

NUTRIENT AND PARTICULATE INPUTS INTO THE MAR MENOR LAGOON (SE SPAIN) FROM AN INTENSIVE AGRICULTURAL WATERSHED

J. VELASCO*, J. LLORET, A. MILLAN, A. MARIN, J. BARAHONA, P. ABELLAN
and D. SANCHEZ-FERNANDEZ

Department of Ecology and Hydrology, University of Murcia, Spain

*(*author for correspondence, e-mail: jvelasco@um.es)*

(Received 27 February 2004; accepted 6 September 2005)

Abstract. The Mar Menor is a Mediterranean coastal lagoon of high conservation interest, but highly threatened by non-point pollution derived from agricultural lands. This is the first comprehensive study that evaluates the inputs into the Mar Menor from a drainage channel and the Albuñón wadi, the main watercourse, and their influence on the trophic state of the lagoon. Discharge variation during the study period was closely related to the precipitation pattern. Suspended sediments and particulate organic matter loads greatly increased with flash floods. Nitrate concentrations, too, increased after heavy autumn rains through washing of the nitrates accumulated in soils, although no significant correlations were found between nitrate concentrations and precipitation or discharge. The nitrate load depended on several factors including the intensity and frequency of precipitation, and the nitrates accumulated in soils as a result of fertilisation. Phosphate concentrations decreased with higher flows. The total input into the lagoon from the two discharges estimated for the period September 2002–October 2003 were 10,142 t.yr⁻¹ of suspended sediments, 389 t.yr⁻¹ of particulate organic matter, 2,010 t.yr⁻¹ of dissolved inorganic nitrogen (93 % as NO₃⁻) and 178 t.yr⁻¹ of soluble reactive phosphorus. The Albuñón wadi exported about 80% of the N load and 70% of the P load. Higher flows contributed approximately 80% of the total discharge and nutrient loads, 99% of suspended sediment and 88% of the particulate organic matter. Mean suspended solids and nutrient concentrations in the lagoon followed a spatial pattern, decreasing with distance from the mouth of the Albuñón wadi. Water nitrate and phosphate concentrations in the Mar Menor lagoon were lower than reference limits for eutrophic conditions, except after heavy rains. Nutrient concentrations were positively correlated with precipitation variables and particulate and nutrient inputs. Phosphorus was the most limiting nutrient in the Mar Menor, the DIN:SRP ratios found being higher than the Redfield ratio on all sampling dates. Phytoplankton bloom in the lagoon was only found next to the Albuñón mouth during late summer and extending 5000 m into the lagoon in autumn as a consequence of large freshwater discharge caused by flash floods. Around 53.6% of the variation in chlorophyll *a* in the lagoon was explained by the NH₄ and NO₃ inputs and distance from the Albuñón mouth. A good deal of P input into the lagoon is retained in the sediments, supporting a high biomass of the benthic macroalga *Caulerpa prolifera* in spring and summer.

Keywords: agriculture, eutrophication, drainage, flashflood, nitrate, nonpoint source pollution, Mar Menor lagoon

1. Introduction

Eutrophication caused by excessive inputs of phosphorus and nitrogen is the most common impairment of surface waters (U.S. EPA, 2002) and the most widespread

pollution problem of estuaries and coastal waters, especially in areas with limited water exchange (Nixon and Pilson, 1983; Bricker *et al.*, 1999; de Jonge *et al.*, 2002; Kennish, 2002).

The Mar Menor, the largest lagoon of the Spanish Mediterranean coast, has a high ecological, fishing and tourism value. It is included in the Ramsar List of Wetlands of International Importance. It is also a Special Protected Area of Mediterranean Interest (SPAMI), Specially Protected Area under the EU Wild Birds Directive (SPA) and Site of Community Importance (SCI) to be integrated in the Nature 2000 Network (EU Habitats Directive). The site is of special importance for its well-developed communities of halophytic and sand dune vegetation, and for nesting, staging and wintering birds. Notable amongst the fish fauna is the threatened endemic *Aphanius iberus*.

Although it is generally accepted that there has been an increase in the inputs into the lagoon during recent decades as a consequence of changes in agricultural practices, there is a remarkable lack of knowledge concerning the actual input of nutrients. In the past, traditional agricultural activities, based on unirrigated land cultivation, have had little influence on the introduction of nutrients, pesticides and other pollutants into the lagoon (Pérez-Rufaza *et al.*, 2000). However, since 1979 the Tajo-Segura river diversion has brought water for irrigation to the Campo de Cartagena, and agriculture in the watershed has changed from extensive dry crops to intensively irrigated crops. The groundwater levels have risen and some previously temporary watercourses maintain a permanent flow into the lagoon. As a consequence of changes in the nutrient input regime, the lagoon has changed from being moderately oligotrophic to be relatively eutrophic, providing ideal growth conditions for two allochthonous jellyfish species (*Rhizostoma pulmo* and *Cotylorhiza tuberculata*), resulting in serious inconveniences for tourism (Pérez-Rufaza *et al.*, 2002). Another eutrophication effect observed has been the change in the composition and distribution of primary producers. In the 1970s, primary production was dominated by the phanerogam *Cymodocea nodosa*. However, since the 1980's a high benthic biomass of the macroalga *Caulerpa prolifera* has begun to cover most of the lagoon beds, restricting the seaweed *Cymodocea nodosa* to small patches in the shallowest areas (Terrados & Ros, 1991).

Under the European Directives 91/271/EEC and 91/676/EEC concerning urban waste water treatment and the protection of waters against pollution caused by nitrates from agricultural sources, respectively, the Mar Menor lagoon was declared a *sensitive area* subject to eutrophication in June 2001, and the Campo de Cartagena was declared a *vulnerable zone* in December 2002. These directives require the regional government to establish and implement action programmes to reduce the concentration of nutrients in discharges from treatment plants and from agricultural drainage to minimise the adverse effects on the environment, and to monitor waters to ensure that any measures taken are effective.

In this context, the objectives of the present study were: 1) to estimate the annual input of particulate organic matter, sediments and nutrients into the Mar Menor from

the Albuji3n wadi and from an effluent of agricultural drainage channels; and 2) to evaluate its impact on the trophic state of the lagoon.

