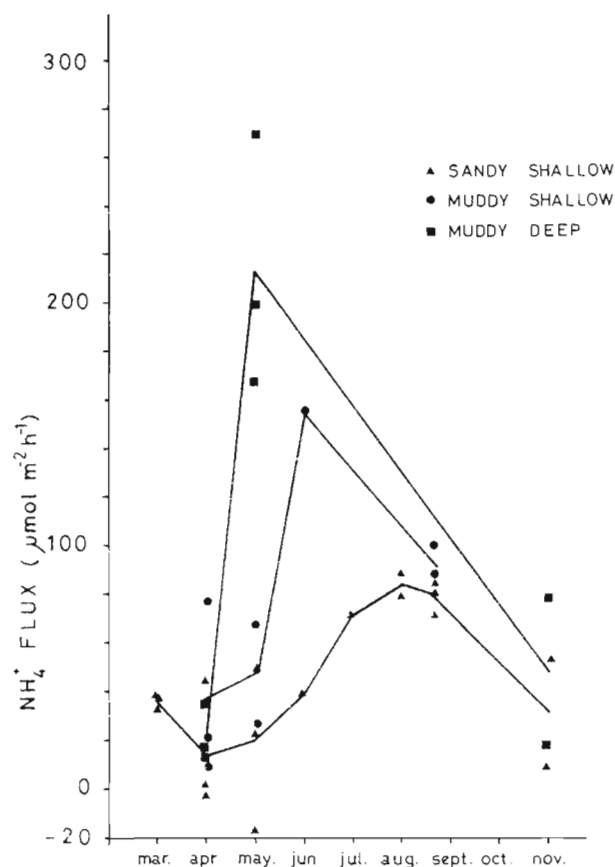


FIG. 4. — Seasonal changes of ammonium fluxes (in $\mu\text{mol m}^{-2} \text{h}^{-1}$). Triangles, station 1; circles, station 2; squares, station 3. The solid lines represent the mean of each station.

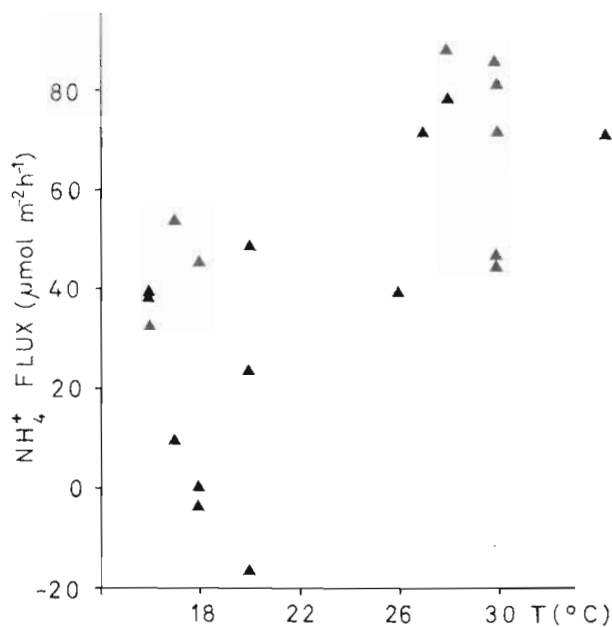


FIG. 5. — Relation between temperature and ammonium flux, following the results of *in situ* experiments.

released (mainly ammonium) to oxygen consumed, which can be called "flux stoichiometry", results from a very complex series of processes. Due to this the ratio is very often undecipherable, as has often been emphasized by various authors (KLUMP & MARTENS, 1983). However, the O:N ratios in Table III are suggestive. All are clearly superior to the theoretical 13.25 which can be expected from the complete and aerobic remineralization of ideal phytoplankton, according to the empirical formulae in use (VALIELA, 1984). Several reasons can be mentioned for explaining these data. On the one hand, the detrital nature of sedimented material shifts the C:N ratio towards higher values (PRAT *et al.*, 1988; the annual seston C:N ratio is around 8.2). On the other hand, denitrification processes may occur. Parallel microbiological studies (FERRER *et al.*, 1987) demonstrate the occurrence of significant denitrifying activity, higher in the mud than in the sand, in agreement with the O:N ratio given (Table III). Moreover, intense denitrification in sediments of estuarine or coastal areas with influxes of organic material is a well known fact (SEITZINGER & NIXON, 1985; GRUNDMANIS & MURRAY, 1977; ENOKSSON & SAMUELSSON, 1987; KOIKE *et al.*, 1984).

A third process accounting for the observed deviations in the stoichiometry is the adsorption of ammonium on particles (ROSENFELD, 1979; BLACKBURN & HENRIKSEN, 1983) which is greater with decreasing grain size of the sediment, again in good agreement with our data.

A final point which merits attention is the absence of a flow of reactive soluble phosphorus from the

sediment to the water. This flux should exist if we take into account DRP concentrations in interstitial water (VIDAL, 1988; VIDAL *et al.*, in press). Therefore, a DRP retaining factor must exist. Our hypothesis is that it may result from either chemical retention (since at high oxygen levels, such as those found in water, phosphorus forms highly insoluble salts) or physico-chemical retention (adsorption on tiny clay particles). Both phenomena are widely described in the literature (KHALID *et al.*, 1977; STIRLING & WORLDWALD, 1977). Our *in situ* measurements do not take into account non-periodic events which, in spite of their short duration, may be of importance in the annual nutrient budget (anoxic periods, storms, etc.). The massive release of phosphorus during these non-periodic events is quite plausible. Thus, laboratory and field experiments have been designed to test this hypothesis, and the preliminary results are summarized in Table IV. Phosphorus release may also occur in other chemical compounds such as soluble organic molecules, and not necessarily as DRP. We have detected sporadic fluxes of this type in our experiments as can be seen in table IV.

TABLE IV. — Phosphorus release (in $\mu\text{mol m}^{-2} \text{h}^{-1}$) found in particular conditions.

Aperiodical events:	Anoxia	1-5
	Anoxia + agitation	50-300
	Resuspension	10-150
Forms other than DRP	Dissolved organic	0-5

Bearing in mind the tentative nature of such values, from table IV we can state that the amount of phosphorus supplied by the sediment in these aperiodic events would be enough to meet (*sensu* the Redfield ratio) and possibly surpass that of nitrogen. Before formulating a hypothesis with regard to which of the two nutrients exerts a limiting role in primary production, it would be necessary to prove that the above mentioned release of phosphorus is irreversible in a short time period (HOLDREN *et al.*, 1980; BOSTROM *et al.*, 1982).

Taking into account the preliminary nature of our results, the only definitive conclusion which we can formulate is that the benthic compartment is of great importance as a nutrient source for plankton, at least with regards to ammonium. The data presented here, along with other data provided by our work in the Ebro Delta system, show that 25 % of the nutritional requirements (nitrogen) of phytoplankton are met by dissolved channel inputs, and 50 % by remineralization in the sediment. In a first approach, the remaining 25 % can be attributed to recycling in the water column.

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