DISTRIBUTION OF DIFFERENT PHOSPHORUS FRACTIONS IN THE SEDIMENT OF PALMONES RIVER (SOUTHERN SPAIN) DURING A DRY SEASON.

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ABSTRACT

Spatial changes of different phosphorus fractions in the sediment of Palmones River, have been studied during the dry season. Results show the dominance of inorganic forms over the organic ones, with values of the ratio IP/OP reaching almost 3. Apatite Inorganic Phosphorus was the most abundant inorganic fraction with a clear dominance in the upper part of the river. **All** fractions showed a depuration effect due to the Reservoir of Charco Redondo (up to 80% for the organic fraction). There was a trend for increasing concentrations downstream, with maximun values reached in the upper part of the estuary. The gradient of accumulation was higher than 20 g P m^{-2} km^{-1} of Total-P.

Key words: phosphorus, sediment, river, Palmones

RESUMEN

Durante la estacidn seca se hun estudiado los cambios espaciales de diferentes fracciones de fósforo en el sedimento del rio Palmones. Los resultados muestran la dominunciu de las formas inorgdnicas sobre las organicus, con valores del cociente IP/OP que casi llegan a 3. El fósforo inorganico en forma de apatito fue la fracción inorgánica más abundante con una clara dominancia en la parte alta del río. Todas las fracciones muestran un efecto de depuración debido al embalse del Charco redondo (por encima del 80 % de la fracción orgánica) seguido por un incremento progresivo de la concentracicin a lo largo del río con valores máximos en la cabecera del estuario. El grudiente de acumulación fue superior a 20 g P m^{-2} km^{-1} para el fósforo total

Palabras clave: fósforo, sedimento, río, Palmones

INTRODUCTION

The transport of phosphorus in rivers from point and diffusive source inputs to coastal waters is of increasing interest because of its ecological impact (Peeters *et al.*, 1991; House et al., 1995). Anthropogenic changes of the freshwater inflow regime of an estuary can affect the currents, suspended solids concentrations, salinities, tides, nutrient levels and morphology (Lepage & Ingram, 1988; Whitfield & Bruton, 1989; Clavero *et al.*, 1999). Water management is the most important problem in subarid regions, and the construction of water reservoirs is frequently the tool. In the early 80s a dam was built in the upper part of the Palmones River which started to store water in 1987.

Palmones River is a small catchment river, typical of Southern Spain rivers. In this area of Spain, the nutrient dynamics are mainly influenced by the distinctive climate of this region which induces an irregular and unpredictable regime of rains, characterized by high-waters during autumn and a very dry summer (Lucena *et al.*, 1983; Carreira et al., 1985). Two main transformations in the catchment area of the Palmones River have occurred in recent years (Clavero *et al.*, 1999): the construction of a dam, and the

Limnetica 19:3 1-38 *(2000)*

accentuated unpredictivility of rains. The reduction of the river discharge in the upper part and climatic vagaries have led to a severe drought affecting the flow of water in the river particularly between the dam and the estuary. The decrease in freshwater input has changed the tidal exchange and therefore the input of phosphate by tidal flux, also contributing to increased eutrophication (Clavero *et al.,* 1997).

The sediment in these productive areas may act as a phosphorus sink, then liberating phosphorus in reducing environments, therby enhancing production in an amplified positive feedback (Van Cappellen & Gaillard, 1996; Furrer *et al.,* 1996). This effect is due mainly to the Non Apatitic Inorganic Phosphorus (NAIP) solubilization of these compounds in reducing conditions and the P-liberation due to the assimilation of Organic Phosphorus by the bacterial community. An increase in the total phosphorus content in the upper layer of the sediment would be an index of progressive eutrophication in subarid areas of southern Spain (Fernandez, 1986; Clavero, 1992), where the P-cycling has been well studied (Pérez-Llorens & Niell, 1990; Clavero *et al.,* 1991, 1992, 1997, 1999; Carreira *et al.,* 1995; Izquierdo, 1996; Palomo, 1999).

The aim of this study is to describe the variation pattern of the different phosphorus fractions during a dry period in river-bed sediment.