2. Study area

The Mar Menor, located in the SE of the Iberian Peninsula (Figure 1), is one of the largest coastal lagoons of the Mediterranean coast (135 km² area, average depth 4 m, maximum 6.5 m). The lagoon is hyperhaline, with salinity levels (42–47) greater than the adjacent Mediterranean Sea because of low precipitation (around 300 mm per year) and high evaporation rates (mean annual temperature 18 °C). It is isolated from the Mediterranean Sea by a 24 km long sandy bar (La Manga), crossed by five channels, the average water residence time being 0.79 years (P3rez-Ruzafa, 1989). As regards human use, fishing in the lagoon is declining, but there are dense urban and tourist developments on the shores of the Mar Menor, industrial activities in the salt pans of San Pedro, and intensive agriculture in the Campo de Cartagena with irrigated horticultural and citric crops. This lowland plain (1200 km²) of clay soils is one of the main horticulture producers in Europe. It is drained by several ephemeral watercourses or wadis, which flow into the lagoon after episodic storm rainfall events, usually in autumn. These wadis are wide, shallow gullies, which are generally inactive, but carry great quantities of water and sediment when it rains. The torrential nature of the supplies is also due to the impermeable soils and the scarce vegetation cover of the headwaters in the watershed areas. There is, also, a web of five subterranean drainage channels running along the inner coast of the

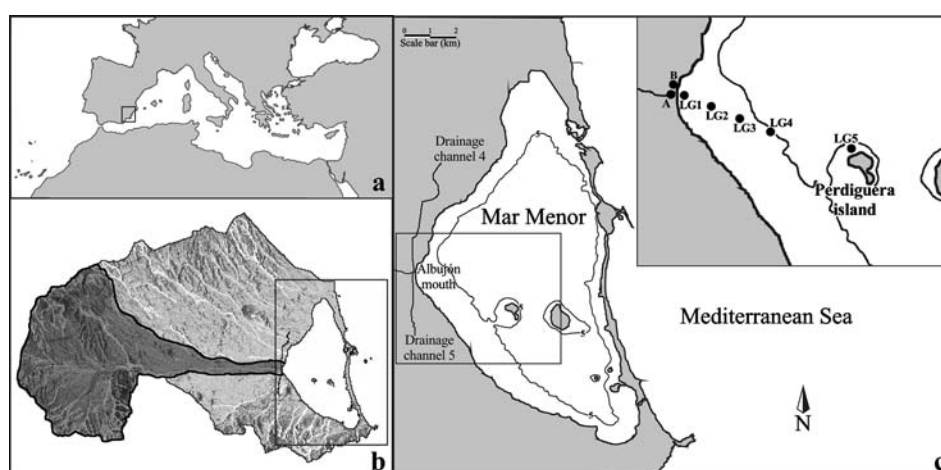


Figure 1. Study area. a) General location, b) Campo de Cartagena and the Albuji3n watershed (shaded), and c) Sampling stations (A: Albuji3n wadi mouth, B: drainage effluent, LG1–LG5: distance gradient in the Mar Menor lagoon).

Mar Menor that collect agricultural water surplus and conduct it to a desalination plant for reuse in irrigation.

The Albuji3n is the principal watercourse, draining a surface of 441 km², about one third of the total surface of the Campo de Cartagena (Figure 1b). From the 1980's it has flowed permanently into the lagoon due to a surplus of irrigation water. The Albuji3n watershed, of 42 km length, presents a fan form with the low section constrained to <2 km width. The drainage network is dendritic, with a low drainage density. The tributaries are concentrated in the upper section of the watershed, the last 20.5 km of the principal channel being without tributaries. The mean watershed slope is 3.02%, but ranges from 25–30% at the head to <1% in the lowland section and the mouth (Conesa, 1992).

In normal local climatic conditions, the Albuji3n wadi is fed by land-based point and diffuse sources. The principal source is the drainage of irrigated crops, but sometimes the Alc3zares waste-water treatment plant, located in the watershed area, discharges large amounts of untreated or insufficiently treated water into the channel. This severe episodic pollution occurs especially after storms, and in summer months, the peak tourist season, when the population increases from 10,000 to 100,000 inhabitants. During heavy rains, the Albuji3n wadi is fed principally by surface runoff.

The drainage waters collected by channels number 4 and 5 (Figure 1c) meet at a pumping plant next to the Albuji3n mouth (at 100 m distance). The water is pumped to a desalination plant, but any surplus water is discharged directly into the lagoon (drainage effluent).

3. Material and Methods

Samples were taken from the mouth of the Albuji3n wadi and the drainage effluent seven times between September 2002 and October 2003 to record the seasonal variability and the influence of flash floods. Additional samples, four times in five localities in the lagoon, were taken along a distance and depth gradient from the mouth of the Albuji3n wadi to Perdiguera Island (Figure 1c) following the water plume determined by the circulation pattern (P3rez-Ruzafa *et al.*, 2002). The study period comprised two heavy storms, one in winter (10–12/1/03, 75.33 mm precipitation) and the other in autumn (16–17/10/03, 35.73 mm precipitation, Figure 2). Mean daily precipitation was calculated from data obtained from four meteorological stations located in the Campo de Cartagena. In the two storm events, samples were taken 1–4 days after the rains.

On each date, water temperature, conductivity, salinity and dissolved oxygen were measured in situ using a multi-parametric recorder (WTW, MultiLine P4). Discharge was estimated from measurements of depth and current velocity along a channel cross-section. Particulate organic matter entering the lagoon was collected with two drift nets of square cross-section (22.5 cm length, and 250 μ m pore size)

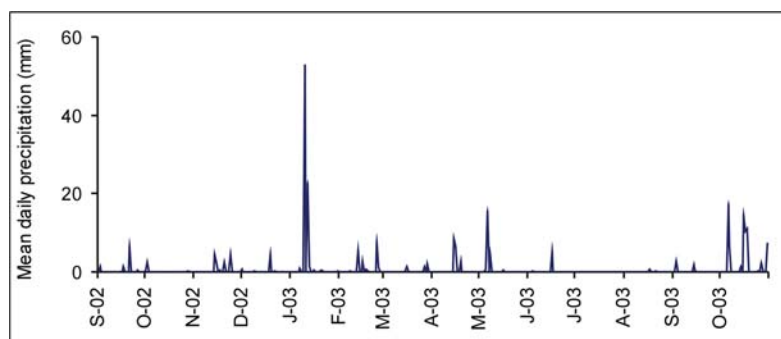


Figure 2. Variation of mean daily precipitation during the study period. Data were obtained from four meteorological stations located in the Campo de Cartagena.

per sampling site. Two water samples were taken to measure suspended solids, chlorophyll *a* and dissolved nutrients (ammonium, nitrate, nitrite and phosphate concentrations). The samples were kept cool until their arrival in the laboratory, where they were filtered onto preashed and preweighed GF/F glass-fiber filters. The filters were oven-dried at 60 °C to constant dry weight and then ashed at 450 °C for 4 h to estimate the input of suspended sediments (SS) and particulate organic matter. The drift net contents were dried and ashed as above to estimate the input of particulate organic matter of size exceeding 250 μm . The total load of particulate organic matter (POM) was the sum of the filter and drift net AFDW. Chlorophyll *a* concentration was determined by spectrophotometry, following extraction in 90% acetone. Ammonium was converted to ammonia by adding 10M NaOH solution and measured with an ammonia electrode connected to a pH/mV meter. The rest of the dissolved inorganic nutrients were determined according to standard methods (APHA, 1992): nitrate by the cadmium reduction method, nitrites by sulfanylic acid colorimetry, and phosphate by ascorbic acid colorimetry. The mean concentration and mean discharge data obtained on the sampling dates were combined to obtain annual estimates of particulate and nutrient inputs, compensating the lack of discharge and concentration data during the high flow peaks.

