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Environmental shaping and carbon cycling in a macrophyte-dominated Mediterranean coastal lagoon

Modulació ambiental i ciclat del carboni en una llacuna litoral Mediterrània dominada per macròfits

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TESI DOCTORAL

Departament d'Ecologia
Universitat de Barcelona
Programa de doctorat: Titulació d'Estudis Avançats en Ecologia
Bienni 2002-2004

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Memòria presentada per Biel Obrador Sala per optar al grau de doctor per la Universitat de Barcelona

Biel Obrador Sala
Barcelona, març de 2009

Vist-i-plau del director de la tesi
Dr. Joan Lluís Pretus Real
Professor titular del Departament d'Ecologia
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A n'Anna i en Guiem,
que des de la pacient espera,
han seguit
i segueixen
enlluernant-me.

Als meus pares,
que m'han ensenyat
la plenitud de les rectes
i la bellesa de les corbes.

– De quin país és aquest estranger?
– No ho sé.
– Com se diu?
– No ho sé.
– Què fa? Quina llengua parla?
– No ho sé.
– Com us dieu, bon home?
– ...
– De quin país veniu? On aneu?
– Sóc d'aquí. Sóc estranger.

L'ESTRANGER
Josep Palau i Fabre
16 d'octubre de 1947
POEMES DE L'ALQUIMISTA. PROA, 8ª ed.

Índex / *Contents*

Agraïments

(com a línia històrica, per a què en quedi constància)

Sembla que ja hi hem arribat. La TESI, en majúscules perquè ara ha passat de quelcom innombrable a poder-se fullejar, m'ha absorbit totalment en els darrers set (...) anys de la meva vida. I ha estat, certament, fantàstic però també esgotador, tant per a mi (segur) com per als que m'envolten (encara més segur). Parlar ara dels moments feliços, intensos, en què la TESI feia un gir i prenia una nova forma, en què es veia la llum sobre com enfocar un dels articles o en què el veies publicat i el final es feia *tocable*, parlar ara, de les cícliques crisis que tan a prop han estat de fer-me abandonar, de les angoixes i els mals de cap, de les nits en blanc, els matins en fosc i les tardes de color gris, parlar dels no-ara-no-puc-...la-tesi, dels riures i somriures den Guiem i n'Anna que m'he perdut, parlar de tot això ara és minimitzar-ne la magnitud. Perquè finalment s'ha acabat i ja puc obrir el congelador de nou (cito a en Rafa).

La tesi està enllestida i fins arribar aquí ha estat molta, moltíssima, l'ajuda que he rebut. En primer lloc, com deia, la inestimable i imprescindible ajuda dels de casa, en Guiem i n'Anna, que tot ho han aguantat somrients. També especialment els meus pares, els avis de Llimpa, i també els ara avis i ara besavis d'Olot, els tiets i tietes de sang o de cor, i tota aquella família indefinida que fa que un se senti acompanyat, potser no del tot entès, però sí recolzat en la seva aposta per invertir tant de temps a fer una cosa tan estranya com ho és una tesi doctoral. A tots, el meu més sincer i sentit agraïment per no voler comparar amb les vares estàndard i per donar, cegament, un suport tan fonamental. Gràcies de tot cor!

Emocions a banda, tot l'aprenentatge i la feina feta durant aquests anys, no hauria estat possible sense l'estímul inicial de tots aquells que em van fer gaudir i intentar entendre això de l'Ecologia. Els primers professors de la carrera, que amb el temps han esdevingut companys, em van transmetre el rigor i aquest abstracte interès: la Pili López (a cicles), en Joan Armengol i la Isabel Muñoz (a eco2) i en Javier Romero (a eco oceànica), entre d'altres, em van fer veure el camí (amb alguns càlculs erronis pel mig, oi Joan?...).

Una vegada decidida l'expiació, va començar s'Albufera amb en Joan, en Pretus del qual jo només sabia que estava sempre en remull per una llacuna de Menorca ('surt des suc'). Ara fa uns deu anys, encara estudiant, vaig tocar les primeres mostres de s'Albufera: vaig fer unes dilucions amb una màquina infernal dels serveis Científico-tècnics per donar un cop de mà al doctorand que aquella època hi havia al grup, en Jordi González, amb qui vaig fer les primeres campanyes i vaig aprendre què volia dir això de fer ciència amb cinta aïllant, brides, claus angleses i tornavisos: volia dir passar per Jaype abans d'embarcar!

Fins a tocar el tema tractat a la tesi, la cosa va donar (i fins fa poc ha donat) moltes voltes. Vaig tremolar amb el fluorhídric i la centrífuga per netejar els ditxosos grans de pòl·len, vaig suar amb el Polyvar al zulo del departament, i vaig aprendre palinologia dels sempre exemplars farmacèutics i geòlegs que em feien veure (o imaginar) l'exina. Va ser en va, perquè el 2002, enmig de la crisi, vaig veure clar que això del sediment estava molt bé si es tractava d'un compartiment més de la llacuna i no només d'un registre històric. Després d'un parell d'anys analitzant les aigües i mostrejant la llacuna, m'havia adonat que per a mi s'Albufera tenia interès per sí mateixa com a sistema, i que a la tesi hi faria una aproximació limnològica. Va ser durant les hores d'autopista amb en Joan, en un viatge a Toulousse per sentir en Guillem Chust en francès explicar-nos la seva tesi, en què vam dibuixar els primers esbossos a una tesi que parlava de carboni, isotopia, macròfits i carbonats. D'aquell enfocament original n'ha quedat un DEA i un parell de capítols al final no inclosos a la TESI, però també un marc conceptual on m'he mogut després.

La fase físicament més intensa va ser el mostreig que va anar del 2002 al 2004, especialment la matada de l'estiu del 2002, en què cada setmana anàvem matí, vespre i matí seguits a mostrejar els quatre punts de s'Albufera amb poc més que un banyador i les ganes (o tanga, eh, Melissa?). Tot el treball del cicle diari (amb son i es ginet a mà) no hauria estat possible sense na Melissa, en Miquel, i en Joan. I la gent de sa Granja que ens va cedir aquell casi-bouer on fèiem alcalinitats i altres animalades.

Durant els mostrejos mensuals va ser molta, moltíssima la gent que em va ajudar. Agraeixo especialment a en Sam i n'Óscar les hores passades dins la barca superant incidències de tota mena. Va ser molta la gent a qui vaig enganar perquè vinguessin a disfrutar de s'Albufera -perquè-és-molt-polit-i-des-de-dins-en-barca-val-molt-la-pena. Tinc molt clar que els que vau venir a remar, acabar plens de fang, empènyer, pesar Ruppia, rotular pots, aixecar caixes, carregar motors i filtrar aigües, ho vau fer per ajudar-me i no per xalar de s'Albufera. Agnès, Cris, Anna Carreras, Nina, Laia, David, Anna, Melisa, Miquel, Marta, Laura, Violeta, Pere, Óscar, Lídia i mon pare, i si me'n descuido algun ho sento moltíssim: gràcies per suar! Van ser unes campanyes amb molts viatges a l'aeroport per part de na Cris (només fins a sa rotonda, eh!), na Laia, en Jaume O., na Pili, en Jaume S., en David, i en què casi sempre queia un dinar, una volteta, un berenar a Sa Grava o una ballada dalt s'era: quines regles tan polides, eh al·lots! També durant aquella època, els irrepetibles platets-amb-quatre-patatetes-frites de s'àvia, els seus somriures i la complicitat que vam aconseguir, són un dels millors records que tinc. A ella també una forta abraçada que segur que rep!

La part analítica de la tesi ha estat menys dolenta per la meva esquena que per a la meva paciència i vista. I és que alguns se sorprenen que tinguem tantes mesures. Després d'haver-ho fet tot jo mateix, ara ho trobo normal. Entre la Tesi i el Seguiment, he fet titulacions potenciomètriques per l'alcalinitat (unes mil), he analitzat nutrients a mà i amb l'Skalar (que encara és viu), he mesurat biomasses, preparat boletes per Anàlisi Elemental, analitzat isòtops, analitzat isòtops (moltes vegades), mesurat valves, mesurat valves i mesurat valves de nou. És a dir he emprat un reguitzell de tècniques i aparells amb noms i sigles estranyes: Gran, ICP-MS, ICP-OES, HPLC, AE, Skalar, IRMS, Delta-C, MAT-252, LOI, ... Això només vol dir una cosa: he rebut l'ajuda de moltíssima gent. Tota la gent dels Serveis Científico-Tècnics (la Pilar Teixidor, la Laia Balart, la Rosa Maria, en Joaquim, la Pili, la Maria, la Pilar Fernàndez, en Santi, en Toni), i la gent que m'ha ensenyat tècniques (la Pili López, en JJ Pueyo), i m'ha deixat material (en Hamper), i també tots els companys de suor al laboratori del departament (Mary, Eusebi, Ainhoa, Violeta, Marta, Lídia!!...).

Del departament no en puc dir sinó que l'ambient ha estat humanament immillorable. Tots els companys, els que ja casi eren veterans quan jo entrava i els que han anat arribant i enriquint, han estat un bon coixí on trobar consells, cafès expiatoris i comprensió: l'Ainhoa, la Núria, l'Eusebi, la Lídia, en Júlio, la Mary, en Gerardo i l'Agnès (se us enyora!), la Mireia, la Tureta, la Blanca, la Rosa, en Raul i tots els Ecobills, en Jaime, en Gonzalo, en Rafa, tots els "marinus", en Xavi, l'Olga, en Pere, en Salva, la Susanna, els emigrats a Blanes... Amb vosaltres, i amb els que per oblit em dec oblidar (disculpeu!), hem rigut pels descosits, i hem fet uns quants gols (pocs...). Fet i fet, hem passat de treballar amb guants i bufanda a tenir estufes, i si us hi fixeu, ja no hi ha cap cartell del sord queixant-se o dient " telèfoooon!". Seriosament, moltes gràcies a tots! Els dinars reclosos a dalt han valgut molt la pena (no pel tupper, és clar....): mira que n'he après de coses en aquests dinars!

L'estada a Londres al final ha quedat poc representada a la Tesi, però ha estat un dels períodes més productius i de major clarividència sobre què feia i cap on anava amb la recerca. Of course you know now that there was a reason why I came a third time! My sincere thanks to Jonathan Holmes, always available. Also my thanks to all the lab, pub and football-match colleagues (George, Jon, and the others!).

A València vaig aprendre a "hacer de modelo" a banda de riure pels descosits amb en Quique, la Marga, en Gonzalo, en Jordi, l'Ana i la Maria: qué collejos! Quique, salió bien el asunto, eh! Una abraçada especial també a la Núria, l'Ainhoa i tota la bona gent jove i limnòloga d'arreu per la implicació conjunta en cada una de les sigles rares dels Jóvenes AIL!

A la Pat i l'Adriana i als arquitectes teòrics, ara ben desperdigats arreu, els hi dec, a banda de la profunda amistat que n'ha quedat, el regust de tantes vetllades cosmopolites, la visió crítica constant, i el plaer de saber qui era Adrià i la seva muralla: Joan, Alberto! És ben cert que m'ha estat d'utilitat!

A ses mutxatxes i es ranxo de Menorca, que sempre m'han convençut per anar a fer qualcuna calamuetjada a Cala Viola, també mil gràcies: que no ho és polit, en tost de Binigaus?

La fase final de la tesi, la d'escriptura, ha durat molt, molt més del que havia pensat. He incomplert no sé quants terminis (mal) previstos amb escreix. M'he exiliat diverses vegades a Llimpa (a fer manguerades), a Cal Governador (veient la Vall den Bas, aïllat per la nevada), o a casa (veient-me a mi, als papers, a l'Excel i al portàtil treient fum) i m'ha anat prou bé. Com deia, hi ha hagut moments d'eufòria i de crisi, però he descobert la il·lusió de tancar un article i d'enfocar un nou tema. Crec que a la casa Toshiba l'hi hauria d'agrair el que facin els portàtils tan resistents, amb uns teclats que ho aguanten tot sense queixar-se....

També en aquesta fase he rebut el suport de molta gent: el 'doctor' Albert, els meta-vinillus imprescindibles amb la LaiaQ, les maques cerverines, i els somriures i saber fer de la Magalí, l'Anna, la Nina, en Guillem, la Laura, els vikings... nois, tornarem a fer calçotades en directe!

Més que mai en aquesta fase, m'he aprofitat del coneixement i el saber fer dels savis del departament. Dec molt a les discussions de resultats amb en Salva, en Rafa, la Margarita, la Núria, la Pili i en Josep Anton, sempre disponibles per resoldre dubtes.

No puc sinó agrair els articles i llibres proporcionats per tants de vosaltres (Quique, Guillermo, Begoña, Biel Moyà i Tom Freeman), així com els comentaris i informació den Miquel Truyol, en Jordi Catalan, en Quique Moreno, en Lluís Pomar, na Laura Piris i en Sam Pons. He fet servir també fotos de molta gent, en Pere Que, en Josep Carbonell, en Sam, na Cris, a qui agraeixo que me les hagin cedit.

També m'han estat de gran ajuda els consells lingüístics i terminològics den Guillem Pujades, en Cice Pasqual, l'Àngels Egea, en Joandomènec Ros, en Santi Sabaté, en Mikel Zabala, així com les correccions del meu anglès de *gentleman* Mediterrani fetes per en George i molt especialment n'Anna, que s'ho ha rellegit tot amb una santa paciència. L'ajuda de mon pare, repassant cada punt, coma i lletra de la bibliografia, ha estat fonamental. La disponibilitat i paciència de la Pili López i de tota la gent de secretaria ha fet moltíssim més manejable l'espinós camí de les normatives i disposicions administratives.

Pel que fa a la supervivència econòmica, la beca que encara no sé com vaig aconseguir m'ha permès tenir l'estabilitat, totalment necessària, durant els primers quatre anys. Quin greu no haver apretat encara més al principi, si és que podia, i haver enllestit abans! La BRD de la Universitat de Barcelona em va posar en contacte amb la docència a la universitat i va tancar la dualitat, totalment necessària al meu parer, entre docència i recerca. Val a dir que la BRD també em va fer fer més de 370 hores de classe durant aquell període: i és clar que tenia excusa per no acabar a temps! No em sap cap greu, en cap cas, haver-les fet. N'he après molt, i no tindria aquesta visió de l'Ecologia (sento que no sé res, i això conforta...) si no hagués suat aquestes classes i totes les que han seguit arreu. La BRD doncs, va fer, que entengués millor tant la Universitat com l'Ecologia (tal i com preveia profèticament en Javier Romero després de la meva primera classe) i que no pretengués separar lo docent de la recerca. És clar que és criticable això de les beques, però veient el que ve després de la fase de becari, un ho veu del tot diferent: què bé que estava amb la beca! I és que una vegada acabada, vaig tenir la sort de trobar aquest xollo que és el ser professor associat a la universitat. Sarcasme a banda, certament he tingut molta sort de, a part de poder menjar una mica, no massa, poder gaudir de la plaça i mantenir el contacte amb la docència i seguir aprenent mentre enllestia la tesi.

Ara que estem als agraïments més formals però no per això més secundaris, també haig d'agrair el suport rebut pel Parc Natural de s'Albufera i el seu personal, i molt especialment el finançament rebut per l'Institut

Menorquí d'Estudis (projectes dels anys 2003 i 2005) i pel Consell Insular de Menorca (projecte del 2007), sense els quals m'hauria estat molt difícil, o gairebé impossible, realitzar aquesta tesi.

Finalment, vull deixar palès el paper fonamental que ha tingut el meu director en aquesta tesi. Amb les discrepàncies habituals en tota relació director-doctorand (o tal vegada algunes més...je, je), veig molt clar que el seu estímul constant i la seva incansable capacitat de sorpresa, si bé m'han esgotat sovint, també m'han fet perdre la por a abordar (de vegades, amb poc realisme, sí) qualsevol dubte que sorgís, qualsevol pregunta, qualsevol volada. És amb en Joan que he après la ciència de la curiositat i l'entusiasme incondicionals, i me'n sento afortunat. Gràcies per creure-hi, Joan!

I citant el geni, que sosté que tot és en tot i tot recomença, necessito agrair novament als de casa el ser-hi sempre i sempre somriure, el corregir i recorregir bibliografies, l'omplir *tuppers* (sense permís), el fer cangurs, l'aguantar massa mocs, i sobretot la fermesa de saber dur el bon rumb amb qualsevol vent. Sense el vostre suport això no hauria passat d'un vers mal escrit encalaixat com una anècdota de televisió barata. Gràcies, polits!

I al lector que ha arribat fins aquí, gràcies per l'interès!

Biel Obrador Sala
Barcelona – Llimpa – Olot, març de 2009

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Variable	Description (units, if appropriate) [Chapter/s]
α	solubility constant for CO_2 (mol m^{-3} atm^{-1}) [C5,C6]
α_c	albedo coefficient [C2]
γ	runoff coefficient [C2]
γ_c	psychrometric constant (kPa $°C^{-1}$) [C2]
Δ	slope of the saturation vapour pressure curve (kPa $°C^{-1}$) [C2]
ΔBi	increase in biomass during time interval *i* [C4]
$\Delta C_{a,d}$	change in the areal concentration of DIC or DO during day (mmol m^{-2} d^{-1}) [C5]
$\Delta C_{a,n}$	change in the areal concentration of DIC or DO during night (mmol m^{-2} d^{-1}) [C5]
$\delta^{13}C$	carbon stable isotope composition (‰) [C6]
$\delta^{13}C_{DIC}$	stable isotope composition of dissolved inorganic carbon (‰) [C6]
$\delta^{15}N$	nitrogen stable isotope composition (‰) [C6]
ε	chemical enhancement factor for CO_2 (dimensionless) [C5,C6]
Ω	saturations state of calcium carbonate [C6]
A	area of the sluice opening (m^2) [C2]
AN	referring to the annual average [C4]
AOP	apparent optical property [C3]
apr	referring to the value for April [C4]
aug	referring to the value for August [C4]
AUT	referring to the value for the autumn months [C4]
bottIrrad	percent bottom irradiance (%) [C4]
c_1	infiltration parameter [C2]
c_2	dry deposition coefficient [C2]
C_{atm}	concentration of gas in atmospheric equilibrium (mmol m^{-3}) [C5,C6]
[Chl-a]	concentration of Chlorophyll-a (µg L^{-1}) [C4,C3]
CDOM	Chromophoric Dissolved Organic Matter (gelbstoff, gilvin) [C3]
cm a.s.l.	centimetres above sea level [C1]
cm b.s.l.	centimetres below sea level [C1]
CR	daily community respiration (mmol m^{-2} d^{-1}) [C5]
C_R	concentration of a given constituent in the riverine endmember [C6]
CR_d	daytime community respiration (mmol m^{-2} d^{-1}) [C5]
CR_n	nighttime community respiration (mmol m^{-2} d^{-1}) [C5]
C_{sw}	concentration of a given constituent in the marine endmember [C6]
C_w	concentration of gas in surface water (mmol m^{-3}) [C5,C6]
D	distance from the sea (m) [C2]
des	referring to the value for December [C4]
[Det]	concentration of detritus (g m^{-3}) [C3]
[Det-C]	concentration of detritic carbon [C6]
D_i	detached biomass of *R. cirrhosa* during time interval *i* [C4]
DIC	concentration of dissolved inorganic carbon (mM) [C1]
$DIC_{h,a}$	DIC expected under hydrological and atmospheric processes [C6]
DIN	total dissolved inorganic nitrogen [C4]
DO	concentration of dissolved oxygen (mg L^{-1}) [C5]
[DOC]	concentration of dissolved organic carbon (g m^{-3}) [C3,C6]
E	evaporation rate (mm d^{-1}) [C2]
E_0	PAR irradiance below water surface (umol m^{-2} s^{-1}) [C3]
E_1	coefficient of efficiency [C2]
e_a	actual vapour pressure (kPa) [C2]
EC	evaporation in the canopy (mm d^{-1}) [C2]
e_s	saturation vapour pressure (kPa) [C2]
ET_0	potential evapotranspiration (mm d^{-1}) [C2]
ET_S	evapotranspiration from the soil (mm d^{-1}) [C2]
E_z	PAR irradiance at depth z (µmol m^{-2} s^{-1}) [C3]
F	flux of CO_2 or O_2 accross the air-water interface (mmol m^{-2} d^{-1}) [C5]
f	fraction of seawater at a given salinity [C6]
$FDIC_{atm}$	flux of CO_2 across the air-water interface (mmol m^{-2} d^{-1}) [C6]
$FDIC_{ni}$	net internal flux of DIC [C6]
$FDIC_{outflow}$	output of DIC through lagoon outflow [C6]
$FDIC_{sw}$	flux of DIC associated to seawater inflow [C6]

(cont.)

feb	referring to the value for February [C4]
F_i	flux of CO_2 or O_2 across the air-water interface at time interval *i* [C5]
G	soil heat flux density (MJ m^{-2} d^{-1}) [C2]
gAFDW m^{-2}	grams of ash-free dry weight per square meter [C1]
gDW m^{-2}	grams dry weight per square meter [C1]
G_i	grazing of *R. cirrhosa* during time interval *i* [C4]
GPP	Gross primary production (mmol m^{-2} d^{-1}) [C5]
h	height of the water column at the sluice (m) [C2]
ICP-OES	Induced Coupled-Plasma Optical Emission Spectroscopy [C6]
IOP	Inherent Optical Property [C3]
IRMS	Isotope Ratio Mass Spectrometry [C6]
[ISS]	concentration of Inorganic Suspended Solids (g m^{-3}) [C3]
jan	referring to the value for January [C4]
jul	referring to the value for July [C4]
jun	referring to the value for June [C4]
K	vertical light attenuation coefficient (m^{-1}) [C3]
k	gas transfer velocity (m s^{-1} or m d^{-1}) [C5]
K.W.	Kruskall Wallis test [C3]
K_{cal}	solubility product for calcite [C6]
K_{chl}	partial attenuation coefficient of Chlorophyll-a (m^{-1}) [C3]
K'_{chl}	specific attenuation coefficient of Chlorophyll-a (m^2 mg^{-1}) [C3]
k_d	decomposition rate of *R.cirrhosa* biomass (d^{-1}) [C4]
K_{det}	partial attenuation coefficient of detritus (m^{-1}) [C3]
K'_{det}	specific attenuation coefficient of detritus (m^2 g^{-1}) [C3]
K_{doc}	partial attenuation coefficient of DOC (m^{-1}) [C3]
K'_{doc}	specific attenuation coefficient of DOC (m^2 g^{-1}) [C3]
K_{iss}	partial attenuation coefficient of ISS (m^{-1}) [C3]
K'_{iss}	specific attenuation coefficient of ISS (m2 g^{-1}) [C3]
K_{of}	free-orifice flow coefficient for filtration outflow [C2]
K_{om}	free-orifice flow coefficient for massive outflow [C2]
K_{sf}	free-orifice flow coefficient for seawater filtration [C2]
K_{sm}	free-orifice flow coefficient for seawtaer flow [C2]
K_T	total light attenuation coefficient (m^{-1}) [C3]
$K_{tripton}$	partial attenuation coefficient of tripton (m^{-1}) [C3]
$K'_{tripton}$	specific attenuation coefficient of tripton (m^2 g^{-1}) [C3]
K_{TSS}	partial attenuation coefficient of TSS (m^{-1}) [C3]
K'_{TSS}	specific attenuation coefficient of TSS (m^2 g^{-1}) [C3]
K_w	partial attenuation coefficient of water (m^{-1}) [C3]
LAI	Leaf Area Index [C2]
LSM	Lagoon Salt Mass submodel [C2]
LWM	Lagoon Water submodel [C2]
M_a	salt atmospheric deposition (Kg d^{-1}) [C2]
MAE	mean absolute error [C2]
mai	referring to the value for May [C4]
mar	referring to the value for March [C4]
MC	macrophytic carbon [C6]
Mg C	megagrams of carbon (10^6g C) [C6]
M_i	natural mortality of *R. cirrhosa* during time interval *i* [C4]
M_o	salt evacuation (Kg d^{-1}) [C2]
M_P	salt input from direct rainfall on the lagoon (Kg d^{-1}) [C2]
M_R	salt input from stream runoff (Kg d^{-1}) [C2]
M_s	seawater salt input (Kg d^{-1}) [C2]
NEP	Daily net ecosystem production (mmol m^{-2} d^{-1}) [C5]
NEP_d	daytime net ecosystem production (mmol m^{-2} d^{-1}) [C5]
NH_4	concentration of ammonia (μM) [C4]
NO_3	concentration of nitrate (μM) [C4]
OC	total organic carbon [C6]
[OSS]	concentration of organic suspended solids (g m^{-3}) [C3]
oct	referring to the value for October [C4]
P	annual production of *R. cirrhosa* (gDW m^{-2} y^{-1}) [C4]
PAR	Photosynthetically Active Radiation (μmol m^{-2} s^{-1}) [C3]

(cont.)

pCO_2	partial pressure of CO_2 (μatm) [C1,C5,C6]
PDB	Pee Dee Belemnite standard [C6]
[Phyt]	concentration of phytoplankton (g m^{-3}) [C3]
[Phyt-C]	concentration of phytoplanktonic carbon [C6]
P_i	net production of *R. cirrhosa* during time interval *i* [C4]
[POC]	concentration of particulate organic carbon [C6]
P_r	rainfall (mm d^{-1}) [C2,C4]
Q_E	evaporation (m^3 d^{-1}) [C2]
Q_o	lagoon outflow (m^3 d^{-1}) [C2]
Q_{of}	lagoon outflow by filtration (m^3 d^{-1}) [C2]
Q_{om}	massive lagoon outflow (m^3 d^{-1}) [C2]
Q_P	direct rainfall on the lagoon (m^3 d^{-1}) [C2]
Q_R	stream runoff (m^3 d^{-1}) [C2]
Q_s	seawater inflow (m^3 d^{-1}) [C2]
Q_{sf}	seawater inflow by filtration (m^3 d^{-1}) [C2]
Q_{sm}	massive seawater inflow (m^3 d^{-1}) [C2]
R^2	coefficient of determination [C2]
RH	relative humidity (%) [C2]
RM	runoff submodel [C2]
RMSE	Root Mean Square Error [C2]
R_n	net radiation (MJ m^{-2} d^{-1}) [C2]
R_{nl}	net longwave radiation (MJ m^{-2} d^{-1}) [C2]
R_{ns}	net shortwave radiation (MJ m^{-2} d^{-1}) [C2]
R_S	surface runoff (mm d^{-1}) [C2]
R_{si}	incoming shortwave radiation (MJ m^{-2} d^{-1}) [C2]
R_T	total runoff (mm d^{-1}) [C2]
S	water salinity (g L^{-1} or in the practical salinity scale) [C2,C4]
S_c	water stored in the canopy (mm) [C2]
S_{cmax}	maximum water stored in the canopy (mm) [C2]
sep	referring to the value for September [C4]
SI_k	sensitivity index for the parameter k [C2]
S_k	sensitivity for the parameter k [C2]
SOM	Sedimentary Organic Matter [C6]
SPR	referring to the value for the spring months [C4]
SR	salinity of the riverine endmember in a mixing model [C6]
SRP	concentration of Soluble Reactive Phosphorus (μM) [C1]
S_s	water content in the soil (mm) [C2]
S_{smax}	soil water capacity (mm) [C2]
S_{sw}	salinity of the marine endmember in a mixing model [C6]
SUM	referring to the value for the summer months [C4]
Sup	lagoon surface (ha) [C2]
t	time (d) [C2]
T	average air temperature (°C) [C2]
TA	total alkalinity (meq L^{-1}) [C5]
Temp	water temperature (°C) [C4]
TF	throughfall (mm d^{-1}) [C2]
T_M	maximum air temperature (°C) [C2]
T_m	minimum air temperature (°C) [C2]
TP	concentration of total phosphorus (μM) [C1]
TS	total salt mass (Kg) [C2]
[TSS]	concentration of Total Suspended Solids or seston (g m^{-3}) [C3]
Turb	water turbidity (m^{-1}) [C4]
u	wind speed (m s^{-1}) [C2]
V	lagoon volume (m^3) [C2]
Wind	mean annual wind speed (m s^{-1}) [C4]
WL	water level (cm a.s.l. or cm b.s.l.) [C2]
WL_{om}	maximum critical water level (cm a.s.l.) [C2]
WL_{sm}	minimum critical water level (cm a.s.l.) [C2]
Z	effective depth (measured) of the water column (m) [C3]
Z_{rel}	relative depth (m) [C3]

I. Introducció

Les llacunes litorals són sistemes aquàtics típicament poc profunds i amb diferents graus de connectivitat amb la mar, que sustenten una elevada biodiversitat, i que es troben entre els sistemes més productius de la biosfera (Barnes 1980; Kjerfve 1994). Es caracteritzen per una elevada variabilitat temporal, tant hidrològica com pel que fa als cicles biogeoquímics que hi tenen lloc o a les dinàmiques de les comunitats biològiques. Aquest caràcter dinàmic es deu, en bona part, a la seva ubicació entre els continents i les aigües marines, rebent grans quantitats de materials de diversa naturalesa (dissolts i particulats, orgànics i inorgànics), alguns dels quals són intensament processats abans d'arribar a la mar (Buddemeier et al. 2002). És en aquest processat de nutrients i matèria orgànica on rau la importància biogeoquímica dels sistemes costaners, que, per una banda, solen tenir una gran importància en les economies locals per l'elevada producció biològica que generen (explotada sovint a través de pesqueries o cultius de mol·luscs), i, per l'altra, tenen un paper important en els cicles globals dels elements (Smith and Hollibaugh 1993; Levin et al. 2001; Gönenç and Wolflin 2004; Crossland et al. 2005). Els sistemes costaners han estat, durant les darreres dècades, intensament afectats per l'acció de l'home, tant per impactes directes com a conseqüència d'alteracions sobre la conca (Lotze et al. 2006; Halpern et al. 2008). Els impactes sobre llacunes litorals inclouen l'eutrofització, la contaminació per metalls, la pertorbació de la geomorfologia i els règims hidrològics, l'alteració de les xarxes tròfiques per sobreexplotació o introducció d'espècies exòtiques, i fins i tot, l'eliminació física directa de llacunes en zones amb elevades pressions urbanístiques i/o turístiques (McComb 1995; Verlaque 2001; EEA 2005; EEA 2006; Viaroli et al. 2007).

El caràcter altament dinàmic de les llacunes litorals és encara més accentuat en les llacunes Mediterrànies, que sovint mostren, a més, un grau de pertorbació antròpica molt elevat (EEA 2005; Viaroli et al. 2005). El clima Mediterrani es caracteritza per una clara estacionalitat tèrmica i pluviomètrica, però també per tenir un règim de precipitacions amb intensos esdeveniments torrencials (Bolle 2003). Això pot generar, en els sistemes aquàtics Mediterranis, importants fluctuacions de nivell de l'aigua, entrades massives de nutrients, canvis sobtats de salinitat o de terbolesa, alteracions brusques dels fluxos químics dels sediments o la ràpida renovació de l'aigua, tots amb marcats efectes damunt els comunitats biològiques (Coops et al. 2003; Beklioglu et al. 2006). A més, la quasi absència de marees a la Mediterrània, fa que les llacunes litorals mediterrànies presentin una variabilitat hidrològica i ecològica especialment elevada i impredictible (Quintana et al. 1998a; Quintana et al. 1998b; Quintana 2002; Pérez-Ruzafa et al. 2005; Viaroli et al. 2005; Badosa et al. 2006; Badosa et al. 2008).