MATERIAL AND METHODS

Study area

Palmones River is located in Campo de Gibraltar (southern Spain). It is a typically Mediterranean river, with strong variations in flow over the year. The river is 35.5 km long and its drainage area covers 95 km^2. Rainfall in the catchment area was irregular. For instance, in 1997 the maximum was in November (317.9 L m^{-2}) and the minimum (0.6 L m^{-2}) in July.

The river is affected by pollution sources mainly located near the estuary as well as other anthropogenic perturbations. The reservoir of Charco Redondo is located at 12 km from the source.

Sampling and analytical methods

Six stations (St.1, St.2, St.3, St.4, St.5 and St.6) were established along the river (Fig. 1) to cover the most important features. St.l was located at 6 Km of its source, St.2 was situated after the dam at 10 Km of St.1; St.3 and St.4 at 20 and 22 Km of the source, respectively, and St.5 and St.6 were located in the estuary. The study was carried out monthly from May to July 1997. Sediment samples were taken using PVC cores, (3 cm iternal diameter, 25 cm long) inserted by hand into the sediment, closed with a silicon stopper and transported in a vertical position to the laboratory in an icebox at 4°C. The sediment was sliced in segments of 2 cm (0 cm to 8 cm depth). Slices were dried at 75°C for 24 hours and divided in two subsamples. One of them was used to determine the inorganic phosphorus fractions (Williams *et al.,* 1971): Non-Apatite Inorganic Phosphorus (NAIP) and Apatite Inorganic Phosphorus (AIP). The Total Inorganic Phosphorus (IP) was considered as the sum of NAIP+AIP. The second subsample was used to determine the Total Organic Phosphorus (OP). It was extracted using Sommer et al.'s (1972) method. The sum of IP and OP was considered to be Total Phosphorus (TP). All the analysis of phosphate were made using the malachite green method (Fernández *et al.,* 1985) in a Technicon model AAII.

RESULTS

The mean concentrations of NAIP during the study period, at different depths in the sediment and down the river are shown in Table 1. From the source to the dam (St. 1), the mean value was 5.7 $\mu g\ g^{-1}{}_{dw}$, after the dam (St. 2) it decrease to 2.7 $\mu g\ g^{-1}{}_{dw}$. From there on an increasing pattern of concentration in the sediment, with the maximum reached in the estuary (172.4 $\mu g\ g^{-1}{}_{dw}$ at St. *5).* The mean values of AIP concentrations followed a similar trend to the NAIP fraction values. The concentrations ranged from 111 $\mu g\ g^{-1}{}_{dw}$ at St. 1 to 214.0 $\mu g\ g^{-1}{}_{dw}$ at St. *5.*

The OP was 1.5 to 3.3 times less abundant than the IP fraction in the sediment along the river and

