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The Control of a Small Dam in Nutrient Inputs to a Hypertrophic Estuary in a Mediterranean Climate

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Abstract A two-year study was carried out in the lower part of the Palmones River to describe the role of a small dam controlling the nutrient fluxes to the estuary. Results showed an important spatial heterogeneity in the nutrient content and water properties of lowland catchment due to the effects of the small dam and the effluents of a sewage treatment work. Taking into account the values of hydraulic retention time, the dam could be considered as an optimally dimensioned pre-dam. Therefore, it removed on average more than 25% of total phosphorus (TP) while no net removal was obtained for TN during the studied period. Palmones River exported 11.3 TonsP year^{-1} of TP and 72.1 TonsN year^{-1} of TN to the estuary showing important seasonal differences. Less than 10% from the total amount of nutrient was exported during low flow conditions, while in four months with important flooding events, the percentage of total nitrogen exported exceeded 64%.

Keywords eutrophication · municipal sewage · nutrient forms · Palmones River · pre-dam · self-depuration

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1 Introduction

Coastal areas all over the world are submitted to an increase in eutrophication levels. This problem is because of the increase in the nutrient content that has led to a decline in environmental quality of shallow estuaries affecting their natural function of estuaries as nurseries for several fish, crustaceans and mollusc species. As a result, important changes in the composition of the primary producers are evident, with the replacement of sea grass meadows by the dominance of phytoplankton and fast-growing macroalgae (e.g., Viaroli et al., 1996; Cardoso, Pardal, Lillebø, & Pardal, 2004). Estuarine processes are therefore of great interest both from the ecological, geochemical, economic and recreational points of view (Zwolsman, 1994). Over the last few decades there has been an increased interest in quantifying the fluxes of nutrients into estuaries and the environmental effects that such nutrients have on water quality (e.g., Nedwell, Dong, Sage, & Underwood, 2002; Tappin, 2002; O'Higgins & Wilson, 2005).

Phosphorus is usually considered the limiting nutrient for primary producers in freshwater, while in marine systems it is nitrogen, thus their reduction from river channels is of paramount importance (Rigler, 1979; Neal, 2001). Several studies have shown the application of riparian vegetation and pre-dams (small dams located immediately upstream from reservoirs or other water masses) as traps that reduce nutrients and suspended particulate matter (SPM) from the water column (e.g., Paul, Schröter & Labahn, 1998; McKergow, Weaver, Prosser, Grayson, & Reed, 2003). In both cases, an important increase of the hydraulic retention time (HRT) is produced and consequently, settling of particles, interactions between sediment and water column and elimination of dissolved nutrients by the primary producers become stronger. According to Benndorf and Pütz (1987) if a pre-dam is optimally dimensioned, the removal of SRP can be expected to be higher than 70% and lower values for inorganic nitrogen can also be expected (Paul, 2003). Furthermore, pre-dams produce important changes in nutrient speciation and nutrient ratios in rivers that could affect the composition and abundance of primary producers in estuaries and coastal regions (Justic, Rabalais, Turner, & Dortch, 1995; Hunt, Loder, & Vörösmarty, 2005).

In the inner part of the estuary of Palmones River (Southern Spain), there is a small dam that acts as a barrier for the seawater at high tide, allowing only freshwater discharge. The hydraulic changes produced by the dam, increase the HRT and the possibility of nutrient removal from the water column. The main sewage treatment works (STW) in the catchment flows into the dammed water, modifying its characteristics and increasing nutrient concentrations (Avilés, 2002).

Climatic conditions influence the behaviour of shallow estuaries in the south of Spain, since they are characterized by small catchment areas and a subarid climate. The hydrology of Palmones River is characterized by low flow conditions during most of the year, with short intense flooding events in winter and spring seasons (Avilés & Niell, 2005). In summer, river discharges could be lower than 0.05 $m^3 s^{-1}$, almost similar to STW discharges.

Since the 1980s several studies have been carried out in the estuary of Palmones River in order to characterize the nutrient concentration in water column and sediments and the progressive eutrophication (Clavero, Fernández, & Niell, 1992; Izquierdo, 2001; Palomo et al., 2004). However, no studies relating to the seasonal inputs from the river and the role of the dam have been made.

The main objectives of this study are to describe the influence of the dam in the seasonal variation of water properties and nutrient concentrations in the lowland catchment of Palmones River and to quantify its role in the fluxes of total phosphorus and nitrogen from the river to the estuary.

2 Study Area

2.1 Palmones river

Palmones River is located in Southern Spain, with a drainage area of 302 km^2 and 42 km in length. In spite of its small surface, there is an extreme variability in geomorphology, land uses and human pressure. Thus, well conserved environments such as the Natural Park of Los Alcornocales contrast with the presence of the reservoir of Charco Redondo in the upper part of the catchment (at 8 km from Site 1) and an important agricultural and industrial activity in its lower part, modifying the natural hydrological and physico-chemical characteristics of stream water.

The annual mean precipitations over the catchment just ranged from 350 mm to over 1,500 mm per year in the last decade. As in other rivers with a Mediterranean climate, precipitation events present irregular patterns of distribution, dominated by short pulses of intense precipitation and long drought periods.

2.2 Dammed water

In 1955 a small dam was built in the catchment at 5.5 km from the mouth of Palmones River, with the purpose of supplying freshwater to a cellulose pulp plant. Nowadays, in spite of it being out of function, it still acts as a barrier for seawater at high tide, allowing only freshwater discharge. Upstream from the dam, a great accumulation of water has been formed, with a volume of 0.21 hm^3, a length of 8.6 km and a very low slope (Table 1). The dammed water presented a dimension big enough to be considered as a pre-dam. The lower part of the Palmones River is characterized by a heterogeneous siliceous and detritic geology and an intensive agriculture of orange trees and irrigated tilled land.

Table 1 Some physiographical characteristics of dammed water

Mean slope (%)	0.15
Longitudinal extent (km)	8.6
Mean width (m)	32
Mean depth (m)	0.75
Dammed volume (hm^3)	0.21
River flow ($m^3 s^{-1}$)	0.0–57.8
Hydraulic retention time (h)	1–>1,000

The main population centre of the catchment (Los Barrios – 15,000 inhabitants) is located near the river with a sewage treatment works (STW) that flows into the dammed water (Fig. 1).