Les llacunes litorals són, a més, uns dels sistemes més productius de la biosfera (Barnes 1980). L'elevada producció d'aquests sistemes pot anar associada a diferents productors primaris que esdevenen dominants en funció de les concentracions de nutrients: essent els principals els macròfits submergits (fanerògames aquàtiques), el fitoplàncton i les macroalgues (Knoppers 1994). Els macròfits submergits són espècies clau en els sistemes aquàtics soms, intervenint en els fluxes biogeoquímics (fluxes del sediment, tamponament de les entrades de nutrients), en l'estabilització fisicoquímica de la columna d'aigua (reducció del material particulat i la resuspensió de sediments, regulació dels nivells d'oxigen), en la determinació de múltiples interaccions biòtiques, i, pel seu rol d'espècies enginyeres, servint d'hàbitat, refugi i aliment per a nombroses espècies de peixos i aus aquàtiques (Heck and Thoman 1981; Carpenter and Lodge 1986; Levin et al. 2001; Jeppesen et al. 1998; Nielsen et al. 2004; Thouzeau et al. 2007). Malgrat que el grau d'eutrofització sembla esser determinant en la dominància d'un o altre productor primari, els mecanismes que en determinen la dinàmica no són ni de bon tros tan coneguts ni estudiats com en els llacs soms d'aigua dolça, en què les alternances entre estats macrofítics i fitoplanctònics han servit de paradigma per la teoria dels estats estables en ecologia (Scheffer et al. 1993; Scheffer et al. 2001; Scheffer and Carpenter 2003). Entre els mecanismes d'estabilització dels diferents règims en llacs soms destaca el paper de la limitació dels macròfits per llum. En el cas dels sistemes costaners soms la disponibilitat de llum juga un paper cabdal en la distribució espacial dels macròfits i altres productors primaris bentònics (Duarte 1991; Koch 2001). Per tot això, la caracterització del règim lumínic subaquàtic pot contribuir a entendre millor la competència entre productors bentònics i planctònics en tota mena de sistemes aquàtics soms.

La degradació dels sistemes costaners, en especial l'eutrofització, ha desplaçat els prats de macròfits submergits afavorint el desenvolupament de *blooms* fitoplanctònics i els creixements de macroalgues, generant importants alteracions ecològiques (Valiela et al. 1997; Raffaeli et al. 1998). En particular, el creixement desmesurat d'aquests productors primaris sol anar associat al desenvolupament d'hipòxies o anòxies amb greus conseqüències ecològiques i econòmiques (Diaz 2001; Rabalais and Turner 2001). En llacunes litorals mediterrànies, les crisis anòxiques estivals, anomenades crisis *distròfiques*, s'associen típicament a l'acumulació de biomassa macroalgal, si bé la d'origen macrofític també pot generar hipòxies intenses (Castel et al. 1996; Viaroli et al. 2001; Duarte et al. 2002; Harzallah and Chapelle 2002; Viaroli and Christian 2003; Giordani et al. 2008). Per tot això, la caracterització del la vegetació submergida és fonamental per a l'avaluació de l'estat ecològic dels sistemes costaners (Austoni et al. 2007). Malgrat la seva importància, però, encara no està clar quins factors determinen la distribució i abundància dels macròfits submergits i les seves dinàmiques espaciotemporals, i, tot i que típicament s'ha atribuït a la salinitat i la disponibilitat de llum un paper fonamental, altres factors hi estarien implicats (Koch 2001; Duarte 2002).

Com s'ha dit abans, l'elevada activitat biogeoquímica dels sistemes costaners els hi confereix un paper important en el cicle global del carboni malgrat la seva relativa petita àrea (Smith and Hollibaugh 1993; Gattuso et al. 1998; Frankignoulle et al. 1998; Borges 2005). L'aproximació metabòlica a l'estudi dels ecosistemes, que suposa un indicador important de la seva funcionalitat, tracta el balanç entre els fluxos de carboni, principalment fotosíntesi i respiració (Dodds and Cole 2007). Els sistemes costaners han estat objecte d'estudi des dels primers treballs metabòlics a nivell de sistema (Odum and Hoskin 1958). La inherent variabilitat i complexitat d'aquests sistemes genera, però, dificultats importants en la determinació de la direcció i magnitud dels fluxos de carboni (Gattuso et al. 1998; Borges et al. 2005). Per altra banda, s'ha suggerit que els macròfits submergits jugarien un paper important en el cicle del carboni, però el seu paper no està ni bon tros quantificat (Smith 1981; Duarte et al. 2005). En particular, manquen estudis comprensius sobre la relació entre els prats de macròfits i els fluxos de CO_2 o la dinàmica del carboni inorgànic dissolt en llacunes costaneres dominades per macròfits (Borges et al. 2005; Borges et al. 2006; Delille et al. 2009).

II. Objectius i estructura de la tesi

En aquesta tesi s'estudien els principals patrons i processos que determinen el funcionament ecològic d'una llacuna litoral Mediterrània dominada per macròfits i relativament poc pertorbada. En primer lloc es caracteritzen la hidrologia, el clima lumínic i la dinàmica espaciotemporal dels prats de macròfits submergits com a elements moduladors del funcionament del sistema. Finalment s'estudia quantitativament el cicle del carboni a la llacuna en un darrer capítol amb una visió integradora. Donada la inherent variabilitat dels sistemes costaners, hem emprat una aproximació centrada en un únic sistema i estesa temporalment, incloent múltiples escales d'anàlisi, que van des de cicles diaris a dinàmiques multianuals.

El sistema estudiat és s'Albufera des Grau, una llacuna litoral situada a la costa nord-oriental de l'illa de Menorca (Illes Balears). Es tracta d'una llacuna de 70 ha i un volum aproximat d'1hm^3, amb una fondària mitjana de 1.37 m i un màxim de 3 m (Pretus 1989). La llacuna constitueix la zona nucli del Parc Natural que du el seu nom i de la Reserva de la Biosfera que designa tota l'illa de Menorca. Se situa en bona part damunt materials impermeables del Paleozoic, per la qual cosa només rep aports d'aigua dolça de tipus superficial, a través de dos torrents que drenen una conca de 56 km^2. La conca, heterogènia geològicament, té com a principals usos del sòl boscos, brolles i bosquines naturals i zones d'agricultura extensiva. En l'actualitat el règim hidrològic de la llacuna és fortament pluvialitzat, amb entrades d'aigua dolça centrades en els períodes de pluges. La comunicació amb la mar no implica una renovació important de l'aigua de la llacuna, i és actualment és gestionada mitjançant un sistema de comportes per tal de maximitzar la diversitat d'hàbitats tot mantenint una dinàmica el més natural possible. L'aigua de la llacuna, que mostra importants fluctuacions estacionals de nivell i salinitat, es classificà com a meso-polihalina als anys 80 (Pretus 1989), tot i que es tenen indicis que en el passat devia de ser euhalina (Vargas-Ponce 1787; Habsburg-Lorena 1890). En les darreres dècades del segle XX s'han observat períodes hipersalins i crisis anòxiques amb importants conseqüències sobre la fauna aquàtica (Pretus, 1989 Cardona and Pretus 1991; Cardona 2001). L'origen d'aquestes crisis anòxiques s'associa típicament a la important acumulació de biomassa de macroalgues d'origen marí, en especial de *Chaetomorpha crassa*, que durant part del segle XX haurien estat dominants (Margalef 1952, Pretus 1989; Cardona 2001), remuntant-se a la dècada dels 90 els primers indicis de presència de macròfits submergits a la llacuna (Cardona 2001).

La tesi s'estructura en sis capítols, dels quals tres estan publicats, i dos més estan en revisió, en diverses revistes internacionals. Els objectius específics de la tesi s'articulen al voltant dels resultats del primer capítol, en el qual es descriu l'estat actual de la llacuna pel que fa als productors primaris, dominats per macròfits que formen densos i extensos prats litorals i que tenen un paper clau en la dinàmica dels principals descriptors limnològics del sistema. Les conclusions i hipòtesis sorgides arran d'aquest primer capítol defineixen els objectius específics de la tesi i estructuren els altres cinc capítols, adreçats a aspectes específics del funcionament de la llacuna. Els resultats del primer capítol, que s'ha d'entendre doncs com un capítol introductori a l'ecologia del sistema, es poden resumir en:

- En l'actualitat s'Albufera des Grau és una llacuna litoral dominada per macròfits, amb densos prats del macròfit eurihalí *Ruppia cirrhosa* i de *Potamogeton pectinatus*, en la dinàmica dels quals hi jugaria un paper important la salinitat i les fluctuacions en el nivell de l'aigua. Al **Capítol 2** s'estudia la hidrologia de la llacuna mitjançant la modelització dinàmica del sistema i la seva conca, amb l'objectiu de desenvolupar un model robust que permeti la simulació de les dinàmiques diàries del nivell de l'aigua i la salinitat així com la quantificació dels fluxos d'aigua i sal a la llacuna.

-Els prats de *R. cirrhosa* mostren a s'Albufera des Grau la màxima biomassa descrita fins ara a la bibliografia per a aquesta espècie (fins a 1760 gDW m^{-2}), i s'hipotetitza l'elevada fondària de la llacuna en comparació amb d'altres llacunes litorals com una possible explicació en el cas que no hi hagués limitació per llum. Al **Capítol 3** s'estudia el règim lumínic subaquàtic de la llacuna, estimant per una banda la potencial limitació per llum dels macròfits, i per l'altra caracteritzant els components responsables de l'atenuació de la llum en la columna d'aigua.

-La distribució espacial i la dinàmica temporal dels macròfits submergits estarien determinades per variacions en la salinitat i el nivell de l'aigua de la llacuna. Al **Capítol 4** s'analitza, des d'una aproximació multianual, la dinàmica espaciotemporal dels prats de macròfits, amb l'objectiu de caracteritzar els factors que en determinen la variabilitat.

-El cicle estacional de producció i descomposició dels prats de macròfits determinaria la dinàmica dels principals descriptors limnològics del sistema, que és capaç de processar les elevades biomasses macrofítiques sense desenvolupar condicions hipòxiques. Al **Capítol 5** s'avalua la variabilitat espaciotemporal en les concentracions i el metabolisme del l'oxigen i el carboni inorgànic dissolt a escala nictemeral durant l'estiu, el període de màxima activitat dels prats de macròfits.

-Com s'ha introduït abans, al **Capítol 6**, que s'alimenta en part dels resultats dels capítols anteriors, s'analitza la dinàmica estacional i interanual del carboni inorgànic dissolt en relació amb els principals fluxos i compartiments de carboni del sistema, alhora que es realitzen balanços anuals de carboni orgànic i inorgànic.

CAPÍTOL 2

MODELITZACIÓ HIDROLÒGICA DINÀMICA

Obrador, B.; Moreno-Ostos, E. and Pretus, J.Ll. 2008. A dynamic model to simulate water level and salinity in a Mediterranean coastal lagoon. *Estuaries and Coasts* 3: 1117-1129

Paraules clau: *hidrologia*; *modelització dinàmica*; *salinitat*; *oscil·lacions de nivell*

Introducció i objectius

La modelització de sistemes dinàmics és una eina àmpliament emprada en l'estudi de la complexitat dels sistemes ecològics (Jørgensen and Bendoricchio 2001). Pel seu caràcter altament variable tant a escala intra com interanual, les llacunes litorals, i especialment les llacunes litorals mediterrànies (Kjerfve 1994; Quintana et al. 1998a; Quintana et al. 1998b; Pérez-Ruzafa et al. 2005; Viaroli et al. 2005), són sistemes l'estudi i gestió dels quals es poden veure substancialment facilitats mitjançant la modelització numèrica. En el cas de s'Albufera des Grau, donada la poca informació hidrològica disponible, un model hidrològic que permeti predir el comportament dels principals descriptors hidrològics pot ser de gran utilitat per la comprensió del funcionament de la llacuna així com per a la seva gestió, i pot servir de base per a futurs balanços biogeoquímics al sistema.

En aquest capítol es desenvolupa un model hidrològic dinàmic per a s'Albufera des Grau. El model s'adreça a simular la dinàmica diària de les dues variables que millor defineixen el comportament del sistema, el nivell de l'aigua, *WL*, i la salinitat, *S*, ambdues amb elevada transcendència ecològica. A banda de la construcció, calibració i validació del model, es realitza també una simulació per a un període històric suficientment llarg, per tal de caracteritzar els balanços anuals d'aigua i sal a la llacuna a partir d'una sèrie de dades ampla i robusta.

El model desenvolupat, basat en balanços diaris de volum d'aigua i de massa de sal total a la llacuna, s'alimenta de dades climàtiques fàcilment disponibles (temperatura, precipitació, vent i humitat relativa) i consisteix en tres submodels acoblats entre ells. El primer component correspon al submodel d'escorrentia de la conca, i consisteix en un balanç d'espai promig a la conca hidrològica que permet calcular l'entrada d'aigua a la llacuna a través dels torrents. El submodel d'aigua de la llacuna modelitza els fluxos d'aigua a la llacuna per tal de calcular un balanç diari en el volum d'aigua continguda al sistema, a partir del qual es calcula el nivell de l'aigua. Finalment, el submodel de sal a la llacuna és un balanç de la massa de sal continguda a la llacuna i permet el càlcul de la salinitat de l'aigua. El model ha estat calibrat per a un període de quatre anys (2002-2005), i posteriorment validat per a un període de dos anys més (2001 i 2006). La simulació històrica s'ha realitzat per al període en què es disposa de dades instrumentals (darrers 30 anys).

Resultats i discussió

Els resultats mostren que el model desenvolupat ha estat capaç de simular correctament la dinàmica de la salinitat i el nivell de l'aigua de la llacuna (Fig. 1). Tant la temporalitat, amb el marcat i característic cicle estacional, com l'interval de variació de les dues variables han estat correctament simulats mostrant una baixa sensibilitat a canvis en els paràmetres. S'ha observat un elevat ajust entre les prediccions i les dades observades, amb un error mitjà de 7.6 cm per al nivell, i de 2.8 g L^{-1} per a la salinitat. El ajustos més baixos s'han donat en les simulacions dels màxims de *WL* durant els esdeveniments torrencials, la qual cosa pot haver estat responsable també de desajustos menors en el balanç de sal i, per tant, en la salinitat de sortida del model. Aquests desajustos, que estan relacionats amb les assumpcions que han permès mantenir el model amb la simplicitat desitjada, en especial l'aproximació d'espai promig a conca i l'assumpció de salinitats constants en els fluxes d'aigua, són acceptables donat el rang de variació de les dues variables considerades. Per altra banda, els resultats de la simulació per als darrers trenta anys han permès una segona validació, de tipus qualitatiu, amb dades històriques de salinitat de la llacuna. El model ha ajustat correctament el rang de variació de la salinitat, i fins i tot ha simulat correctament un període d'hipersalinització ocorregut a la llacuna als anys 90 del segle XX malgrat haver estat calibrat en un rang molt inferior de salinitat. Així doncs, el model desenvolupat descriu, a partir d'una sèrie reduïda de dades climàtiques de fàcil obtenció, la dinàmica hídrica de s'Albufera des Grau amb suficient exactitud com per a ser utilitzat en futurs balanços biogeoquímics o en la gestió del sistema.

Pel que fa a la caracterització dels balanços d'aigua i sal a la llacuna efectuats sobre els resultats de la simulació per als darrers trenta anys s'ha observat una elevada variabilitat interanual. La llacuna es caracteritza per una dominància de les entrades d'aigua per escorrentia (59%) per damunt la precipitació directa (27%) i l'entrada d'aigua de mar (14%). L'evaporació és responsable del 62% de les sortides d'aigua anuals, i són la seva dinàmica temporal i l'estacionalitat de les precipitacions els factors determinants del patró temporal de nivell i salinitat de la llacuna. Pel que fa als balanços de sal, la deposició d'aerosol marí tindria un paper negligible, i aquests estarien determinats pels fluxes d'entrada d'aigua marina i evacuació d'aigua llacunar, amb una important contribució dels inputs de sal per escorrentia. Pel que fa a la salinitat, s'ha observat una clara relació entre la salinitat mitjana anual i la precipitació total anual, la qual cosa ha permès calcular la precipitació anual necessària per mantenir constant la salinitat de la llacuna. Aquesta "precipitació d'equilibri" ha estat de 547 mm, un valor molt proper a la precipitació mitjana anual durant el període històric estudiat (549 ± 136 mm). La salinitat corresponent és de 17.3 g L^{-1}, un valor que es pot considerar com una salinitat diana on encarar els esforços de la gestió de la llacuna, suggerint que les gestions que s'allunyessin d'aquest valor resultarien inapropiades i insostenibles.

Els resultats del model han permès determinar que la hipersalinització observada a la llacuna als anys 90 estaria relacionada amb causes naturals i que l'aportació d'aigua dolça de les fonts que abocaven als torrents i que es van assecar als anys 1960 o 1970, no serien necessàries per al manteniment de la llacuna en un estat òptim de salinitat, en concordança amb observacions prèvies (Pretus 2003). S'Albufera des Grau es defineix, doncs, com una llacuna confinada amb una dinàmica hidrològica influenciada pel patró de precipitacions i evaporació, més que no pas per l'intercanvi amb la mar.

CAPÍTOL 3

RÈGIM LUMÍNIC I COMPONENTS DE L'ATENUACIÓ DE LA LLUM EN LA COLUMNA D'AIGUA

Obrador, B. and Pretus, JLl. 2008. Light regime and components of turbidity in a Mediterranean coastal lagoon. *Estuarine, Coastal and Shelf Science* 77: 123-133

Paraules clau: *clima lumínic*; *atenuació de la llum*; *partició de la terbolesa*; *macròfits*

Introducció i objectius

El règim lumínic és un factor fonamental en l'ecologia dels sistemes aquàtics soms, per l'efecte que la disponibilitat de radiació fotosintèticament activa, *PAR*, té sobre la distribució i abundància dels productors primaris bentònics (Dennison 1987; Scheffer 1998). El règim lumínic subaquàtic està determinat, a banda de per la radiació incident, pel comportament de la llum en el medi aquàtic, que depèn al seu torn dels components òpticament actius que es troben a la columna d'aigua, dividits en la pròpia aigua, la matèria particulada i la matèria dissolta (Kirk 1994). En llacs soms la terbolesa de l'aigua, que juga un paper fonamental en les interaccions entre fitoplàncton i macròfits (Scheffer et al. 1993), se sol associar típicament a l'absorció i dispersió de la llum per part del fitoplàncton i els sòlids inorgànics en suspensió (Cristofor et al. 1994; van Duin et al. 2001).

En aquest capítol s'estudia el clima lumínic subaquàtic a s'Albufera des Grau. Per una banda s'analitza la variabilitat en la radiació en fondària per estimar la potencial limitació per llum en el creixement des macròfits submergits, i per l'altra, es quantifica la contribució dels diferents components en l'atenció de la llum en la columna d'aigua.

Durant quatre anys es van realitzar perfils verticals de PAR al llarg de l'eix major de la llacuna. Els perfils es van ajustar a una funció exponencial per a determinar el coeficient d'atenuació de la llum, *K* (m^{-1}). La potencial limitació lumínica al bentos es va estimar en base a la comparació entre la radiació percentual en fondària i els valors crítics descrits a la bibliografia per a l'espècie de macròfit dominant (Duarte 1991; Menéndez and Peñuelas 1993). La partició dels components de l'atenuació de la llum es va realitzar mitjançant regressions múltiples de *K* sobre la concentració de fitoplàncton, DOC, detritus i sòlids inorgànics en suspensió (*ISS*).

Resultats i discussió

Durant el període estudiat, els valors de *K* han mostrat una elevada variabilitat temporal, mentre que a escala espacial no s'han observat diferències significatives, de manera que la llacuna es pot considerar homogènia pel que fa a l'atenuació de la llum. Els valors observats de *K* s'han mogut entre 0.63 m^{-1} i 3.80 m^{-1}, amb un valor mitjà de 1.42 m^{-1}.

Els resultats mostren que la producció fitoplanctònica a s'Albufera des Grau no està limitada per llum llevat de durant es esdeveniments puntuals de màxima terbolesa. Els macròfits, en canvi, sí que poden estar sotmesos a limitació per llum en les zones més fondes de la llacuna durant l'hivern, que és el període més tèrbol de l'any. Durant primavera i estiu, períodes de màxim creixement de *Ruppia cirrhosa*, la llacuna té respectivament, un 17% i un 7% de la superfície amb el bentos potencialment limitat per llum. La disponibilitat de llum en fondària a les zones profundes de la llacuna (>2m) estaria més relacionada amb canvis en la terbolesa de l'aigua (*K*) que amb variacions en el nivell de l'aigua. Tanmateix, a fondàries intermèdies (1.5 m), que suposen el 45% de la superfície de la llacuna, el nivell de l'aigua sí que influeix la disponibilitat lumínica bentònica per a valors de *K* entre 1.8 m^{-1} i 3.3 m^{-1}.

La partició de l'extinció de la llum ha mostrat que, malgrat que el fitoplàncton és el responsable de la dinàmica temporal de *K*, aquest només explica un 44% del valor promig d'atenuació de la llum a la llacuna. S'ha observat una contribució similar dels components particulats i els dissolts. La contribució mitjana dels altres components al valor de *K* és: DOC (47%), tripton (6%) i aigua (3%). La baixa contribució dels fitoplàncton i els sòlids inorgànics en suspensió, que en el cas dels darrers podria ser major si es considerés una escala temporal menor (Banas et al. 2005), contradiu la visió habitual dels components de l'atenuació de la llum en sistemes soms (Cristofor et al. 1994; van Duin et al. 2001; Jackson 2003). Destaca l'elevada contribució del DOC a l'atenuació de la llum a s'Albufera des Grau, ja que en situacions de baixa terbolesa, el DOC és responsable de fins al 75% de l'atenuació de la llum, suposant un nivell basal de terbolesa proper a 0.6 m^{-1}. En altres sistemes estuàrics o costaners on el DOC té un paper important en el règim lumínic, el DOC sol ser al·lòcton (Branco and Kremer 2005; Xu et al. 2005). En el cas de s'Albufera des Grau, on el DOC semblaria tenir un origen majoritàriament macrofític, aquest fet podria suposar un mecanisme d'interacció entre els macròfits i el fitoplàncton. Els resultats d'aquest capítol han permès la derivació d'una equació per a predir *K* a partir dels components de l'aigua, que explica un 93% de la variança.

CAPÍTOL 4

DINÀMICA ESPACIOTEMPORAL DELS PRATS DE MACRÒFITS

Obrador, B. and Pretus, JLl. 2008. Spatiotemporal dynamics of submerged macrophytes in a Mediterranean coastal lagoon. *Estuarine, Coastal and Shelf Science*, submitted

Paraules clau: *macròfits*; *Ruppia cirrhosa*; *distribució espacial*; *biomassa*; *producció*

Introducció i objectius

En els sistemes costaners, les comunitats de productors primaris estan típicament dominades per macròfits submergits, macroalgues o fitoplàncton (Knoppers 1994; Duarte 1995). En aquests sistemes, com en d'altres sistemes aquàtics soms, els macròfits submergits juguen un paper estructural i funcional fonamental (Levin et al. 2001; Nielsen et al. 2004). No obstant això, encara no està clar quins factors determinen la distribució i abundància dels macròfits (Koch 2001). En les darreres dècades, la degradació dels sistemes costaners, en especial l'eutrofització, ha generat un important retrocés dels prats de macròfits afavorint el desenvolupament de macroalgues o de fitoplàncton (Castel et al. 1996; Valiela et al. 1997), per la qual cosa la caracterització de la vegetació submergida és de gran utilitat per a l'avaluació del seu estat ecològic. Per altra banda, l'estudi de les propietats i dinàmica dels prats de macròfits en sistemes poc o gens pertorbats, pot contribuir a un major coneixement dels factors implicats en les dinàmiques espaciotemporals, contribuint així a augmentar la capacitat de conservació i gestió d'aquests espais.

En aquest capítol s'estudia la producció i la dinàmica espaciotemporal dels prats de macròfits a s'Albufera des Grau. Durant tres anys s'han fet estimes de producció de *Ruppia cirrhosa* a partir de mètodes d'extracció de biomassa (Menéndez 2002). La distribució espacial i la dinàmica estacional i interanual dels macròfits s'han analitzat durant un període de sis anys. Per una banda s'ha avaluat el paper de diferents descriptors morfomètrics i dels gradients horitzontals de salinitat sobre la distribució espacial dels macròfits. També s'han mesurat els principals descriptors limnològics de la llacuna per tal de determinar els factors implicats en la dinàmica temporal dels prats. Per a l'anàlisi de les variacions interanuals s'han incorporat també dades d'anys anteriors descrites a Obrador et al. (2007).

Resultats i discussió

Els prats de macròfits estan dominats per *R. cirrhosa*, que mostra un marcat cicle estacional amb quiescència hivernal, i la seva fenologia estaria determinada en gran mesura per la temperatura dels mesos de primavera, en concordança amb observacions prèvies (Verhoeven 1979).

La comparació de diferents mètodes de càlcul de la producció anual de *R. cirrhosa* ha fet aconsellable realitzar les estimes en base a la biomassa màxima assolida, obviant altres mètodes més complexes que requereixen un major esforç mostral (Menéndez 2002; Casagranda and Boudouresque 2007). La producció anual, que ha mostrat una elevada variabilitat interanual, es troba en el rang 327-919 gDW m^{-2}. Aquests valors, si bé no són tan alts com els observats per Obrador et al. (2007), es troben entre els valors més alts descrits per a aquesta espècie a la bibliografia (Verhoeven 1980b; Menéndez 2002; Pergent et al. 2006; Casagranda and Boudouresque, 2007). Aquests resultats posen de manifest l'elevada producció macrofítica a s'Albufera des Grau.

La distribució espacial dels prats de macròfits no està relacionada, contràriament al que és habitual en d'altre sistemes (Menéndez et al. 2002; Lirman et al. 2008), amb gradients horitzontals de salinitat, ja que a l'escala treballada la llacuna es pot considerar espacialment homogènia pel que fa a la salinitat. Els descriptors més relacionats amb la distribució espacial dels prats han estat la fondària i una combinació de fondària, orientació i pendent, suggerint que els factors determinants de la distribució espacial dels macròfits serien la disponibilitat de llum i l'exposició a l'onatge, amb les màximes abundàncies situades a les zones someres, amb pendents suaus i exposades al sud, a redossa dels forts vents de tramuntana.

S'han observat importants variacions interanuals en els descriptors macrofítics analitzats (extensió dels prats, fondària mitjana i biomassa màxima). Aquestes variacions estan principalment relacionades amb la terbolesa i la salinitat de l'aigua, estant els efectes d'aquestes variables, però, restringits als mesos de primavera i estiu, respectivament. Per altra banda, s'ha observat una relació significativa entre l'extensió de *R. cirrhosa* i el nivell de l'aigua al final de l'any hidrològic anterior, la qual cosa suggeriria un possible efecte positiu de la dessecació damunt la cobertura del macròfit. Aquest resultat es contraposa al que s'espera per a aquesta espècie, que si bé tolera un cert grau de dessecació, aquesta no pot ser superior a unes poques hores (Verhoeven 1979; Adams and Bate 1994). Tot i que el mecanisme pel qual es donaria aquest estímul no està clar, s'hipotetitza que pugui estar relacionat amb una major producció de llavors. Després de sis anys d'aparent estabilitat dels prats, els macròfits van desaparèixer sobtadament de la llacuna. Els mecanismes implicats en aquest canvi no estan clars, i estarien relacionats amb la combinació de diversos factors.

CAPÍTOL 5

METABOLISME I VARIACIONS NICTEMERALS DE CARBONI I OXIGEN DISSOLTS

Obrador, B. and Pretus, JLl. 2009. Variability in dissolved inorganic carbon and oxygen concentrations and ecosystem metabolism in a macrophyte-dominated Mediterranean coastal lagoon. *Estuaries and Coasts*, under revision

Paraules clau: *metabolisme a nivell de sistema*; *mètode d'aigües lliures*; *carboni inorgànic dissolt*; *oxigen dissolt*; *variabilitat espacial*; *macròfits*

Introducció i objectius

L'elevada activitat biogeoquímica dels sistemes costaners ha fet que fossin dels primers sistemes estudiats pel que fa al seu metabolisme (Odum and Hoskin 1958). El metabolisme dels ecosistemes fa referència al processat biogeoquímic del carboni, principalment per fotosíntesi i respiració, i és un indicador important de la seva funcionalitat (Dodds and Cole 2007). Un dels mètodes més interessants per estimar el metabolisme dels sistemes aquàtics es basa en els canvis, al llarg d'un cicle diari, de la concentració en aigües lliures dels soluts afectats per l'activitat metabòlica (Odum 1956; Kemp and Boynton 1980). Aquest mètode, amb un ressorgit interès en l'actualitat (Hanson et al. 2003; Gazeau et al. 2005; Torgersen and Branco 2007), facilita la extrapolació dels resultats perquè integra el metabolisme pelàgic i el bentònic. Tradicionalment s'ha emprat l'oxigen com a traçador, però la relació entre oxigen i carboni no és constant, sinó que està determinada pels processos anaeròbics que tenen lloc al sediment, processos de cabdal importància en els sistemes soms (Torgersen and Branco 2007).

En aquest estudi s'estudia la variabilitat espacial i temporal, a escala nictemeral, en les concentracions de carboni inorgànic dissolt, DIC, i d'oxigen dissolt, DO, a s'Albufera des Grau durant el període de màxima activitat dels macròfits. Durant l'estiu del 2002 s'ha avaluat la magnitud de la hipòxia al sistema, així com la possible limitació dels macròfits per carboni. A través del mètode de canvi de concentració en aigües lliures s'han fet estimes dels descriptors metabòlics a nivell de sistema: fotosíntesi, *GPP*, respiració de la comunitat, *CR*, i producció neta ecosistèmica, *NEP*. Les estimes metabòliques s'han efectuat a partir de DIC i de DO, i la comparació des resultats s'ha emprat per discutir els principals processos biogeoquímics que els determinen.

Resultats i discussió

Els resultats han mostrat una elevada variabilitat espacial i temporal en les concentracions de DIC i DO a la llacuna. A l'albada, la llacuna és espacialment homogènia com a conseqüència d'una homogeneïtzació dels processos biogeoquímics. Per contra, a l'ocàs la llacuna mostra un doble gradient s'observa un doble gradient espacial de concentració en les dimensions horitzontal i vertical, com a resultat de la dominància de diferents processos entre aigües de superfície i de fons, i entre localitats litorals amb macròfits i localitats centrals sense macròfits. La variabilitat espacial a l'escala observada s'explicaria per l'activitat fotosintètica en l'aigua superficial al si dels prats de macròfits, més que no pas per diferències en el metabolisme del sediment.

Només en algunes ocasions es van observar valors hipòxics en l'aigua de fons de les zones litorals a l'albada, però la seva baixa ocurrència situen la hipòxia com un factor de poca importància per a la llacuna, contràriament el que passa en d'altres llacunes Mediterrànies (Castel et al. 1996; Souchu et al. 1998; Viaroli et al. 2001; Duarte et al. 2002; Harzallah and Chapelle 2002).