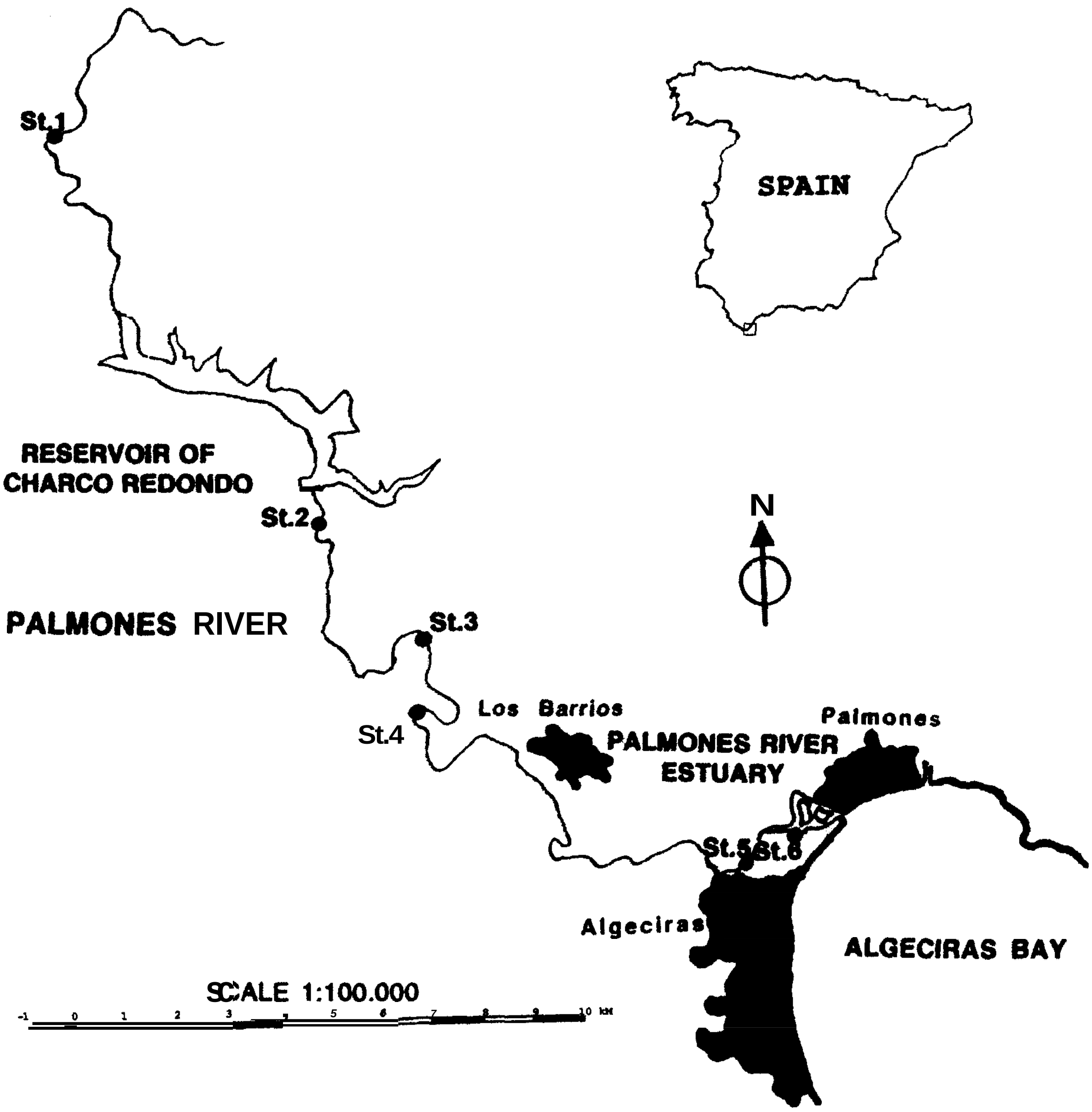

Figure 1. Map of Palmones River, showing location of sediment sampling sites. *Mapa del río Palmones mostrando la situación **de** los puntos **de** muestreo **del** sedimento.*

ranged between 12.9 $\mu g\ g^{-1}{}_{dw}$ (St. 2) and 305 $\mu g\ g^{-1}{}_{dw}$ (St. 5).

The variation of the NAIP, AIP and OP in space and depth are show in figure 2. The trends of inorganic and organic fractions were very similar i.e. an increase in concentrations from the dam to St. 5, followed by a decrease at St. 6. The results were analyzed using a two-way ANOVA (Table 2). The analysis showed that all the phosphorus fractions considered increased significantly with space (i.e. down the river) and not with depth (i.e. down the sediment profile).

Table 1. *Comparison of the mean concentrations of different phosphorus fractions in river bed-sediment. Concentrations are expressed in μg $g^{-1}{}_{dw}$.* Comparacidn de las concentraciones medias de las diferentes fracciones de fdsforo en el sedimento del lecho del rio. Concentraciones expresadas en μg $g^{-1}{}_{dw}$.

Station	NAIP	AIP	IP	OP	TP
St.1	5.7k3.5	111.0±35.8	116.7±36.0	64.4±20.5	181.1±41.4
St.2	2.7±0.3	36.3±5.5	39.1±5.5	12.9±4.1	51,9±6,9
St.3	25.1±1 1.3	27.8±12.8	52.9±17.1	35.5±52.4	88.4±55.1
St.4	11.4±4.9	102.9±50.2	114.4±50.4	79.9k58.2	197.1±77.0
St.5	172.4±26.7	214.0±5 1.9	386.4±58.3	304.9±136.8	691.3±148.7
St.6	161.4k149.7	159.1±7 1.2	320.5±165.8	141.9±124.5	462.4±207.3