2.3 The Palmones estuary

The estuary of Palmones River is a small, shallow and hypertrophic system with small tidal movements (maximal amplitude of 2 m) and a long emersion period (Niell, Espejo, Fernández, & Algarra, 1989). The grain size composition in the estuary sediment presents a great heterogeneity with sandbanks and important mudflats (Moreno & Niell, 2004). As a consequence of the construction of the reservoir of Charco Redondo (that produces a great reduction of river discharge and sediment scouring) and some severe droughts in the last two decades, an increase of estuary eutrophication has been expected, modifying the nutrient fluxes and the biota composition (Carreira et al., 1995; Clavero, Izquierdo, Palomo, Fernández, & Niell, 1999).

3 Materials and Methods

3.1 Sample collection

As the study reported in this paper uses the ‘upstream and downstream’ approach to investigate the role of the dam in the nutrient fluxes to the estuary, samples from the water column were collected in three sampling sites (Fig. 1). Site 1 is located up to the limit of dammed water. This site acts as a control point, allowing the calculation of nutrient input from the upper and middle part of the catchment. Site 2 is placed only a few metres upstream from the dam, quantifying the water and nutrient export to the estuary. Finally, site 3 is located in the inner part of the estuary (just after the dam) that allows us to verify the role of the dam in the inner part of the estuary. From April 1999 to May 2001, eight samples were collected with a frequency conditioned by river discharge in order to complete monthly results of total nitrogen and phosphorus obtained by the Environmental Agency

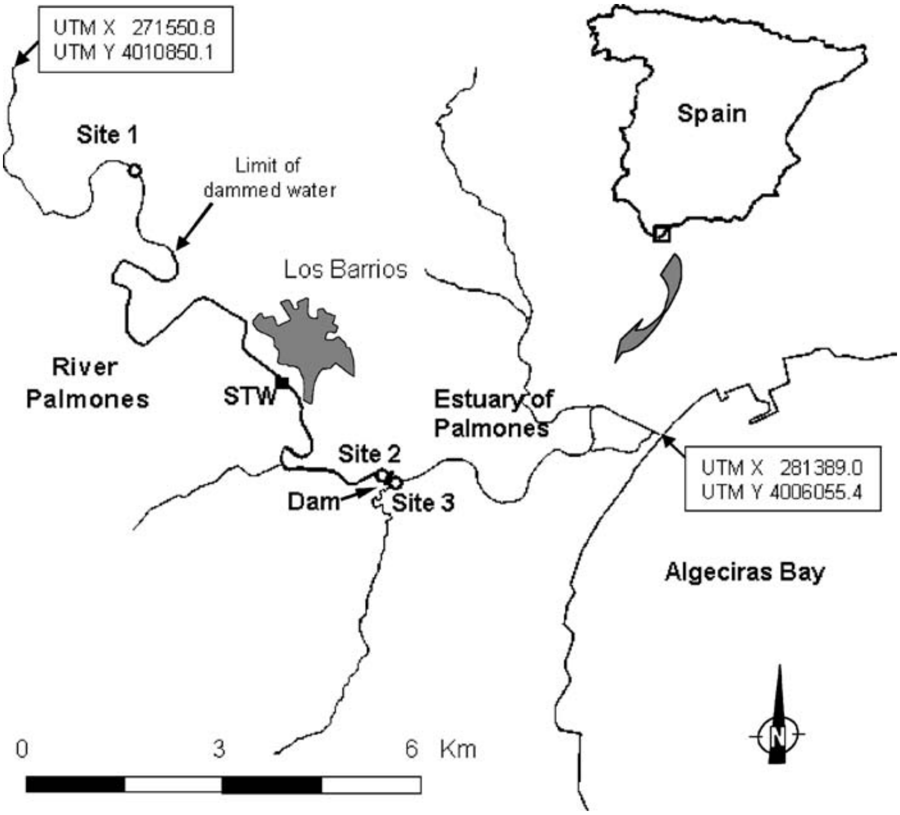

Fig. 1 Map of the lower part of Palmones River showing the location of sampling points

of the Junta de Andalucía. Governmental data were used only for the quantification of sewage flows and nutrient inputs from the river to the estuary.

Temperature and pH were measured using a multisonde WTW P3 pH/OXI and salinity with a WTW conduktometer LF191. Two litres of water were collected from 0.25 m below the surface in the middle of the channel at each sampling sites and placed in ice for transport to the laboratory. For the determination of particulate forms of phosphorus and nitrogen, suspended particulate matter (SPM) and chlorophyll *a* (Chl *a*), subsamples of water were filtered through Whatman GF/F membranes, using the filtered water for the analysis of soluble nutrients, carbonate and calcium, and unfiltered subsamples for the determination of total forms of phosphorus and nitrogen.

3.2 Sample processing and analytical procedures

An exhaustive analysis of phosphorus and nitrogen forms from the water column was carried out through this study. Soluble reactive phosphorus (SRP) was determined using the malachite green method (Fernández, Niell, & Lucena, 1985) in a Technicon Autoanalyzer AAII. From unfiltered water, filtered water and filters, total phosphorus (TP), total soluble phosphorus (TSP) and total particulate phosphorus (TPP) respectively, were analysed by acid digestion with nitric and perchloric acids (Sommers & Nelson, 1972), followed by the determination with the malachite green method. The concentration of soluble unreactive phosphorus (SUP) was obtained by difference between TSP and SRP according to Rigler (1973). The inorganic nutrients nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) were analysed using a BRAN & LUEBBE Technicon TRACCS 800. Nitrate and nitrite analysis were performed according to the Industrial Method N° 818-87T based on Shinn (1941) and Wood, Armstrong and Richards, (1967). Ammonium ion was analysed using the Industrial Method N° 786-86T (Slawyk & MacIsaac, 1972). The term DIN refers to the sum of all soluble inorganic nitrogen species ($NO_3^- + NO_2^- + NH_4^+$). Total particulate nitrogen from filters were obtained with a CHN autoanalyzer Perking Elmer (model 2400 C), while total nitrogen (TN) was determined according to Grasshoff,