Les estimes metabòliques per a *GPP* i *CR* per a tot el sistema han estat 1169 ± 619 mmol m^{-2} d^{-1}, i 1027 ± 747 mmol m^{-2} d^{-1}, respectivament. Aquests valors, que se situen en el rang alt descrit per a sistemes costaners (Duarte and Agustí 1998), han mostrat una elevada variabilitat, amb importants diferències entre les localitats estudiades. L'intercanvi atmosfèric de CO_2 i de O_2 suposa un flux de menor importància en comparació amb la magnitud dels canvis de concentració observats.

S'ha observat una discrepància important entre el metabolisme basat en carboni i el basat en oxigen, com a conseqüència dels intensos processos anaeròbics i les reaccions químiques que tenen lloc a la interfase sediment/aigua i a la columna d'aigua. Donada l'elevada variabilitat observada, es conclou que les estimes precises de metabolisme basades en el mètode de canvi nictemeral de concentració en aigües lliures requereixen múltiples localitats d'estudi i aproximacions conjuntes entre DIC i DO en sistemes soms dominats per macròfits.

CAPÍTOL 6

CICLE DEL CARBONI: BALANÇOS DE CARBONI ORGÀNIC I INORGÀNIC

Obrador, B. and Pretus, JLl. 2009. The carbon cycle in a macrophyte-dominated coastal lagoon (Albufera des Grau, Western Mediterranean). *in prep.*

Paraules clau: *cicle del carboni; carboni inorgànic dissolt; macròfits; fluxes atmosfèrics; DOC*

Introducció i objectius

Els sistemes costaners són uns dels ecosistemes més actius des del punt de vista biogeoquímic de la biosfera (Gattuso et al. 1998). Els macròfits submergits són, a més d'uns components fonamentals en les llacunes litorals pel seu paper estructural i funcional, uns elements a considerar en els balanços globals del cicle del carboni (Smith 1981; Duarte et al. 2005). Malgrat tot, encara no es té clara la dinàmica del carboni inorgànic dissolt en llacunes costaneres dominades per macròfits o la relació entre els prats de macròfits i els fluxes de CO_2 (Borges et al. 2005; Borges et al. 2006; Delille et al. 2009). Per entendre el paper dels macròfits en aquests sistemes és fonamental avaluar també el destí de la producció primària que s'hi dóna (Duarte and Cebrián 1996).

En aquest capítol s'estudia la dinàmica del carboni inorgànic dissolt, DIC, a s'Albufera des Grau durant tres anys. L'objectiu principal és la comprensió de la dinàmica del DIC a través de la quantificació dels fluxes i els compartiments de carboni al sistema, així com realitzar balanços estacionals i anuals de DIC. També s'avalua el destí de la producció primària mitjançant balanços anuals de carboni orgànic, OC, i d'una exploració isotòpica dels principals compartiments orgànics de la llacuna.

La dinàmica del DIC, avaluada mensualment, s'ha complementat amb l'anàlisi de la seva composició isotòpica, $\delta^{13}C_{DIC}$. Els balanços de DIC s'han basat en estimacions dels fluxes hidrològics de carboni (a partir dels fluxos d'aigua simulats amb al model hidrològic descrit a Obrador et al. 2008); de l'intercanvi de CO_2 amb l'atmosfera, i de fluxes interns, com ara els fluxes metabòlics (a partir de les estimes d'Obrador et al. 2009b i de valors bibliogràfics) o la precipitació de $CaCO_3$ (a partir d'un balanç paral·lel de calci a la llacuna). Els compartiments de carboni es van quantificar a partir de la concentració (areal o volumètrica) dels diferents compartiments del sistema. El destí de la producció primària es va avaluar mitjançant isotopia estable del carboni i el nitrogen en diferents components de la xarxa tròfica, i estimant taxes d'acumulació de matèria orgànica al sediment.

Resultats i discussió

Els resultats han mostrat que la dinàmica temporal del CO_2 a la llacuna està determinada pel cicle estacional de producció i descomposició dels prats de macròfits, i fortament modificada pels pics de fitoplàncton i pels esdeveniments torrencials. El flux atmosfèric de CO_2 ha oscil·lat estacionalment de direcció, absorbint netament CO_2 en els mesos amb macròfits i emetent-ne en l'època no vegetada, en concordança amb d'altres sistemes costaners dominats per macròfits (Knoppers 1994; Gattuso et al. 1998). L'emissió de CO_2 en els mesos sense macròfits estaria més determinada pel metabolisme intern del sistema, que no pas per entrades externes d'aigua saturada de CO_2 que estimulessin el metabolisme heterotròfic. Pel que fa al DIC, la seva dinàmica s'explica principalment pels intensos fluxes metabòlics que tenen lloc a la llacuna, i secundàriament per fluxes fisicoquímics com la precipitació de carbonats, l'intercanvi amb l'atmosfera o els fluxos hidrològics.

El canvis de DIC al sistema estan determinats per la combinació de diversos fluxes molt majors en magnitud que els canvis observats de concentració. Aquesta intensitat en el ciclatge del DIC queda palesa amb el temps de residència del DIC, estimat en 3.7 dies i 18.6 dies en els períodes amb i sense macròfits, respectivament. Aquests valors són extremadament menors que el temps de residència de l'aigua, de manera que el DIC circula entre 65 i 13 vegades més ràpid que no pas l'aigua. Aquesta elevada taxa de renovació del DIC presumiblement ha emmascarat la senyal isotòpica dels diferents processos que afecten al carboni, de manera que la dinàmica de la $\delta^{13}C_{DIC}$ sembla estar més lligada a la signatura isotòpica dels diferents compartiments que no pas a la magnitud dels fluxes. El balanç anual de DIC ha mostrat una elevada variabilitat interanual depenent en bona mesura del grau de pertorbació del cicle basal d'activitat estacional dels macròfits per part dels pics de fitoplàncton i els esdeveniments torrencials.

Pel que fa als compartiments de carboni, el carboni inorgànic i l'orgànic estan força balancejats, essent dominant el segon només durant els mesos amb vegetació submergida. Els principals compartiments orgànics han estat els macròfits durant l'època vegetada (70% de tot el OC) i el DOC durant l'època no vegetada (75%). Aquest DOC estaria clarament associat a un origen macrofític més que no pas al·lòcton. El paper dels fluxes hidrològics de caboni orgànic sobre el balanç anual ha estat de menor importància, i aniria més associat a la desestabilització de l'estructura i oxigenació de la columna d'aigua i al desenvolupament de pics fitoplanctònics que no pas a l'entrada de matèria orgànica *per se*.

La llacuna no ha exportat netament OC, i l'elevada producció macrofítica no sembla tenir un paper important com a entrada de carboni a la xarxa tròfica bentònica ni pelàgica. El destí majoritari d'aquest carboni produït internament seria la descomposició, i l'enterrament al sediment, que suposa un 15-30% de la producció anual macrofítica.

CONCLUSIONS GENERALS

Les conclusions generals d'aquesta tesi es poden resumir de la següent manera:

1. S'Albufera des Grau és un sistema simple pel que fa as processos hidrològics que hi tenen lloc. Un model dinàmic simple amb pocs requeriments de dades externes desenvolupat específicament per a s'Albufera des Grau és capaç de simular correctament la dinàmica temporal dels principals descriptors hidrològics de la llacuna a escala diària.

2. L'anàlisi de les simulacions hidrològiques per a un període històric de 30 anys permet definir s'Albufera des Grau com una llacuna confinada amb poca influència marina, on l'aigua es troba en el rang d'oligo-polyhalinitat i té un temps de residència de 8 mesos. El cicle estacional de precipitació i evaporació i els esdeveniments torrencials que en pertorben el patró basic són responsables de la dinàmica temporal del nivell de l'aigua i la salinitat.

3. La llacuna està dominada per vegetació submergida, amb densos i extensos prats dominats per *Ruppia cirrhosa*. La producció anual d'aquesta espècies es troba entre les més altes descrites a la bibliografia i dibuixa s'Albufera des Grau com un sistema costaner altament productiu.

4. La distribució espacial dels macròfits està determinada per la disponibilitat de llum i l'exposició a l'onatge, més que no pas per gradients horitzontals de salinitat, que són insignificants a la llacuna. La dinàmica interanual dels prats de macròfits està determinada per la salinitat, el nivell de l'aigua i la disponibilitat de llum, cadascun amb efectes restringits a determinats períodes del cicle anual. La disponibilitat de llum és un factor important pels macròfits a les parts fondes de la llacuna, però no sembla tenir un paper important en la dinàmica dels macròfits en zones somes.

5. La llacuna es pot considerar espacialment homogènia pel que fa a l'atenuació de la llum a l'aigua. Les variacions espacials en el règim lumínic subaquàtic estan relacionades, doncs, només amb la fondària de la columna d'aigua. La variació temporal del règim lumínic a fondàries intermèdies està relacionada tant amb l'atenuació de la llum a l'aigua com amb oscil·lacions en el nivell de l'aigua de la llacuna.

6. El fitoplàncton és el principal causant de l'atenuació a llum a la columna d'aigua, però hi ha una important contribució del DOC, que sembla tenir un origen macrofític. Els sòlids inorgànics en suspensió juguen un paper molt secundari en l'atenuació de la llum a l'escala temporal considera.

7. La intensa activitat metabòlica nictemeral al sí dels prats de macròfits genera una elevada variabilitat en les concentracions de DIC i DO. La llacuna passa de condicions homogènies a l'albada, a un doble gradient espacial a l'ocàs, manifestat en les dimensions vertical i horitzontal.

8. El metabolisme de la llacuna és molt variable a escala diària i entre punts de mostreig, i està fortament influenciat pel metabolisme anaeròbic i per reaccions químiques d'oxidació. El flux atmosfèric de DIC i DO suposa una contribució menor en comparació amb la magnitud dels fluxos interns.

9. L'aplicació del mètode de canvi nictemeral de concentració en aigües lliures per a realitzar estimes metabòliques en llacunes costaneres dominades per macròfits s'hauria de basar en múltiples localitats i en l'anàlisi combinat de DIC i DO.

10. El ciclat del DIC a la llacuna és extremadament ràpid, amb una taxa de renovació entre 13 i 65 vegades més gran que la de l'aigua. La dinàmica estacional del DIC s'explica per la combinació de múltiples fluxos molt majors en magnitud que el balanç net final, amb una clara dominància dels fluxos metabòlics, i una alta influència de la precipitació de carbonats i de fluxos atmosfèrics i hidrològics

11. La dinàmica de la pCO_2 a la llacuna s'explica en bona mesura pel cicle estacional de producció i descomposició dels prats de macròfits, amb intenses pertorbacions originades per pics de fitoplàncton i per entrades d'aigua. El flux atmosfèric de CO_2 oscil·la estacionalment, i la llacuna es comporta com una font o un embornal de carboni depenent de la presència de vegetació submergida.

12. L'elevada producció macrofítica no suposa una entrada important de carboni a la xarxa tròfica bentònica ni pelàgica, que se sustentaria en d'altres fonts de matèria orgànica. El destí de la producció dels macròfits sembla ser la descomposició i secundàriament l'enterrament al sediment, mentre que el consum tròfic o l'exportació serien negligibles.

13. El balanç anual de DIC i OC és altament variable, aparentment relacionat amb el grau de pertorbació del cicle basal estacional dels macròfits. L'efecte de les entrades torrencials d'aigua i de l'entrada d'aigua marina està relacionat amb el desenvolupament de pics de fitoplàncton i amb l'alteració de l'estructura vertical de la columna d'aigua i l'afavoriment ocasional d'hipòxies en fondària, més que no pas amb una entrada de carboni al·lòcton.

14. Malgrat l'elevada acumulació de biomassa a l'estiu, les condicions hipòxiques a les zones litorals són poc rellevants, com tampoc ho són les hipòxies causades per estratificacions a la columna d'aigua a les zones més fondes de la llacuna.

Informe del director de la Tesi Doctoral referent al factor d'impacte i a la contribució del doctorand en cadascun dels articles publicats

En Joan Lluís Pretus Real del Departament d'Ecologia (UB), director de la Tesi Doctoral elaborada pel Sr. Biel Obrador Sala, amb el títol "Environmental shaping and carbon cycling in a macrophyte-dominated Mediterranean coastal lagoon (Modulació ambiental i ciclat del carboni en una llacuna litoral Mediterrània dominada per macròfits)",

INFORMA

Que els treballs de recerca duts a terme pel Sr. Biel Obrador Sala com a part de la seva formació predoctoral i inclosos a la seva Tesi Doctoral han donat lloc a 3 publicacions i 2 manuscrits enviats a revisió. A continuació es detalla la llista d'articles així com els índexs d'impacte (segons el SCI de la ISI web of Knowledge) de les corresponents revistes.

1- Obrador, B., Pretus, J.Ll., and Menéndez, M. 2007. Spatial distribution and biomass of aquatic rooted macrophytes and its relevance in the metabolism of a Mediterranean coastal lagoon. *Scientia Marina* 71: 57-64

L'índex d'impacte de la revista *Scientia Marina* és en l'actualitat 0.945 Aquesta revista està inclosa a la categoria "Marine and Freshwater Biology", que té una mediana d'índex d'impacte de 1.155 i inclou un total de 86 revistes. Tenint en compte l'índex d'impacte de *Scientia Marina*, aquesta ocupa el 52è lloc de la seva categoria.

2- Obrador, B.; Moreno-Ostos, E. and Pretus, J.Ll. 2008. A dynamic model to simulate water level and salinity in a Mediterranean coastal lagoon. Estuaries and Coasts 31: 1117-1129

L'índex d'impacte de la revista *Estuaries and Coasts* es en l'actualitat 1.124. Aquesta revista està inclosa a la categoria "Marine and Freshwater Biology", que té una mediana d'índex d'impacte de 1.155 i inclou un total de 86 revistes. Tenint en compte l'índex d'impacte de *Estuaries and Coasts*, aquesta ocupa el 46è lloc de la seva categoria. La revista *Estuaries and Coasts* ha canviat recentment de títol, de manera que el 2008 és el primer any que té índex d'impacte sota aquest nom (amb el títol anterior, *Estuaries*, l'índex d'impacte és 2.133 i ocupa 19è lloc de la seva categoria).

3- Obrador, B. and Pretus, J.Ll. 2008. Light regime and components of turbidity in a Mediterranean coastal lagoon. *Estuarine, Coastal and Shelf Science* 77: 123-133

L'índex d'impacte de la revista *Estuarine, Coastal and Shelf Science* es en l'actualitat 1.799. Aquesta revista està inclosa a la categoria "Marine and Freshwater Biology", que té una mediana d'índex d'impacte de 1.155 i inclou un total de 86 revistes. Tenint en compte l'índex d'impacte de *Estuarine, Coastal and Shelf Science*, aquesta ocupa el 24è lloc de la seva categoria.

4- Obrador, B. and Pretus, JLl. 2009. Spatiotemporal dynamics of submerged macrophytes in a Mediterranean coastal lagoon. *Estuarine, Coastal and Shelf Science* (submitted)

L'índex d'impacte de la revista *Estuarine, Coastal and Shelf Science* es en l'actualitat 1.799. Aquesta revista està inclosa a la categoria "Marine and Freshwater Biology", que té una mediana d'índex d'impacte de 1.155 i inclou un total de 86 revistes. Tenint en compte l'índex d'impacte de *Estuarine, Coastal and Shelf Science*, aquesta ocupa el 24è lloc de la seva categoria.

5- Obrador, B. and Pretus, J.Ll. 2009. Variability in dissolved inorganic carbon and oxygen concentrations and ecosystem metabolism in a macrophyte-dominated Mediterranean coastal lagoon. *Estuaries and Coasts* (under revision)

L'índex d'impacte de la revista *Estuaries and Coasts* es en l'actualitat 1.124. Aquesta revista està inclosa a la categoria "Marine and Freshwater Biology", que té una mediana d'índex d'impacte de 1.155 i inclou un total de 86 revistes. Tenint en compte l'índex d'impacte de *Estuaries and Coasts*, aquesta ocupa el 46è lloc de la seva categoria. La revista *Estuaries and Coasts* ha canviat recentment de títol, de manera que el 2008 és el primer any que té índex d'impacte sota aquest nom (amb el títol anterior, *Estuaries*, l'índex d'impacte és 2.133 i ocupa 19è lloc de la seva categoria).

A més CERTIFICA

Que el Sr. Biel Obrador Sala ha participat activament en el desenvolupament del treball de recerca associat a cadascun dels articles, així com en la seva elaboració. En concret, la seva participació en cadascun de les tasques ha estat la següent:

- Plantejament inicial dels objectius de cadascun dels treballs
- Disseny i desenvolupament de la part de mostreig de camp i posada punt de les metodologies analítiques associades a cadascun dels capítols. Una part d'aquesta tasca va comportar una estada a *l'Environmental Change Research Center* de la *University College of London* per l'aprenentatge de metodologies i interpretació de resultats de temàtiques afins a la tesi.
- Realització dels mostrejos de camp.
- Processat i anàlisi de les mostres obtingudes.
- Desenvolupament, calibració i validació d'un model dinàmic
- Càlcul de resultats i anàlisi de dades.
- Redacció dels articles i seguiment del procés de revisió dels mateixos.

Finalment, certifico que cap dels coautors dels articles abans esmentats i que formen part de la Tesi Doctoral del Sr. Obrador ha utilitzat o bé té previst utilitzar implícita o explícitament aquests treballs per a l'elaboració d'una altra Tesi Doctoral.

Atentament,

Barcelona, 16 de març de 2009

Joan Lluís Pretus Real

General introduction and objectives

I. Coastal lagoons in context

Coastal lagoons are inland water bodies, usually shallow, that have varying degrees of connection with the open ocean (Barnes 1980). Due to their location in the interface between the continents and the sea, coastal lagoons are subject to intense external forcings, such as the hydrochemical fluxes associated with river inputs and seawater exchange, or the combined effects of tidal dynamics, wind stress, heat balance and storm effects (Kjerfve 1994). The complex coupling between these systems and the adjacent terrestrial and marine ecosystems renders coastal lagoons a highly dynamic character that is reflected in high spatial and temporal variability in their physicochemical and biological descriptors, what results in their wide recognition as highly unpredictable environments (Margalef 1969; Comín et al. 2004).

As transitional environments, coastal ecosystems receive substantial amounts of water and of dissolved and particulate materials, and buffer the transport of sediment, nutrients and organic matter from the continents to the sea, acting as sources or sinks of a wide variety of compounds, including anthropogenic pollutants (Buddemeier et al. 2002). Apart from this, coastal lagoons and their associated wetlands are hot spots for bird biodiversity and serve as feeding and nursery habitats for many fish species (Yáñez-Arancibia et al. 1994; Levin et al. 2001). Highly productive, these systems often sustain considerable economic activities, mainly related to the fishery and clam farming industries, but also to tourist and recreational activities. All these features make that, despite they occupy 13% of the world coastline, coastal lagoons are considered to be the most valuable components of the coastal areas from a biological, biogeochemical and socioeconomic perspective (Gönenç and Wolflin 2004). Apart from their local and regional significance, coastal ecosystems in general act as reservoir of biodiversity and play an important role in the regulation of the land-ocean biogeochemical interactions at a global scale (Smith and Hollibaugh 1993; Gattuso et al. 1998; Levin et al. 2001; Crossland et al. 2005). They are also amongst the most important ecosystems of the biosphere in terms of ecosystem services (Costanza et al. 1997).

With regard to their ecological status, coastal ecosystems are nowadays amongst the most impacted marine ecosystems (Halpern et al. 2008), and during the last century they have been subject to a fast world-wide degradation as a result of intense anthropogenic impacts (Lotze et al. 2006). The environmental alterations in coastal lagoons range from direct pressures on the lagoonal ecosystems to perturbations at the watershed level, and the resulting impacts include eutrophication, chemical pollution, geomorphological impacts, alteration of the hydrological regimes, direct modifications of the trophic structure (introduction of exotic species, overexploitations of fisheries...) and even the physical destruction of lagoon ecosystems in regions under intense tourist and urbanization pressures (McComb 1995; Verlaque 2001; EEA 2006; Viaroli et al. 2007). Coastal lagoons are also highly vulnerable to sea eustatism in the context of global change (EEA 2005; Viaroli et al. 2007). The threats and important values of coastal environments are nowadays recognised by the high degree of protection of these systems worldwide, and several international projects to define sustainable uses and management of coastal areas are being or have been launched in the last years (e.g. WADI, LEMSM, or DITTY projects).

Sources of variability: a note on terminology

An authoritative operational definition of a coastal lagoon, the one which will be implicitly used here, is that proposed by Kjerfve (1994): *a coastal lagoon is a shallow coastal water body separated from the ocean by a barrier, connected at least intermittently to the ocean by one or more restricted inlets, and usually oriented shore-parallel.* Despite much effort has been done to define the different types of coastal aquatic ecosystems, the literature is far from being terminologically consistent, what probably reflects the difficulty in classifying these environments. It is thus frequent to find a confusing use of the terms estuary, coastal lagoon, coastal pond and coastal wetland, among others, when referring to coastal lagoons. Interestingly this is also manifested in the high diversity of terms that designate different coastal environments in the local terminologies (in Catalan and other Latin-derived languages, for instance, the terms Albufera (from the Arab *al buhayra*, the lake) are combined with *llacuna*, *bassa*, *estuari*, *braç de mar*, *badia*, *aiguamoll*, *aigua moix*, and others; González-Bernáldez 1992). There have been several attempts to properly classify these environments (Kjerfve 1994; Elliot and McLusky 2002), and the classical classifications of coastal ecosystems rely on geomorphological attributes, salinity levels, tidal range, mixing behaviours of the water masses or degree of confinement (IUBS 1959; Barnes 1980; Guelorget and Pertuisot 1983; Kjerfve 1986; Kjerfve 1994; Basset et al. 2006). A relevant example of the difficulty in classifying coastal ecosystems is the controversy generated by the European Water Framework Directive (EU 2000), which does not group coastal lagoons into a single water category, but allows its classification into two separate categories (*Transitional Waters* and *Coastal Waters*) depending on whether they are or not "substantially influenced by freshwater flows". Apart from the suitability of the term *transitional waters* (McLusky and Elliot 2007) and avoiding the consequences of this surprising duality on the correct implementation of the Directive (Tagliapietra and Volpi 2006), this issue likely reflects the high variability and diversity of coastal lagoons. Without entering on the discussion of which descriptors are more adequate to functionally classify coastal environments (physiography, geomorphology, hydrology,....) it is clear that the inherent variability of coastal environments, which should be reflected in any typology aimed to be operational, ultimately reflects the multiplicity of factors that determine the ecological behaviour of these systems (geomorphological features, salinity levels, hydrological permanence regime, temporality and extent of the seawater and freshwater flows, degree of confinement....). The most characteristic feature of coastal lagoons may be the intense and asynchronic interaction of continental, atmospheric and marine processes, what, as stated above, results in a high degree of unpredictability.

This variability is even more pronounced in Mediterranean coastal lagoons. In the Mediterranean region there is a strong climatic seasonality, with a dry hot summer season, and wet winters and autumns. Despite the seasonal distribution of precipitation, a significant fraction of the total annual precipitation can be concentrated in a few number of heavy rainfall events (Bolle 2003). Mediterranean shallow aquatic systems of any type, but especially coastal lagoons, are therefore highly influenced by seasonal variations in water level and by the torrential punctuations of this seasonal pattern (Álvarez-Cobelas et al. 2005; Beklioglu et al. 2007). The torrential character of freshwater inputs to coastal lagoons can imply severe water level fluctuations, high nutrient inputs, rapid salinity changes, small-scale sediment-based turbidity changes, alterations of the sediment-water chemical fluxes, or even complete water renewal of the system, all of them with substantial consequences on the biological communities (Coops et al. 2003; Beklioglu et al. 2006). The same applies for the seawater inflow if this is irregular and related to unpredictable storm events. The intensity and timing of the freshwater and seawater flows are thus not only important for the associated flux of materials and the consequent change in the material status (nutrient concentrations or salinity levels, for instance), but also for the immediate effect on the biotic communities. All this processes are especially significant in Mediterranean coastal lagoons, which are not subject to tidal forcing given the absence of regular tides in the Mediterranean Sea, and which exhibit a specially high hydrological and ecological variability (Quintana et al. 1998a; Quintana et al. 1998b; Quintana 2002; Pérez-Ruzafa et al. 2005; Viaroli et al. 2005; Badosa et al. 2006; Badosa et al. 2008). Mediterranean coastal lagoons can show sudden salinity and turbidity changes, can turn from the flooding of the adjacent ecosystems to the desiccation of extensive littoral areas, can suffer drastic nutrient enrichments and can move from the strict confinement without marine influence to an absolute opening to the sea. Mediterranean coastal lagoons are thus highly dynamic systems characterised by variability at multiple temporal scales, and any approach to the knowledge of these ecosystems should take into account this variability and design sampling strategies accordingly.

Macrophytes in coastal lagoons

In shallow coastal ecosystems the primary producers are either dominated by rooted macrophytes, macroalgae or phytoplanktonic communities[1], and secondarily by periphyton (Knoppers 1994; Valiela

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[1] Throughout this thesis, the term 'macrophyte' will be used *sensu* Knoppers (1994), who differentiates macroalgae and macrophytes (vascular plants) as different macroscopic benthic primary producers. In contrast, it is common to find in the literature the use of 'macrophyte' as a generic term to designate all macroscopic primary producers, including both seaweeds (macroalgae) and seagrasses (marine vascular plants) (e.g. Duarte and Cebrian 1996; Viaroli et al. 1996; Sfriso and Marcomini 1997; Fox et al. 2008). Given that the main macrophyte species treated here (*Ruppia cirrhosa*) is strictly not considered a true seagrass because it does not occur at consistently high salinities (den Hartog 1970 in Borum et al. 2004), we decided to use the term 'macrophyte' to refer to rooted aquatic angiosperms, on the understanding that everything said here with regard to macrophytes is likely applicable to seagrasses in general.

et al. 1997; Sand-Jensen and Nielsen 2004). Each group of primary producer has different functional properties, and the dominance of one or another is mostly related to nutrient levels despite other factors appear to be also involved (Knoppers 1994; Duarte 1995; Taylor et al. 1995; Taylor et al. 1999; Trobajo et al. 2002; Hauxwell and Valiela 2004).

In shallow aquatic ecosystems submerged macrophytes are key species with important structural and functional roles (Carpenter and Lodge 1986; Levin et al. 2001; Jeppesen et al. 1998). The macrophyte beds serve as habitat and food resources not only for numerous aquatic organisms but also for many waterbird species (Heck and Thoman 1981; Heck and Thoman 1984; Orth et al. 1984; Brown and Lodge 1993; Perry and Deller 1996; Bortolus et al. 1998; Moreno-Ostos et al. 2008). Thus, part of the importance of coastal lagoons in maintaining regional biodiversity levels is based on the role of macrophytes as direct food resources and as engineering species creating habitat for refuge, feeding and breeding for aquatic and terrestrial species (Levin et al. 2001). But macrophyte beds intervene in many other ecological processes: they influence hydrodynamics, affect water temperature, enhance sedimentation and reduce sediment resuspension, influence the nutrient and oxygen levels, affect the sediment-water chemical fluxes, and intensely determine multiple biotic interactions (Carpenter and Lodge 1986; Sand-Jensen and Borum 1991; Viaroli et al. 1996; Asaeda and van Bon 1997; Barko and James 1998; Madsen et al. 2001; van Donk and van de Bund 2002; Plus et al. 2003; James et al. 2004; Thouzeau et al. 2007; see compilations in Jeppesen et al. 1998 and Nielsen et al. 2004).

In freshwater shallow lakes the competition between benthic and pelagic primary producers has been intensely studied during the last decades, resulting in the alternative stable states theory that defines the existence of two stable states, macrophytic and phytoplanktonic, stabilised by several mechanisms that control the shift from one state to the other (Scheffer et al. 1993). The shallow-lake model of sudden changes between phytoplanktonic and macrophytic regimes is nowadays considered an archetypical example of the regime shifts theory that predicts alternative regimes in many different ecosystems (Scheffer et al. 2001; Scheffer and Carpenter 2003; Folke et al. 2004; Scheffer and van Nes 2007). Among the stabilizing mechanisms involved in shallow lakes, it is especially important the role of light limitation of macrophytes due to attenuation of light by phytoplankton or by wind-induced sediment resuspension (Scheffer 1998). In shallow coastal environments light availability is a fundamental factor in the abundance and distribution of macrophytes and other benthic primary producers in relation to water depth (Dennison 1987; Duarte 1991; Koch 2001). Thus, the characterisation of the underwater light environment must contribute to a better understanding of the factors involved in the competence and dynamics of benthic and pelagic primary producers in any particular shallow aquatic system.

Some of the biotic stabilizing mechanisms of freshwater shallow lakes have been described in oligo-mesohaline lagoons, thus leading to the interpretation of its dynamics under the view of the regime shifts theory (Moss 1994; Jeppesen et al. 1994; Jakobsen et al. 2003; Romo et al. 2005; Cardona 2006; Jeppesen et al. 2007). However, different assemblages of primary producers are proposed as characteristic of stable states in coastal environments (Duarte 1995; Valiela et al. 1997; Trobajo et al. 2002; Troell et al. 2005; Chomérat et al. 2007), and there are still few well-documented evidences of regime-shifts in meso-polyhaline coastal lagoons and other coastal ecosystems (Gunderson 2001; Chomérat et al. 2007; Petersen et al. 2008). In a recent review, Viaroli et al. (2008) defined a specific framework for the regime shifts theory in coastal lagoons, and depicted the benthic and sedimentary biogeochemical processes as key regulatory functions controlling the stability of these systems, in accordance with previous observations in Mediterranean coastal lagoons (de Wit et al. 2001; Bartoli et al. 2008; Giordani et al. 2008).

The worldwide degradation of coastal environments, particularly the increased nutrient inputs, has favoured the occurrence of phytoplankton blooms and the spread of fast-growing macroalgae, replacing the original rooted macrophytes and leading to strong environmental alterations (Valiela et al. 1997; Raffaeli et al. 1998; McGlathery 2001). Among the consequences of excessive phytoplanktonic and macroalgal development are the periodic hypoxic or anoxic crises that affect many coastal environments with dramatic ecological and economical consequences (Diaz 2001; Rabalais and Turner 2001).

In this context of fundamental functional role of submerged macrophytes in coastal lagoons, an assessment of the ecological status of these systems must necessarily include a detailed characterization of the submerged vegetation, and different indexes using macrophyte diversity and biomass have been proposed as indicators of environmental status (Mouillot et al. 2006; Austoni et al. 2007; Orfanidis et al. 2007). However, there is still a poor understanding of the factors that determine the distribution and abundance of submerged macrophytes in both space and time (Duarte 2002). Salinity variations and light availability have traditionally received major attention, but the need to consider other factors (physical, geological and geochemical) has been recently highlighted (Koch 2001).

Carbon cycling in coastal ecosystems

Coastal lagoons are amongst the most productive ecosystems of the biosphere (Barnes 1980, Knoppers 1994). A first consequence of the high production in coastal ecosystems is the above-mentioned occurrence of intense hypoxias with important ecological and economical consequences (Diaz 2001; Rabalais and Turner 2001). In many Mediterranean coastal lagoons episodic anoxic crises, usually termed *dystrophic* crises, are a common phenomena that seriously affect the status of the system and the survival of animals and vegetation due to the low oxygen levels and the sulfide release from anaerobic metabolism (Castel et al. 1996; Souchu et al. 1998; Viaroli et al. 2001; Harzallah and Chapelle 2002; Viaroli and Christian 2003; Giordani et al. 2008). The hypoxic conditions in Mediterranean coastal lagoons are usually related to the accumulation of large amounts of organic matter of macroalgal origin, although macrophytic biomass may also lead to such oxygen deficits (Duarte et al. 2002).