In the lagoon, geographic co-ordinates of each sampling point were measured using GPS. Photosynthetic active radiation was measured at different depths in the water column using a LI-COR 1000 photometer. The light extinction coefficient (*k*) in the water column was obtained from photometer measurements, using the Lambert-Beer equation:

$$L_z = L_o \cdot e^{-k \cdot z}$$

where L_z = light at *z* depth, L_o = light at water surface and *k* = light extinction coefficient.

Surface water samples were collected in each location and analysed following the same methods described above.

Because of the nature of the data, Spearman rank correlations were used to determine significant relationships between the variables. Finally, a stepwise multiple regression was used to explain the variation of the chlorophyll *a* concentration in the lagoon using precipitation, physical (water temperature, depth, distance to the mouth, extinction coefficient, transparency) and nutrient and particulate inputs as independent variables. We used different precipitation variables (monthly precipitation, maximum daily precipitation, total precipitation during storm event), as measures of the intensity of perturbation; and the number of days after storm events with daily precipitation ≥ 20 mm, as a measure of disturbance frequency. Statistical analyses were performed using Statistica v4.5.

4. Results

4.1. TEMPORAL VARIATION OF PARTICULATE AND NUTRIENT CONCENTRATIONS IN FRESHWATER DISCHARGES

The composition and variation patterns of the physical and chemical variables of the Albuñón wadi and the drainage effluent were very similar, reflecting the same predominant nutrient source, agriculture (Table I and Figure 3). High nutrient values were measured during the study period, generally exceeding the European Community limits for drinking water and freshwater fish (Directives 80/778/EEC and 78/659/EEC, respectively).

Discharge variation (Figure 3a) during the study period was closely related to precipitation pattern (Figure 2). There were significant positive correlations between discharge and precipitation variables, with monthly precipitation showing the greatest coefficient ($r = 0.60$, $p \leq 0.05$). The mean discharge of the Albuñón wadi was about 127 L s^{-1} , except following rainfall in January and October, when it reached values higher than $1 \text{ m}^3 \text{ s}^{-1}$. The mean discharge of the drainage effluent to the Mar Menor was less than one third of the stream discharge, with peaks after the January and October rains.

Mean annual conductivity was about 11 mS cm^{-1} at both discharge points, with maximum values in summer and minimum values in the flash floods events. Conductivity was negatively correlated with maximum daily precipitation ($r = -0.54$, $p \leq 0.05$).

The load of suspended sediments increased greatly with flash floods (Figure 3c). The autumn event showed a higher erosive and carrying capacity than the winter event, despite the lower rainfall, because of the cutting of *Phragmites australis* along the floodplain one month earlier. Suspended sediment was positively correlated with discharge ($r = 0.57$, $p \leq 0.05$) and precipitation variables. However, the variation pattern in POM did not show significant correlations with precipitation

TABLE I
Physical and chemical parameters measured in the two discharges and in the Mar Menor lagoon

	Albujón wadi ($n = 7$)				Drainage effluent ($n = 7$)				Mar Menor lagoon ($n = 20$)			
	Mean	Min	Max	Std.Dev.	Mean	Min	Max	Std.Dev.	Mean	Min	Max	Std.Dev.
Discharge (L.s^{-1})	638.57	34.58	2687.03	981.86	230.12	22.36	1127.03	402.84				
Water temperature ($^{\circ}\text{C}$)	18.90	11.70	24.40	4.37	18.00	10.20	23.10	4.78	22.24	9.80	31.20	7.92
Salinity	6.16	3.60	7.90	1.64	6.50	3.60	8.20	1.47	44.85	40.80	46.30	1.98
Conductivity (mS.cm^{-1})	10.83	6.66	13.60	2.69	11.47	6.74	14.05	2.39				
Dissolved oxygen (mg.L^{-1})	10.60	4.00	26.20	7.39	5.06	0.47	9.25	3.68	9.05	7.22	11.30	1.03
SS (mgADWL^{-1})	266.80	0.20	1766.50	661.72	657.17	0.50	4507	1697.81	9.64	2.53	17.67	5.63
POM (mgAFDW.L^{-1})	11.25	0.11	26.88	8.31	12.57	3.75	38.50	11.88	3.80	1.47	6.60	1.94
Chl a (mg.L^{-1})	28.42	3.46	104.53	36.59	10.14	0.91	47.68	16.65	2.39	0.49	12.73	2.75
NH_4 (mg.L^{-1})	4.42	0.22	12.75	4.06	3.67	0.34	11.13	4.11	0	0	0	0
NO_2 (mg.L^{-1})	0.74	0.17	1.60	0.56	0.79	0.09	2.09	0.72	0.008	0.0009	0.037	0.008
NO_3 (mg.L^{-1})	72.70	11.59	151.38	44.16	56.51	10.77	98.33	32.34	0.42	0.0016	3.42	0.75
SRP (mg.L^{-1})	6.23	0.10	21.54	9.00	7.30	0.34	26.41	10.72	0.003	0	0.015	0.005