Table 2 Water quality summaries for sampling sites

Date	Site	Discharge ($m^3\ s^{-1}$)	T^a (°C)	pH	Salinity	LogSI$_{calcite}$	SPM (mg l^{-1})	Chl a (μg l^{-1})
Apr–99	Site 1	0.1	16.9	7.82	0.13	−0.39	6.8	1.7
	Site 2	0.3	19.8	7.71	0.03	−0.12	18.4	56.6
	Site 3		22.5	7.40	7.60	1.35	41.6	85.9
May–99	Site 1	0.6	15.3	7.51	0.12	−0.84	45.3	2.2
	Site 2	0.8	18.1	7.37	0.16	−0.64	7.7	9.6
	Site 3		18.5	7.34	0.92	0.48	19.5	23.0
Jul–99	Site 1	0.0	24.9	7.10	0.20	−0.47	10.5	11.0
	Site 2	0.0	26.2	7.22	0.16	0.08	27.0	7.6
	Site 3		30.6	8.52	25.49	3.21	121.0	41.8
Feb–00	Site 1	0.7	11.5	7.41	0.08	−0.95	6.9	1.1
	Site 2	1.1	15.3	7.25	0.12	−0.88	27.4	45.6
	Site 3		17.6	7.32	8.89	1.08	30.2	11.0
May–00	Site 1	1.4	15.2	7.34	0.14	−0.85	15.8	0.9
	Site 2	1.9	18.1	7.35	0.23	−0.59	39.7	38.0
	Site 3		17.9	6.95	1.54	0.88	20.0	8.4
Jun–00	Site 1	0.1	22.3	6.80	0.19	−1.05	9.3	1.6
	Site 2	0.0	27.1	8.80	0.26	0.95	63.4	98.2
	Site 3		24.2	7.88	28.80	2.50	16.4	56.7
Jan–01	Site 1	6.0	12.3	7.95	0.10	−0.78	35.2	0.0
	Site 2	7.1	13.4	7.56	0.12	−0.82	97.3	0.5
	Site 3		13.2	8.01	0.14	−0.35	64.6	0.0
May–10	Site 1	1.0	18.0	7.20	0.12	−1.21	13.5	0.3
	Site 2	1.4	18.7	7.38	0.20	−0.54	45.5	16.7
	Site 3		20.0	7.60	3.40	0.60	45.0	32.2

Ehrhardt, and Kremling, (1983) method. Dissolved organic nitrogen (DON) was obtained by difference between TN and the sum of DIN and TPN.

Carbonate was determined by titration 100 ml of water with 0.01 N HCl down to pH 4.2 (Stumm & Morgan, 1981) and calcium was analysed by ion chromatography in a Metrohm 732. According to Neal et al., (2002), the saturation index of calcite ($SI_{Calcite}$) is defined in a logarithmic form as:

$$\begin{aligned}\mathrm{Log}(\mathrm{SI}_{\mathrm{calcite}}) &= \log_{10}\left(\left\{\mathrm{Ca}^{2+}\right\} * \left\{\mathrm{CO}_3^{2-}\right\}\right) \\ &\quad - \log_{10}\left(\mathrm{K}_{\mathrm{Calcite}}\right) \\ \mathrm{K}_{Calcite} &= 13.534 - (0.040\mathrm{T}) - (3000/\mathrm{T})\end{aligned}$$

where K_{Calcite} is the solubility product of calcite at the temperature of the reaction (Plant & House, 2002) and T is the temperature (°K).

In order to find out the determination of suspended particulate matter (SPM), filters were dried and later weighed. Phytoplankton chlorophyll *a* was measured spectrophotometrically after extraction with N-N Dimethylfornamide (Stricklan & Parson, 1972).

Benndorf and Pütz (1987) proposed a coefficient $\bar{t}_{\mathrm{rel}}$ to predict the SRP elimination in pre-dams:

$$\bar{t}_{\mathrm{rel}} = \frac{\bar{t}_{\mathrm{theor}}}{\bar{t}_{\mathrm{crit}}} \quad \bar{t}_{\mathrm{theor}} = \frac{V_{\mathrm{R}}}{Q_{\mathrm{in}}} \quad \bar{t}_{\mathrm{crit}} = \frac{24.7}{T_{\mathrm{M}}}\left(1+\frac{2}{P_{\mathrm{M}}}\right)\left(1+\frac{21}{I_{\mathrm{M}}}\right)$$

where the volume V_{R} of the 'reaction space', the mean discharge Q_{in}, the monthly means of the temperature T_{M} (°C), underwater light intensity I_{M} (J cm^{-2} d^{-1}) in the reaction space and the SRP concentration P_{M} (μgP l^{-1}) of the inlet.

3.3 Statistical analyses

Analyses of covariance between water variables were carried out. Two-way ANOVAs have been used to examine the spatial and seasonal effects on the concentration of nutrients (Sokal & Rohlf, 1995). Multiple *a posteriori* comparisons between means were tested by Tukey test using the program SPSS 12.0.

Table 3 Nutrient concentrations in water column

Date	Site	SRP (mgP l^{-1})	SUP (mgP l^{-1})	TPP (mgP l^{-1})	NO_3^- (mgN l^{-1})	NO_2^- (mgN l^{-1})	NH_4^+ (mgN l^{-1})	DON (mgN l^{-1})	TPN (mgN l^{-1})	DIN/SRP ratio	C/N ratio
Apr–99	Site 1	0.01	0.03	0.01	1.21	0.02	0.11	0.87	0.11	93	11.0
	Site 2	0.08	0.09	0.10	2.17	0.15	1.82	0.60	0.49	52	8.2
	Site 3	0.12	0.05	0.11	0.83	0.18	1.08	0.69	0.69	19	7.3
May–99	Site 1	0.01	0.09	0.02	1.19	0.05	0.07	0.98	0.33	50	9.6
	Site 2	0.39	0.12	0.05	1.47	0.22	1.43	0.43	0.22	9	9.9
	Site 3	0.24	0.15	0.08	1.61	0.21	0.75	0.73	0.35	9	6.4
Jul–99	Site 1	0.02	0.04	0.08	0.07	0.01	0.18	0.66	0.84	24	8.0
	Site 2	0.01	0.03	0.02	0.09	0.00	0.16	0.06	0.21	26	9.9
	Site 3	0.04	0.09	0.14	0.55	0.01	0.10	0.39	0.91	11	8.1
Feb–00	Site 1	0.01	0.03	0.01	0.95	0.03	0.05	0.68	0.10	71	7.5
	Site 2	0.15	0.12	0.12	1.66	0.13	2.26	0.58	0.38	31	8.6
	Site 3	0.23	0.10	0.07	0.09	0.15	2.11	0.65	0.27	16	6.7
May–00	Site 1	0.02	0.01	0.02	2.01	0.04	0.06	1.33	0.10	49	14.7
	Site 2	0.09	0.40	0.13	0.50	0.28	1.76	0.40	0.51	40	8.2
	Site 3	0.12	0.09	0.06	0.53	0.46	1.61	0.70	0.19	27	8.6
Jun–00	Site 1	0.00	0.10	0.02	1.33	0.02	0.05	0.92	0.13	159	8.3
	Site 2	0.03	1.05	0.23	0.02	0.00	0.00	0.27	2.02	1	7.1
	Site 3	0.22	0.79	0.16	0.02	0.00	0.23	0.48	1.68	2	5.6
Jan–01	Site 1	0.13	0.04	0.04	1.02	0.01	0.01	0.72	0.16	4	14.5
	Site 2	0.05	0.01	0.11	1.03	0.03	0.29	0.24	0.51	21	8.9
	Site 3	0.01	0.01	0.07	2.06	0.45	0.13	0.77	0.41	132	10.2
May–01	Site 1	0.01	0.02	0.02	0.94	0.01	0.00	0.63	0.11	85	11.1
	Site 2	0.04	0.08	0.12	0.68	0.14	2.18	0.49	0.73	96	7.0
	Site 3	0.15	0.11	0.12	0.31	0.15	0.87	0.65	0.3	4	7.3