On the other hand, the high biogeochemical activity in coastal environments renders them an important role in the global carbon cycle despite their comparatively small surface area (Smith and Hollibaugh 1993; Frankignoulle et al. 1998; Thomas et al. 2004; Borges 2005). The intensity of carbon cycling in these highly productive systems has been a subject of study since the earliest whole-system metabolic works (Odum and Hoskin 1958, in Swaney and Hall 2004). The metabolic approach to the study of aquatic ecosystems deals with the balance between the two major pathways of carbon (primary production and respiration) and is a useful indicator of ecosystem function (Dodds and Cole 2007). In coastal environments, the intrinsic complexity and variability results in large uncertainties in the determination of the direction and magnitude of carbon fluxes (Gattuso et al. 1998; Borges et al. 2005). Of particular interest is the role that macrophytes play in the global carbon cycle, which is believed to be significant but is still poorly quantified (Smith 1981; Duarte et al. 2005a). The effects of macrophytic beds on air-water carbon fluxes and on the dynamics of dissolved inorganic carbon are still to be fully understood, and there is a lack of comprehensive approaches to carbon cycling and its inter-annual variability in both tidal and non-tidal lagoons and in macrophyte-dominated ecosystems (Borges et al. 2005; Borges et al. 2006; Delille et al. 2009).

II. Objectives and structure of the thesis

The main objective of this thesis is to comprehensively characterise the main patterns and processes that determine ecosystem functioning in a Mediterranean coastal lagoon (Albufera des Grau, Balearic Islands). This includes a quantitative assessment of carbon cycling as a superior descriptor of the functioning of the system, a challenging approach that is articulated as a final integrative chapter that feeds from the results of all the previous chapters. Given the high variability inherent to coastal lagoon ecology, we used a temporally extended single-site design, applying a multi-scale approach that ranges form diel cycles to multiannual dynamics.

The thesis is articulated in six chapters, all of them published or in progress of publication in international journals. **Chapter 1** is a description of an annual cycle of the macrophyte meadows and its relationship with the main limnological descriptors of the studied system. The results described in this chapter, which should be considered an introductory paper to the ecology of the lagoon, articulate the specific objectives of the other chapters, and can be summarised as follows:

-The lagoon is nowadays dominated by dense and extensive macrophyte meadows. The temporal dynamics of macrophytes appears to be driven by salinity and water level fluctuations. In **Chapter 2**, the hydrology of the lagoon is explored through a dynamic modelling approach, aiming to produce a reliable model which allows the quantification of water and salt flows in the lagoon.

-The high macrophytic biomass measured in the studied lagoon is hypothesized to be explained by the relatively high depth of the system in comparison with other coastal lagoons, what depending on the underwater light availability could favour higher biomass due to higher water volume per surface area. In **Chapter 3**, we describe the underwater light regime in the system, characterizing on the one hand those water components that are responsible for the light attenuation in the water column, and on the other, performing estimates of potential light limitation for macrophytes.

-The water level and salinity variations in the lagoon may explain the spatial distribution and the temporal dynamics of macrophytes. In **Chapter 4** we explore, from a multiannual perspective, the spatiotemporal dynamics of macrophyte meadows, aiming to determine the main factors that explain its variability.

-The seasonal macrophyte production-decomposition cycle appears to drive the main limnological descriptors of the lagoon, and there is a fast processing of the huge macrophytic biomass without the development of hypoxic conditions. In **Chapter 5** we quantify summer whole-system metabolism variability and relate the carbon and oxygen metabolic measures with macrophyte metabolism and sediment fluxes.

-As described above, in **Chapter 6** we finally aim to understand the seasonal and interannual dynamics of dissolved inorganic carbon and perform annual budgets of both inorganic and organic carbon in the lagoon.

Study site

What follows is a brief description of the study system, to outline its main environmental features and significance and to bring the reader with an overall synthesis of the present knowledge about its ecological functioning, explicitly avoiding an overlap with the more detailed site descriptions given in each of the following chapters.

Site description

The Albufera des Grau is a coastal lagoon located in the northeast coast of the island of Menorca (Balearic Islands, Western Mediterranean). It constitutes the open free waters of the most important wetland of the island of Minorca and is one of the most well-preserved lagoons of the Balearic Islands, especially due to a high number of resident and migrating birds. The lagoon was declared Nature Park in 1995 and is the nucleus area of the UNESCO designation of Biosphere Reserve for the island of Minorca since 1993.

The lagoon, with a surface area of 78 ha and a mean volume of 1.0 hm^3, is oligo-mesohaline and has a mean depth of 1.37m and a maximum of 3m (Pretus 1989). It is connected to the sea by a narrow 500 m long channel and receives freshwater inputs from two streams. The watershed, mainly composed of Palaeozoic siliciclastic turbidites and Mesozoic dolomites and sandstones, covers an area of 56 Km^2, comprising similar proportions of extensive dry farming land and natural vegetation (Mediterranean Holm oak and Aleppo pine forests and shrublands) as the main land covers. Attached to the lagoon there are spotted satellital salt marshes and brackish wetlands, with a most extensive freshwater wetland at the landward side.

Anthropogenic impacts and pressures

Like most Mediterranean coastal lagoons, the Albufera des Grau has been used for centuries as fishery ground, mainly focusing on sand smelt (*Atherina boyeri* (Osteichthyes, Atherinidae)), on different species of grey mullets (Osteichthyes, Mugilidae), on a nowadays locally extinct mysid (*Mesopodopsis slabberi*, 'Gambó de sa Bufera', Ferrer-Aledo 1923), and since the late XXth century exclusively on the European eel (*Anguilla anguilla* (Osteichthyes, Anguillidae)) (Cardona et al. 2002). The lagoon has never been exploited for aquaculture or mollusc farming and the economic activities supported in the lagoon probably never exceeded the familiar small-scale fishing industry (Buenaventura 2002). Nowadays, the exploitation of European eel in the lagoon is regulated by the Nature Park managers and can be considered a minor pressure to the lagoon.

The hydrology of the lagoon was modified a few decades ago with the drought of the springs in the watershed, probably due to aquifer overexploitation, what supposed the disappearance of a permanent freshwater flow into the lagoon known to have existed until the 1960s. Thus, freshwater inputs into the lagoon are nowadays exclusively centred on the rainy periods. This alteration is believed to be behind the huge hypersalinisation and subsequent bottom hypoxia observed in the lagoon in the 1990s (Pretus 1996). This led the Nature Park authority to manage the sea-lagoon connection through a small floodgate in the outlet channel that allows the regulation of the water exchange when the sand barrier at the end of the channel is opened. Such water management is aimed to ensure the maximum connectivity with the sea while maintaining the water level and salinity within adequate ranges to maximize the diversity of habitats in the lagoon (Pretus 2003).

The most serious threat that has ever focused the lagoon was a project, developed in the 1970s, that planned to construct a residential extensive area in the surroundings, which included the dredge of the lagoon to favour its conversion into a marina for recreational boating. The popular clamour against such threat, with important social and political consequences (Piris 2006) resulted in the first protection figure of the Albufera des Grau, which was designated an ANEI (Natural Area of Special Interest) by the Balearic Government in 1986.

With regard to the anthropogenic impacts in historic times, it is known that in the XVIII century the natural outlet was dredged and modified to favour the presence of marine species in the lagoon (Pretus 2003), a situation that appears to be frequent during the first decades of that century (Habsburg-Lorena 1890; Vargas-Ponce 1787). It is also in the local knowledge that probably during the British rule of Minorca in the XVIII century, an extensive wetland which connected the lagoon with a marine embayment located a few kilometres westward (Port d'Addaia) was desiccated to obtain farming grounds (Buenaventura 2002), as many field evidences suggest. Such engineering action is believed to have affected substantially the ecology of the lagoon, and an authors' ongoing project dealing with palaeolimnological reconstruction of the Albufera des Grau during the last millennium will probably contribute to assess the impacts associated with such perturbation.

Fortunately, and unlike many other coastal lagoons in the Mediterranean, the lagoon has never been subject to intense anthropogenic pressures of chemical nature, and it has never been used as outlet for domestic or industrial wastewaters. This does not imply an absence of nutrient agriculture-derived inputs into the lagoon, which strongly affect its ecological dynamics, but these are by far smaller than in other areas with more intense agricultural (rice fields, intensive agriculture) or industrial pressures. In the case of the Albufera des Grau, the farming practises in the watershed are mostly extensive and only locally intensive, and implicate moderate nutrient loads into the streams (Cirach 2007). Apart from this a recent study revealed that metal concentrations in the lagoon water and its sediments are comparable to those of unpolluted sites (Cañas 2008). The lagoon can be considered to be well preserved, especially in comparison with other Mediterranean coastal lagoons, most of which are hypereutrophic, highly polluted, geomorphologically altered or intensely exploited for aquaculture (Vicente and Miracle 1992; Chapelle et al. 2000; Aliaume et al 2001; Viaroli et al. 2001; Frascari et al. 2002; Pastres et al. 2004; Lloret et al., 2005; Viaroli et al. 2005; Chomérat et al. 2007).

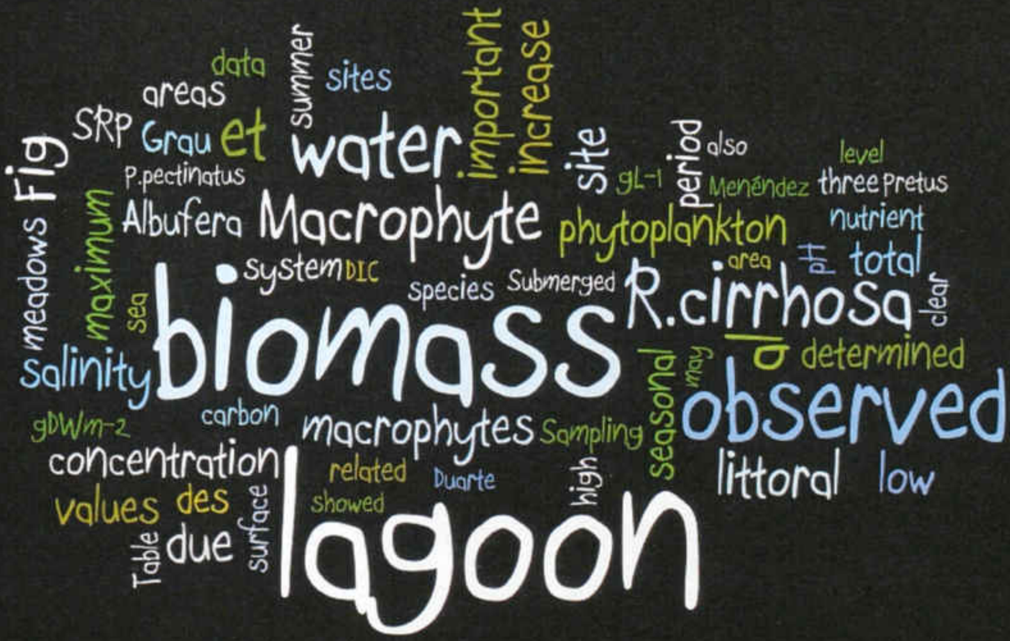
Current knowledge on the ecology of the lagoon

The first sources with data of biological interest describe the Albufera des Grau as a lagoon with a marked marine character, given the high salinity of its waters (Vargas-Ponce 1787) and the existence of a high diversity of marine fish species in the XVIII century (Habsburg-Lorena 1890). In the XXth century the lagoon was described as dominated by marine macroalgae (*Chaetomorpheto-Polysiphonietum*, Margalef 1952).

The first ecological studies were performed in the 1980s, with a first complete limnological description of the lagoon (Pretus 1989). In that period, the dense beds of *Chaetomorpha crassa* that covered the whole surface of the lagoon were responsible for severe hypoxic crises (Pretus 1989) with important consequences on the fish communities (Cardona and Pretus 1991). Afterwards the lagoon has been studied as part of major research projects focusing on specific processes of coastal environments: the ecology of fish communities in brackish waters (Cardona 1994; 1999; 2000; 2001; Cardona et al. 2002), and the phosphorus biogeochemistry at the sediment-water interface in coastal environments (López 2003; 2004a; 2004b). Together with these, there are a number of specific studies dealing with descriptions of zooplankton diversity (Pretus et al. 1992), ostracod assemblages (González and Pretus 2003), polichaete reefs (Fornós et al. 1997) or essays about the ecological management of the lagoon (Pretus 2003). There are also several unpublished studies and technical reports focusing on a high diversity of aspects related to the lagoon ecology: the hydrodynamics, the organic (Grimalt 2001) and metal (Cañas 2008) pollutants, the nutrient loads into the streams of the watershed (Pascual 2005; Cirach 2007), the descriptions of the benthic and pelagic invertebrate communities (Pretus and Pons 2005) and of the parasite communities of fishes (Montoliu et al. 2004), and the calibration of palaeolimnological proxies based on stable isotope and trace element geochemistry of ostracod shells (Obrador 2004). All this diversity of approaches has been substantially complemented with the information generated by a limnological monitoring program started in the 1980s that, more or less uninterruptedly, has arrived to our days (Pretus 1996; Pretus and Obrador 2004).

In conclusion, the knowledge of the ecology of the Albufera des Grau is depicted as highly diverse in nature and based on studies focusing on specific aspects usually treated unconnectedly. This thesis is challenged to portray the ecosystem functioning of the lagoon through a comprehensive and integrative systemic approach.

NOTE TO THE READER: Throughout this thesis the crossed references between the different chapters follow consistently the usual citation criteria for published literature. Thus, the citation Obrador et al. (2007) addresses to Chapter 1, Obrador et al. (2008) addresses to Chapter 2, and Obrador and Pretus (2008) addresses to Chapter 3. For those chapters that are not yet published, the citations Obrador and Pretus (2009a), Obrador and Pretus (2009b) and Obrador and Pretus (in prep) refer to the Chapters 4, 5 and 6 of this thesis, respectively.



Chapter 1

Spatial distribution and biomass of aquatic rooted macrophytes and its relevance in the metabolism of a Mediterranean coastal lagoon

ABSTRACT / RESUM / RESUMEN

Obrador, B., Pretus, J.Ll., and Menéndez, M. 2007. Spatial distribution and biomass of aquatic rooted macrophytes and its relevance in the metabolism of a Mediterranean coastal lagoon. *Scientia Marina* 71: 57-64

This work aims to characterize the current autotrophic compartment of the Albufera des Grau coastal lagoon (Menorca, Balearic Islands) and to assess the relationship between the submerged macrophytes and the limnological parameters of the lagoon. During the studied period the submerged vegetation was dominated by the macrophyte *Ruppia cirrhosa*, which formed dense extensive meadows covering the 79% of the surface. Another macrophyte species, *Potamogeton pectinatus*, was also observed but only forming small stands near the rushing streams. Macroalgae were only occasionally observed. Macrophyte biomass showed a clear seasonal trend with maximum values in July. The biomass of *R. cirrhosa* achieved 1760 gDW m^{-2}, being this value the highest biomass ever reported for this species in the literature. The seasonal production-decomposition cycle of the macrophyte meadows appears to drive the nutrient dynamics and carbon fluxes in the lagoon. Despite the significant biomass accumulation and the absence of a wash out of nutrients and organic matter to the sea, the lagoon did not experience a dystrophic collapse. These results point out the importance of internal metabolism above exchange processes in the lagoon.

RESUM (*en català*)

El present treball té per objectiu la caracterització del component autotròfic de la llacuna litoral de s'Albufera des Grau (Menorca, Illes Balears) i determinar la relació entre els macròfits aquàtics i la dinàmica de les principals variables limnològiques del sistema. Durant el període d'estudi, la vegetació submergida va estar dominada pel macròfit *Ruppia cirrhosa*, formant extenses praderies a tota la llacuna. També s'observà una altra espècie de macròfit, *Potamogeton pectinatus*, però només en petites formacions a prop de l'entrada dels torrents a la llacuna, mentre que la presència de macroalgues va ser ocasional. La biomassa dels macròfits submergits va mostrar un clar cicle estacional, amb màxims centrats a l'estiu. La biomassa de *R. cirrhosa* assolí valors de fins a 1760 gDW m^{-2}, que suposa el valor més elevat de biomassa descrit per a aquesta espècie. El cicle estacional de producció i descomposició dels prats de macròfits sembla ser el responsable de la dinàmica de nutrients i dels fluxes de carboni la llacuna. Malgrat les elevades biomasses observades i que no es produí una evacuació de nutrients o matèria orgànica cap al mar, la llacuna no mostrà cap col·lapse distròfic, suggerint la importància del metabolisme intern de la llacuna per sobre dels processos d'intercanvi amb el mar.

RESUMEN (*en castellano*)

El presente estudio pretende caracterizar el componente autotrófico de la laguna litoral de s'Albufera des Grau (Menorca, Islas Baleares) y determinar la relación entre los macrófitos acuáticos y la dinámica de los principales parámetros limnológicos del sistema. Durante el periodo estudiado, la vegetación sumergida estuvo dominada por el macrófito *Ruppia cirrhosa*, que formaba extensas praderas en toda la laguna. También se observó otra especie de macrófito, *Potamogeton pectinatus*, pero sólo formando pequeñas formaciones cerca de la entrada de los torrentes a la laguna. La biomasa de macrófitos mostró un claro ciclo estacional, con los valores máximos centrados en verano. La biomasa de *R. cirrhosa* alcanzó 1760 gDW m-*2*, que supone el valor más alto de biomasa descrito para esta especie en la literatura. El ciclo estacional de producción-descomposición de las praderas de macrófitos parece ser el responsable de la dinámica de nutrientes y de los flujos de carbono en la laguna. A pesar de las elevadas biomasas acumuladas y de la ausencia de un lavado de nutrientes y materia orgánica hacia el mar, la laguna no mostró un colapso distrófico, sugiriendo la importancia del metabolismo interno de la laguna por encima de los procesos de intercambio con el mar.

1.1. Introduction

Submerged aquatic macrophytes account for an important part of the primary production in shallow lakes (Margalef 1983). In coastal lagoons, which are amongst the most productive ecosystems of the world (Barnes 1980), the primary production is either performed by macrophytes, macroalgae or, to a lesser extent, periphyton or phytoplankton (Castel et al. 1996; McGlathery et al. 2001). The dominance of one of these groups of primary producers can be related to nutrient levels, but many factors appear to be involved (Duarte 1995; Taylor et al. 1995; Valiela et al. 1997). Nonetheless, the accumulation of significant biomass of either macroalgae or rooted macrophytes together with the highly dynamic character of coastal lagoons can periodically lead these systems to dystrophic crises (Castel et al. 1996; Viaroli et al. 1996; Duarte et al. 2002).

The Albufera des Grau is a coastal lagoon located in the northeast coast of Menorca, Balearic Islands. The lagoon is the most important wetland of the island and one of the most well preserved coastal lagoons of the western Mediterranean. The few previous studies of the Albufera des Grau described different submerged vegetation in its recent history (Margalef 1952; Pretus 1989; Cardona 2001). In the early 50s the eminent ecologist Ramon Margalef described the flora of the lagoon as *Chaetomorpheto-Polysiphonietum*, with no indication of the presence of aquatic submerged phanerogams (Margalef 1952). During the decade of 1980s the green macroalgae *Chateomorpha crassa* formed extensive beds covering the 100% of the surface most of the time (Pretus 1989). A dystrophic crisis was reported due to a massive mortality of macroalgal beds after the entrance of seawater to the lagoon and subsequent salinity changes (Pretus 1989). The presence of rooted macrophytes in the lagoon was first reported in the 90s in the seaward littoral areas, with an estimated cover of 40% (Cardona 2001).

The lagoon is isolated in the sense that the communication with the sea does not imply an important water renewal of the system. This means that the export of organic matter and nutrients to the sea is not as important as lagoons with more intensive lagoon-sea exchanges (Duarte et al. 2002). In such situation, we would expect the internal metabolism of the lagoon to play an important role on the trophic status of the system. As a consequence, the knowledge of the trophic status including the relative importance of the different primary producers is essential for the understanding and further management of the lagoon.

This study aims to characterize the current autotrophic component of the lagoon and to assess the spatial and temporal variability of aquatic rooted macrophytes on a seasonal basis. A parallel description of the basic chemical parameters is also conducted to briefly discuss the relation of the production cycle with the metabolism of the lagoon.

1.2. Material and methods

1.2.1 Study site

The Albufera des Grau has a surface area of 78 ha and a volume of 1 hm^3 (Fig. 1.1). The average depth is 1.37 m and reaches a maximum of 3 m (Pretus 1989). Climate is typically Mediterranean, with a mean air temperature of 17 °C and 599 mm annual precipitation during the last three decades. The lagoon receives freshwater inputs from two streams that drain an area of 56 Km^2, being the watershed mainly composed of Palaeozoic siliciclastic sands and silts and Mesozoic dolomites. Freshwater inputs are irregular and centred on spring and autumn. The lagoon is connected to the sea by a narrow channel of 500 m long, Sa Gola, where a small floodgate allows the regulation of the lagoon-sea connection when the sand-barrier is opened. The water of the lagoon is oligo-mesohaline with a range of salinity between 5 and 20 g L^{-1} during the last five years. There is a marked seasonality in salinity and water level due to Mediterranean evaporation/precipitation regime, which can potentially lead the system to critical situations such as hypersaline events (up to 60 g L^{-1} in 1995, authors' unpublished data), haline stratification and dystrophic events (Pretus 1989; Cardona 2001).

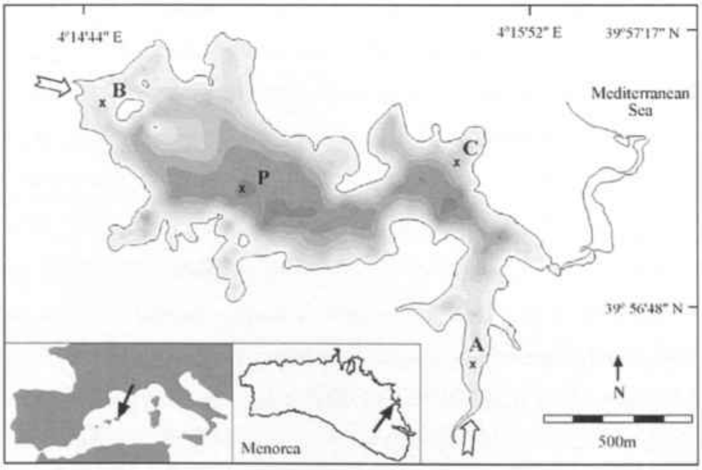


Figure 1.1. Location and bathymetric map of the Albufera des Grau in the island of Menorca, Western Mediterranean. Isobaths are every 50 cm. Sampling sites (crosses) and freshwater inputs (arrows) are shown.

1.2.2 Sampling methods

During year 2000 the biomass of submerged macrophytes was determined at approximately monthly intervals at three littoral sites (~1m depth) beneath dense meadows. Sites A and B were located near the rushing streams, while site C was located on the northern coast of the lagoon (Fig. 1.1). Three replicates were conducted at each sampling site. Biomass samples were collected with a cylindrical core sampler of 16 cm of diameter (Menéndez 2002) and aboveground biomass was sorted by hand from the core. The sediment was sieved through a 1 mm mesh to collect belowground biomass (rhizomes and roots). After sorting and cleaning with tap water, samples were dried (70 °C to constant weight) and weighted.

Macrophyte cover was determined in July 2000 by visual observation from a boat. Repeated diving immersions were done in order to identify macrophyte species when necessary. The surface of the lagoon was divided in a 50x50m grid, and the abundance of the macrophyte species was determined for each unit. The whole lagoon was surveyed. Macrophyte abundance was determined by a percent cover scale.

During the studied period the basic limnological parameters of the lagoon were determined monthly at a 3m-depth site in the central area of the lagoon. All samplings were conducted at the same time of the day. Five water samples were taken at different depths every 50 cm from surface to bottom. Water salinity, pH, temperature and oxygen concentration were determined in situ with field sensors (WTW Multiline P3 and WTW Cond315i). Water samples were filtered, stored frozen and analyzed in the laboratory as soon as possible. Nutrient concentration (nitrate, nitrite, ammonia, total phosphorus and SRP) were determined following standard methods (Hansen and Koroleff 1999). Alkalinity was determined by potentiometric titration with H_2SO_4 and Gran evaluation (Stumm and Morgan 1981). The parameters of the carbonate system (total dissolved inorganic carbon and partial pressure of CO_2) were calculated from the pH and alkalinity values using the dissociation constants for seawater (Millero 1995). Phytoplankton biomass was evaluated from pigment concentrations in water, which were extracted in 90% Acetone and determined by the trichromatric method (Jeffrey and Humphrey 1975).

1.3. <u>Results</u>

1.3.1 Spatial distribution and biomass of submerged vegetation

Two vascular submerged macrophytes were found during the survey of aquatic vegetation in the lagoon, *Ruppia cirrhosa* (Petagna) Grande and *Potamogeton pectinatus* L., which formed dense extensive meadows all along the lagoon. Occasional occurrence of red algae (*Polysiphonia spp.*, *Gracillaria sp.*) and filamentous green algae (*Chaetomorpha crassa*) was observed. In the study site emerged macrophytes (*Scirpus maritimus* and *Phragmites australis*) were also observed in narrow vegetated belts in some areas along the shoreline.

The spatial extent of macrophytes was dominated by *R. cirrhosa*. It was distributed through large areas of the lagoon, forming the denser beds in the littoral parts (Fig. 1.2). Individual stands were also found at intermediate depths (1-2m), with shoots arriving to the top of water column. *R. cirrhosa* was only absent in the deepest part of the lagoon (>2m). The total area of appearance of *R. cirrhosa* was estimated to be 59 ha. On the other hand, *P. pectinatus* only appeared forming small stands among *R. cirrhosa* meadows and its distribution was limited to the areas near the entrance of freshwater streams to the lagoon (Fig. 1.2).

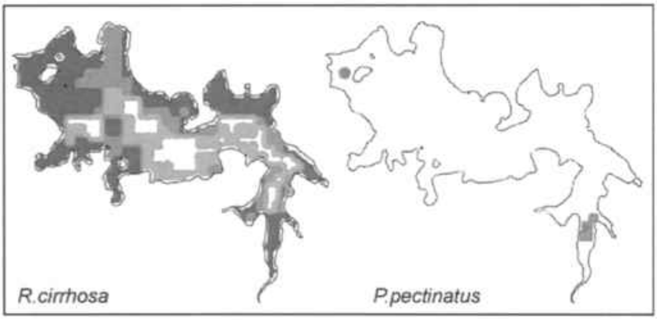


Figure 1.2. Spatial distribution of *R. cirrhosa* (left) and *P. pectinatus* (right) in summer 2000, including both living and recently desiccated littoral stands. Cover scale from dark grey to white: 100%, >50%, <50%, and absence or scarce individuals.

The main species, *R. cirrhosa*, was present in the three sampling sites during all studied period and showed a clear seasonal trend in terms of biomass at the three sampling sites (Fig. 1.3). Similar trends in aboveground (shoots and leaves) and belowground (roots and rhizomes) biomass were observed. Aboveground biomass was below 300 gDW m^{-2} from January to April. In spring increasing values of biomass were observed until July, when it peaked with more than 1000 gDW m^{-2} at the three sites. Maximum achieved biomass was 1760 gDW m^{-2} at site A. The maximum belowground biomass was also observed in July at sites A and B, but never above 300 gDW m^{-2}. During the summer the contribution of belowground biomass to total biomass was very small, and aboveground biomass accounted for more than 85% of total plant biomass on average. Beyond the biomass maximum, *R. cirrhosa* progressively declined and both above and belowground biomass decreased, reaching quickly the low values of the previous winter (below 300 gDW m^{-2}) and then absolutely disappearing from the lagoon.

Potamogeton pectinatus only appeared at sites A and B (Fig. 1.3). The maximum observed aboveground biomass of *P. pectinatus* was 576 gDW m^{-2} at site B, being 80% of total plant biomass. With the little data available, no clear seasonal trends can be inferred, but it's worth mentioning its absolute disappearance from the lagoon beyond July.

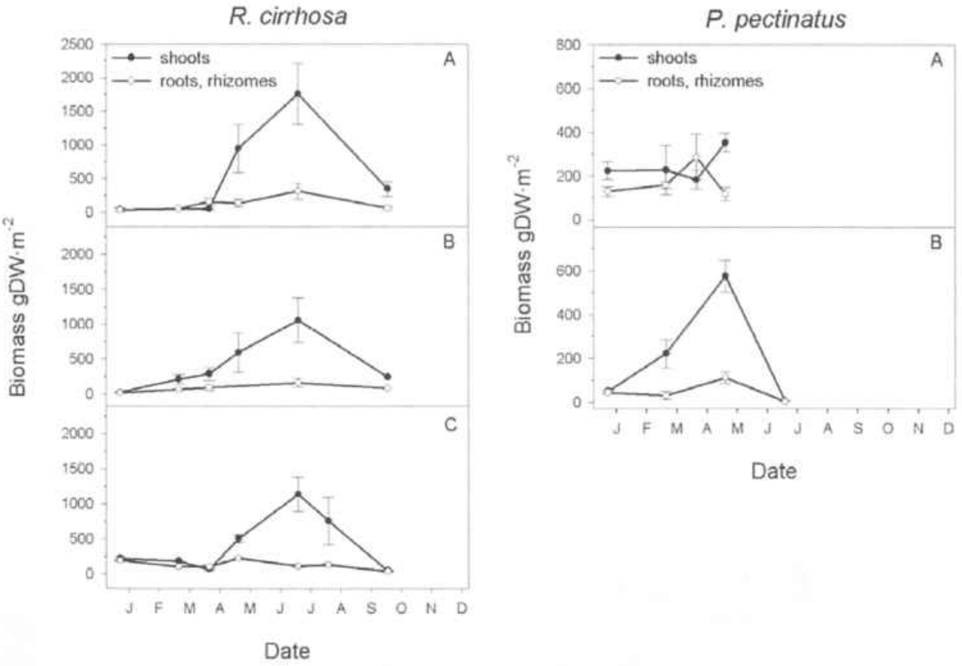


Figure 1.3. Temporal dynamics of *R. cirrhosa* (left) and *P. pectinatus* (right) biomass at the three sampling sites. Aboveground (filled circles) and belowground (open circles) biomass is shown.

1.3.2 Water parameters

During the study period, water level was always below sea level (s.l.) and showed clear seasonal fluctuations with extremely low values in summer (Fig. 1.4). Minimum level was reached in September, with -85 cm below s.l., leading to important littoral desiccation. From the bathymetry of the lagoon (Pretus, 1989 and authors' unpublished data) we could estimate the desiccated area in approximately 31 ha. This value accounts for the 40% of the total lagoon surface and the 90% of the surface corresponding to littoral areas (<1m depth). Average salinity was 17 g L^{-1}, but an important seasonal variation was observed (Fig. 1.4). Winter values of 12 g L^{-1} progressively increased until October, when maximum salinity was observed (25 g L^{-1}). Such increase was related to the evaporation balance and to the sporadic entrance of small amounts of seawater to the lagoon due to low water levels. During the studied period the water column was always mixed and only smooth vertical gradients in salinity were observed. A clear seasonal trend in pH was observed, with a slight progressive increase reaching the maximum of 9.3 in June (Fig. 1.4). A fast decrease below seawater pH values was observed at the end of the summer. Such a variation in pH (range 7.3 - 9.3) occurred despite the high alkalinity of the water (Table 1.1).