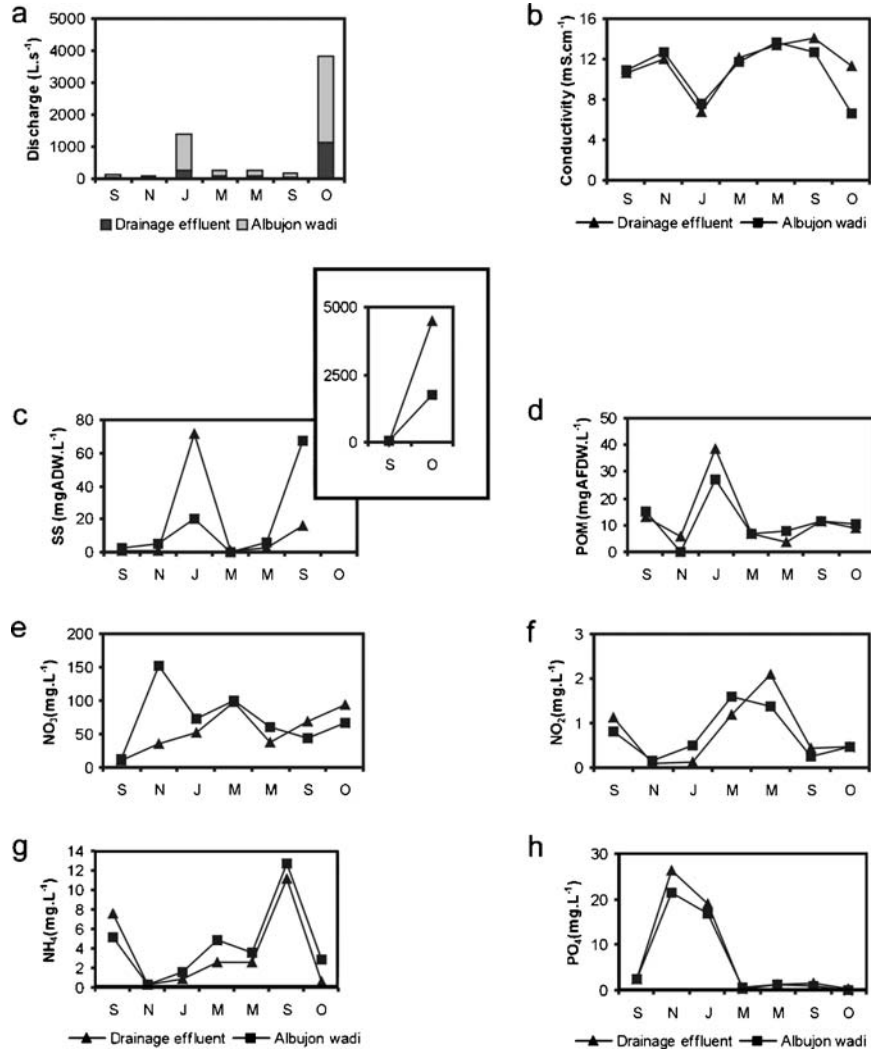


Figure 3. Temporal variation in discharge levels (a), conductivity (b), suspended sediment (c), particulate organic matter (d) and water nutrient concentrations (e, f, g, h) in the two studied discharges into the lagoon.

variables, although the former reached its highest loads in the January flash flood (Figure 3d).

Nitrate concentrations also increased after heavy autumn rains through the washing of nitrate-charged soils, although a contrary effect was observed in stream nitrate concentration after January rains (Figure 3 e), probably due to the low level of fertilisers accumulated in the top soil of the basin in winter. However, the washing of nitrate accumulated in deeper soils led to an increase of the nitrate concentration in the drainage channels. High nitrate concentrations were also found in both

discharge points in March, coinciding with maximum crop fertilisation activity in the watershed. We found no significant correlations between nitrate concentrations and precipitation and discharge.

Nitrite concentrations showed a slight increase during high flow conditions (Figure 3f), while ammonium increased its concentration with the winter rains but strongly decreased with autumn rains (Figure 3g). Ammonium and nitrite concentration peaks were found in summer, coinciding with the period of highest remineralisation intensity. The ammonium concentration was positively correlated with water temperature and chlorophyll *a* concentration ($r = 0.72$, $p \leq 0.005$ and $r = 0.77$, $p \leq 0.001$, respectively), and negatively correlated with monthly precipitation ($r = -0.65$, $p \leq 0.01$). Nitrite was negatively correlated with total precipitation during the storm event ($r = -0.55$, $p \leq 0.01$).

Phosphate concentration showed a different pattern, decreasing with higher flows (Figure 3h). High values were found throughout the study period, although the maximum concentrations in November were probably due to failures in the wastewater treatment plant. Non-significant correlations were found between phosphate and the studied variables.

4.2. TOTAL ANNUAL INPUTS

Table II shows the annual inputs from the Albujón wadi and the drainage effluent, and the total input into the lagoon. Total annual discharge into the lagoon was estimated at $27.4 \text{ Hm}^3 \cdot \text{yr}^{-1}$, of which the Albujón wadi accounted for $20.14 \text{ Hm}^3 \cdot \text{yr}^{-1}$, almost 73.5% of the total. The combined inputs amount to $10,142 \text{ t} \cdot \text{yr}^{-1}$ of SS, $389 \text{ t} \cdot \text{yr}^{-1}$ of POM ($1.5 \text{ t} \cdot \text{yr}^{-1}$ of particle size $> 250 \mu\text{m}$), $2,010 \text{ t} \cdot \text{yr}^{-1}$ of dissolved inorganic nitrogen (DIN), 93 % as NO_3^- , and $178 \text{ t} \cdot \text{yr}^{-1}$ of soluble reactive phosphorus (SRP). In base-flow conditions, excluding the sampling dates after heavy rains, the total agricultural inputs to the lagoon from the two discharges were estimated at $71 \text{ t} \cdot \text{yr}^{-1}$ SS, $46 \text{ t} \cdot \text{yr}^{-1}$ POM, $402 \text{ t} \cdot \text{yr}^{-1}$ DIN and $31 \text{ t} \cdot \text{yr}^{-1}$ SRP. Higher flows contributed approximately 80% of the total discharge and nutrient loads, and 99% of SS and 88% of POM.

Of the total inputs, the Albujón wadi exported about 53% SS, 75% POM, 78% DIN and 70% SRP. Stream N and P fluxes varied between $7\text{--}33 \text{ kgNO}_3^- \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ and $0.5\text{--}3 \text{ kgPO}_4^- \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ depending of the occurrence of flood events.

4.3. PARTICULATE AND NUTRIENT CONCENTRATIONS IN THE LAGOON

The levels of sediments and POM suspended in the lagoon were substantially lower than in the two discharges studied (Table I). The greatest differences corresponded to the mean nitrite and nitrate concentrations, which were two-orders of magnitude lower in the lagoon, and to the phosphate concentration, which differed by three-orders of magnitude. Ammonium concentrations were always below the detection limit ($0.001 \text{ mg} \cdot \text{L}^{-1}$).

TABLE II

Annual inputs of particulates and nutrients into the Mar Menor lagoon estimated for the period September 2002–October 2003 including two storm events (a), and in base flow conditions (b)

		Albujón wadi	%	Drainage effluent	%	Total
Discharge ($\text{Hm}^3 \text{ y}^{-1}$)	a	20	100	7	100	27
	b	4	20	1	21	5
SS (t.y^{-1})	a	5373	100	4769	100	10142
	b	65	1	6	0	71
POM (t.y^{-1})	a	293	100	97	100	390
	b	35	12	11	11	46
NH_4 (t.y^{-1})	a	89	100	27	100	116
	b	21	24	7	27	28
NO_3 (t.y^{-1})	a	1464	100	410	100	1874
	b	295	20	74	18	369
NO_2 (t.y^{-1})	a	15	100	6	100	21
	b	3	20	1	17	4
DIN total (t.y^{-1})	a	1568	100	442	100	2010
	b	320	20	83	19	403
SRP (t.y^{-1})	a	125	100	53	100	178
	b	21	17	10	18	31

In general, mean suspended solids and nutrient concentrations in the lagoon followed a spatial pattern, decreasing with distance from the Albujón mouth (Table III). Site LG1, located 315 m from the principal discharge point, presented higher light extinction coefficients, SS and POM concentrations than more distant sites. Sites LG2 and LG3, at 720 and 1550 m distance, showed similar concentrations in these variables, with intermediate levels between those recorded at LG1 and the most distant sites (at 2400 m and 5150 m distance). However, the mean nitrite and nitrate levels were higher in sites LG2 and LG3 than in LG1, while the highest mean phosphate concentration was found in LG2, followed by LG1. No differences in mean particulate and nutrient concentrations were found between LG4 and LG5, which presented the lowest values.