4 Results and Discussion

4.1 Water chemistry and nutrient concentrations

A summary of the water quality is presented in Table 2. Discharges measured in sites 1 and 2 showed a wide variability, with an alternation of short flooding events and low flow periods with discharges lower than 0.05 $m^3 s^{-1}$. During the summer, such low discharges, doses of photosynthetic active radiation (PAR) higher than 14,000 kJ $d^{-1} m^{-2}$ (Aguilera et al., 2004) and temperatures up to 25°C promoted an elevated phytoplankton growth. Chl *a* presented values higher than 10 μg l^{-1} in sites 2 and 3 (almost reaching a value of 98.2 μg l^{-1} in site 2) that is often taken to indicate persistent algal blooms and eutrophic level (Iriate & Purdie, 2004). Samples are characterized by basic pH with mean values higher than 7.4 and a maximum of 8.80 obtained in site 2 during the summer 2000. The seasonal variation of salinity in the inner part of the Palmones Estuary (site 3) is strongly influenced by the river discharge, showing salinities lower than 0.2 during flooding events and up to 25 during drought periods. The absence of significant differences of suspended particulate matter (SPM) between sampling sites (ANOVA, $n=24$, $P<0.05$) show that its reduction from the water column was lower than in other pre-dams (Paul et al., 1998).

It is well known that the precipitation of calcium carbonate reduces phosphate pollution in freshwater because the co-precipitation caused by the interaction between phosphate and the calcite surface during crystal growth (House & Donaldson, 1986; Neal, 2001). For instance, in River Kennet, Neal et al. (2002) showed the high importance of this process in the removal of phosphorus from waters that receive effluents of STW. However, the water from sampling sites 1 and 2 are in general, undersaturated with respect to calcite by a factor from 1.3 to 16 times (−0.12 and −1.21 on a logarithmic scale). In site 2, lower values of oversaturation were obtained during the summer samplings. Only site 3 showed always positive $LogSI_{calcite}$ values, with a maximum of 3.21 that was obtained during summer 1999. Results showed that the effect of calcite precipitation and co-precipitation of phosphate as a self-cleansing phosphate mechanism could only be important in site 3 and during dry seasons in site 2, having in general a scarce importance in the phosphate depletion in the dammed water.

In Table 3 a summary of the most important phosphorus and nitrogen forms is presented. On average, soluble unreactive phosphorus (SUP) comprised the highest phosphorus form in the study area, with the highest concentration of 1.05 mgP l^{-1} in site 2. Soluble reactive phosphorus (SRP) and total particulate phosphorus (TPP) presented lower concentrations than SUP

Table 4 Correlation coefficients between water variables in the study area ($n=24$; $n=16$ for discharge and $n=8$ for HRT)

	Disch.	T^a	SPM	Chl *a*	HRT	SRP	SUP	TPP	TP	NO_3^-	NO_2^-	NH_4^+	DON	TPN	TN
Disch.	1														
T^a	−0.57*	1													
SPM	0.63**	0.23	1												
Chl *a*	−0.26	0.55**	0.23	1											
HRT	−0.52	0.88**	0.01	0.89**	1										
SRP	0.14	−0.04	−0.21	0.17	−0.30	1									
SUP	−0.20	0.43*	0.09	0.67**	0.76*	0.16	1								
TPP	0.08	0.48*	0.51*	0.82**	0.68	0.19	0.72**	1							
TP	−0.10	0.40	0.09	0.71**	0.72	0.45	0.94**	0.79**	1						
NO_3^-	0.06	−0.53**	−0.14	−0.25	−0.19	−0.02	−0.44*	−0.37	−0.41*	1					
NO_2^-	−0.04	−0.28	0.00	−0.02	−0.50	0.30	−0.14	0.05	−0.01	0.25	1				
NH_4^+	−0.06	−0.12	−0.11	0.23	−0.48	0.49*	−0.06	0.26	0.14	0.05	0.52**	1			
DON	−0.15	−0.43*	−0.39	−0.34	−0.13	−0.15	−0.35	−0.52**	−0.40	0.52**	0.08	−0.17	1		
TPN	−0.13	0.60**	0.35	0.75**	0.80*	0.03	0.85**	0.85**	0.82**	−0.47*	−0.21	−0.09	−0.43*	1	
TN	−0.10	−0.29	−0.11	0.26	−0.13	0.36	−0.04	0.22	0.12	0.58**	0.58**	0.74	0.25	−0.05	1

* $P<0.05$, ** $P<0.01$.

with very similar values between them. There were spatial differences in SRP concentrations between sites 1 and 3 and between site 1 and sites 2–3 for TPP (Tukey test, $n = 24$, $P < 0.05$). In unperturbed systems, SUP proceeds from exudation of organic compounds by the cellular metabolism and lysis (Christman & Minear, 1971). This phosphorus form usually has little importance in the phytoplankton growth because the use of enzymatic activity is necessary for its transformation to SRP. Therefore, Hernández, Pérez-Pastor, and Pérez-Lloréns, (2000) showed that in Palmones River, alkaline phosphatase is only used actively as a phosphate source by bacteria and phytoplankton in the estuary.

Nitrate and DON were the most abundant forms in site 1, while nitrate and ammonium were in sites 2 and 3 (Table 3). DON showed spatial differences with minimum values in site 2 (Tukey test, $n = 24$, $P < 0.05$), just where maximum values of nitrate (2.17 mgN l^{-1}), ammonium (2.26 mgN l^{-1}) and TPN (2.02 mgP l^{-1}) were found.