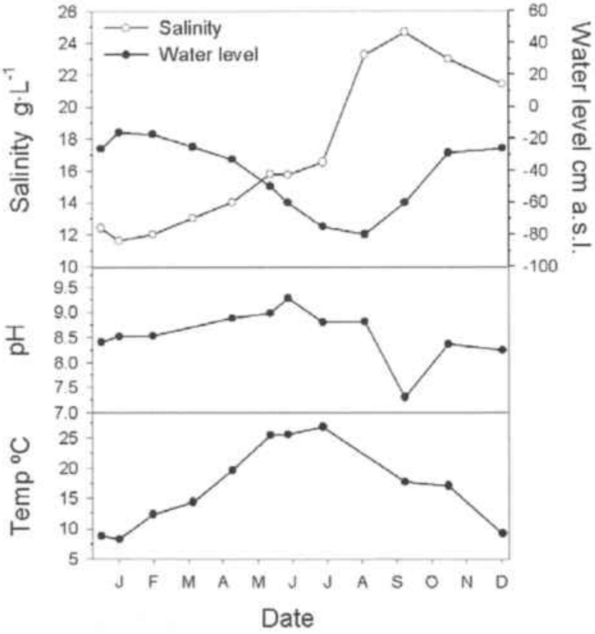


Figure 1.4. Temporal evolution of salinity, water level, pH and temperature during the studied period.

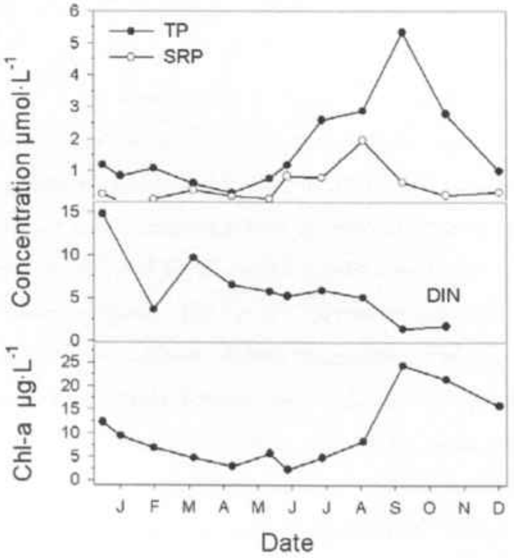


Figure 1.5. Temporal evolution of nutrient (total phosphorus, TP, SRP-phosphorus and dissolved inorganic nitrogen, DIN) and chlorophyll-a concentrations during the studied period.

Nutrient concentrations were low during the studied period (Table 1.1). Dissolved inorganic nitrogen, DIN, ranged 1-15 µmol L^{-1} and a progressive reduction was observed all along the year (Fig. 1.5). Soluble reactive phosphorus, SRP, showed a clear seasonal trend, peaking in summer (2 µmol L^{-1} ; Fig. 1.5). The total phosphorus, TP, including both dissolved and particulate forms of phosphorus, showed a similar trend (Fig. 1.5). The lower values (<1.5µmol L^{-1}) were found during winter and spring months, and concentration started a progressive increase from June. The maximum TP was achieved in October with 5.3 µmol L^{-1}. Chlorophyll-a concentration was at intermediate levels during the winter months (5-12 µg L^{-1}) and decreased during spring (Fig. 1.5). By mid-summer concentration progressively increased and achieved the maximum value of 25 µg L^{-1} in October, but from this date the eutrophic situation started to revert.

Table 1.1. Summary of water characteristics in s'Albufera des Grau

	range
Water level (cm a.s.l)	-85 - 16
Volume (x1000 m^3)	921 - 1026
Salinity (g L^{-1})	11.6 - 24.7
Temperature (°C)	8.2 - 26.8
pH	7.3 - 9.3
Oxygen (%saturation)	70 - 133
Oxygen (mg L^{-1})	6.7 - 12.2
Phosphorus SRP (µmol L^{-1})	0.02 - 2.0
TP (µmol L^{-1})	0.26 - 5.34
NH_4^+ (µmol L^{-1})	0 - 9.18
NO_3^- (µmol L^{-1})	0.30 - 4.62
Alkalinity (meq·L^{-1})	1.93 - 3.64
pCO_2 (µatm)	10 - 3870
HCO_3^- (mmol L^{-1})	1.39 - 3.16
CO_2 (mmol L^{-1})	0.0004 - 0.1431

Interestingly, the dissolved inorganic carbon, DIC, showed a clear seasonal trend. During the growing period of *R. cirrhosa*, DIC concentration showed a progressive decrease and pCO_2 was below atmospheric equilibrium (Fig. 1.6). After the summer minimum in DIC concentration, a huge increase was observed presumably due to the release of carbon from macrophyte biomass decomposition. A fast and dramatic supersaturation of CO_2 in the lagoon occurred in October (up to 3870 µatm, ten fold the atmospheric partial pressure), but two months later the 370 µatm range of atmospheric equilibrium was recovered.

1.4. Discussion

The Albufera des Grau is a macrophyte-dominated system with *R. cirrhosa* the most important species. The low diversity of macrophytes is typical of brackish systems such as this lagoon (Remane and Schlieper 1971). The meadow is densely distributed all along the lagoon especially in the littoral areas. The total estimated macrophyte cover was 80% of the lagoon surface, of which only 2% corresponds to mixed *Ruppia-Potamogeton* meadows (Table 1.3). The dominance of *R. cirrhosa* over *P. pectinatus* is probably due to the salinity range observed in the lagoon, which is in accordance with the salinity tolerance of these species (Verhoeven 1980a). Indeed, *P. pectinatus* disappears in July when salinity increases sharply from 16 to 23 g L^{-1}.

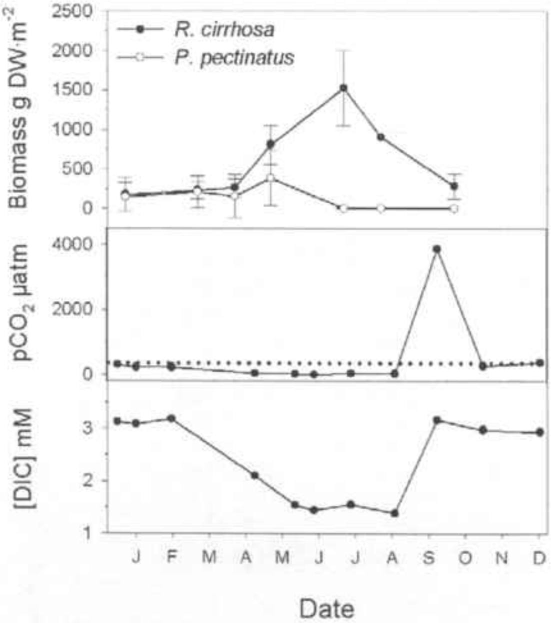


Figure 1.6. Temporal evolution of average total biomass of *R. cirrhosa* and *P. pectinatus* in relation with the partial pressure of CO_2 and the concentration of dissolved inorganic carbon in water. The dotted line is the partial pressure of CO_2 at atmospheric equilibrium.

The high biomass of *R. cirrhosa* observed in this study is clearly the highest value ever reported for this species in the literature (Table 1.2) and points out the importance of benthic production in the lagoon. Such high biomass may be related to the higher irradiance and warmer temperatures typical of the Mediterranean climate. Moreover, in a situation without light limitation, the greater depth of the littoral areas of the Albufera des Grau in comparison with other reported Mediterranean coastal lagoons could presumably be involved in the achievement of such high biomass values.

Table 1.2. Range of biomass values reported in the literature for *R. cirrhosa*. ([a] calculated from original data in gDW m^{-2}, assuming 20% ash content)

Biomass gAFDW m^{-2}	Locality	Source
8-90[a]	Murcia, Spain	Ballester (1985)
20-106[a]	Certes fishponds, France	Viaroli et al. (1996)
90-140	Tvärminne, Finland	Verhoeven (1980b)
50-160	Camargue, France	Verhoeven (1980b)
55-190	Coastal ponds, Netherlands	Verhoeven (1980b)
128-282	Badia del Fangar, Spain	Pérez and Camp (1986)
226-365[a]	Buda lagoon, Spain	Menéndez et al. (2002)
72[a]-438	St. André lagoon, Portugal	Duarte et al. (2002)
473-642[a]	Fra Ramon, Spain	Gesti et al. (2005)
75-672	Tancada Lagoon, Spain	Menéndez (2002)
380-1408[a]	Albufera des Grau, Spain	This study

A clear seasonal trend in the production and decomposition of the *Ruppia* meadows was observed at the three sampling sites, which only differed in the maximum values of *Ruppia* biomass. The lower biomass at site B may be related to the high biomass of *P. pectinatus* at the sampling site (Fig. 1.3) but further work would be required to confirm this (Verhoeven 1980a; Menéndez et al. 2002). Similarly, the lower biomass at site C may be related to differences in sediment composition and to the presence of macroalgae at the sampling site (346 gDW m^{-2} of *Polysiphonia sp*., authors' unpublished data).

The macrophyte production-decomposition cycle seems to drive most of the limnological parameters of the lagoon. During the macrophyte growing period nutrient concentrations are low, presumably limiting phytoplankton growth. From mid-summer the macrophyte beds decline and decomposition of macrophyte biomass takes place (Menéndez et al. 2003), as suggested by the increase in SRP and DIC in the water column. The increase in DIC is actually delayed in relation to SRP and could also be related to carbonate dissolution due to low pH, but such a hypothesis can not be discussed with the available data. On the contrary a fast release of nutrients is expected due to the high decomposition rate of *R. cirrhosa* biomass (Menéndez et al. 2003; Menéndez et al. 2004). The average expected time to decompose the 50% of *R. cirrhosa* biomass in the Albufera des Grau is 2 months (calculated from measured decomposition rates in the Albufera des Grau, authors' unpublished data), and the whole macrophyte community is mineralised after a year cycle (230 days to decompose the 95% of biomass).

The nutrient release is presumably responsible for the autumn proliferation of phytoplankton, as suggested by the synchronous peak in chlorophyll-a and TP concentrations. The increase in TP could be explained by a release of SRP from the sediments due to low pH, but such an increase in SRP was not observed and actually SRP decreased. This observation, together with the increase in chlorophyll-a, strongly suggests that SRP is incorporated into phytoplankton and that the peak in TP is thus reflecting phytoplankton growth. The constant or even decreasing DIN, which is synchronous with the increase in SRP, may be due to a fast incorporation of nitrogen into phytoplankton or due to denitrification beneath the dense littoral meadows. Thus, anoxic conditions near the bottom are expected to be common in the littoral areas with large amounts of biomass (Calado and Duarte 2000). However, the system did not fall into dystrophy as no hypoxia was observed in the open water (the oxygen saturation concentration in the open waters never decreased below 70%; Table 1.1).

The great reduction of DIC during the macrophyte growing period may cause both phytoplankton and macrophytes to be limited by carbon. Indeed, the minimum CO_2 concentration was below the compensation point described for *R. cirrhosa* (Table 1.1, Peñuelas and Menéndez 1990). *R. cirrhosa*, however, is highly adapted to low CO_2 values because of its ability to use HCO_3^- (Peñuelas and Menéndez 1990; Hellblom and Axelsson 2003). Nonetheless, HCO_3^- concentration below *R. cirrhosa*'s compensation point have been observed in the littoral waters of the Albufera des Grau on a typical summer daily cycle, suggesting growth limitation by inorganic carbon during extremely productive periods (authors' unpublished data).

On the view of the important role that macrophyte meadows play on the lagoon carbon cycle, the question of the stability of such a productive system in relation to the fluctuating physical factors (salinity and water level) emerges. In summer 2001 a new macrophyte mapping was conducted in order to evaluate the recovery of the meadows after the littoral desiccation of the previous summer. In 2001 only monospecific meadows of *R. cirrhosa* were observed with no presence of *P. pectinatus*. This may be due to the higher observed salinities during the growing period (up to 14-20 g L^{-1}, author's unpublished data). Similar to 2000, dense stands of *R. cirrhosa* occupied littoral areas and sparse individuals were found in the central part of the lagoon. The total meadow area was estimated at 64 ha (Table 1.3), slightly higher than that observed in 2000. This expansion of *R. cirrhosa*, despite the very low water levels of the previous year, is consistent with the high tolerance to desiccation described for this species (Adams and Bate 1994; Gesti et al. 2005).

Table 1.3. Comparison of macrophyte cover and percentage of cover of each species for years 2000 and 2001

	2000	2001
Macrophyte cover (ha)	59	64
Percentage of total surface (%)		
absence of macrophytes	21	15
monoespecific meadows of *R. cirrhosa*	77	85
R. cirrhosa - *P. pectinatus*	2	0
monoespecific meadows of *P. pectinatus*	0	0

In conclusion, despite the magnitude of carbon fluxes in the lagoon, as exemplified by the huge pCO_2 increase in autumn, the system did not collapse into a dystrophic crisis, as would probably have been the case in a macroalgae-dominated situation in which a faster return of nutrients is expected (Viaroli et al. 1996; Viaroli and Christian 2003). The phytoplankton proliferation due to nutrient release did not achieve extreme chlorophyll-a concentrations. Because the water level was below s.l. throughout the year, no outputs to the sea occurred. Consequently, the fast recovery of spring conditions (low phytoplankton and nutrient levels and pCO_2 near atmospheric equilibrium) occurred without the washout of nutrients or organic matter to the sea and was more related to the internal metabolism of the lagoon. This is in discordance with other similar systems where an export of organic matter and nutrients to the sea or even a harvesting of macrophyte biomass help prevent eutrophication (Calado and Duarte 2000; Duarte et al. 2002).

1.5. Acknowledgements

This work was partially funded by the Albufera des Grau Nature Park. We are especially grateful to Miquel Truyol for his assistance during field work and to George Swann for the English corrections. We also thank Dr. Xavier Quintana and an anonymous reviewer for their valuable comments.

Chapter 2

A dynamic model to simulate water level and salinity in a Mediterranean coastal lagoon

ABSTRACT / RESUM / RESUMEN

Obrador, B.; Moreno-Ostos, E. and Pretus, J.LL. 2008. A dynamic model to simulate water level and salinity in a Mediterranean coastal lagoon. *Estuaries and Coasts* 3: 1117-1129

In this study, a dynamic model for a Mediterranean coastal lagoon (Albufera des Grau, Menorca, Western Mediterranean) is presented. A simple model with limited data requirements was constructed to simulate the daily variations in water level (*WL*) and water salinity (*S*) in the lagoon. Both parameters constitute the main descriptors of the lagoon hydrology and have substantial ecological significance. The model consisted of three coupled submodels: a submodel for the water balance in the watershed, a submodel for the water balance in the lagoon, and a submodel for the salt mass balance in the lagoon.

The results of the study revealed that the model simulated the temporal dynamics of both *WL* and *S* with reasonable accuracy (mean error of 7.6 cm and 2.8 g L^{-1} for *WL* and *S*, respectively). The model made it possible to determine the annual water and salt budgets, which were characterised by intense inter-annual variability. A simulation carried out for the last 30 years accurately predicted the long term range of variation of salinity, and even severe hyperhaline periods were correctly simulated. The model is believed to be a useful tool in predicting the occurrence of ecologically degraded situations and could contribute to future biogeochemical studies.

RESUM (*en català*)

El present treball presenta un model hidrològic dinàmic per a una llacuna litoral Mediterrània (s'Albufera des Grau, Menorca, Illes Balears). Es va desenvolupar, calibrar i validar un model simple destinat a la simulació diària dels dos principals descriptors hidrològics del sistema, el nivell de l'aigua (*WL*) i la salinitat (*S*), ambdós amb elevada transcendència ecològica. El model, alimentat per dades climàtiques fàcilment disponibles, va consistir en tres submodels acoblats entre ells: un primer submodel per al balanç d'aigua a la conca hidrològica, un segon submodel per al balanç d'aigua a la llacuna, i un tercer submodel per al balanç de sal total a la llacuna.

Els resultats van mostrar que el model va ser capaç de simular correctament la dinàmica de *S* i *WL* amb errors acceptablement baixos (error mitjà de 7.6 cm i de 2.8 g L^{-1} per a *WL* i *S*, respectivament). Les simulacions efectuades per als darrers trenta anys van permetre una caracterització precisa dels balanços anuals d'aigua i sal a la llacuna, que van mostrar una elevada variabilitat interanual. El model va predir correctament el rang de variació de la salinitat durant el període històric analitzat, i també simulà correctament un esdeveniment d'hipersalinitat ocorregut a la llacuna als anys noranta.

El model, doncs, pot contribuir a millorar el coneixement de molts processos que tenen lloc a la llacuna, servint de base per a futurs balanços biogeoquímics, aixi com suposar un eina útil en la gestió hidrològica del sistema.

RESUMEN (*en castellano*)

El presente trabajo presenta un modelo hidrológico dinámico para una laguna litoral Mediterránea (s'Albufera des Grau, Menorca, Islas Baleares). Se desarrolló, calibro y validó un modelo dirigido a simular la dinámica diaria de los dos descriptores hidrológicos principales del sistema, el nivel del agua (*WL*) y la salinidad (*S*), ambos con elevada trascendencia ecológica. El modelo, alimentado por datos climáticos de fácil obtención, consistió en tres submodelos acoplados entre sí: un primer submodelo para el balance de agua en la cuenca hidrológica, un segundo submodelo para el balance de agua en la laguna, y un tercer submodelo para el balance de sal total en la laguna.

Los resultados mostraron una elevada capacidad del modelo para simular correctamente la dinámica del *WL* y *S* con errores aceptables (error medio de 7.6 cm y de 2.8 g L^{-1} para *WL* y *S*, respectivamente). Las simulaciones efectuadas para un período de los últimos treinta años permitieron una descripción precisa de los balances anuales de agua y sal en la laguna, que se caracterizaron por una elevada variabilidad interanual. El modelo predijo correctamente el intervalo de variación de la salinidad durante el período histórico analizado, e incluso simuló correctamente un evento de hipersalinización que tuvo lugar en la laguna en los años noventa.

El modelo desarrollado puede contribuir a mejorar el conocimiento de la laguna, sirviendo de base para futuros balances biogeoquímicos, así como suponer una herramienta útil en la gestión hidrológica del sistema.

2.1. Introduction

Mediterranean shallow lakes and lagoons are characterised by complex limnological dynamics, which result from the vast temporal variability in hydrogeochemical and meteorological forcings (de Vicente et al. 2006; Beklioglu et al. 2007; Moreno-Ostos et al. 2007). Salinity variations, nutrient dynamics and water level fluctuations are important factors in the functioning of these water bodies, and influence the alternations between macrophytic and phytoplanktonic regimes (Beklioglu et al. 2007).

The Albufera des Grau (island of Menorca, Balearic archipelago, western Mediterranean) is an enclosed coastal lagoon without tidal influence and is one of the most well-preserved lagoons in the Balearic Islands. The ecological status of the lagoon is highly dependent on the hydrology, mainly described by water level (*WL*) and salinity (*S*). Unusual variations in these hydrological parameters can lead the system to critical situations with important ecological consequences. These include haline stratification and consequent bottom anoxia due to the massive entrance of seawater (Pretus and Obrador 2004), mid-term salinisation, which can result in hypersalinity (Pretus 1989; Cardona 2001; Pretus 2003), and littoral desiccation, which is caused by low water levels and can lead to large-scale mortality of the dense and extensive macrophyte meadows that are found throughout the lagoon (Obrador et al. 2007).

To prevent such undesirable situations, the water exchange between the lagoon and the sea is regulated by two sluices. The management of this system mainly focuses on the maintenance of *WL* and *S* within the optimal range for the conservation of the macrophyte meadows and the consequent effect on waterbird species (Noordhuis et al. 2002; Moreno-Ostos et al. 2008). The hydrological management is subject to a trade-off between *WL* and *S* because the entrance of seawater (to minimise summer littoral desiccation) can lead to quick salinity shifts and increase the risk of vertical density stratification and consequent bottom anoxia (Pretus and Obrador 2004). Since there are no gauging stations in the streams or in the outlet channel, the management practices are not fed by direct data of the water flows in the lagoon. The hydrological information currently available consists of a time series of water level and salinity, from which rough estimates of monthly water and salt flows are calculated (Pretus and Obrador 2004). These estimates are inaccurate and cannot be used for evaluating small flows or assessing the lagoon hydrology on a daily basis.

Given the limited possibilities for hydrological management on the lagoon (only the outflow or the seawater inflow can be modified) and the lack of information, a simple dynamic model to simulate *WL* and *S* with few data requirements would be a useful tool in the management of the lagoon. The quantification of the water fluxes could also serve as a basis to calculate nutrient loads into the lagoon. The model could also help identify effective management schemes under changing climate scenarios. Besides this, a hydrological model run on a daily basis would also improve the understanding of the hydrological regime and serve as a basis for further nutrient budget calculations in the Albufera des Grau.

The objective of the present study was to model the hydrological regime of the Albufera des Grau using daily water and total salt mass balances. Water level and water salinity were the desired output variables. The quantification of water and salt flows and the determination of the mean annual water and salt budgets in the lagoon were also objectives of the present study.

2.2. Study site

The Albufera des Grau (surface area 78 ha, volume 1 hm^3) is a brackish coastal lagoon located in the northeast coast of the island of Menorca (Balearic Islands; Fig. 2.1). The average depth is 1.37 m with a maximum of 3 m (Pretus 1989). The climate is typically Mediterranean; mean air temperature is 17 °C and annual precipitation is 549 mm. The lagoon is located on Palaeozoic siliciclastic turbidites and receives only surface water inputs from inland. The system is connected to the sea by a narrow channel, which is 500 m long; here, a small floodgate (c.a. 2 m^2) regulates the lagoon-sea connection when the sand barrier at the end of the channel is opened. The water exchange with the sea is irregular and does not represent an important renewal of water in the system (Pretus and Obrador 2004). The freshwater inputs are frequently torrential and are supplied by two streams that drain an area of 56 km^2. These water inputs are nowadays strongly intermittent and typically occur during the autumn and winter; but the permanent flow of freshwater to the lagoon has been documented until the 1960s, when the springs that supplied water to the streams were dry, probably due to aquifer overexploitation.

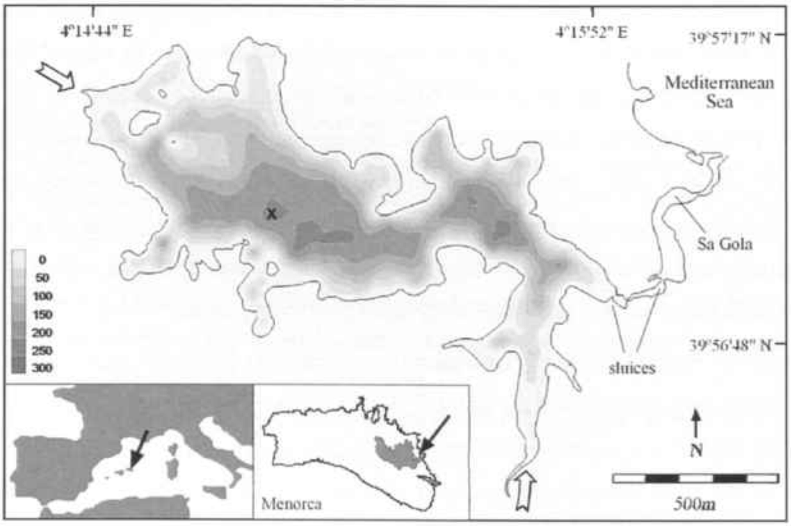


Figure 2.1. Location and bathymetric map (50 cm isobaths) of the Albufera des Grau coastal lagoon. The freshwater inputs (arrows) and the fixed sampling site (cross) are shown. The dashed area in the inset corresponds to the catchment area.

The watershed is mainly composed of Palaeozoic siliciclastic sands and silts (26%) and Mesozoic dolomites (40%). The main land covers in the watershed comprises 47% woodlands, composed of Mediterranean Holm oak and Aleppo pine forests, 9% shrublands, and 41% extensive dry farming land (authors' unpublished data).

Currently, the lagoon is a macrophyte-dominated system with dense and extensive meadows of the euryhaline macrophyte *Ruppia cirrhosa*. In these meadows, the highest biomass ever reported for this species is found (up to 1760 gDW m^{-2}; Obrador et al. 2007). Intense phytoplankton peaks, which are the main drivers of turbidity dynamics in the lagoon (Obrador et al. 2008), are observed every year usually in relation to the entrance of nutrients from the watershed or from the decomposition of the macrophyte meadows (Obrador et al. 2007). In the past, the lagoon has been described as a macroalgae-dominated system (Margalef 1952; Pretus 1989); and hyperhaline events (up to 60 g L^{-1} in 1995, authors' unpublished data), haline vertical stratifications, and dystrophic crises have also been reported (Pretus 1989; Cardona 2001).

2.3. Methods

2.3.1 Model description

The model consisted of three coupled submodels and simulated water level and salinity on a daily basis (Fig. 2.2). The Runoff Model (RM) was a water balance in the watershed (in mm) and allowed the calculation of the stream runoff entering the lagoon. The Lagoon Water Model (LWM) dealt with the water flows in the lagoon to calculate a daily balance of the lagoon water volume (in m^3), from which the water level was calculated. The LWM was fed by climatic data and by the runoff calculated in the RM submodel (Table 2.1). Finally, the Lagoon Salt Mass Model (LSM) was a balance of the total salt mass contained in the lagoon (in kg) and was fed by climatic data and by the water flows of the LWM. The relationships between the submodels and the respective inputs and outputs are shown in Table 2.1. The model was built and run using STELLA software (High Performance Systems).

The Runoff submodel (RM)

The total runoff was calculated from a water balance between precipitation and evapotranspiration in the catchment using a simplified version of a global hydrological model for runoff (Döll et al. 2003). The data inputs required to run the RM were daily average, maximum and minimum temperature, wind speed, relative humidity and rainfall. The fraction of the rainfall converted into runoff was determined by daily water balances in the canopy and in the soil from the following equations:

$$\frac{dS_c}{dt} = P_r - E_c - TF \qquad \text{Eq. (2.1)}$$

$$\frac{dS_S}{dt} = TF - ET_S - R_T \qquad \text{Eq. (2.2)}$$

where S_c is the water stored in the canopy (mm), P_r is precipitation (mm d^{-1}), E_c is the evaporation in the canopy (mm d^{-1}), TF is the throughfall (mm d^{-1}), S_S is the water content in the soil (mm), ET_S is the evapotranspiration from the soil (mm d^{-1}), and R_T is the total runoff (mm d^{-1}).

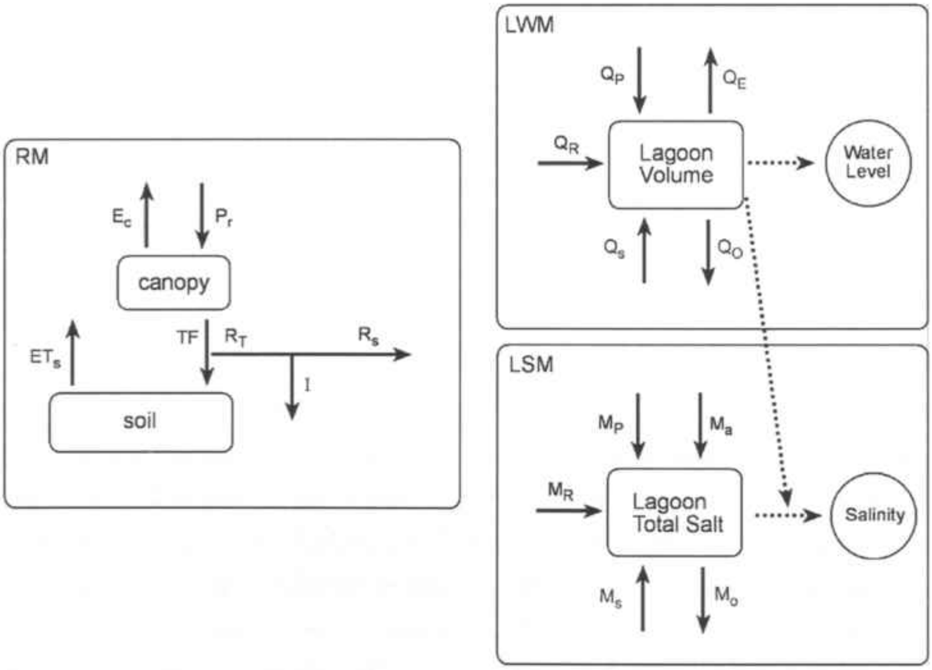


Figure 2.2. Schematic diagram of the Albufera des Grau hydrological model. The watershed model (RM) generates runoff inputs to the lagoon water model (LWM), from which the water level is computed. The salt mass model in the lagoon (LSM) together with the LWM allows the calculation of lagoon water salinity. Symbols are as follow: P_r: precipitation; E_C: evaporation in the canopy; TF: throughfall; ET_S: evapotranspiration from the soil; R_T: total runoff; I: infiltration; R_S: surface runoff; Q_P: direct rainfall; Q_R: stream runoff; Q_E: evaporation; Q_S: seawater flow; Q_O: lagoon outflow; M_P: salt input from precipitation; M_R: salt input from stream runoff; M_a: atmospheric deposition of salt; M_S: salt input from seawater flow; M_O: salt output due to lagoon outflow.

The evaporation of the water stored in the canopy E_c (mm d^{-1}) was calculated as (Deardorff 1978 in Döll et al. 2003):

$$E_c = ET_o\left(\frac{S_c}{S_{C\max}}\right)^{2/3} \qquad \text{Eq. (2.3)}$$

where ET_o is potential evapotranspiration (mm d^{-1}), and $S_{c\max}$ is the maximum water stored in the canopy (mm). $S_{c\max}$ was calculated assuming that each leaf is covered by a 0.3 mm-thick water film

(Döll et al. 2003):

$$S_{c\max} = 0.3 \cdot LAI \qquad \text{Eq. (2.4)}$$

where *LAI* is the average Leaf Area Index. A constant value of 3 was taken for *LAI* from GIS data of land cover in the catchment (authors' unpublished data). Throughfall F (mm d^{-1}) was calculated from the daily balance between precipitation and E_c.

Potential evapotranspiration ET_o (mm d^{-1}) was calculated from the Penman-Monteith equation (Penman 1948) for the energy and mass balance during evaporation of water following the FAO guidelines (Allen et al. 1998):

$$ET_o = \frac{0{,}408\Delta(R_n - G) + \gamma_c \dfrac{900}{T + 273} u(e_s - e_a)}{\Delta + \gamma_c(1 + 0{,}34u)} \qquad \text{Eq. (2.5)}$$

where Δ is the slope of the saturation vapour pressure curve (kPa °C^{-1}), R_n is net radiation on the soil surface (MJ m^{-2} d^{-1}), G is soil heat flux density (MJ m^{-2} d^{-1}), γ_c is the psychrometric constant (kPa °C^{-1}), T is mean daily air temperature (°C), u is wind speed (m s^{-1}), e_s is saturation vapour pressure (kPa) and e_a is actual vapour pressure (kPa). Net radiation R_n corresponds to the difference between the incoming net shortwave radiation R_{ns} and the outgoing net longwave radiation R_{nl} (Allen et al. 1998). Net shortwave radiation R_{ns} was calculated as (Allen et al. 1998):

$$R_{ns} = (1 - \alpha_c)R_{si} \qquad \text{Eq. (2.6)}$$

where R_{si} is the estimated incoming radiation and α_c is the albedo coefficient (set to 0.18; Linacre 1992). Details of the computation of R_{si}, R_{nl}, G, γ_c, Δ, e_s and e_a from air average, maximum and minimum temperature, relative humidity and wind speed can be found elsewhere (Allen et al. 1998; Xu and Singh 2001).