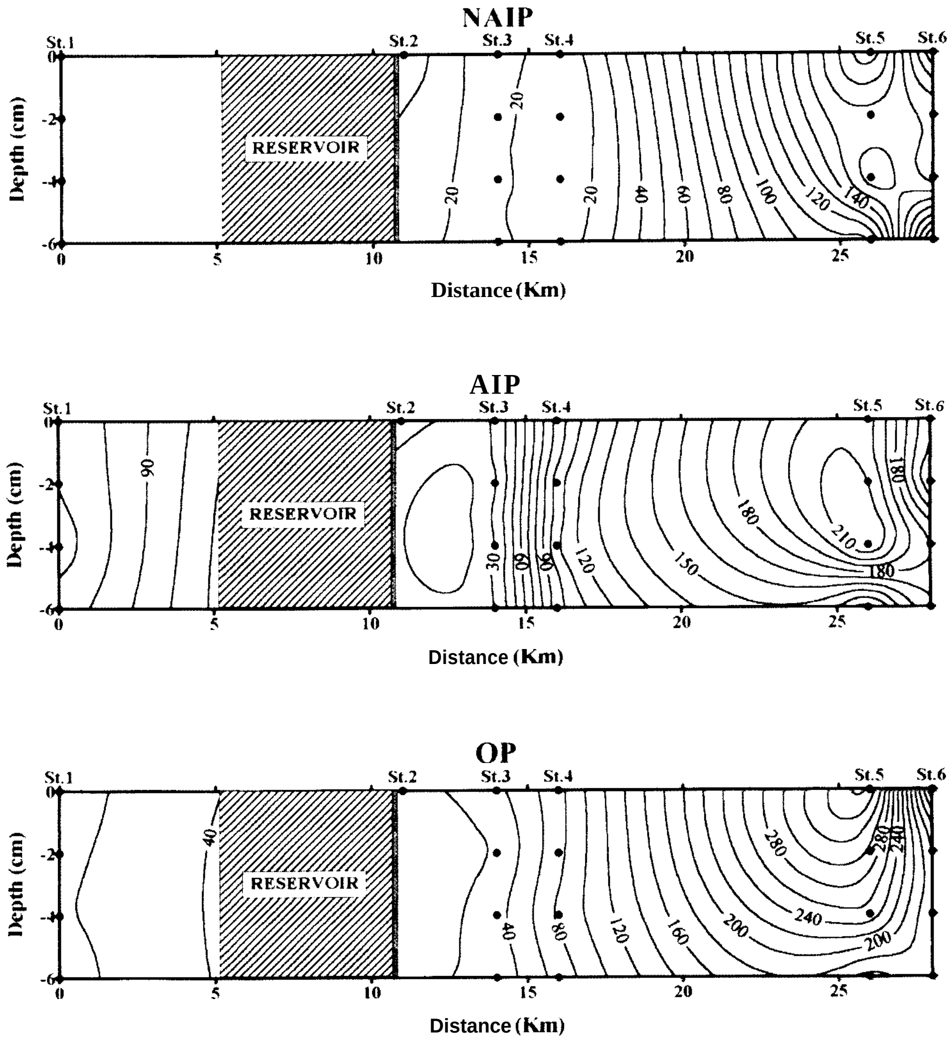

Figure 2. Horizontal versus depth variation in mean concentration of Non-Apatite Inorganic Phosphorus (NAIP), Apatite Inorganic Phosphorus (AIP) and Total Organic Phosphorus (OP) expressed as (μg$g^{-1}{}_{dw}$). *Variacidn horizontal respecto a la projundidad en la concentración media respecto a la defdsforo inorgdnico no apatítico (NAIP), fósforo inorgdnico apatítico (AIP)y fósforo organico total (OP) expresado como (μg$g^{-1}{}_{dw}$).*

Table 2. *ANOVA table for NAIP; AIP and OP concentrations in the sediment over distance and at different depth., (* significant for a = 0.05).* Tabla de un **ANOVA** de las concentraciones de NAIP, **AIP** y OP en el sedimento respecto a la distancia a diferentes profundidades