The STW of Los Barrios flows 1.84 $\mathrm{hm}^3\ \mathrm{year}^{-1}$ with mean concentration of 3.5 mgP l^{-1} of TP and 23.6 mgN l^{-1} of TN, producing a great impact in the nutrient content downstream. The application of a Tukey test ($n = 24$, $P < 0.05$) showed significant differences between site 1 and sites 2 and 3 in the concentration of TPP, ammonium and DON, showing the effect of STW effluents in the increase of nutrient concentrations.

Table 5 Annual nutrient loads in site 1, STW and site 2, and percentage of total phosphorus and nitrogen removed by the dam

	Site 1 Input	STW Input	Site 2 Output	Removal %
TP (TonsP year^{-1})	9.6	5.5	11.3	25.2
TN (TonsN year^{-1})	27.8	44.1	72.1	−0.3

Average concentrations of nitrate and phosphate in the sampling sites were higher than average world river values obtained by Meybeck (1982), including site 1 that is not affected by STW effluents. Taking into account TP concentrations, the trophic states on sampling sites over the year are usually hypertrophic (Fosberg & Ryding, 1980). In an attempt to evaluate the control of nutrient over primary producer growth, lineal correlations between nutrient content (SRP, NO_3^- and NH_4^+) and Chl *a* were made (Table 4). Results indicated that nutrients did not correlate with phytoplankton biomass variability. According to Danielidis, Spartinou, and Economou-Amilli, (1996) in base to nutrient requirements of phytoplankton, there is in general a phosphorus limitation if DIN/SRP ratio is

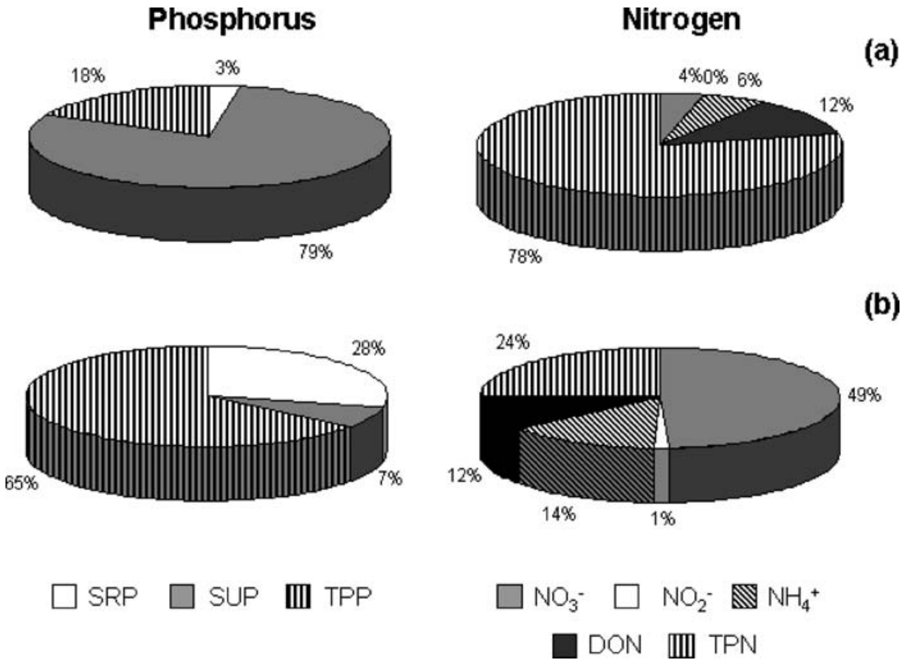

Fig. 2 Average relative percentage of phosphorus and nitrogen forms in site 2. Low flow periods (a) and flooding events (b)

higher than 20 and nitrogen limitation if DIN/SRP ratio is lower than 10. Data of mean DIN/SRP ratios (Table 3) show values higher than 20, so probably P-limited. However, during the summer 2000, results obtained in sites 2 and 3 presented nitrogen as the limiting nutrient, with values of 1 and 2, respectively. The C/N ratio showed maximum values that are double than the relation proposed by Redfield, Ketchum, and Richards, (1963) for planktonic composition (14.7 in site 1), indicating the detritic origin of SPM. Interestingly, is the decrease of C/N ratio from site 1 to site 3, in a clear relation with the increase of phytoplankton biomass.

4.2 The role of the dam in the removal of nutrients

The purpose of pre-dams is to improve the quality of the inflowing water by reduction of the loads of suspended particulate matter and dissolved nutrients (Paul, 2003). Benndorf and Pütz (1987) developed a procedure to predict the SRP elimination in pre-dams, which can be expected to be higher than 70% if the relative retention time $\bar{t}_{\mathrm{rel}} > 1\ \mathrm{d}^{-1}$. Results of $\bar{t}_{\mathrm{rel}}$ in the dammed water showed a markedly seasonal variability ranging from 0.1 d^{-1} in winter 2001 to more than 30 d^{-1} in summer 1999. Values of $\bar{t}_{\mathrm{rel}}$ were lower than one only during the odd flooding events,