The water balance in the soil (Eq. (2.2)) was calculated using the throughfall, the water content of the soil, the total runoff, and the evapotranspiration from the soil ET_s (mm d^{-1}). Evapotranspiration from the soil was calculated as (modified from Döll et al. 2003):

$$ET_s = (ET_o - E_c)\frac{S_s}{S_{s\max}} \qquad \text{Eq. (2.7)}$$

where $S_{s\max}$ is the soil water capacity (mm). The value of $S_{s\max}$ for the soils of the watershed was taken from Estradé (2003).

Total runoff R_T (mm d^{-1}) was calculated as (Bergström 1995 in Döll et al. 2003):

$$R_T = (P_r - E_c)\left(\frac{S_s}{S_{s\max}}\right)^{\gamma} \qquad \text{Eq. (2.8)}$$

where P_r is rainfall (mm d^{-1}), and γ is a calibration parameter. The ratio $S_s/S_{s\max}$ determines the fraction of throughfall that is derived to runoff (Döll et al. 2003).

Total runoff was divided into surface runoff R_s (mm d^{-1}) and infiltration I (mm d^{-1}). Infiltration was considered as a fraction of the total runoff as $I = c_I R_T$, and c_I was used as a calibration parameter.

The lagoon water submodel (LWM)

A simple one-dimensional model was developed to simulate the water balance in the lagoon. For each time step, a balance between the inputs and the outputs in the lagoon was performed assuming an instantaneous (one-day) effect. All the fluxes in the LWM were calculated in m^3 d^{-1} and the volume of the lagoon V (m^3) was transformed to water level WL (cm a.s.l.) using the hypsographic curve of the lagoon (authors' unpublished data). The water balance equation is:

$$\frac{dV}{dt} = Q_P + Q_R + Q_s - Q_E - Q_o \qquad \text{Eq. (2.9)}$$

where Q_P is direct rainfall on the lagoon, Q_R is stream runoff, Q_s is seawater flow, Q_E is evaporation and Q_o is lagoon outflow.

Runoff inputs Q_R were calculated from R_s (the surface runoff of the WM) and the surface of the watershed (56 km^2). Direct precipitation on the lagoon Q_P was calculated from rainfall P (mm d^{-1}) and lagoon surface (ha) at each time step. Similarly, Q_E was calculated from the surface of the lagoon and the evaporation rate (E, in mm d^{-1}). The Penman equation (Eq. (2.5)) multiplied by a calibration parameter c_E, was used to calculate E assuming an albedo of 0.08 for water (Stumpf et al. 1999; Linacre 1992). The effect of salinity on evaporation was considered negligible for the range of salinity observed in the lagoon (Asmar and Ergenzinger 1999).

The fluxes between the lagoon and the sea (Q_S and Q_o) were computed with a simple hydraulic formula assuming a free-orifice flow (USBR 2001; Chauvelon et al. 2003):

$$Q = kA\sqrt{h} \qquad \text{Eq. (2.10)}$$

where Q is the discharge (m^3 s^{-1}), A is the area of the sluice opening (m^2), h is the height of the water column (m) and k is a calibration parameter that includes the gravity and the contraction and velocity coefficients of the free-orifice flow (USBR 2001). The model distinguished between two types of flow: a massive flow corresponding to the sluice opening (Q_{om} and Q_{sm}) and a flow resulting from filtration through the dam (Q_{of} and Q_{sf}). Massive lagoon outflow Q_{om} takes place when the water level is above a critical water level (WL_{om}) and the sluice is open. This flow results from the management of the sluice and reproduces the natural overflow of the lagoon at very high water levels. In this case, the height of the water column *h* in Eq. (2.10) was calculated from the difference between *WL* and WL_{om}, the sluice opening *A* was set to 2 m^2 and a calibration parameter K_{om} was used. On the other hand, the lagoon outflow resulting from filtration (Q_{of}) was computed when *WL* was above the critical level that results in filtration (WL_{of}); *h* was then computed from the difference between *WL* and WL_{of}. In this case, *A* was set to 0.025 m^2 and a specific calibration parameter (K_{of}) was used.

Seawater inflow (Q_s) only occurs when the lagoon is below sea level ($WL<0$). This flow was composed by a massive seawater flow (Q_{sm}) and a filtration flow (Q_{sf}). For the computation of Q_{sm}, a critical water level WL_{sm} was considered, below which, the sluice is opened. In this case *h* was calculated from the difference between *WL* and WL_{sm}, and a calibration parameter K_{sm} was used. Massive seawater inputs caused by extremely low water levels in the lagoon occur when the dam is opened to avoid littoral desiccation and large-scale mortality of macrophytes (Obrador et al. 2007). The natural equivalent of this flux occurs when the sand-bar naturally opens under pressure exerted by seawater in the channel. For Q_{sf}, *h* was calculated directly from *WL*, and K_{sf} was used as a calibration parameter. The values of *A* for the massive and the filtration flows were taken as in the lagoon outflow (2 m^2 and 0.025 m^2 respectively). The critical water levels of outflow and seawater flow, WL_{om} and WL_{sm}, were also used as calibration parameters.

The lagoon salt mass submodel (LSM)

The LWM was coupled with a submodel of the salt mass in the lagoon (LSM). The water salinity (*S*, in g L^{-1}) was calculated from the total salt mass and the lagoon water volume. The salt mass balance equation was expressed as:

$$\frac{dTS}{dt} = M_P + M_R + M_a + M_s - M_o \qquad \text{Eq. (2.11)}$$

where TS is the total salt content in the lagoon (kg), M_P is the salt input from direct precipitation, M_R is the salt input from stream runoff, M_a is atmospheric deposition, M_s is the salt input from seawater flow, and M_o is the salt output caused by lagoon outflow. The fluxes in the LSM were expressed as salt loads (kg d^{-1}) and those fluxes related to water fluxes were calculated from the corresponding water volume (m^3 d^{-1}) and salinity (g L^{-1}) of each flux. Thus, M_P was computed from Q_P taking the value of 0.11 g L^{-1} for the salinity of rainwater (Alcalá-García 2005); M_R was computed from Q_R and the average salinity of the streams entering the lagoon (authors' unpublished data); M_s was estimated from Q_s and the mean seawater salinity (38 g L^{-1}), and finally M_o was derived from Q_o and the lagoon water salinity at the previous time step. Both M_s and M_o were calculated in the same way, independently of the massive or filtration type of flow. Dry deposition of sea aerosol was computed as a function of wind speed following Gustafsson and Franzen (1996):

$$M_a = c_D(0.728 \cdot e^{0.478u}) \cdot D^{0.011} / D^{0.024u} \qquad \text{Eq. (2.12)}$$

where M_a is the salt deposition (mg m^{-2} h^{-1}), D is the distance from the sea (m), u is wind speed (m s^{-1}) and c_D is a calibration parameter that was used to fit the calculated deposition into the reported range of annual salt deposition in the island of Menorca (Jansà 1982).

Table 2.1. Summary of the characteristics and relationships between the submodels (see text for details)

	Watershed (RM)	Lagoon Water Volume (LWM)	Lagoon Salt Mass (LSM)
State variables	canopy water S_c (mm) soil water S_s (mm)	Water Volume V (m^3)	Total Salt TS (kg)
Output variables	surface runoff R_S (mm)	Water level WL (cm a.s.l.)	Salinity S (g L^{-1})
Inputs			
Climatic Data	P_r, T, T_M, T_m, u, RH	P_r, T, T_M, T_m, u, RH	u
Variables	-	R_S (from RM)	Q_P, Q_R, Q_S, Q_O, V (from LWM)
Calibration parameters	γ, c_I	c_E, WL_{om}, K_{om}, WL_{of}, K_{of}, WL_{sm}, K_{sm}, K_{sf}	c_D

2.3.2 Climatic and lagoon data

Daily values of rainfall (P_r), average temperature (T), maximum and minimum temperature (T_M and T_m), relative humidity (RH) and wind speed (u) were obtained from the nearest (7 Km) meteorological station (Spanish Meteorological Institute).

Daily values of WL (cm a.s.l.) in the lagoon were measured with a fixed scale near the outlet channel and provided by the Albufera des Grau Nature Park. The gaps in the data set were always lower than 10 days and were corrected by linear interpolation. A WTW-Cond315i conductivity probe was used to determine the water salinity at six depths (0, 50, 100, 150, 200 and 250 cm) on a monthly basis using a fixed sampling station located in the centre of the lagoon. The salinity values used here correspond to the average salinity of the entire water column. The Albufera des Grau is vertically homogeneous most of the time with vertical stratifications only observed occasionally (Pretus and Obrador 2004). A weighted salinity to correct the differences in the volume of each depth layer was not used because differences with the non-weighted average are minimal even during the stratification events (Obrador and Pretus, unpublished data).

2.3.3 Calibration and validation

The model was calibrated from January 2002 to December 2005 by tuning the eleven parameters to get the best fit in *WL* and *S*. The model performance was evaluated with measures of "goodness of fit" and of the absolute error between the observed and predicted daily values of the model outputs (*WL* and *S*). Despite its limitations (Legates and McCabe 1999) the coefficient of determination R^2 between the observed and predicted values was used as a first measure of the goodness of fit for the model. The modified coefficient of efficiency E_1 (Nash and Sutcliffe 1970 in Legates and McCabe 1999) was also used:

$$E_1 = 1 - \frac{\sum |O_i - P_i|}{\sum |O_i - \overline{O}|} \qquad \text{Eq. (2.13)}$$

where O_i and P_i are the observed and predicted values of the variable (*WL* or *S*) at each time step *i*, and $\overline{O}$ is the mean of the observed values of the variable.

The root mean square error (RMSE) and the Mean Absolute Error (MAE) were used as estimates of the absolute error:

$$RMSE = \sqrt{\frac{1}{n} \sum (O_i - P_i)^2} \qquad \text{Eq. (2.14)}$$

$$MAE = \frac{1}{n} \sum |O_i - P_i| \qquad \text{Eq. (2.15)}$$

where n is the number of observations.

A sensitivity analysis of the lagoon state variables (*V* and *TS*) and of the output variables (*WL* and *S*) was performed by running the model with a +10% and -10% relative change in the parameters. A sensitivity index was calculated for *V* and *TS* (Haefner 2005):

$$SI_k = \frac{1}{n} \frac{\sum \left(|P_i - P_i'| / P_i \right)}{0.1} \qquad \text{Eq. (2.16)}$$

where SI_k is the standardised sensitivity index of the variable (*V* or *TS*) to a change of 10% in the parameter k, P_i is the value of the variable at the nominal value of the parameter, and P_i' is the value of the variable at the modified value of the parameter.

The sensitivity of the output variables *WL* and *S* was expressed as RMSE:

$$S_k = \sqrt{\frac{1}{n}\sum\left(P_i - P_i'\right)^2} \qquad \text{Eq. (2.17)}$$

where S_k is the sensitivity of the variable (*WL* or *S*) to a change of 10% in the parameter k. For both SI_k and S_k the average of the measure for 10%-increase and 10%-decrease runs was computed.

The model was validated for the years 2001 and 2006, and the model performance was assessed and compared to the results of the calibration.

2.3.4 Historical data

Data of water salinity for the period 1975-2000 were used to assess the capability of the model to predict long term changes in the salinity of the lagoon and to determine the mean annual water and salt budgets. The observed data set consisted of irregular records of water salinity obtained from several sources, including published literature (Pretus 1989; Pretus et al. 1992), technical reports (Moyà et al. 1988; Pretus 1996; Pretus and Obrador 2004) and authors' unpublished data. In some cases, the methodology or the exact sampling date for a given salinity value were missing or unclear, in which case, the salinity value was assigned to the central day of the reported period (month or season). The mean annual water and salt budgets in the Albufera des Grau were calculated from the model outputs for the period 1975-2006 and hydrological years (from September to August) were used.

2.4. Results

2.4.1 Model performance

The calibration of the model resulted in a general good agreement between the observed and predicted values of the output variables (Fig. 2.3). For water level, both the marked seasonal trend and the range of variable were correctly simulated. The upper limit of *WL* during the torrential events (e.g. February 2003 and October 2003) was slightly underestimated, but the timing of the events closely agreed with the observed data. A negative slope in the *WL* trend was correctly reproduced during the dry season due to evaporation in the lagoon. The R^2 coefficient for *WL* was 0.84, and the coefficient of efficiency E_1 was 0.62 (Table 2.2). For salinity, the seasonal trend was correctly simulated and a good agreement between the simulated and observed series was achieved (Fig. 2.3). The R^2 and E_1 coefficients computed for salinity were 0.87 and 0.62, respectively. In terms of the absolute error, the model outputs showed a RMSE of 11 cm (MAE of 8 cm) for *WL*, and 1.8 g L^{-1} (MAE of 1.5 g L^{-1}) for *S* (Table 2.2).

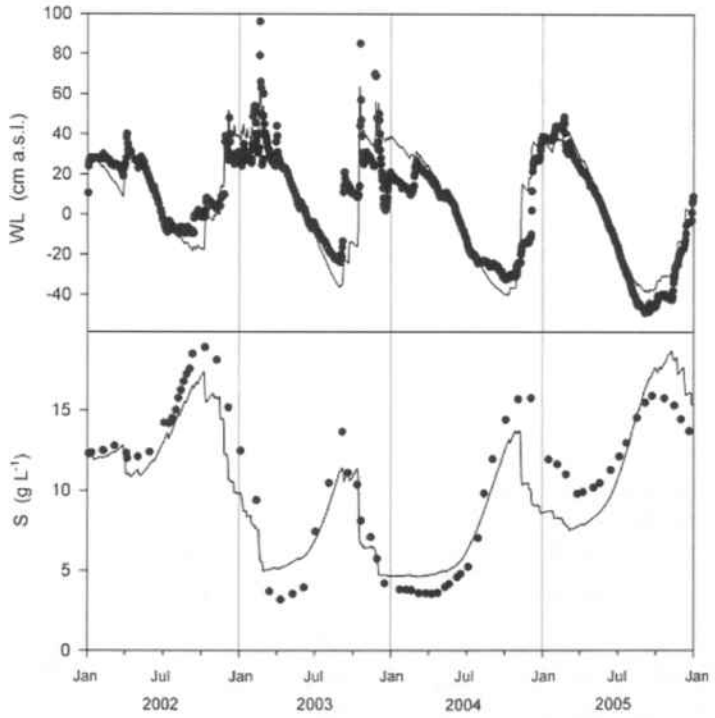


Figure 2.3. Temporal variation in the observed (dots) and predicted (line) values of water level and salinity for the calibration period.

Table 2.2. Measures of model performance based on the comparison between the observed and predicted values of WL and S. The R2 coefficient, the Efficiency coefficient (E1), the Root Mean Square Error (RMSE) and the Mean Absolute Error (MAE) are shown for the calibration (2002-2005) and validation (2001 and 2006) periods.

		Calibration	Validation 2001	Validation 2006	Whole period
R^2					
	Water Level	0.84	0.86	0.98	0.89
	Salinity	0.87	0.82	0.94	0.69
RMSE					
	Water Level	11.0	13.5	5.7	10.4
	Salinity	1.8	3.1	5.3	3.6
MAE					
	Water Level	8.0	8.9	4.9	7.6
	Salinity	1.5	2.6	4.4	2.8
E_1					
	Water Level	0.62	0.66	0.83	0.55
	Salinity	0.62	0.12	-0.56	0.52

The results of the sensitivity analysis carried out on the parameters of the model are summarised in Table 2.3. The sensitivity of the state variables was always below 0.5 for *V* and below 3 for *TS*, which means that the response of the model to a 10% change in any parameter is below 5% for *V* and below 30% for *TS*. The equivalent sensitivity in terms of RMSE in the output variables was 5.5 cm for *WL* and 3.2 g L^{-1} for *S*. The *WL* was not sensitive to any parameter of the LSM submodel. The highest sensitivities were found on parameters of the RM and LWM submodels, being *WL* and *S* most sensitive to c_I. The model showed low sensitivity to changes in the initial values of the state variables.

Table 2.3. Sensitivity of the state variables to a 10% change in the parameters. The sensitivity of *WL* and *S* is expressed as the average RMSE of the 10%-increase and 10%-decrease runs of the model. (^{c}: calibration parameter)

			Sensitivity Index		Sensitivity (RMSE)	
	Parameter	Value	*V*	*TS*	*WL* (cm)	*S* (g L^{-1})
RM						
	c_I ^{c}	0.799	0.26	2.96	5.5	3.2
	S_{smax}	100 mm	0.05	0.29	1.2	0.3
	γ ^{c}	3.093	0.05	0.26	1.0	0.3
	albedo watershed	0.18	0.02	0.17	0.4	0.2
	initial S_s	60 mm	0.01	0.05	0.4	0.1
LWM						
	c_E ^{c}	0.796	0.22	0.95	3.7	1.5
	initial *WL*	24 cm	0.08	0.39	3.0	0.7
	WL_{om} ^{c}	40	0.13	0.13	2.4	0.2
	A (filtration)	0.025 m^2	0.05	0.31	0.9	0.4
	K_{of} ^{c}	1.467	0.05	0.07	0.8	0.1
	K_{sf} ^{c}	0.895	0.03	0.24	0.7	0.3
	albedo water	0.08	0.02	0.07	0.3	0.1
	K_{om} ^{c}	1.224	0.01	0.01	0.2	0.0
	WL_{of} ^{c}	7.4 cm	0.01	0.03	0.2	0.0
	A (massive flow)	2 m^2	0.00	0.42	0.2	0.0
	K_{sm} ^{c}	0.689	0.00	0.00	0.0	0.0
	initial *S*	12.4 g L^{-1}	0.00	0.42	0.0	0.6
	WL_{sm} ^{c}	-62 cm	0.00	0.00	0.0	0.0
LSM						
	Seawater salinity	38 g L^{-1}	0.00	0.35	0.0	0.5
	Stream salinity	1.9 g L^{-1}	0.00	0.22	0.0	0.2
	Rainfall salinity	0.11 g L^{-1}	0.00	0.00	0.0	0.0
	c_D ^{c}	12.3	0.00	0.00	0.0	0.0

The validation of the model for 2001 and 2006 resulted in an overall good agreement between the observed and the predicted values (Fig. 2.4). The R^2 for *WL* and *S* were similar to, and at times higher than, those obtained with the calibration data set (Table 2.2). The RMSE for *WL* was 13.5 cm and 5.7 cm for 2001 and 2006, respectively. Nevertheless, results for salinity did not match the observed data very precisely, and despite the high R^2 coefficients, the RMSE was twice that found in the period 2002 to 2005 (3.1 g L^{-1} and 5.3 g L^{-1} for 2001 and 2006, respectively; Table 2.2). The poor match between observed and predicted salinity was especially apparent during 2006, when a negative efficiency coefficient was found. This indicates that the simulated salinity is not as good a predictor as the mean of the observed data (Legates and McCabe 1999). It is likely that the differences found for *S* in 2006 are related to an overestimation of the variable at the end of the year (Fig. 2.4).

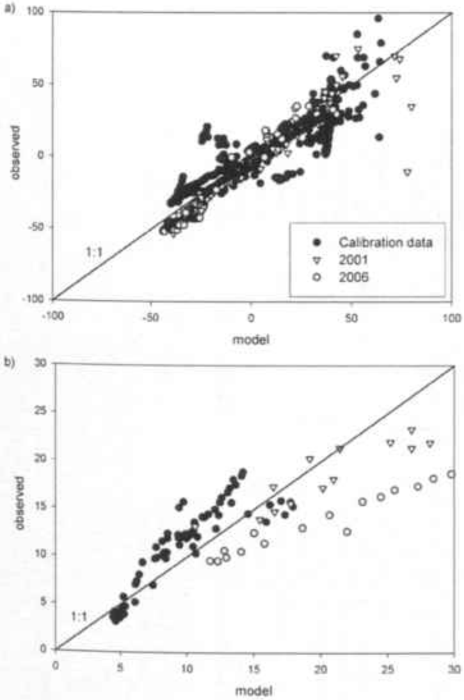


Figure 2.4. Scatterplot of the predicted water level (a) and salinity (b) for the calibration and validation periods.

2.4.2 Historical period

The salinity predicted by the model for the period 1975-2000 showed a clear seasonal trend but an important inter-annual variability was observed (Fig. 2.5). The range of the modelled salinity corresponded with the available observed data. The model correctly simulated the hyperhaline period ($S>40$ g L^{-1}) observed in the lagoon during 1994 and 1995, and it also successfully predicted the recovery of the polyhaline range (18-30 g L^{-1}) observed in the following years.

The water balance in the watershed was dominated by evapotranspiration, which accounted for 82% of the total water outputs in the catchment (Table 2.4). Surface runoff only accounted for 4% of the total annual precipitation on average. However, the daily runoff ratio (i.e. ratio between runoff and precipitation) was between 0.1% and 16% (mean 3%), which indicates that a higher proportion of precipitation turned into runoff during certain precipitation events.

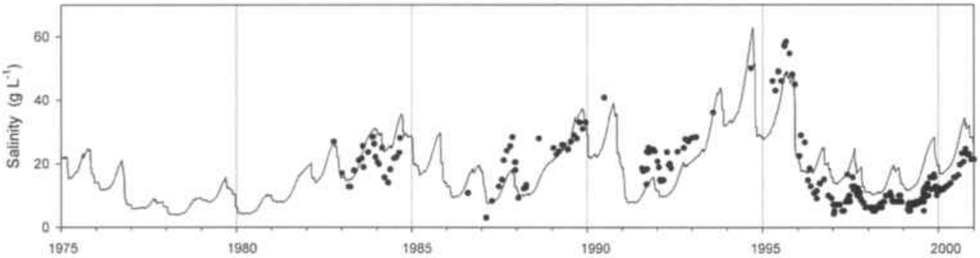


Figure 2.5. Temporal variation of the predicted (line) and observed (dots) water salinity for the period 1975-2000.

Table 2.4. Average annual water budgets (mean ± s.d.) in the watershed for the period 1975-2006. The mean of the percent contribution of each flux to total annual outputs is shown in brackets.

Component	Water budget (mm)	
Rainfall	549 ± 136	(100%)
Evapotranspiration	437 ± 76	(82%)
Infiltration	88 ± 56	(14%)
Runoff	22 ± 14	(4%)

Table 2.5. Average annual water and salt budgets (mean ± s.d.) in the Albufera des Grau during the period 1975-2006. The mean of the percent contribution of each flux to total annual inputs or outputs is shown in brackets.

Component	Annual Water Flux (x 1000 m^3)		Annual Salt Flux (x 1000 kg)	
Rainfall	387 ± 118	(27%)	43 ± 13	(0.7%)
Runoff	970 ± 602	(59%)	1844 ± 1178	(27%)
Seawater inflow	153 ± 75	(14%)	5808 ± 2582	(72%)
Aerosol deposition	-		16 ± 4	(0.3%)
Outflow	692 ± 637	(38%)	7798 ± 6616	(100%)
Evaporation	823 ± 39	(62%)	-	

The lagoon annual water and salt budgets for the period 1975-2006 are shown in Figure 2.6. High variability in the water budget was observed between years, especially in those fluxes directly or indirectly related to precipitation: rainfall and runoff, and lagoon outflow, respectively. Evaporation was the most constant water flux with values of $823 \cdot 10^3 \pm 39 \cdot 10^3$ m^3. Stream runoff and direct precipitation accounted for an average of 59% and 27%, respectively, of total water inputs (Table 2.5). Evaporation played an important role in the water balance and was the most important water output (an average of 62% of the total water outputs; Table 2.5). From the total annual water inputs (mean 1.51 hm^3) and the mean water volume in the lagoon (1.03 hm^3) the mean water residence time was calculated as 8 months.

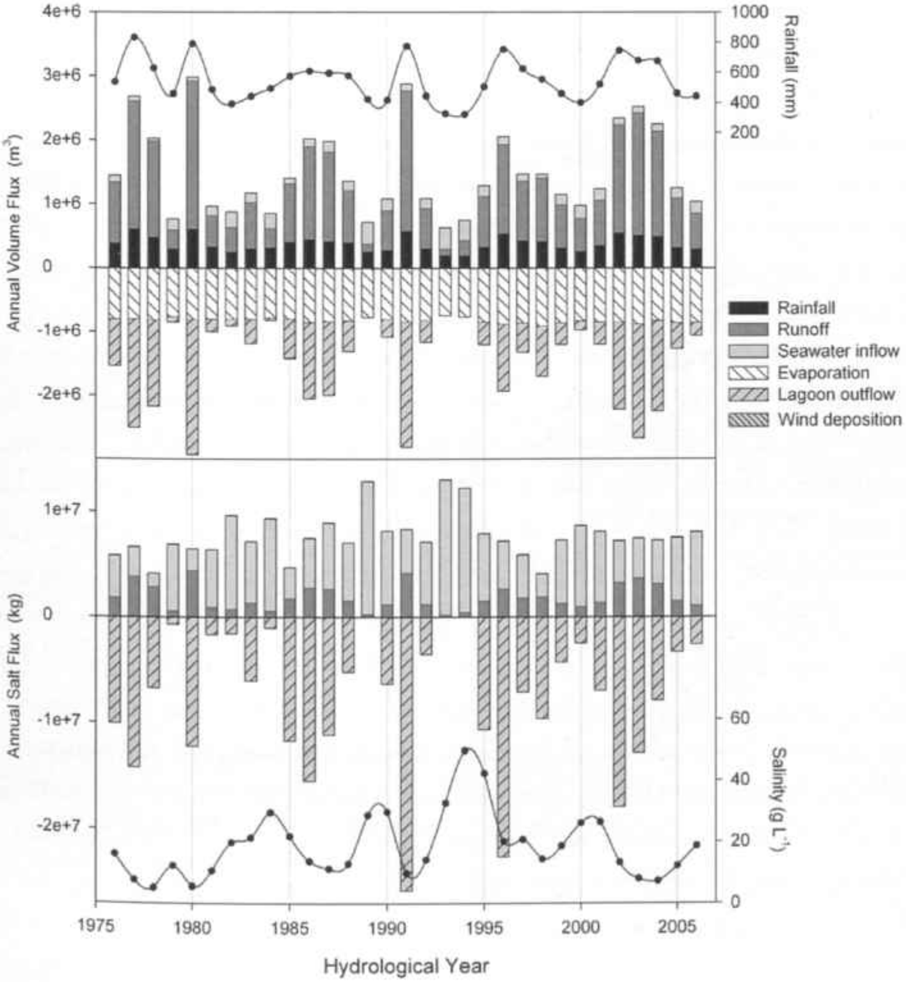


Figure 2.6. Annual water and salt budgets in the lagoon for the period 1975-2006. The annual precipitation and mean summer salinity are also shown for each hydrological year

The salt budget also reflected the high inter-annual variability observed in the water fluxes (Fig. 2.6). The salt inputs from direct rainfall and marine aerosol deposition had a negligible effect on the annual salt balance, and seawater inflow was responsible for an average of 72% of the annual salt inputs (Table 2.5). It is important to highlight that the contribution of the salt input from the watershed accounted for 27% of the total salt inputs on average (Table 2.5). The salt evacuation associated to the lagoon outflow was highly variable and was negligible in some years with very low water levels (1993 and 1994; Fig. 2.6).

During the historical period the mean annual salinity was related to the total precipitation of the previous hydrological year (Fig. 2.7a). From the relationship between the change in the mean annual salinity and the total annual precipitation (Fig. 2.7b), an "equilibrium" precipitation was calculated as 547 mm. This precipitation corresponded to the annual precipitation that would be necessary to maintain the lagoon without an inter-annual trend in salinity.

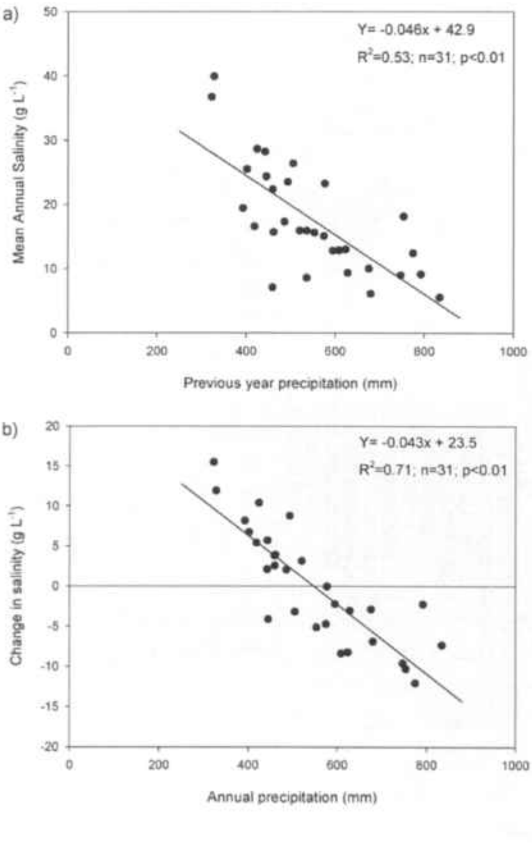


Figure 2.7. Relationships between mean annual salinity and total precipitation of the previous year (a), and between the change in the mean annual salinity and total annual precipitation (b). Each point corresponds to a hydrological year for the period 1975-2006.

2.5. Discussion

The model correctly simulated the basic hydrological processes of the lagoon. The seasonal trends were correctly simulated, and a reasonable adjustment between the observed and the predicted series of both *WL* and *S* was obtained. The model outputs showed low sensitivity to changes in most of the parameters or in the initial values of *WL* and *S*, and the highest sensitivities were observed in the parameters of the runoff submodel.

With regard to the lagoon model, the mean MAE for *WL* was 7.6 cm, which is an acceptable value given the range of variation of *WL* and the depth distribution of macrophytes (Obrador et al. 2007). On average, the RMSE was 30% higher than the MAE for *WL*, indicating the presence of outliers in the series. These outliers corresponded to the peaks in *WL* during the torrential events, which were slightly underestimated. Given the higher sensitivity of the model to the parameters of the runoff submodel, an inaccurate prediction of the torrential inputs is suggested. This could be due to spatial heterogeneity in the rainfall, which is described as being important in the island (Jansà 1979). More probably, the inaccurate prediction of the torrential events may be explained by the spatially averaged approach used to model the watershed. More detailed approaches based on a spatially explicit hydrology of the watershed would help to improve the accuracy of the model during such torrential events. This would be desirable if nutrient loads are to be calculated, since most of the nitrogen inputs enter the lagoon during these events (authors' unpublished data). However, despite the inaccuracies in the peaks, the model correctly predicted the dynamics of *WL*, properly adjusting the slope during the dry season and giving the appropriate response when the lagoon had low *WL* values. Moreover, the hydrology of the watershed was realistic in terms of the annual water budget. The mean annual water balance in the watershed for the historical period (considering hydrological years) was similar to the water budgets for the island of Menorca reported in the literature (Fayas 1999; Estradé 2003). Furthermore, the runoff ratio (below 16%) was within the reference values for similar Mediterranean areas (Martin-Vide et al. 1999; Rulli et al. 2006).