Maximum nutrient levels were found after rain events, principally after the intense winter flash flood, when levels greater than $50 \mu\text{molNO}_3^-\text{.L}^{-1}$ and $0.15 \mu\text{molPO}_4^-\text{.L}^{-1}$ were recorded (Figures 4 a and b). Typical background concentrations of nitrates and phosphates in the lagoon were lower than $5 \mu\text{mol.L}^{-1}$ and $0.01 \mu\text{mol.L}^{-1}$, respectively, values lower than reference limits defining eutrophic conditions (Thyssen, 1999). Nitrate and phosphate concentrations were highly correlated ($r = 0.70$, $p \leq 0.0005$). Both concentrations were positively correlated with precipitation variables and particulate and nutrient inputs, and negatively with the number of days after precipitation ≥ 20 mm (Table III).

TABLE III
Mean (\pm 1SE) values of physical and chemical parameters in the Mar Menor lagoon measured in the distance gradient from the mouth of the Albujón wadi

	LG1	LG2	LG3	LG4	LG5
Distance to the mouth (m)	315	720	1550	2400	5150
Temperature ($^{\circ}$ C)	23 ± 4.5	22.3 ± 3	22.1 ± 2.4	22 ± 2	22 ± 2
Salinity	44.8 ± 1	44.6 ± 0.8	44.7 ± 0.5	45 ± 0.5	45 ± 0.5
Dissolved oxygen (mg.L^{-1})	9.6 ± 0.6	8.7 ± 0.3	9.1 ± 0.3	9.3 ± 0.2	9.3 ± 0.2
Light extinction coefficient	0.74 ± 0.21	0.37 ± 0.03	0.37 ± 0.02	0.3 ± 0.02	0.22 ± 0.02
SS (mgADW.L^{-1})	11.75 ± 2.7	10.04 ± 2.2	10.17 ± 1.9	8.08 ± 1.1	8.08 ± 1.1
POM (mgAFDW.L^{-1})	4.18 ± 0.74	3.9 ± 0.78	3.95 ± 0.65	3.32 ± 0.45	3.32 ± 0.45
NO_2 ($\mu\text{mol.L}^{-1}$)	0.006 ± 0.001	0.016 ± 0.005	0.008 ± 0.001	0.006 ± 0	0.006 ± 0
NO_3 ($\mu\text{mol.L}^{-1}$)	0.224 ± 0.068	1.135 ± 0.504	0.471 ± 0.115	0.217 ± 0.047	0.217 ± 0.047
SRP ($\mu\text{mol.L}^{-1}$)	0.004 ± 0.004	0.005 ± 0.002	0.001 ± 0	0.003 ± 0.001	0.003 ± 0.001
Chl <i>a</i> (mg.m^{-3})	4.97 ± 2.7	2.08 ± 0.6	2.02 ± 0.36	1.78 ± 0.2	1.78 ± 0.2

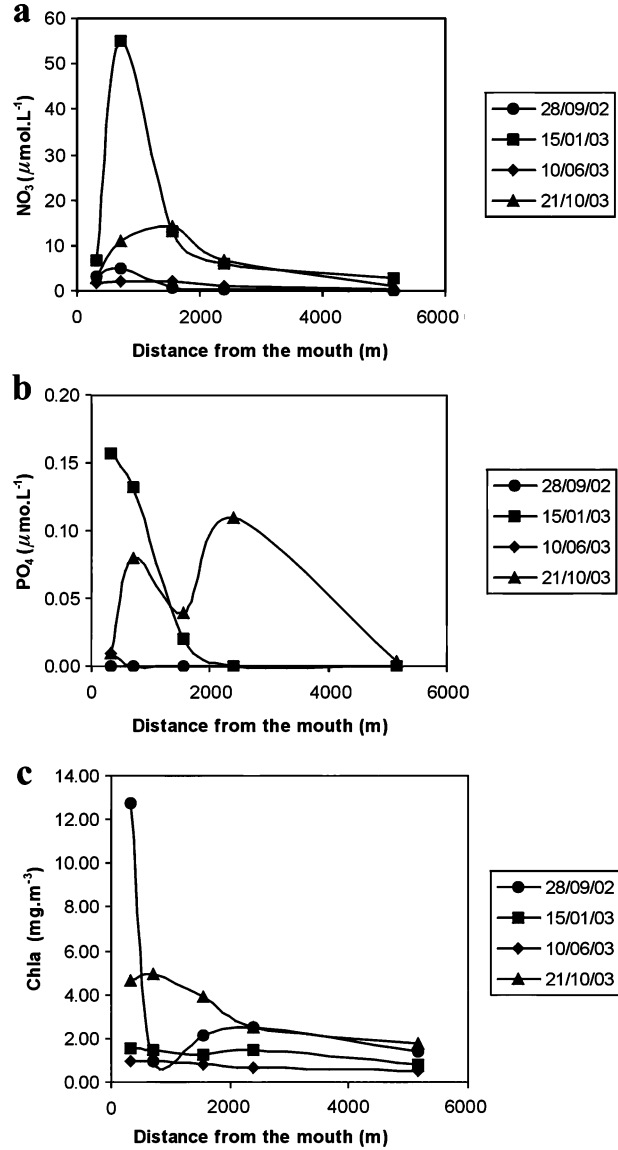


Figure 4. Temporal variation in nitrate (a), phosphate (b) and chlorophyll *a* (c) in the Mar Menor lagoon along the distance gradient from the mouth of the Albuñón wadi.