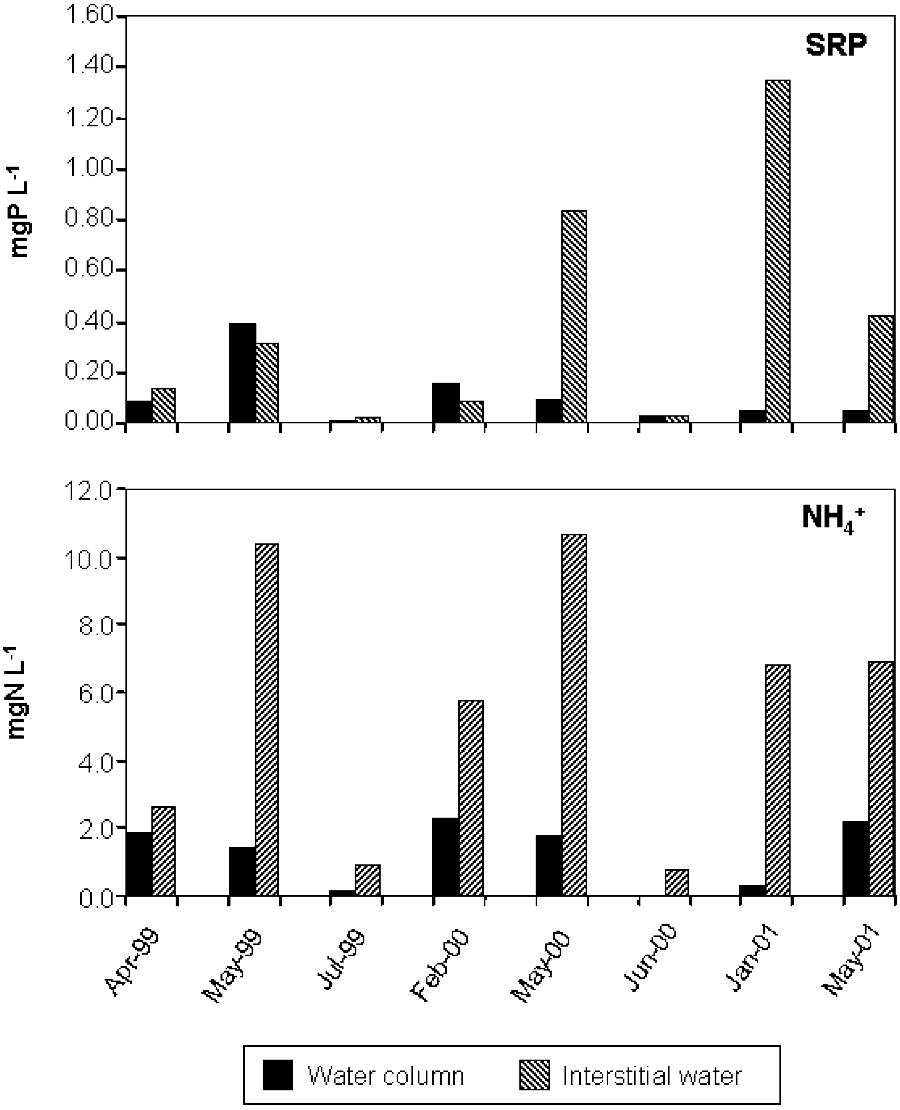

Fig. 3 Comparison between SRP and ammonium concentrations in water column and interstitial water in site 2

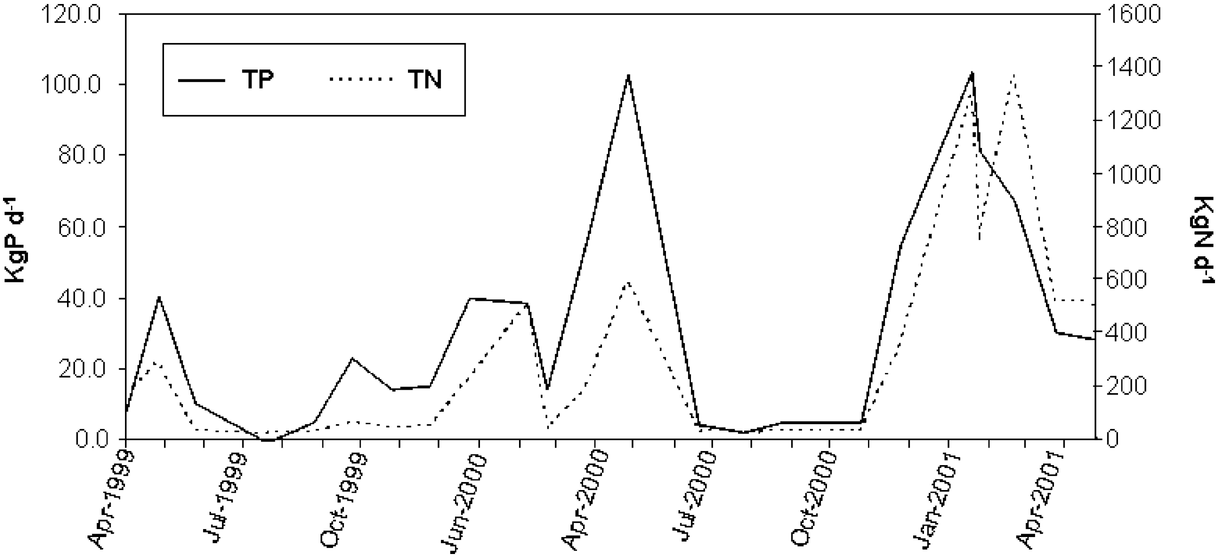

Fig. 4 Variability of total phosphorus and total nitrogen loads from river Palmones to the estuary

so it could be concluded that in spite of the different purpose of the erected dam, it could be considered as an optimally dimensioned pre-dam in attention to its potential on SRP removal.

A summary of annual phosphorus and nitrogen loads in site 1, site 2 and STW effluent is given in Table 5. From site 1 to site 2, TP and TN loads changed from 9.6 to 11.3 TonsP year^{-1} and from 27.8 to 72.1 TonsN year^{-1}, respectively. These differences show the importance of sewage effluents in the increase of nutrient fluxes to the estuary. Table 5 also shows the annual percentage of nutrient removed by the dam by a balance between the outputs (site 2) and the inputs (site 1 and STW).Thus, the annual removal of TP was higher than 25%, while no net removal was obtained for TN. Paul (2003) obtained that TP elimination did not outreach 25% even in the largest pre-dams in summer, showing the great efficiency of the studied dam in the phosphorus elimination from the water column. Nevertheless, the removal efficiency presented strong seasonal differences. Thus, the mean percentage of TP and TN loads removed in July 1999 were up to 95%; while in January 2000 only a removal of 13% of TP has been estimated and also an increase of 14% of TN.

The HRT values obtained in this study ranged between one hour and more than 1,000 h (Table 1). This high seasonal variability is probably the most important factor that controls the relative percentage of phosphorus and nitrogen forms obtained in site 2 (Fig. 2). While SUP with 79% and TPN with 78% were the dominant phosphorus and nitrogen forms in summer; during flooding events TPP was the most abundant form of phosphorus (65%) and nitrate the dominant form of nitrogen (49%). HRT is also the main factor controlling the Chl *a* concentration, as proof of the high correlation obtained between the HRT and the concentration of Chl *a* (Table 4), in agreement with the results shown by Kawara, Yura, Fujii, and Matsumoto, (1998) in the Asahi River Dam reservoir. The high concentration of Chl *a* obtained in this sampling point (Table 2) illustrates that SRP elimination does mainly result from the biological transformation of dissolved to particulate phosphorus by the phytoplankton. During low flow conditions, the increase of HRT values produce settling of particles and the development of phytoplankton, but it would favour the sediment-water biochemical interactions such as the nutrient fluxes from the sediment to the water column (e.g., Clavero, Izquierdo, Fernández, & Niell, 2000). However, when the HRT were highest, concentrations of SRP and ammonium in

Table 6 Total load and percentage of total load in site 2 during low flow and high flow conditions

Site 2	Total (Tons)	Low flow (%)	High flow (%)
TP	26.3	7.7	41.3
TN	168.7	4.4	64.5

the interstitial water in site 2 were the lowest (Avilés, 2002) with values very similar to those obtained in the water column (Fig. 3). Therefore, in spite of the need to perform exhaustive studies of sediment-water interactions, it is reasonable to assume that the nutrient fluxes from the sediment to the water in the dammed water has less influence in the nutrient loads than the HRT.