With regard to salinity, the model correctly simulated the temporal dynamics and the range of the variation of the variable. The mean MAE for the whole period was 2.8 g L^{-1}, which is acceptable for the management of the lagoon. Despite a good agreement was obtained in the calibration, a significant overestimation of salinity was observed in the validation of the year 2006 (Fig. 2.4). This could be due to a misdetermination of the water fluxes between the lagoon and the sea. It is important to highlight that the wood sluices were changed the previous winter, which could have changed the flow conditions for the year 2006 and the end of 2005 (M. Truyol, pers. comm., 2007). On the other hand, assuming a constant level of salinity for each water flux could also be criticised. Firstly, the salinity of the so-termed seawater inflow does not actually correspond to the salinity of seawater because intense evaporation and dilution can occur all along the outlet channel, which is intermittently connected to the sea. Similarly, it is unrealistic to assume constant stream salinity because it naturally decreases with discharge. A variable salinity was not used because robust data of the salinity-discharge relationship for the streams of the Albufera des Grau was not available; using it otherwise would have added another element of uncertainty to the model. The salinity of the lagoon outflow is also subject to a certain degree of variation because during very intense torrential events the output salinity can be slightly higher than the average salinity of the lagoon. This is explained by incomplete mixing and a forced hypolimnetic discharge (Pretus and Obrador 2004). Nonetheless, the very simple hydraulic equations used in the model resulted in a reasonable degree of accuracy in the determination of the seasonal dynamics and the range of variation of water salinity. Moreover, the simulation of the historical period 1975-2000 revealed that the model could predict long-term dynamics in the salinity of the lagoon. The low quality of the historical salinity data set prohibited a formal validation of the salinity simulation, and only the range of the variable was considered. High salinity ranges (30-40 g L^{-1}) and even a hyperhaline period in the lagoon (years 1994 and 1995) was correctly simulated despite the model being calibrated in a much lower range (between 2 and 20 g L^{-1}).

In conclusion, the model is believed to be a useful tool to simulate the dynamics of water level and salinity in the Albufera des Grau. Both variables have substantial ecological significance and are highly informative descriptors of the risk of critical situations such as the hypersalinisation of the lagoon and the littoral desiccation due to low water levels, both with severe adverse effects on the macrophyte meadows and the fish community (Cardona 2000; Pretus 2003). Numerous models have been developed to simulate the hydrology of Mediterranean costal lagoons; most of them are two- or three-dimensional models designed to describe circulation patterns resulting from wind, river or tidal forcing (Covelli et al. 2002; Chauvelon et al. 2003; Umgiesser et al. 2004; Ferrarin and Umgiesser 2005; Marinov et al. 2006; Niedda and Greppi 2007). In the Albufera des Grau, a detailed hydrodynamic model would be useful in describing the risk of haline stratification and bottom anoxia. It would also be useful to evaluate the suitability of different management strategies related to the height of the sluice opening (Pretus 2003). Nonetheless, in the case of the Albufera des Grau, an enclosed lagoon without tidal influence, the fluctuations in water level are driven mainly by the precipitation-evaporation regime. In this context, and given the existing difficulties in applying detailed two- or three-dimensional models for shallow waters (D'Alpaos and Defina 2007), a simple model referred not to hydrodynamics but to the water and salt balances would be the most appropriate approach. This is especially relevant in the absence of a robust dataset for the hydrology of the system, as in the case of the Albufera des Grau. In this sense, the advantage of the model comes from its simplicity and the fact that it does not require a large data set (Jørgensen and Bendoricchio 2001).

The results of the simulations during the historical period allowed us to determine the water and salt budgets in the lagoon on an annual basis. As expected, the salt fluxes were characterised by a dependence on the water fluxes, and the direct aerosol deposition on the lagoon was insignificant in the annual salt budget. Despite the high inter-annual variability observed in the water fluxes, total water input was dominated by the runoff input (59% of total water inputs) followed by direct rainfall (27%) and seawater inflow (14%). Evaporation accounted for 62% of the water outputs in the lagoon, however, its temporal dynamics combined with the seasonality of the precipitation, appeared to determine the temporal trend in water level and salinity.

In this study, a description of the annual water budget of the lagoon is given as a first application of the model outputs. A detailed exploration of the hydrological processes that control the dynamics in *WL* and *S* was not within the purpose of this paper. Nonetheless, a brief exploration into the inter-annual variability in salinity revealed a clear relationship with the total annual precipitation. The hypersalinisation of the years 1994 and 1995 occurred after two consecutive dry years characterised by annual precipitation below 400 mm. The low freshwater inputs were responsible for a null outflow over a two–year period (1993 and 1994), thus increasing the total salt in the lagoon and consequently water salinity.

By establishing the relationship between precipitation and water salinity (Fig. 2.7) the level of annual precipitation required to maintain a constant salinity in the lagoon could be calculated. The resulting "equilibrium" precipitation was 547 mm, which is very close to the mean annual precipitation during the historical period (549 ± 136 mm; Table 2.4). This suggests that the springs that supplied permanent freshwater inputs to the streams, which suffered drought in the 1960s, are not essential in maintaining the lagoon in an optimal state. These findings are in accordance with previous observations (Pretus 2003). The corresponding salinity at "equilibrium" precipitation is 17.7 g L^{-1}, which is an appropriate salinity target for the management of the lagoon and thus indicates the inappropriateness of any management targets significantly outside this value. However, this should be confirmed by a detailed evaluation of the seasonal timing of the fluxes and not just by conclusions based on annual averages. Historical records with information on the ecological status of the lagoon during the last decades, together with palaeolimnological studies designed to reconstruct the palaeosalinity of the system, may also improve the understanding of the hydrology of the lagoon before the anthropogenic alteration of the water cycle in the watershed.

2.6. Conclusions

The model simulated the dynamics of the hydrological descriptors of the Albufera des Grau coastal lagoon with reasonable accuracy. Both the timing, with a marked seasonal trend, and the range of water level and water salinity were accurately modelled with low sensitivity to parameter changes. The simulations carried out over a period of 30 years accurately predicted the long term range of variation of salinity in the lagoon, even at salinity levels above the usual range of variation. The simplicity of the model and the fact that it does not require a large data set makes it an attractive tool for lagoon management in assessing the risk of adverse ecological situations in the lagoon. However, the model cannot accurately predict torrential water inputs; this would probably require a more explicit approach in the modelling of the watershed hydrology. The model made it possible to describe the annual water and salt budgets, which were characterised by high inter-annual variability.

2.7. Acknowledgements

This project was funded by the Consell Insular de Menorca. BO was supported by a BRD grant from the University of Barcelona. We would like to thank the staff of the Albufera des Grau Nature Park for their assistance in the field work. We would also like to thank Sonia Estradé (Social and Environmental Observatory of Menorca) for providing data on watershed edaphology. We are very grateful to Rafa Marcè and Salva Pueyo for their valuable assistance during the modelling process. Finally, we would like to thank Prof. S.E. Jørgensen for his valuable comments and suggestions during the early stages of this project.

Chapter 3

Light regime and components of turbidity in a Mediterranean coastal lagoon

ABSTRACT / RESUM / RESUMEN

Obrador, B. and Pretus, JLl. 2008. Light regime and components of turbidity in a Mediterranean coastal lagoon. *Estuarine, Coastal and Shelf Science* 77: 123-133

The underwater light regime of a Mediterranean coastal lagoon (Albufera des Grau, Balearic Islands) was studied during four years in order to characterise the spatial and temporal variations in the light attenuation coefficient (K) and to assess the relative contribution of the different water components to total light attenuation.

During the studied period K averaged 1.42 m^{-1} and ranged from 0.63 m^{-1} to 3.80 m^{-1}. High temporal variability was observed in light attenuation coefficients, but the lagoon was spatially uniform. Percentage bottom irradiance in relation to specific requirements for the dominant macrophyte species (*Ruppia cirrhosa*) was used as an indicator of benthic light limitation. Macrophyte light limitation was expected to occur in the deepest areas of the lagoon during winter, the most turbid period of the annual cycle. During the macrophyte growing season, higher bottom irradiances were observed but a significant percentage of the lagoon benthos (17% in spring and 7% in summer) was expected to be light limited. In the deepest areas of the lagoon (>2m) changes in bottom irradiance were related more to variations in the light attenuation coefficient than to variations in water level. However, water level appeared to play an important role in determining benthic light limitation at intermediate depths (1.5 m) for the range of K from 1.8 m-1 to 3.3 m^{-1}. The partitioning of the light attenuation coefficient showed that phytoplankton was the main driver of the temporal dynamics of K, but only accounted for 44% of total light attenuation on average. The mean contributions of the other water components to K were: DOC (47%), tripton (6%), and water (3%). At low values of K, attenuation by DOC was responsible for up to 75% of total attenuation. An equation to predict K from the concentration of water components explained 93% of the variance.

RESUM (*en català*)

En aquest treball es presenta un estudi del clima lumínic d'una llacuna litoral Mediterrània (Albufera des Grau, Illes Balears). Durant quatre anys es va caracteritzar la variabilitat espacial i temporal en el coeficient d'atenuació vertical de la llum (*K*) i es va determinar la contribució relativa dels diferents components de l'aigua implicats en l'atenuació total de la llum.

Durant el període estudiat, els valors de *K* van mostrar una elevada variabilitat temporal, mentre que a escala espacial no es van observar diferències significatives. Els valors observats de K es van moure entre 0.63 m^{-1} i 3.80 m^{-1}. La limitació lumínica al bentos es va avaluar a partir del percentatge de radiació en fondària en relació als requeriments lumínics específics per a l'espècie de macròfit dominant (*Ruppia cirrhosa*). Els resultats van mostrar que els macròfits poden patir limitació per llum a les zones més fondes de la llacuna durant l'hivern, que és el període més tèrbol de l'any. Durant primavera i estiu, períodes de màxim creixement macrofític, la llacuna mostrà respectivament, un 17% i un 7% de la superfície amb el bentos potencialment limitat per llum. La disponibilitat de llum en fondària a les zones profundes de la llacuna (>2m) estigué més relacionada amb canvis en la terbolesa de l'aigua (*K*) que amb variacions en el nivell de l'aigua. Tanmateix, a fondàries intermèdies (1.5 m), que suposen el 45% de la superfície de la llacuna, el nivell de l'aigua sí que va influir en la disponibilitat lumínica bentònica per a valors de *K* entre 1.8 m^{-1} i 3.3 m^{-1}. La partició de l'extinció de la llum mostrà que malgrat que el fitoplàncton és el responsable de la dinàmica temporal de *K*, només un 44% del valor promig d'atenuació de la llum a la llacuna s'explica pel component fitoplanctònic. La contribució mitjana dels altres components al valor de *K* fou: DOC (47%), tripton (6%) i aigua (3%). En situacions de baixa terbolesa, el DOC fou responsable de fins al 75% de l'atenuació de la llum. Amb aquests resultats es derivà una equació per a predir *K* a partir dels components de l'aigua explicant un 93% de la variança.

RESUMEN (*en castellano*)

Este trabajo presenta un estudio del clima lumínico de una laguna litoral Mediterránea (Albufera des Grau, Islas Baleares). Durante cuatro años se caracterizó la variabilidad espacial y temporal en el coeficiente de atenuación vertical de la luz (*K*) y se determinó la contribución relativa de los distintos componentes del agua implicados en la atenuación total de la luz.

Durante el período estudiado, los valores de *K* mostraron una elevada variabilidad temporal, pero no se observaron diferencias espaciales significativas. Los valores observados de *K* se movieron entre 0.63 m^{-1} i 3.80 m^{-1}. La limitación por luz en el bentos se evaluó a partir del porcentaje de radiación en el fondo de la laguna en relación con los requerimientos lumínicos específicos para la especie de macrófito dominante (*Ruppia cirrhosa*). Los resultados mostraron que la actividad de los macrófitos puede estar sometida a limitación por luz en las zonas más profundas de la laguna durante el invierno, que es el período más turbio del año. Durante la primavera y el verano, que son los períodos de crecimiento macrofítico, la laguna mostró respectivamente un 17% y un 7% de la superficie bentónica potencialmente limitada por luz. La disponibilidad de luz en el fondo de la columna de agua estuvo, para las zonas más profundas de la laguna (>2 m), más relacionada con cambios en la turbidez del agua (*K*) que con variaciones en el nivel del agua. Por contra, a profundidades intermedias (1.5 m) el nivel del agua sí que influyó en la disponibilidad lumínica bentónica para valores de *K* entre 1.8 m^{-1} y 3.3 m^{-1}. La partición de la atenuación de la luz mostró que a pesar de que el fitoplancton es el principal responsable de la dinámica temporal de *K*, éste sólo contribuye en promedio a un 44% de la atenuación lumínica. La contribución media de los otros componentes a *K* fue: DOC (47%), tripton (6%) y agua (3%). En condiciones de baja turbidez, el DOC fue responsable de hasta el 75% de la atenuación de la luz. A partir de estos resultados se obtuvo una ecuación para predecir *K* a partir de los componentes del agua explicando el 93% de la varianza.

3.1. Introduction

The underwater light environment is a fundamental factor in the ecology of aquatic ecosystems (Wetzel 2001). The quality and quantity of light in the wavelengths 400-700 nm (PAR, Photosynthetically Active Radiation), is crucial for the photosynthesis of benthic and pelagic primary producers (Kirk 1994). Underwater light availability depends on the properties of the incoming irradiance and on the behaviour of light in the aquatic medium (Kirk 1994). The attenuation of light with depth is quantified by the vertical attenuation coefficient, K, which is an Apparent Optical Property, AOP, in contraposition to the Inherent Optical Properties, IOP. The difference between AOPs and IOPs is that the latter depend only on the concentrations of the optically active components in water and not on the angular nature of the light field in the aquatic medium (Kirk 1994). The absorption coefficient, a, and the scattering coefficient, b, are both IOPs and have the same units as K (m^{-1}).

The attenuation of light with depth depends on the absorbance and scattering of photons, which in turn depend on the concentrations of the optically active constituents in the medium. Water components responsible for light attenuation are typically divided in three categories: the water itself, the particulate matter and the dissolved matter. The absorption by water typically contributes to a small fraction of the total absorption of light in natural aquatic systems, and its contribution to the scattering is negligible (Kirk 1994). Chromophoric Dissolved Organic Matter, CDOM (also known as gelbstoff, yellow substance or gilvin), is the coloured fraction of the total dissolved organic matter. Particulate materials (Total Suspended Solids, TSS, or seston) include both the organic (OSS) and inorganic (ISS) fractions. OSS can be divided into living (Phytoplankton) and non-living (Detritus) organic materials. The term Tripton refers to the sum of the non-living organic and inorganic particulate materials, and it is common to use the terms organic Tripton and inorganic Tripton to refer to detritus and inorganic suspended solids respectively.

In shallow aquatic ecosystems light availability plays an important role in the distribution and abundance of submersed aquatic vegetation. In shallow estuaries and coastal waters in particular light availability is a fundamental factor in the distribution of seagrasses and other benthic primary producers in relation to water depth (Dennison 1987).

Moreover, the underwater light regime is believed to be determinant in the alternative equilibria in shallow lakes, that is the existence of two stable states, one clear and one turbid, over different levels of nutrient concentrations (Scheffer et al. 1993). Although many stabilizing mechanisms appear to be involved (Weisner et al. 1997; Jeppesen et al. 1998; Scheffer 1998), one simple graphical illustration of the alternative stable states theory of shallow lakes is based upon water turbidity as the critical variable that describes the shift from one state to the other (Scheffer et al. 1993). Some of the reported stabilizing mechanisms are based on a limitation of macrophyte growth by light limitation due to attenuation of light by phytoplankton or by wind-induced sediment resuspension in the absence of macrophytes (Scheffer 1998). Characterising the underwater light environment can thus contribute to the understanding of the factors involved in the competence and dynamics of benthic and pelagic primary producers in any particular system.

In this paper the underwater light regime of a Mediterranean coastal lagoon is studied. The Albufera des Grau is a coastal lagoon located in the northeast coast of Menorca, Balearic Islands. The lagoon is the most extensive wetland of the island and was declared Nature Park in 1995. Severe dystrophic collapses due to massive mortality of the extensive macroalgal beds were reported in the 1980s (Pretus 1989). In recent years, the lagoon was described as a macrophyte dominated system with dense and extensive meadows of the euryoic macrophyte *Ruppia cirrhosa* (Obrador et al. 2007). Intense phytoplankton peaks are observed each year, usually related to the entrance of nutrients form the watershed or from the decomposition of the macrophyte meadows (Obrador et al. 2007).

The objective of the present study is to characterise the light regime in the Albufera des Grau coastal lagoon by describing the spatial and temporal variability in the light attenuation coefficients to determine the light availability for pelagic and benthic primary producers. Furthermore, the partial contribution of the different optically active water constituents to total light attenuation is also assessed by means of empirical partitioning methods to better understand the interannual phytoplankton-macrophyte equilibria.

3.2. Methods

3.2.1 Study site

The Albufera des Grau has a surface area of 78 ha and a volume of 1 Hm^3 (Fig. 3.1). The average depth is 1.37 m and it reaches a maximum of 3 m (Pretus 1989). Climate is typically Mediterranean, with a mean air temperature of 17 °C and 599 mm annual precipitation. Freshwater inputs are irregular and typically centred on autumn and winter. The lagoon is connected to the sea by a narrow channel 500 m long, where a small floodgate allows the regulation of the lagoon-sea connection when the sand-barrier is opened. Exchange with the sea is irregular and does not result in an important water renewal of the system. The water of the lagoon is oligo-mesohaline with a range of salinity between 5 and 20 during the last five years (salinity in practical salinity units). There is a marked seasonality in salinity and water level due to a naturally preserved Mediterranean evaporation/precipitation regime. Macrophyte meadows of *Ruppia cirrhosa* and *Potamogeton pectinatus* are found all along the lagoon except in the deepest areas (>2 m) and the dense littoral beds of *R. cirrhosa* in the Albufera des Grau have the highest biomass reported for this species (Obrador et al. 2007).

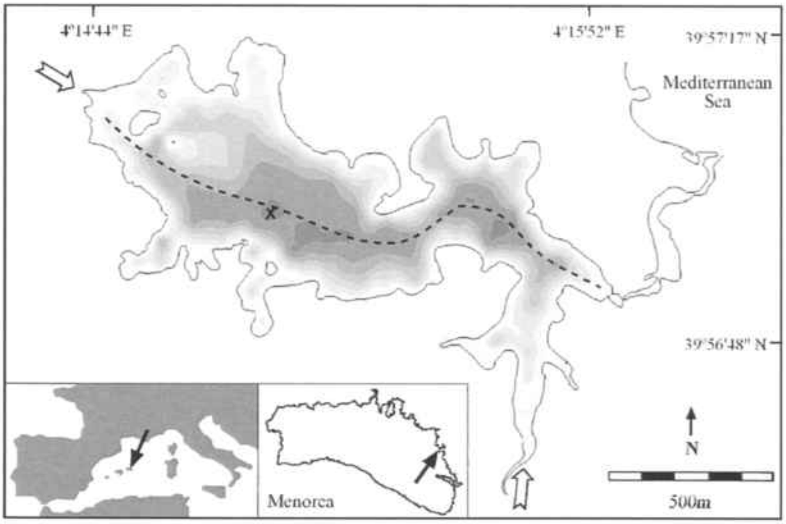


Figure 3.1. Location and bathymetric map (50 cm isobaths) of the Albufera des Grau coastal lagoon. The EW transect for the vertical profiles (dotted line) and the fixed sampling site (cross) are shown. Arrows correspond to the freshwater inputs.

3.2.2 Light attenuation coefficients

Monthly samplings of the lagoon were conducted from February 2001 to December 2004 to determine the spatial and temporal variability in the underwater light environment. The sampling design is part of a general research program to study phytoplankton-macrophyte dynamics. The vertical light attenuation coefficient was determined at five to seven sites distributed along the major axis of the lagoon (east-west), and their UTM coordinates were recorded with a GPS device (Fig. 3.1). The sampling sites were always in open water to avoid shading by macrophytes and covered the entire range of depths of the lagoon. At each site, Photosynthetically Active Radiation, PAR, was measured at different depths with a spherical quantum sensor (LI-193SA) for the measurement of diffuse light irradiance (in µmol m^{-2} s^{-1}). Measurements were done every 50 cm from surface to bottom, and two vertical profiles were conducted at each site. The vertical profiles of PAR were assumed to follow an exponential attenuation of irradiance with depth:

$$E_z = E_0 \cdot e^{-k \cdot z} \qquad \text{Eq. (3.1)}$$

where E_Z and E_0 are the scalar PAR irradiances at depth z (m) and below the water surface respectively, and K is the attenuation coefficient (m^{-1}). The values of K for each profile were determined by linear regression between depth and $\ln(E_z/E_0)$. Only those significant regressions ($p<0.05$) with $R^2>0.90$ were considered.

To test the statistical differences between sampling sites and dates, a nonparametric Kruskall-Wallis test was carried out with the factors EW coordinate and Date. The EW coordinate was categorised in four zones 200m wide.

3.2.3 Light availability for primary producers

For each sampling site the euphotic depth, the depth at which irradiance reaches 1% of E_0, was calculated from the measured light attenuation coefficient. The euphotic depth refers to the depth below which phytoplankton photosynthesis is expected to be light limited (Kirk 1994), but macrophytes are expected to have higher light compensation points in order to compensate for higher respiratory demands (Dennison 1987). Light availability for macrophyte growth was expressed as the percentage of surface irradiance reaching the bottom of the water column (Phlips et al. 1995b). It was calculated for each PAR profile from the light attenuation coefficient and the maximum depth of the site. Two values of bottom irradiance were taken from the literature as indicative of light limitation for macrophytes. A general value of 11% was selected from worldwide depth distribution of seagrasses (Duarte 1991) and a more specific value was selected for the dominant macrophyte species in the Albufera des Grau. The physiological light requirements described for *Ruppia cirrhosa* to maintain net production at the average water temperature of the lagoon is on the order of 3% (Menéndez and Peñuelas 1993). The depths of the 3% and 11% critical light levels were determined for each date. The surface area of the lagoon in which *R. cirrhosa* was expected to be light-limited was calculated for each sampling date from the critical depths and the bathymetry of the lagoon (authors' unpublished data).

The bottom irradiance values were plotted on a plane defined by the water level and the light attenuation coefficient in order to examine the relative contribution of these factors to benthic light availability. Critical isolines of expected light limitation were calculated for different depths from a rearrangement of Eq. (3.1). The relationship between effective depth (*Z*, the measured water depth), relative depth, (Z_{rel}, the distance between the bottom of the lagoon and sea level) and the water level of the lagoon at each sampling date, *WL*, was used ($Z_{rel} = Z - WL$). Eq. (3.1) was rearranged to express the water level as a function of *K*, Z_{rel} and the critical bottom irradiance (3% or 11%): $WL = -(1/K)(\ln(E_Z/E_0)) - Z_{rel}$. The water level of the lagoon was measured with a fixed scale near the outlet channel and expressed in cm above sea level (cm a.s.l.).

3.2.4 Components of light attenuation

The contribution of the different optically active constituents to light attenuation was evaluated from January 2003 to December 2004. Together with PAR profiles, water samples for the physicochemical analyses were taken at a 3 m depth site in the central area of the lagoon (Fig. 3.1). Six water samples were taken at different depths every 50 cm from surface to bottom. Water samples were filtered in pre-combusted GF/F fibre filters, stored frozen and analysed in the laboratory as soon as possible. Pigments were extracted in 90% acetone and the concentration determined by the trichromatic method (Jeffrey and Humphrey 1975). The presence of phaeopigments was monitored with the ratio of the optical density at 430 nm to that at 410 nm (Moss 1967). The concentration of Dissolved Organic Carbon, [DOC], was determined in a TOC-500 Shimadzu as an approximation to CDOM. The concentration of Total Suspended Solids, [TSS], was determined gravimetrically on pre-combusted fibre filters after the filtration of a known volume of water (APHA 1985). The concentration of Inorganic Suspended Solids, [ISS], was determined by weight loss on the same filters before and after ignition (APHA 1985), and the concentration of Organic Suspended Solids, OSS, was determined from the difference between [TSS] and [ISS].

The concentration of Detritus or organic Tripton, [Det], was calculated from the difference between [OSS] and the concentration in dry weight of phytoplankton, [Phyt], which was determined from the Chlorophyll-a concentration assuming the relationship $[Phyt]/[Chl]=100$, where [Chl] is the concentration of Chlorophyll-a in mg m^{-3} (Reynolds 1984; Phlips et al. 1995b). Individual correlations between *K* and the water parameters and between the water components were evaluated with the Pearson r coefficient.

To examine the contribution of each water component to the total light attenuation coefficient (*K*) it was assumed that the relative contributions of the components are additive. Although this is not strictly true for the Apparent Optical Properties such as *K*, this assumption has proved to be very useful leading to minimal errors (Gordon 1989; Gallegos 2001). Under this assumption the light attenuation coefficient can be partitioned into:

$$K_t = K_w + K_{doc} + K_{chl} + K_{det} + K_{iss} \qquad \text{Eq. (3.2)}$$

where K_t refers to the total attenuation coefficient and K_w, K_{doc}, K_{chl}, K_{det} and K_{iss} are the partial attenuation coefficients (in m^{-1}) of water, DOC, Chlorophyll-a, Detritus and ISS respectively (McPherson and Miller 1987; Gallegos 2001; Christian and Sheng 2003; Kelble et al. 2005). Each partial attenuation coefficient was expressed as a function of the concentration of each component multiplied by the specific attenuation coefficient of the component, yielding the equation:

$$K_t = K_w + K'_{doc}[DOC] + K'_{chl}[Chl] + K'_{det}[Det] + K'_{iss}[ISS] \qquad \text{Eq. (3.3)}$$

where K'_{doc}, K'_{chl}, K'_{det} and K'_{iss} are the specific attenuation coefficients of DOC, Chlorophyll-a, Detritus, and ISS respectively, and the terms in brackets refer to the concentrations of the components (all in g m^{-3} except Chl, in mg m^{-3}). The units of the specific attenuation coefficients are m^2 g^{-1} except for Chl, in $m^2\ mg^{-1}$. The attenuation coefficient of water, K_w, was taken to be 0.0384 m^{-1} (Lorenzen 1972).

In a first approach, a Stepwise Multiple Linear Regression of the water components concentrations (DOC, Chl, Det and ISS) on K was performed to determine the specific attenuation coefficients $K_{doc}^{'}$, $K_{chl}^{'}$, $K_{\mathrm{det}}^{'}$ and $K_{iss}^{'}$.

A least squares linear regression method based on a sequential evaluation of the constant of the fitted models (Reynolds 1984; described in detail in Armengol et al. 2003) was also used to estimate the relative contributions of the components. The method is based on simple linear regressions between K and each component, considering in this case DOC, Tripton (Trip) and Chlorophyll-a (Chl). Note that Trip includes both the organic (Detritus) and inorganic (ISS) fraction of Tripton, and that the contribution of particulate matter is represented by $K_{chl} + K_{tripton}$. The partition of light attenuation is

$$K_t = K_w + K_{doc} + K_{chl} + K_{tripton} \qquad \text{Eq. (3.4)}$$

which substituting $K_{chl} + K_{tripton}$ by K_{TSS}, can be written as:

$$K_t = K_w + K_{doc} + K_{TSS} \qquad \text{Eq. (3.5)}$$

In a first step, a regression of TSS on K_t of the form $K_t = a_1 + b_1[TSS]$ was performed and the values of a_1 and b_1 determined. The constant of the function, a_1 must correspond to the contribution of the non-particulate components (in m^{-1}). In this case a_1 equals $K_w + K_{doc}$ (Eq. (3.5)), thus yielding the determination of K_{doc} by subtracting K_w from a_1.

In the next step, the same procedure was applied on Chl. A simple regression between K_t and Chl was performed, with the form $K_t = a_2 + b_2[Chl]$. In this case the constant a_2 corresponds to the non-Phytoplankton components, that is $K_w + K_{doc} + K_{Tripton}$ (Eq. (3.4)), thus allowing the determination of $K_{Tripton}$ by difference with a_1. The slope of the function, b_2 corresponds to the specific attenuation coefficient of Chlorophyll-a ($K_{chl}^{'}$ in $m^2\ mg^{-1}$). All the statistics were performed in STATISTICA software.

3.3. Results

3.3.1 Spatial and temporal variation in light attenuation

From the 229 available profiles of PAR, 221 linear regressions to determine light attenuation coefficients were significant and had R^2 higher than 0.90 (the mean R^2 was 0.98). Measured K

averaged 1.42 m^{-1} and ranged from 0.63 m^{-1} (in May 2002) to 3.80 m^{-1} (in March 2004). The values of *K* were skewed towards high values and centred on a median value of 1.21 m^{-1} (Fig. 3.2).

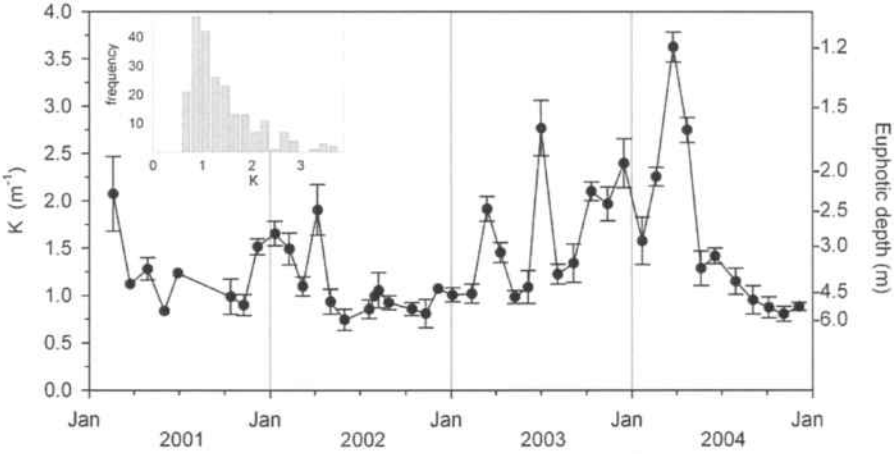


Figure 3.2. Temporal dynamics (mean ± s.d.) of light attenuation coefficient (m^{-1}) during the studied period. The equivalent scale of euphotic depth (m) is shown on the right axis. The inset shows the frequency distribution of the light attenuation coefficients.

During the studied period, there were no significant differences in *K* between the categorised EW coordinates of the sites (Kruskall Wallis=5.18; d.f.=7; p=0.61). On the contrary, *K* showed important temporal variations (Fig. 3.2), and significant differences between sampling dates were observed (K.W.=181.8; d.f.=43; p<0.001). A clear seasonal trend was not observed, but a very general pattern could be inferred with a turbid period in winter or early spring (Fig. 3.2). The trend for 2003 broke this general pattern with a peak in summer. The maximum values were found in March 2004 (3.63 m^{-1} on average) and July 2003 (2.77 m^{-1} on average). The existence of a basal value of *K* about 0.70 m^{-1} was observed during the studied period.