Source of variation	gl	SS	Ms	Fs
NAIP				
Distance	5	403361.3	80672.3	37.75*
Depth	3	769.7	256.6	0.12
Distance vs. Depth	15	63519.1	4234.6	1.98*
Error	35	74795.6	2137.0	
AIP				
Distance	5	272844.8	54568.9	27.01*
Depth	3	7411.4	2470.4	1.22
Distance vs. Depth	15	214335.5	1428.9	0.71
Error	35	70699.1	2019.9	
OP				
Distance	5	502225.2	100445.0	23.21*
Depth	3	5144.1	1714.7	0.40
Distance vs. Depth	15	94331.1	6288.7	1.45
Error	35	151471.3	4327.7	

$F_{0.05}(3,35) = 2.87$; $F_{0.05}(5,35) = 2.49$; $F_{0.05}(15,53) = 1.96$

Integrated values of NAIP, AIP and OP in sediment

During the sampling period, the variation of different phosphorus fraction concentrations were mainly due to their location in the catchment and not to the different date. This is the reason why we are presenting only mean differences in distance and depth ignoring time differences.

The depth-integrated P concentrations were used to calculate the percentage and the phosphorus gradient concentrations of the different fractions along the river. The percentages of each fraction are shown in Table 3. From source to the dam the most abundant fraction was AIP, which accounted for 61-70% of the total phosphorus; NAIP ranged between 3 and 35%. After the dam, except in St. 6, the most abundant fraction was OP, accounting for 30 to 44% of TP. The ratio IP/OP ranged between 2 and 3 at the upper part of the river, and was close to unit at the other stations, except in St. 6.

Table 3. *Spatial changes (i.e. across samplig stations) in mean percentage of each phosphorus fraction values are depth-integrated total phosphorus concentrations.* Cambios espaciales en el tanto por ciento medio de las fracciones de fosforo usando la concentración de fosforo total integrada para toda la profundidad muestreada.

Station	NAIP	AIP	IP	OP	IP/OP
1	3.1	61.3	64.4	35.6	1.8
2	5.3	69.9	75.2	24.8	3.0
3	28.4	31.5	59.9	40.1	1.5
4	5.8	52.2	58.0	42.0	1.4
5	24.9	31.0	55.9	44.1	1.3
6	34.9	34.4	69.3	30.7	2.2

Phosphorus concentration gradient along the river

The phosphorus concentration gradient was obtained by calculating the integral from surface to depth P-concentrations for each fraction and distance interval. The values obtained were plotted against distance (km) and the function that exhibited the best fit was calculated for the stretch going from the dam to the upper part of the estuary (Fig. 3). The value of the first derivative (dP/dX) of this function was considered to be the phosphorus gradient concentration (g P m^{-2} km^{-1}). The accumulation from St. 2 to St.5 was estimated at 2.73 g P m^{-2} km^{-1} of NAIP; 8.56 g P m^{-2} km^{-1} of AIP and 9.26 g P m^{-2} km^{-1} of OP, which means total phosphorus accumulation along the whole river was 20.8 g P m^{-2} km^{-1}. In the estuary, the trend was different, with a loss of 1.01, 5.05, 15.0 and 21.0 g P m^{-2} km^{-1} of NAIP, AIP, OP and TP respectively.