Paul (2003) stated that the nitrate reduction obtained during the summer in pre-dams of Saidenbach reservoir (southeast Germany) were mainly due to the microbial denitrification at the sediment more than the phytoplankton growth. This does not seem to be the case in this study due to the great dominance of particulate nitrogen and the low percentages of nitrate and ammonium obtained in site 2 that prove the importance of phytoplankton in the DIN removal.

During high flows, SPM and particulate nutrients that were stored during low flow periods are resuspended and flow to the estuary. Thus, the percentage of TPP increased from 18% in summer to 65% during flooding events, as a consequence of scouring processes (Fig. 2). Nevertheless, nitrogen showed a different trend with nitrate as the dominant form during events (49%), although in a less percentage than in site 1 (66%).

4.3 Nutrient export to the estuary

The annual river loads of TP and TN from Palmones River to the estuary during the study period was 11.3 TonsP year^{-1} and 72.1 TonsN year^{-}1, respectively (Table 5). Although these loads were lower than those obtained by Nedwell et al. (2002) in rivers with similar catchment areas, their effects over this shallow estuary are evident. Therefore, the increase of nutrient concentration in the estuary of Palmones River has caused benthic red algae (*Gracilaria bursa-pastoris*) and polichaetes (*Hedistis diversicolor*) to disappear (Carreira et al., 1995) and the drastic reduction in the capture of species with commercial interest such as shellfish *Venerupis decussata* (Briones, personal communication).

Results show a great seasonal variability of nutrient loads to the estuary (Fig. 4). In order to establish the latter variability, a comparison between low flow (from June to September) and high flow conditions (January to April 2001) was made in Table 6. Thus, during low flow (31% of total sampling time) the TP and TN loads were lower than 8% and 5% of total loads, respectively; while during four months of high flow conditions (15% of total sampling time) the loads of TP and TN corresponded to 41.3% and 64.5% of total loads, respectively.

The dammed water studied in this work plays an important role in the control of estuarine eutrophication. Thus, during the summer, there is an important depletion of inorganic nutrient forms by the phytoplankton biomass in the dammed water that contributes to reduce the appearance of blooms of *Gyrodinium sp*. in the estuary (Mercado, personal communication). In high flooding events, the nutrients that were stored in the dammed water and in the estuarine sediment by settling during the low flow periods are scoured and exported out of the estuary to the Algeciras Bay (Avilés & Niell, 2005).

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References

Aguilera, J., de Gálvez, M. V., Conde, R., Pérez-Rodríguez, E., Viñegla, B., Abdala, R., et al. (2004). Series temporales de medida de radiación solar ultravioleta y fotosintética en Málaga. *Actas Dermosifiliograficas*, *95*(1), 25–31.

Avilés, A. (2002). El papel del sector fluvial en la biogeoquímica del Río Palmones, *PhD Thesis*, Departament of Ecology, University of Málaga, 189 pp.

Avilés, A., & Niell, F. X. (2005). Pattern of phosphorus forms in a Mediterranean shallow estuary: Effects of flooding events. *Estuarine, Coastal and Shelf Science*, *64*, 786–794.

Benndorf, J., & Pütz, K. (1987). Control of eutrophication of lakes and reservoirs by means of pre-dams – I. Mode of operation and calculation of the nutrient elimination capacity. *Water Research*, *21*, 829–838.

Cardoso, P., Pardal, M. A., Lillebø, A. I., & Pardal, M. A. (2004). Dynamic changes in seagrass assemblages under eutrophication and implications for recovery. *Journal of Experimental Marine Biology and Ecology*, *303*, 233–248.

Carreira, J. A., Clavero, V., Gálvez, J. A., Guevara, J. M., Hernández, I., Lucena, J., et al. (1995). Eutrophication progresses in the estuaries site at the end of small catchment areas. In P. Kamermans & P. H. Nienhuis (Eds.), *Eutrophication and macrophytes* (pp. 113–116). The Netherlands: Kamermans and Nienhuis.

Christman, R. F., & Minear, R. A. (1971). Organics in lakes. In S. D. Faust & J. O. Hunter (Eds.), *Organic compounds in* *aquatic environments* (pp. 119–143). New York: Marcel Dekker.

Clavero, V., Fernández, J. A., & Niell, F. X. (1992). Bioturbation by Nereis sp. And its effects on the phosphate flux across the sediment–water interface in the Palmones River estuary. *Hydrobiologia*, *235*, 387–392.

Clavero, V., Izquierdo, J. J., Fernández, J. A., & Niell, F. X. (2000). Seasonal fluxes of phosphate and ammonium across the sediment-water interface in a shallow small estuary (Palmones River, Southern Spain). *Marine Ecology. Progress Series*, *198*, 51–60.

Clavero, V., Izquierdo, J. J., Palomo, L., Fernández, J. A., & Niell, F. X. (1999). Water management and climate changes increases the phosphorus accumulation in the small shallow estuary of the Palmones River (Southern Spain). *Science of the Total Environment*, *228*, 193–202.

Danielidis, D. B., Spartinou, M., & Economou-Amilli, A. (1996). Limnological survey of Lake Amavrakia, Western Greece. *Hydrobiologia*, *318,* 207–218.

Fernández, J. A., Niell, F. X., & Lucena, J. (1985). A rapid and sensitive automated determination of phosphate in natural waters. *Limnology and Oceanography*, *30*(1), 227–230.

Fosberg, C., & Ryding, S. O. (1980). Eutrophycation parameters and eutrophic state indices in 30 Swedish waste-receiving lakes. *Archiv fur Hydrobiologie*, *89*, 189–207.

Grasshoff, K., Ehrhardt, M., & Kremling, K. (1983). *Methods of seawater analysis, 2nd edn.* (p. 419). Weinheim: Verlag Chemie.

Hernández, I., Pérez-Pastor, A., & Pérez-Lloréns, L. (2000). Ecological significance of phosphomonoesters and phosphomonoesterase activity in a small Mediterranean river and its estuary. *Aquatic Ecology*, *34*, 107–117.