Mean chlorophyll *a* concentration changed along the distance gradient in the lagoon, the highest values being recorded near to the Albuñón wadi mouth (Table III and Figure 4 c). There was a significant positive correlation between chlorophyll *a* and the light extinction coefficient (*k*) in the water column ($r = 0.64$, $p \leq 0.005$). According to the guideline values for still waters (OECD, 1982), the site

LG1 changed from oligotrophic ($\leq 1.5 \text{ mg Chl } a.m^{-3}$) in winter and spring to mesotrophic ($4.7 \text{ mg Chl } a.m^{-3}$) in autumn and to eutrophic ($13 \text{ mg Chl } a.m^{-3}$) in late summer. The other locations in the lagoon presented oligotrophic conditions ($\leq 2.5 \text{ mg Chl } a.m^{-3}$) during the studied period, except after autumn rains, when mesotrophic levels were reached. There were highly significant positive correlations between chlorophyll *a* and ammonium input and less significant correlations with nitrite concentration and phosphate concentrations in the lagoon (Table IV). The best multiple regression model obtained explains 54% of the variance in chlorophyll *a* concentration in the lagoon. It included ammonium input, with positive sign, and nitrate input and distance from the Albuji3n mouth, with negative sign (Table V).

5. Discussion

In the United States and Europe, only 30% of the P input and 18% of the N input in fertilisers is incorporated in crops, resulting in an average accumulation rate of $22 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ and $174 \text{ kg.ha}^{-1}.\text{yr}^{-1}$ of surplus P and N, respectively (Carpenter *et al.*, 1998). The phosphorus and nitrogen compounds accumulated in agricultural lands are exported to surface and ground waters by erosion and leaching. The flux of nutrients to water are influenced by many factors, including the rate, season, chemical form, and method of nutrient application; the amount and timing of rainfall after application (Carpenter *et al.*, 1998), and vegetative cover and soil texture (Berka *et al.*, 2001).

Nutrient surplus from agricultural lands, the underlying cause of non-point pollution, was the main cause of the N and P inputs into the Mar Menor. Continuous nutrient flux from agricultural lands through the saturated subsurface flow system sustains the stream base flow discharging into the lagoon, while the inputs from wastewater treatment plants were discontinuous and of lower magnitude.

Similar nutrient concentrations were found in the Albuji3n wadi and the drainage effluent, reflecting the same predominant nutrient source. The greatest differences between the two discharge levels were found for suspended sediment and nitrate concentrations after storm events. The drainage effluent transported more sediment per litre than the Albuji3n wadi. In addition, the differences in nitrate concentration may have been due to differential nitrate accumulation rates in the top and deeper soil layers, depending on the season, and differential leaching by surface or subsurface runoff. Surface runoff erodes and leaches the nitrate accumulated in the top soil, and an increase in the nitrate concentrations of the stream can be observed very quickly after the autumn rains, when the soils would have contained heavy nutrient loads as a result of fertilisation activity. However, infiltration creates subsurface saturated flow, which leaches the deeper nitrates that provide delayed peaks of nitrate concentration a few days after a storm event (Burt & Arkell, 1987).

In our study, nutrient inputs showed a strong temporal variation linked to heavy precipitation events and seasonal agricultural activity. The higher flows following

TABLE IV
Significant Spearman correlation coefficients between nitrate, phosphate and chlorophyll *a* concentrations in the lagoon and precipitation and input variables

	Monthly <i>P</i>	Storm <i>P</i>	Days after <i>P</i> > 20 mm	NO ₂ input	NH ₃ input	NO ₃ input	PO ₄ input	SS input	POM input	NO ₂	PO ₄
NO ₃	0.674***	0.703***	-0.662***	0.597*	0.613**	0.597*	0.675***	0.597**	0.653**	0.773***	0.703***
PO ₄	0.56*	0.624**	-0.705***	0.713**	0.649**	0.713***	0.56*	0.713**	0.48*	0.546*	-
Chl <i>a</i>	n.s.	n.s.	n.s.	n.s.	0.675***	n.s.	n.s.	n.s.	n.s.	0.45*	0.44*

p* = 0.05–0.01 ** *p* = 0.005–0.001 **p* < 0.001.

TABLE V

Regression summary for dependent variable chlorophyll *a* concentration in the Mar Menor lagoon

	B	St. Err. of B	<i>t</i> (16)	<i>p</i> -level
Intercept	0.5434	0.0876	6.2034	0.00001
InputNH ₄	−0.8894	0.2055	4.3288	0.0005
InputNO ₃	−0.2654	0.0822	−3.2273	0.0053
Distance from the mouth	−0.00005	0.0000	−2.3802	0.0301

Dependent and independent variables, except distance to the mouth, were log ($x + 1$) transformed.
 $n = 4$, $R^2_{\text{adj.}} = 0.54$, $p < 0.0015$.

rainfall contributed to approximately 80% of the total discharge and nutrient loads, 99% of suspended sediment and 88% of the particulate organic matter yields. In addition, the fluxes of N to surface and ground waters increased in spring and summer, the seasons of highest fertilisation.

Our estimates of the area-specific stream loads for the Albuñón watershed were 1.65 times and 2.3 times higher, respectively, for N and P, than those suggested by Vollenweider (1975) as being excessive. The loading was similar to the highest loads found in some agricultural drainage basins to Baltic Sea (Stalnacke *et al.*, 1999) but lower than in freshwater discharges to other Mediterranean coastal lagoons in NE Spain (Lucena *et al.* 2002) and those obtained by Molénat *et al.* (2002) in one of the most intensively agricultural watersheds in French Brittany. Based on our estimates of N and P stream fluxes, and considering that Albuñón wadi could be responsible for almost half of the total nutrients discharged into the Mar Menor, we estimate the total inputs derived from the Campo de Cartagena at 640–3136 t DIN.yr^{−1} and 43–251 t SRP.yr^{−1} depending on the occurrence of flood events. Predictions made from a dynamic model for estimating the nutrient inputs from agricultural sources into the Mar Menor (Martínez and Esteve, 2000) are consistent with our empirical results. The model predicted inputs of 2000 t N.yr^{−1} and 60 t P.yr^{−1}, and showed that nutrient export presents a clearly dynamic character that depends on both exogenous factors, mainly the monthly rainfall, and endogenous factors, such as the level of fertilisers accumulated in the basin.

To ascertain the extent of any changes that may have occurred in discharge and nutrient concentrations during the last decade, we compared our mean results for the Albuñón wadi, in base-flow conditions, with the mean data obtained in 1996, a dry year (SACYR, 1997), since these are the only previous data for the Albuñón wadi. Although more data are needed to test for statistical differences, base-flow discharge seems to have increased almost two-fold (Table VI). However, phosphate concentrations have remained nearly constant, while nitrates and ammonium have slightly increased. These trends are indicative of an increase in the irrigation area in the watershed and consequently of an increase in nutrient surplus and potential nutrient inputs in rainstorm events.