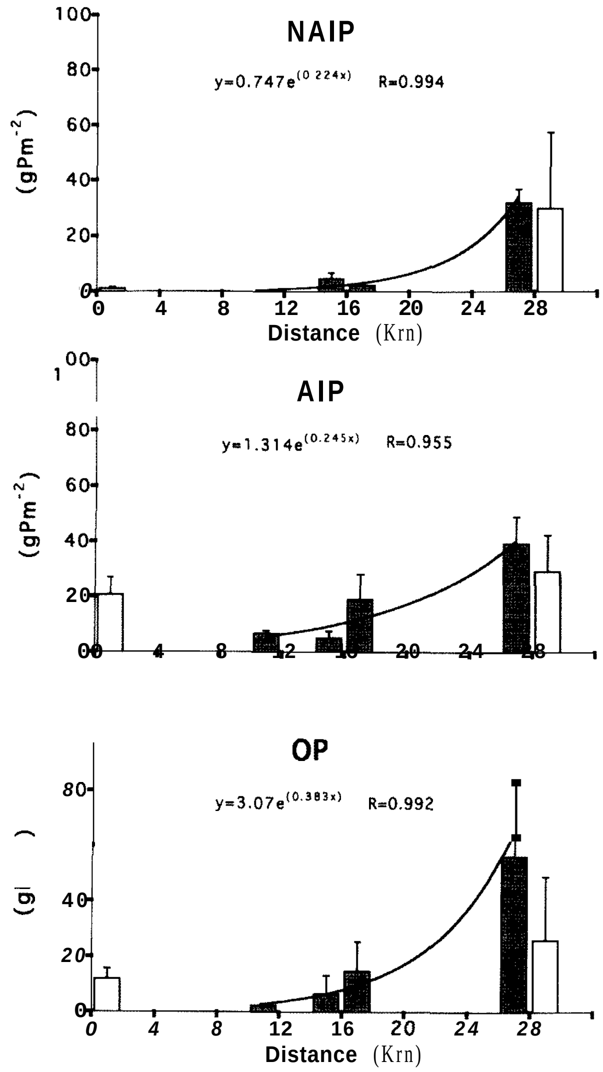

Figure 3. Exponential regression coefficients between changes in Non-Apatite Inorganic Phosphorus (NAIP), Apatite Inorganic Phosphorus (AIP) and Total Organic Phosphorus (OP) mean concentration along the study period and distance from St *2* to St 6 (grey colour). Correlations were significant at $\alpha = 0.05$. *Correlacidn exponencial entre los cambios* **en** *la concentración media de fósforo inorgánico no apatitico (NAIP), fdsforo inorganico apatítico (AIP)y fdsforo orgánico total (OP)a lo largo del periodo estudiado respecto a la distancia entre las estaciones 2 y 6 (color gris). Cada correlacidn* **es** *significante a* $\alpha = 0.05$.

DISCUSSION

Reservoirs are known to be able to retain an important amount of phosphorus, thus affecting this biochemical cycle downatream of it (Carreira *et al.,* 1995). In Palmones River the "retention" of different fractions of phosphorus by the reservoir is very high and can be calculated as the relation between the concentration of NAIP, AIP and OP after and before the dam. NAIP was retained at 53%, AIP at 67% and OP near to 80%. Accumulation of OP can occur by rapid phosphorus burial (Clavero *et al.,* 1998). The phosphorus profiles in the reservoir (Lucena *com. pers.*) were related to high production in the eutrophic reservoir, and to the consequently increased organic matter settling onto the sediment. OP has been considered a source of dissolved phosphate in interstitial water in sediment due to bacterial regeneration (Berner, 1980). The change of the IP/OP ratio before and after the dam showed, however, a different pattern of retention in this reservoir, with higher "depuration rates" in the organic phosphorus fractions than in the inorganic ones. This depuration effect of the reservoir on the OP fraction may produce a significat reduction of the release of phosphorus from the sediments.

AIP was the most abundant fraction of inorganic phosphorus. Its concentration increased up to 10 fold from dam to estuary. This could be due to either catchment area erosion, or to reprecipitation as calcium-bound phosphorus (Jahnke *et al.,* 1995) when water presents a positive redox, when oxygenated by photosynthesis or directly by aireation (Clavero *et al.,* 1997). In contrast to **AIP,** NAIP decreased almost 2-fold. This is why the ratio AIP/NAIP strongly decreased from the source down to the mouth of river Palmones. The ratio IP/OP indicates the importance of inorganic phosphorus in the catchment. Maximum values after the dam are probably due to preferential retention of the organic fraction by the reservoir. The minimum value at St. *5*, where the concentration of OP was the highest, may be related at its maximum bacterial abundance at this site (Clavero *et al.,* 1995).

There were important differences between St. *5* and St. 6 (both estuarine stations), observed as high changes in concentrations and fundamentally in the spatial gradients of every phosphorus fraction. A general accumulation of P from the dam to St. *5* is followed by an important loss within the estuary, with values of only 15.0 g P m^{-2} km^{-1} of OP. The variation in salinity, the highly variable topography, the different tidal ranges and the physical mixture of two different water masses result in a complex pattern of deposition that make possible the huge differences across less than two kilometres.

ACKNOWLEDGEMENTS

This work has been supported by the grant AMB99-1088 of the Spanish Commission Interministery Science and Technology. We warmly thank E. Briones for his assistance in the field.

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