House, W. A., & Donaldson, L. (1986). Adsorption and co-precipitation of phosphate and calcite. *Journal of Colloid and Interface Science*, *112*(2), 309–324.

Hunt, C. W., Loder, T., & Vörösmarty, C. J. (2005). Spatial and temporal patterns of inorganic nutrient concentrations in the Androscoggin and Kennebec Rivers, Maine. *Water, Air and Soil Pollution*, *163*, 303–323.

Iriate, A., & Purdie, D. A. (2004). Factors controlling the limiting of major spring blooms events in an UK south coast estuary. *Estuarine, Coastal and Shelf Science*, *61*, 679–690.

Izquierdo, J. J. (2001). Aspectos del ciclo de los nutrientes no conservativos en el estuario del Río Palmones, *PhD Thesis*, Departament of Ecology, University of Málaga, 233 pp.

Justic, D., Rabalais, N. N., Turner, R. E., & Dortch, Q. (1995). Changes in nutrient structure of river-dominated coastal waters: Stoichiometric nutrient balance and its consequences. *Estuarine, Coastal and Shelf Science*, *40*, 339–356.

Kawara, O., Yura, E., Fujii, S., & Matsumoto,T. (1998), A study on the role of hydraulic retention time in eutrophication of the Asahi River Dam reservoir. *Water Science and Technology*, *37*, 245–252.

McKergow, L. A., Weaver, D. M., Prosser, I. P., Grayson, R. B., & Reed, A. E. G. (2003), Before and after riparian management: Sediment and nutrient exports from a small agricultural catchment, Western Australia. *Journal of Hydrobiology*, *270*, 253–272.

Meybeck, M. (1982). Carbon, nitrogen and phosphorus transport by World Rivers. *American Journal of Science*, *282*, 401–450.

Moreno, S., & Niell, F. X. (2004). Scales of variability in the sediment chlorophyll content of the shallow Palmones River estuary, Spain. *Estuarine, Coastal and Shelf Science*, *60*, 49–57.

Neal, C. (2001). The potential for phosphorus pollution remediation by calcite precipitation in UK freshwaters. *Hydrology and Earth System Sciences*, *5*(1), 119–131.

Neal, C., Jarvie, H. P., Williams, R. J., Neal, M., Wickham, H., & Hill, L. (2002). Phosphorus-calcium carbonate saturation relationships in a lowland chalk river impacted by sewage inputs and phosphorus remediation: An assessment of phosphorus self-cleansing mechanisms in natural waters. *Science of the Total Environment*, *282–283*, 295–310.

Nedwell, D. B., Dong, L. F., Sage, A., & Underwood, G. J. C. (2002). Variation of the nutrient loads to the mainland U.K. estuaries: Correlation with catchment areas, urbanization and coastal eutrophication. *Estuarine, Coastal and Shelf Science*, *54*, 951–970.

Niell, F. X., Espejo, M., Fernández, J. A., & Algarra, P. (1989). Performances and uses of energy in intertidal systems related to random disturbances and thermal stress. *Scientia Marina*, *53*, 293–299.

O'Higgins, T. G., & Wilson, J. G. (2005). Impact of the river Liffey discharge on the nutrient and chlorophyll concentrations in the Liffey estuary and Dublin Bay (Irish Sea). *Estuarine, Coastal and Shelf Science*, *64*, 323–334.

Palomo, L., Clavero, V., Izquierdo, J. J., Avilés, A., Becerra, J., & Niell, F. X. (2004). Influence of macrophytes on sediment phosphorus accumulation in a eutrophic estuary (Palmones River, Southern Spain). *Aquatic Botany*, *80*, 103–113.

Paul, L. (2003). Nutrient elimination in pre-dams: Results of long term studies. *Hydrobiologia*, *504*, 289–295.

Paul, L., Schröter, K., & Labahn, J. (1998). Phosphorus elimination by longitudinal subdivision of reservoirs and lakes. *Water Science and Technology*, *37*(2), 235–243.

Plant, L. J., & House, W. A. (2002). Precipitation of calcite in the presence of inorganic phosphate. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *203*, 143–153.

Redfield, A. C., Ketchum, B. H., & Richards, F. A. (1963). The influence of organisms on the composition of sea water. In M. N. Hill (Ed.), *The Sea, vol. 2* (pp. 26–27). New York: Interscience.

Rigler, F. H. (1973). A dynamic view of the phosphorus cycles in lakes. In E. J. Griffith, A. Beeton, J. M. Spencer & D. T. Mitchel (Eds.), *Environmental phosphorus handbook* (pp. 539–568). New York: Wiley.

Rigler, F. H. (1979). The export of phosphorus from Darmoor catchment: A model to explain variations of phosphorus concentrations in streamwater. *Journal of the Marine Biological Association of the United Kingdom*, *59*, 659–687.

Shinn, M. B. (1941). A colorimetric method for the determination of nitrite. *Industrial and Engineering Chemistry, Analytical Edition*, *13*, 33–35.

Slawyk, G., & MacIsaac, J. J. (1972). Comparison of two automated ammonium methods in a region of coastal upwelling. *Deep-Sea Research*, *19*, 521–524.

Sokal, P. R., & Rohlf, F. J. (1995). *Biometry* (p. 850). New York: Freeman.

Sommers, L. E., & Nelson D. W. (1972). Determination of total phosphorus by a rapid perchloric acid procedure. *Soil Science Society of America Proceedings*, *36*, 902–904.

Stricklan, J. D. H., & Parson, T. R. (1972). A practical approach handbook of seawater analysis. *Fisheries Research Board of Canada Bulletin*, *167*, 191–194.

Stumm, W., & Morgan, J. J. (1981). *Aquatic Chemistry*, 2nd edn. (p.780). New York: Wiley.

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.

Viaroli, P., Bartoli, M., Bondavalli, C., Christian, R. R., Giordan, G., & Naldi, M. (1996). Macrophyte communities and their impact benthic fluxes of oxygen, sulphide and nutrients in shallow eutrophic environments. *Hydrobiologia*, *329*, 105–119.

Wood, E. D., Armstrong, F. A. J., & Richards, F. A. (1967). Determination of nitrate in sea water by cadmium-copper reduction to nitrite. *Journal of the Marine Biological Association*, *47*, 23–31.

Zwolsman, J. J. C. (1994). Seasonal variability and biochemistry of phosphorus in the Scheldt Estuary, Southwest Netherlands. *Estuarine, Coastal and Shelf Science*, *39*, 227–248.