TABLE VI

Comparative of mean annual values of discharge and nutrient concentrations ($n = 5$) in the Albuñón wadi in base flow conditions during 2002/2003 (this study) and 1996 (SACYR, 1997)

	1996	2002/2003
Discharge (L.s^{-1})	63	127
Conductivity (mS.cm^{-1})	10	11
NO_3 (mg.L^{-1})	63	74
NO_2 (mg.L^{-1})	6.75	0.84
NH_4 (mg.L^{-1})	3.9	5.3
SRP (mg.L^{-1})	5	5.3

Pérez-Rufaza *et al.* (2002), in a comparison of nutrient concentrations in the lagoon over a 9-year period between 1988 and 1997, pointed to a considerable increase in nitrate concentration and a reduction in phosphate concentration, which were related to the increase in irrigated lands, the amount of agricultural fertilisers and wastewater treatment plants. The spatial distribution of nitrates in the lagoon waters during 1997 showed a close relationship with watercourse mouths, especially with the Albuñón wadi. At the present time, peak nutrients levels after rainstorm events have increased in the lagoon, although similar concentrations have also been found in dry seasons.

The nitrate levels measured in the Mar Menor lagoon corresponded to moderately to heavily eutrophic areas in the Mediterranean Sea (GESAMP, 1990), although the phosphate levels were very low, rarely exceeding water quality criteria guidelines of 0.01 mg.L^{-1} , despite the high freshwater inputs observed. Phosphorus was the most limiting nutrient in the Mar Menor lagoon, the DIN:SRP ratios on all sampling dates being higher than the Redfield ratio. High DIN:SRP ratios are frequent in other Mediterranean coastal lagoons that receive high levels of freshwater discharge (Lucena *et al.*, 2002). The greatest part of phosphate input to the lagoon might be trapped in lagoon sediments as insoluble phosphate and then liberated in anoxic conditions (Perkins, 1974) or by wind induced resuspension of particulate matter (Krogerus and Ekholm, 2003).

The chlorophyll *a* concentrations were characteristic of oligotrophic conditions, except in late summer and early autumn when they reached mesotrophic to eutrophic levels. These data, both for nutrients and chlorophyll, are much lower than those observed in most Spanish Mediterranean coastal lagoons (Vicente, 1992; Comín, 1994; Quintana *et al.*, 1998, Lucena *et al.*, 2002) where the eutrophy is the result of high nutrient discharges maintained over many years (Lucena *et al.*, 2002). The participation of macrophytobenthos in the overall production of the Mar Menor is 64% (Terrados and Ros, 1991) which is higher than in other places, such as the bays of the Ebro delta where phytoplanktonic production predominates (Pérez, 1989).

These differences may be due to a shorter period of strong human impact in the watershed (important changes in land-use occurred in the last decade) compared to other Mediterranean areas, and/or specific physical boundary conditions of the system (de Jonge *et al.* 2002).

In the Mar Menor, muddy substrates, low hydrodynamism and shallow waters determine that sufficient light reaches the bottom to allow the development of submerged vegetation, such as the macroalga *Caulerpa prolifera*, which is capable of using the nutrients present both in water and sediments (Terrados and Ros, 1991). Only in late summer and early autumn was there any proliferation of the phytoplankton, principally near the Albuñón mouth, as a result of increased inputs of NH_4 and the concurrence of high water temperature and strong easterly winds. These conditions produced an acceleration in the P exchange across the sediment-water interface, increasing the availability of water P for phytoplankton. This increased development of phytoplankton, which cause a reduction in the quantity of light that reaches the bottom and affect the survival of the dominant seaweed, *C. prolifera* (Terrados and Ros, 1991). Furthermore, from the middle of September and throughout the winter, the water temperature would not allow optimal growth of the macroalga (Terrados and Ros, 1995).

Autumn floods fed the system by flushing large material and nutrient loads, and disturbing the lagoon sediments, thus increasing turbidity and the eutrophication effect of phytoplankton proliferation along a 5000 m gradient from the Albuñón mouth. However, freshwater inputs into the lagoon as a result of winter floods, did not have the same effect on phytoplankton development because of the low water temperature, but promoted a higher production of macrophytes during spring and summer periods. The relative importance of each primary producer component depends on the level of availability of nutrients in the water or in the sediment and the turbidity conditions, so the effect on local eutrophication changes from phytoplankton blooms in the late summer and early autumn to the growth of the opportunistic macroalga, *C. prolifera*, in spring and summer. Although algae blooms are limited by dissolved P, the nutrients trapped in sediments constitute a reservoir that may make eutrophication of the Mar Menor a persistent problem.

On the other hand, the feeding activities of the two allocthonous jellyfish species (*Rhizostoma pulmo* and *Cotylorhiza tuberculata*) may play an important role in controlling the consequences of eutrophication within the Mar Menor coastal lagoon. Pérez-Ruzafa *et al.* (2002) suggest a strong top-down control mechanism of size structure of phytoplankton by large jellyfishes that feed predominantly on large diatoms, which are most favoured by the increasing nutrient input. Jellyfish gut contents indicated clearly their preference for large diatoms, tintinnids, veliger larvae and copepods.

The development of action programmes to reduce the inputs of nitrates and phosphates from agricultural sources is an urgent task, which must include source and landscape management measures (Carpenter *et al.*, 1998). In the case of the Mar

Menor, these must involve: 1) limiting the land-application of fertilisers to match crop needs especially during the time when crops are growing rapidly (Sharpley *et al.*, 1994); 2) the restoration of wetlands and floodplains in littoral areas as buffer zones (Gren, 1995); and 3) an improvement in agricultural drainage water reutilization in the Campo de Cartagena. Among these, the second measure, including the appropriate management of *Phragmites australis* in the watercourses as a green filter may be the most cost-effective method for decreasing non-point N pollution in the Mar Menor lagoon. Information programmes, environmental education and codes of good agricultural practice are also necessary (Thyssen, 1999).

Acknowledgements

This work was funded by the Consejería de Agricultura, Agua y Medio Ambiente of the Murcia Region, Programa Séneca, 2001 (Project AGR/24/FS/02). We thank R. Alcántara, M.M. Ruíz, C. Gutierrez and J. Hernández for assistance in the field work; M.T. Pardo and F. Carreño for analysis assistance and Figure 1; and J. Martínez, M.A. Esteve and two anonymous reviewers for their helpful comments on the manuscript.

References

- American Public Health Association (APHA): 1992, *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, Washington, DC.
- Berka, C., Schreier, H. and Hall, K.: 2001, 'Linking water quality with agricultural intensification in a rural watershed', *Water, Air and Soil Pollut.* **127**, 389–401.
- Burt, T.P. and Arkell, B.P.: 1987 'Temporal and spatial patterns of nitrate losses from an agricultural watershed', *Soil Use and Management* **3**, 138–142.
- Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N. and Smith, V.H.: 1998, 'Nonpoint pollution of surface waters with phosphorus and nitrogen', *Ecological Applications* **8**, 559–568.
- Bricker, S.B., Clement, C.G., Pirhalla, D.E., Orlando, S.P. and Farrow, D.R.G.: 1999, 'National Estuarine Eutrophication Assessment: A Summary of Conditions, Historical Trends, and Future Outlook'. *NOAA's Technical Report*, National Ocean Service, National Oceanic and Atmospheric Administration, Silver Spring, MD, pp.71 <http://cammp.nos.noaa.gov/spo/prodlist.taf?alltype=1>
- Comín, F.A., Armengol, J., Lopez, P., Ballesteros, E. and Romero, J.: 1994, 'Introducció a l'estudi limològic dels aiguamolls de l'Empordà', *Treballs de l'Institut Català d'Història Natural* **13**, 254–271.
- Conesa, C.: 1992, *El Campo de Cartagena. Clima e hidrología de un medio semiárido*, Universidad de Murcia, Ayuntamiento de Cartagena y Comunidad de regantes del Campo de Cartagena, Murcia.
- De Jonge, V.N., Elliot, M. and Orive, E.: 2002, 'Causes, historical development, effects and future challenges of a common environmental problem: eutrophication', *Hydrobiologia* **475/476**, 1–19.
- GESAMP: 1990, 'The State of the Marine Environment', *Technical report*, IMO/ FAO/ UNESCO/ WMO/ IAEA/ UN/ UNEP, Joint Group of Experts on the Scientific Aspects of Marine Pollution, Reports and Studies N° 39, Nairobi.

- Gren, I.M.: 1995, 'The value of investing in wetlands for nitrogen abatement', *European Review of Agricultural Economics* **22**, 157–172.
- Kennish M.J.: 2002, 'Environmental threats and environmental future of estuaries', *Environmental Conservation* **29**, 78–107.
- Krogerus, K. and Ekholm, P.: 2003, 'Phosphorus in settling matter and bottom sediments in lakes loaded by agriculture', *Hydrobiologia* **492**, 15–28.
- Lucena, J.R., Hurtado, J. and Comín, F.A.: 2002, 'Nutrients related to the hidrologic regime in the coastal lagoons of Viladecans (NE Spain)', *Hydrobiologia* **475/476**, 413–422.
- Martínez, J. and Esteve, M.A.: 2000, 'Estimación de la entrada de nutrientes de origen agrícola en el Mar Menor mediante un modelo dinámico', *Mediterranea*, Serie de estudios biológicos, 19–25.
- Molénat, J., Durand, P., Gascuel-Odoux, C., Davy, P. and Gruau, G.: 2002, 'Mechanisms of nitrate transfer from soil to stream in an agricultural watershed of French Brittany', *Water, Air and Soil Pollut.* **91**, 183–189.
- Nixon, S.W. and Pilson, M.E.Q.: 1983, 'Nitrogen in estuarine and coastal marine ecosystems' in E.J. Carpenter and D.G. Capone (eds.), *Nitrogen in the Marine Environment*, Academic Press, New York, NY, USA.
- OECD: 1982, 'Eutrophication of Waters: Monitoring, Assesment and Control', *Technical Report*, Organisation for Economic Development and Co-operation, Report of the OECD cooperative programme on eutrophication, Paris.
- Pérez, M.: 1989, 'Fanerógamas marinas en sistemas estuáricos: producción, factores limitantes y algunos aspectos del ciclo de nutrientes', *Ph.D. Thesis*, University of Barcelona, Spain.
- Pérez-Ruzafa, A., Gilabert, J., Gutiérrez, J.M., Fernández, A.I., Marcos, C. and Sabah, S.: 2002, 'Evidence of a planktonic food web response to changes in nutrient input dynamics in the Mar Menor coastal lagoon, Spain', *Hydrobiologia* **475/476**, 350–369.
- Pérez-Ruzafa, A., Navarro, S., Barba, A., Marcos, C., Cámara, M.A. and Salas, F.: 2000, 'Presence of pesticides through trophic compartments of the food web in the Mar Menor lagoon (SE Spain)', *Marine Pollution Bulletin* **40**, 140–151.
- Pérez-Ruzafa, A.: 1989, 'Estudio ecológico y bionómico de los poblamientos bentónicos del Mar Menor (Murcia, SE de España)', *Ph.D. Thesis*, University of Murcia, Spain.
- Perkins, E.J.: 1974, *The Biology of Estuaries and Coastal Waters*, Academic Press, London, 678 pp.
- Quintana, X.D., Moreno-Amich, R. and Comín F.A.: 1998, 'Nutrient and plankton dynamics in a Mediterranean salt marsh dominated by incidents of flooding. Part 1. Differential confinement of nutrients', *J. Plankton Res.* **20**, 2089–2107.
- SACYR S.A.: 1997 'Análisis y caudales de los drenajes y ramblas del campo de Cartagena', *Technical Report*, Confederación Hidrográfica del Segura, Murcia, Spain, 21pp.
- Sharpley, A.N., Chapra, S.C., Wedepohl, R., Sims, T., Daniel, T.C. and Reddy, K.R.: 1994, 'Managing agricultural phosphorus for protection of surface waters: issues and options', *Journal of Environmental Quality* **23**, 437–451.
- Stalnake, P., Grimvall, A., Sundbland, K. and Tonderski, A.: 1990, 'Estimation of riverine loads of nitrogen and phosphorus to the Baltic Sea, 1970–1993', *Environmental Monitoring and Assessment* **58**, 173–200.
- Terrados, J. and Ros, J.D.: 1991, 'Production dynamics in a macrophyte-dominated ecosystem: the Mar Menor coastal lagoon (SE Spain)', in J.D. Ros and N. Prat (eds), *Homage to Ramon Margalef; or, Why there is such Pleasure in Studying Nature?* Oecol. Aquatica **10**, 255–270.
- Terrados, J. and Ros, J.D.: 1995, 'Temporal variation of the biomass and structure of *Caulerpa prolifera* (Forsskal) Lamourous meadows in the Mar Menor lagoon (SE Spain)', *Scientia Marina* **59**, 49–56.
- Thyssen N. (ed.): 1999, 'Nutrients in European Ecosystems', *Technical Report*, European Environment Agency, Environmental Assessment Report, 4, Copenhagen, pp.155 <http://reports.eea.eu.int/ENVIASSRP04/en/enviassrp04.pdf>

- U.S. EPA: 2002, '2000 National Water Quality Inventory', *Technical Report*, Office of Water. U.S. Government, Washington, D.C., USA. <http://www.epa.gov/305b/2000report/>
- Vollenweider, R.A.: 1975, 'Input-output models with special reference to the phosphorus loading concept in Limnology', *Schweiz. Z. Hydrol.* **37**, 53–84.
- Vicente, E. and Miracle, M.R.: 1992, 'The coastal lagoon albufera de Valencia: an ecosystem under stress', *Limnetica* **8**, 87–100.