3.3.2 Estimates of light availability for phytoplankton and macrophytes

The values of euphotic depths calculated from the light attenuation coefficients are shown in Figure 3.2. The mean euphotic depth was 3.8 m, a value slightly deeper than the maximum depth of the lagoon (3 m). However, minimum euphotic depth was 1.2 m (in March 2004) which is slightly shallower than the average depth of the lagoon (1.37 m). Figure 3.3 shows percentage irradiance at the bottom of the water column for each sampling site and date. Benthic light availability averaged 13% of surface irradiance, but high spatial and temporal variability was observed and it ranged from 0.02% to 69% with a median value of 9% (Fig. 3.3). The spatial and temporal distribution of bottom irradiance shows that some sampling dates have very low values in all sampling sites and that low bottom irradiance is more frequent in the central areas of the lagoon than at the edges of the transects (Fig. 3.3) due to the deeper depths.

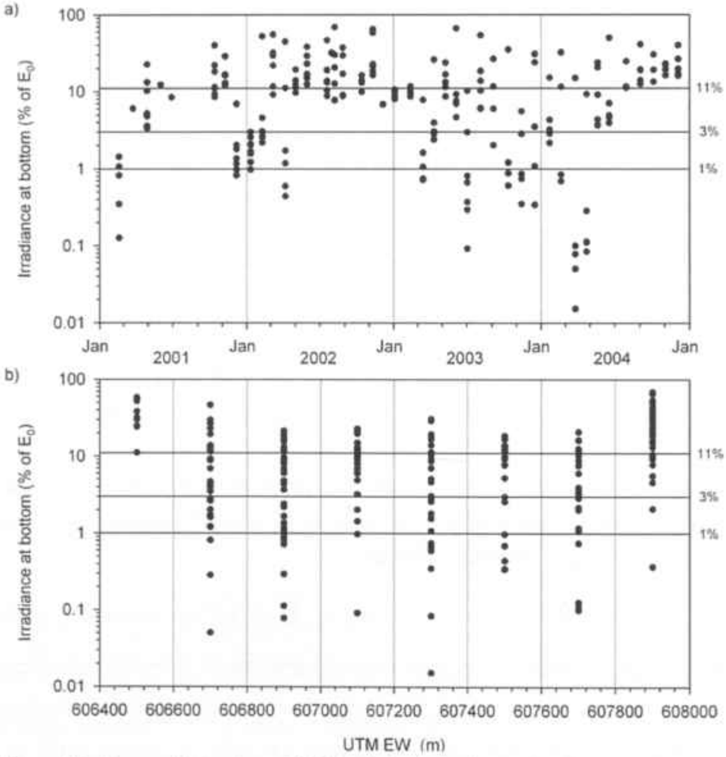


Figure 3.3. Temporal (a) and spatial (b) variation in the bottom irradiance expressed as a percentage of water surface irradiance. Reference critical levels of 11%, 3% and 1% (euphotic depth) are shown.

3.3.3 Temporal dynamics in *K* and water parameters in the period of 2003-2004

During the period of 2003-2004, *K* at the fixed central site averaged 1.59 m^{-1} and ranged from 0.75 to 3.58 m^{-1} (Fig. 3.4). Chlorophyll-a concentration was very high (mean 51 mg m^{-3}) and showed high temporal variability, peaking in March 2004 and July 2003 at 190 and 128 mg m^{-3} respectively. Phytoplankton concentration, inferred from the Chlorophyll-a concentration, was on average 39% of total suspended solids. Detritus and ISS were 40% and 21% of TSS on average. During the phytoplankton bloom observed in spring 2004, the weight contribution of Phytoplankton, Detritus and ISS to Total Suspended Solids was 47%, 50% and 3% respectively. The concentration of DOC showed a seasonal trend around high values, with values ranging from 7.8 to 12.8 mg L^{-1}. The minimum and maximum concentrations were observed in early spring and autumn, respectively.

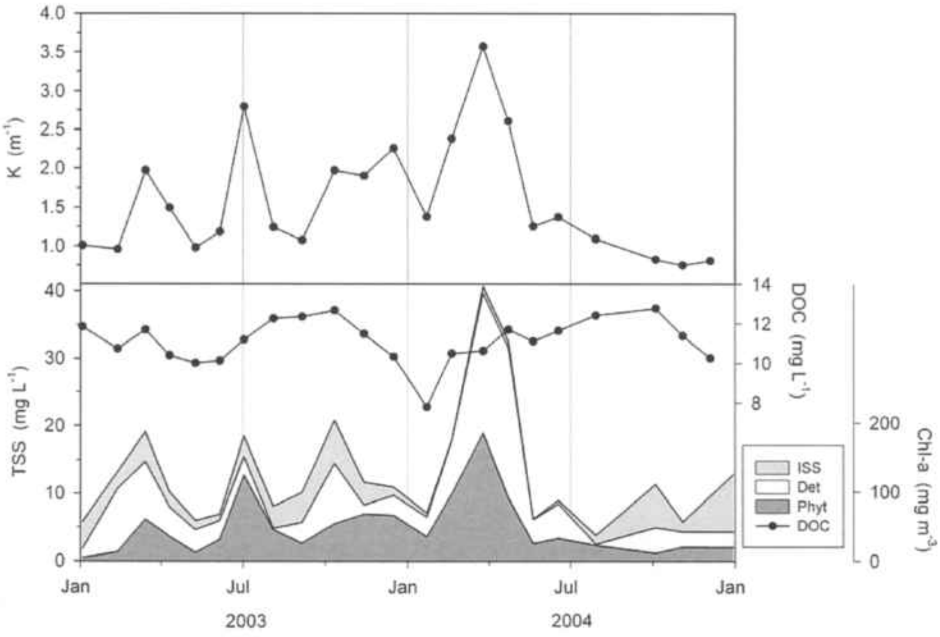


Figure 3.4. Temporal dynamics of *K* and water optically active components at the central sampling site for the period 2003-2004. For the concentration of phytoplankton, the equivalent scale in terms of Chlorophyll-a concentration is shown.

3.3.4 Partitioning of light attenuation

Significant positive correlation was observed between *K* and Chlorphyll-a, Detritus, OSS and Tripton and positive correlations were also observed between some water components (Table 3.1). A multiple regression of *K* versus Chl, ISS, Detritus and DOC was only significant in relation to Chlorophyll-a, and showed no significant relationship between *K* and DOC, ISS and Detritus. The same results were obtained if Tripton instead of its organic and inorganic fractions was considered in the model (regression between *K* and Chl, Tripton and DOC). The resulting model was:

$$K = 0.0163 \cdot [Chl] + 0.7627 \quad (R^2=0.93;\ n=22;\ p<0.001) \qquad \text{Eq. (3.6)}$$

The Root Mean Square Error (RMS) between the observed and the predicted values of *K* calculated with Eq. (3.6) was 0.21 m^{-1}, approximately 13% of the mean measured value. From Eq. (3) the value of the intercept (0.7627 m^{-1}) can be interpreted as the combined contribution of the non-phytoplankton components to light attenuation, i.e. $K_w + K_{doc} + K_{iss} + K_{det}$. By substituting the mean Chlorophyll-a concentration (51 mg m^{-3}) in Eq. (3.6), we get that the average contribution by Chlorophyll-a is 0.8313 m^{-1}, which is only the 52% of total attenuation at average conditions. The unspecified contribution of all the other components together accounts for 48% of total light attenuation on average.

The results of the second empirical method are shown in Fig. 3.5. The simple linear regression between K and TSS showed a significant relationship:

$K = 0.0694 \cdot [TSS] + 0.6728$ (R^2=0.68; n=22; $p<0.001$) Eq. (3.7)

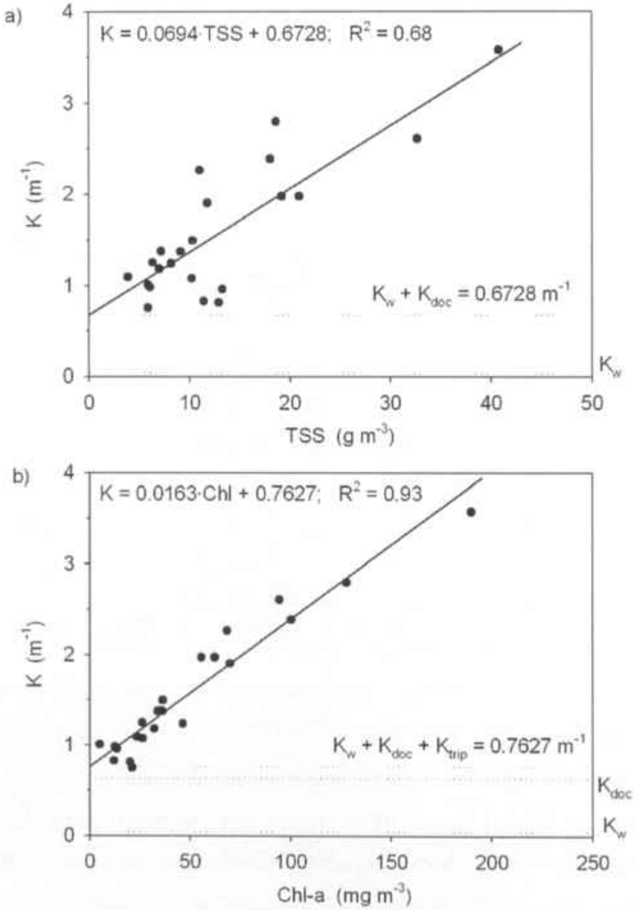


Figure 3.5. Simple linear regressions between K and a) Total Suspended Solids and b) Chlorophyll-a concentrations. From the constants of the fitted functions, the partial attenuation coefficients for DOC and Tripton are obtained (see text for details).

From K_w and the value of the constant in the model, 0.6728 m^{-1}, the resulting partial attenuation coefficient for DOC K_{doc} is 0.6344 m^{-1}. The specific attenuation coefficient for DOC, K'_{doc}, was not calculated because no significant correlation between DOC and K was observed (Table 3.1).

Table 3.1. Correlation matrix for the water components and the light attenuation coefficient. The mean and standard deviation of the water components during the studied period are also shown. (*: $p<0.001$; **: $p<0.01$)

		Pearson r						
Component	Mean ± s.d.	Detritus	ISS	DOC	Tripton	OSS	TSS	K
Chlorophyll-a	51 ± 45 mg m^{-3}	0.63^{**}	n.s.	n.s.	0.54^{**}	0.88^{*}	0.84^{*}	0.96^{*}
Detritus	5.3 ± 5.8 mg L^{-1}		n.s.	n.s.	0.92^{*}	0.93^{*}	0.91^{*}	0.66^{**}
ISS	2.7 ± 2.3 mg L^{-1}			n.s.	n.s.	n.s.	n.s.	n.s.
DOC	11.2 ± 1.1 mg L^{-1}				n.s.	n.s.	n.s.	n.s.
Tripton	8.1 ± 5.9 mg L^{-1}					0.84^{*}	0.91^{*}	0.56^{**}
OSS	10.5 ± 9.3 mg L^{-1}						0.97^{*}	0.88^{*}
TSS	13.2 ± 9.1 mg L^{-1}							0.83^{*}

In the next step a significant relationship between K and Chlorophyll-a concentration was obtained (Fig. 3.5b). The resulting equation is the same as Eq. (3.6) ($K = 0.0163 \cdot [Chl] + 0.7627$). The slope of the fitted function corresponds to the specific attenuation coefficient for Chlorophyll-a, 0.0163 m^2 mg^{-1} (Table 3.2). The average partial coefficient for Chlorophyll-a, K_{chl}, can be obtained by multiplying this value by the mean concentration of Chlorophyll-a, obtaining that $K_{chl} = 0.8313$ m^{-1}. From the constant in the fitted function, 0.7627, the partial attenuation coefficient for Tripton $K_{tripton}$ is calculated, and equals 0.0899 m^{-1}. The resulting average specific coefficient for Tripton , $K'_{tripton}$ is then 0.0111 m^2 g^{-1} (Table 3.2).

Table 3.2. Partitioning of light attenuation by the simple linear regression method with the mean percent contribution of each component during the studied period.

Component	Specific attenuation coefficients (K')	Partial attenuation coefficients (K)	Mean percent contribution
Chlorophyll-a	0.0163 m^2 mg^{-1}	0.8313 m^{-1}	44%
Tripton	0.0111 m^2 g^{-1}	0.0899 m^{-1}	6%
DOC	-	0.6344 m^{-1}	47%
Kw	-	0.0384 m^{-1}	3%

These results were used to describe the partial contribution of water components for each date because the effect of Tripton and DOC are included. The average contribution of each component was estimated as the mean of the contribution for all the sampling dates. Phytoplankton (expressed as the concentration of Chlorophyll-a) accounted for 44% of total attenuation, DOC for 47%, Tripton for 6% and water for 3% (Table 3.2).

To evaluate the relative importance of the water constituents over the entire range of variation of *K* and not only on the average values, the percentage contribution of each component for each sampling date was plotted against total attenuation in Fig. 3.6. At low values of K, DOC accounted for the 60-75% of total attenuation, whereas Phytoplankton only accounted for 10-35%. The opposite situation was observed at high values of K, the contribution of DOC diminished to the 15% and Phytoplankton accounted for up to the 80% of total light attenuation. Tripton had a constant contribution around 6%.

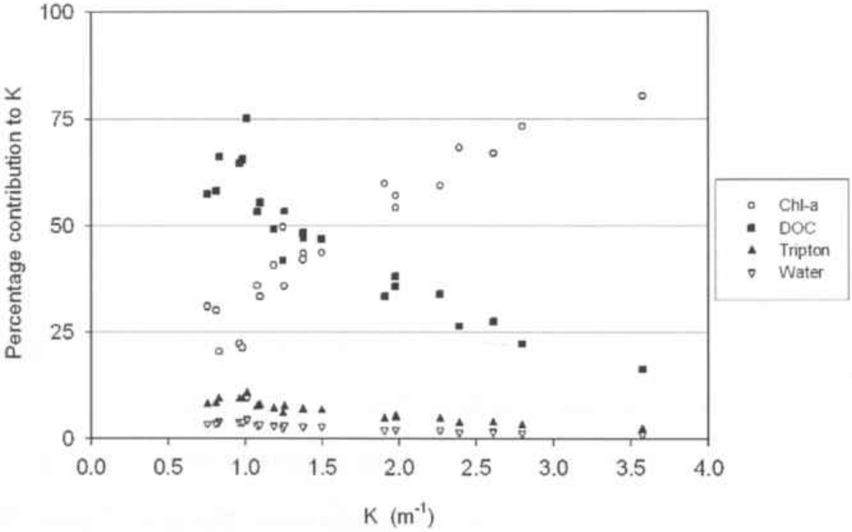


Figure 3.6. Partial contributions of water components to light attenuation over the entire range of light attenuation observed during the studied period. The contribution of each component is expressed as a percentage of total attenuation.

3.4. Discussion

3.4.1 Light availability

During the studied period the lagoon was spatially uniform with respect to light attenuation, and had higher variability on a temporal basis than on a spatial basis. The light attenuation coefficients had a mean of 1.42 m^{-1}, but large variation was observed. Even though the minimum observed euphotic depth was shallower than the average depth of the lagoon, the average euphotic depth was deeper than the maximum depth most of the time (75% of sampling dates, Fig. 3.2). This suggests that light limitation would not play an important role in controlling the planktonic primary production of the lagoon except during the very turbid events such as the observed in March 2004.

The percentage of light reaching the bottom is used in this study as an indicator of light limitation for macrophytes, and it results from the effect of light attenuation in the aquatic medium and the depth of the water column at each site. The spatial distribution of bottom irradiance (Fig. 3.3) shows that benthic light limitation is presumed to take place during the most turbid periods in the central area of the lagoon due to the higher depths found there. This is in accordance with the observed distribution of macrophytes in the lagoon, which are usually scarce or absent in the central areas (Obrador et al. 2007).

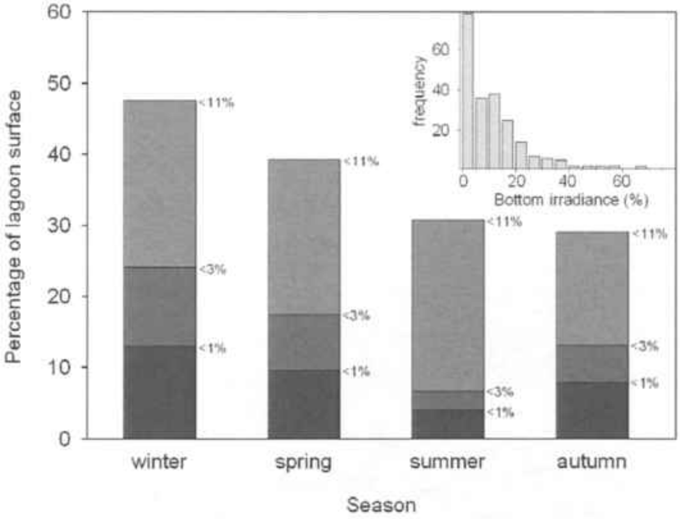


Figure 3.7. Percentage of the lagoon surface with expected light limitation. The average area with bottom irradiance lower than the critical levels of 11% (upper specification), 3% (intermediate specification) and 1% (lower specification) of surface irradiance is shown for each season in relation to the surface area of the lagoon. The overall frequency distribution of the percentage bottom irradiance in the 221 vertical profiles is also shown (inset).

The evaluation of the mean bottom irradiance for each date shows that light limitation of macrophyte growth was expected to occur on 16% of the sampling dates if the specific light requirement for *R. cirrhosa* is considered, and up to 43% of the sampling dates if we consider the more general reference value of 11% for seagrasses (Fig. 3.3). Seasonally, winter is the period with the lowest values of benthic light availability independently of whether the 11% or the 3% critical level is considered (Fig. 3.7). During the winter months, up to 24% and 48% of the lagoon area had bottom irradiance lower than 3% and 11% respectively (Fig. 3.7). It must be noted that throughout the annual cycle, at least 30% of the benthos of the lagoon was expected to receive less than 11% of surface irradiance on average (Fig. 3.7). Spring and summer are the main growing period for *R.cirrhosa* in the Albufera des Grau, but it can occasionally extend to autumn (Obrador et al. 2007). Considering the 3% critical value for *R. cirrhosa*, 17% of the lagoon is expected to be light limited in spring (Fig. 3.7). Summer would be the optimal growth period in relation to benthic light availability, but even then 7% of the lagoon was observed to have benthic light limitation.

From these results, light limitation is expected to play an important role in the primary production and spatial distribution of benthic primary producers in the lagoon during certain periods of the year. The specific effect on the distribution and abundance of each macrophyte species should be examined in detail, especially during the growing season.

For a given site benthic light limitation can result from either high light attenuation coefficients or high water levels in the lagoon. In order to assess the contribution of each factor to benthic light availability, the bottom irradiance values were plotted on a plane defined by the water level and the light attenuation coefficient (Fig. 3.8). The critical lines of expected light limitation (taking 3% of surface irradiance as a critical level) are shown for different depths. On the right of each reference line, the points corresponding to that depth are expected to be light limited (bottom irradiance lower than 3%). Points on the left of the line will have bottom irradiance higher than 3%.

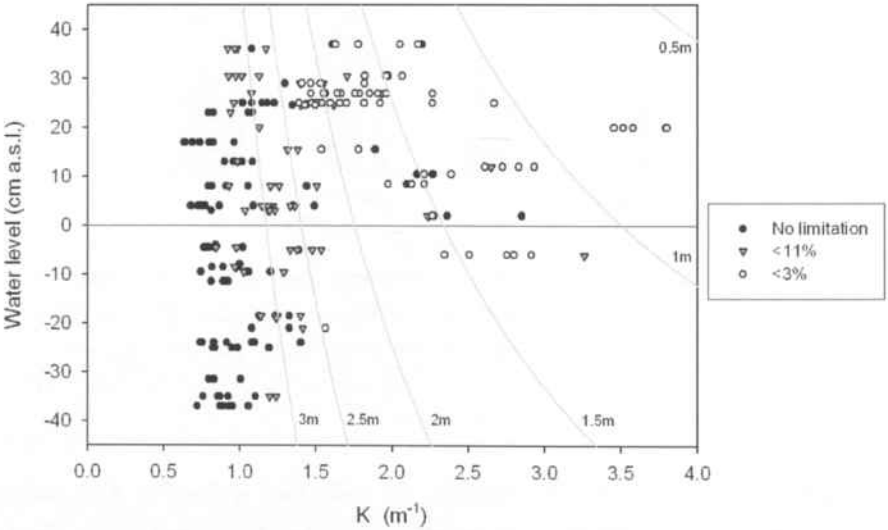


Figure 3.8. Pot of the benthic light availability in the plane defined by the water level of the lagoon (in cm above sea level) and the light attenuation coefficient (in m^{-1}). Each point corresponds to a vertical profile and the different symbols correspond to different values of bottom irradiance in relation to the critical levels of 3% and 11%. The critical lines of the 3% of surface irradiance are shown for different depths (see text for details).

As expected, bottom irradiances lower than 3% were mainly found in the upper-right quadrant of the plane, i.e. high *K* and high water level (Fig. 3.8). At low values of *K* (<1.3 m^{-1}), benthic irradiance was always higher than 3% independently of the water level of the lagoon. The lower-right quadrant of the plane (high *K* and low water level) was poorly represented in the data set. The slightly vertical distribution of the isolines of high depths (>2 m) suggests that light availability in the deepest areas of the lagoon is mainly driven by changes in light attenuation and not by changes in water level. The shallower areas (<0.5 m), with a more oblique isoline at the top of the plane, would not be light limited for any combination of *K* and water level. The intermediate depths show oblique isolines, suggesting that benthic light limitation is influenced by both *K* and water level. The upper and lower cutting points of the 1.5m-isoline are 1.8 m^{-1} and 3.3 m^{-1} respectively (Fig. 3.8). These points are defined from the water levels of 45 cm and -45 cm, which are not the maximum and minimum physical values of the lagoon but describe well the usual range of variation of water level in the lagoon (authors' unpublished data). These cutting points can be interpreted in the sense that for *K* higher than 3.3 m^{-1}, all areas deeper than 1.5 m are expected to be light limited, and for *K* lower than 1.8 m^{-1}, shallower areas will have bottom irradiance higher than 3%. The depth of 1.5 m is significant because the bathymetry of the lagoon distributes 47% of the surface in areas shallower than 1.5 m (authors' unpublished data). These results are assumed to include enough variance in both *K* and water level due to the temporal extension of the data set. However, the results should be interpreted carefully because the selection of a constant threshold in bottom irradiance is not an absolute but a suggestive measure of light limitation. Moreover, the temporal resolution of the data set does not include the short term variation in underwater irradiance, which is believed to play a role in the limiting effect of light on benthic primary producers (Banas et al. 2005).

3.4.2 Components of light attenuation

The empirical partitioning of light attenuation in the Albufera des Grau resulted in a dominance of the phytoplanktonic component as the main driver of the temporal dynamics in light attenuation coefficients. The resulting specific attenuation coefficient for Chlorophyll-a (0.0163 $m^2\ mg^{-1}$; Table 3.2) falls well between the previously reported values (Reynolds 1984; Phlips et al. 1995b; Kelble et al. 2005). An equation describing *K* as a linear function of Chlorophyll-a, Eq. (3.6), accounts for 93% of the variance. Available data of Chlorophyll-a for the period 2001-2002 (authors' unpublished data) allowed the validation of Eq. (3.6) on an independent data set (Fig. 3.9). This period was not included in the partitioning of light attenuation because data of suspended solids was not available. Observed and predicted values agreed well but explained less variance than for the period 2003-2004 (R^2=0.44; n=21; p<0.01). This could be due to the lower range of *K* and Chlorophyll-a concentration observed in the validation period (Fig. 3.9). The overall agreement between observed and predicted values for the whole period 2001-2004 was significant and explained 83% of the variance (R^2=0.83; n=43; p<0.001; Fig. 3.9). In conclusion, for modelling purposes Eq. (3.6) ($K = 0.0163 \cdot [Chl] + 0.7627$) is a useful equation to predict the light attenuation in the lagoon, but this equation should be used carefully especially on the lower range of concentrations and light attenuation coefficients used in the present study.

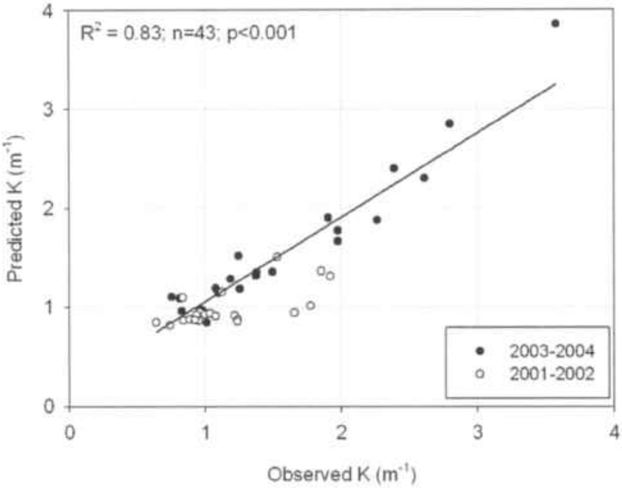


Figure 3.9. Observed versus predicted values of the light attenuation coefficient. The data sets used for the calibration (2003-2004) and for the validation (2001-2002) of Equation 6 are shown. The fitted line refers to the overall data set.

The results show that despite phytoplankton is the major driver of K, it only accounts for less than half of the total light attenuation on average (Table 3.2). The particulate component is responsible for 50% of light attenuation, whereas the dissolved matter accounts for 47%. The low Tripton contribution to light attenuation is not in accordance with other reported estuarine and lagoonal systems (Phlips et al. 1995a; Phlips et al. 1995b; Pfannkuche 2002; Christian and Sheng 2003; Lund-Hansen 2004; Kelble et al. 2005) or with the prevailing view of turbidity components in freshwater shallow lakes (van Duin et al. 2001; Jackson 2003). In this study the contribution of Tripton to light attenuation could not be separated into the inorganic (sediment) and organic (Detritus) fractions. By weight, the inorganic fraction of Tripton, ISS, averaged 21% of TSS and 33% of total Tripton, and it only occasionally contributed to more than 50% of total Tripton (Fig. 3.4). A shallow aquatic system located in a very windy location such as the north of Menorca, is expected to have high contribution of ISS to total Tripton due to sediment resuspension (Phlips et al. 1995a; van Duin et al. 2001; Banas et al. 2005). The origin of ISS in the Albufera des Grau could be assigned not only to wind-driven sediment resuspension but also to the clays entering the lagoon during torrential events. Such events drive the main hydrological pattern in water level fluctuations in this lagoon (authors' unpublished data). On the other hand, the high Chlorophyll-a concentration observed in the lagoon could explain the low contribution of inorganic Tripton to TSS by weight.

It must be noted that the organic fraction of Tripton corresponds to detritus originated from phytoplankton and macrophytes, which are both pigmented particles not easily differentiated from living phytoplankton. In this study Chlorophyll-a concentration was not corrected for phaeophytin following the suggestions of Stich and Brinker (2005). From the ratio 430:410 of the pigment extracts (Moss 1967), the presence of phaeopigments in the samples was expected to be 20-50% of total chlorophyll. Moreover, the conversion between Chlorophyll-a and phytoplankton with the fixed ratio 1:100 could be responsible for a misdetermination of the living and non-living fractions of the organic suspended solids. This could have resulted in an erroneous determination of the contribution of Tripton to total light attenuation. In order to check for this effect, the simple linear regression method was applied again on the directly measured variables that do not depend on the chlorophyll determination and on the conversion of chlorophyll to phytoplankton (i.e. DOC, ISS and OSS). Similarly as above, simple linear regressions were performed on TSS and OSS to obtain respectively the contributions by DOC and ISS from the constants of the fitted functions. Both regressions were significant at $p<0.001$ ($R^2=0.68$ and 0.76 respectively) and the results are summarised in Table 3.3. As can be seen the resulting partial contributions of OSS, ISS and DOC are 41%, 12%, and 44% respectively. These results are similar to the above conclusions in the sense that on average the particulate and the dissolved components account for half of light attenuation each one. The contradictory lower contribution of OSS (41%; Table 3.3) in relation to that of Clorophyll-a (44%; Table 3.2), may be assigned to a consequence of the assumed linear partitioning of *K* or to the inaccuracy in the determination of the Chlorophyll-a concentration due to the presence of phaeopigments. In relation to the low contribution of ISS to light attenuation, it must be noted that higher contribution would be expected if shorter time scales were considered (van Duin et al. 2001; Banas et al. 2005).

Table 3.3. Partitioning of light attenuation by the simple linear regression method applied on the directly measured water components.

Component	Specific attenuation coefficients (K')	Partial attenuation coefficients (K)	Mean percent contribution
OSS	$0.0711\ m^2\ g^{-1}$	$0.7466\ m^{-1}$	41%
ISS	n.s.	$0.1680\ m^{-1}$	12%
DOC	n.s.	$0.6344\ m^{-1}$	44%
Kw	-	$0.0384\ m^{-1}$	3%

The relative contribution of DOC to light attenuation is highlighted, specially considering that no correlation with *K* was observed. The lack of correlation between DOC and *K* could be a consequence of the use of DOC as an approximation to CDOM, because only the coloured fraction of the dissolved organic matter is related to light absorption (Ferrari et al. 1996). Further research on the variation of light attenuation including the different size fractions of DOC over a wide range of Chlorophyll-a concentrations is needed. More mechanistic approaches based on the specific spectral variations in absorption and scattering must contribute to obtain a more precise partitioning of the light attenuation (Bracchini et al. 2005; Gallegos et al. 2005).

In the previous studies reporting high contribution of DOC to light attenuation an allochthonous origin of DOC from adjacent terrestrial systems is usually assumed, even for estuarine systems (Branco and Kremer 2005; Xu et al. 2005) or inland waters (Bukaveckas and Robbins-Forbes 2000; Álvarez-Cobelas et al. 2002). In the case of shallow lakes and lagoons, the autochthonous DOC released from submerged macrophyte meadows is believed to be significant (Bertilsson and Jones 2003). However, turbidity in these systems is typically attributed to phytoplankton and inorganic suspended solids (Cristofor et al. 1994; van Duin et al. 2001; Jackson 2003), and reports of high contribution of DOC to light attenuation are not frequent in the literature. In the few studies where high DOC contribution to light attenuation is reported in shallow lakes, an allochthonous origin of DOC is described (Squires and Lesack 2003; Bracchini et al. 2005; Loiselle et al. 2005). In the Albufera des Grau the dynamics of DOC seems to be related to the macrophyte cycle, with high DOC values during the decomposition period of the dense macrophyte meadows (authors' unpublished data[2]). Given the high contribution of DOC to total light attenuation described in this study, the hypothesized macrophytic origin of DOC would suggest the possibility of interference in the interaction between macrophytes and phytoplankton. Such extent should be explored and possible thresholds determined, especially in systems where wide variations in light attenuation and water components concentrations make them difficult to be classified in the classical optical water classifications (Morel and Prieur 1977; Reinart et al. 2003).

3.5. Conclusions

The underwater light environment in the Albufera des Grau coastal lagoon was characterised by high temporal variability in the light attenuation coefficient. Light limitation was expected to play an important role in the primary production and spatial distribution of the benthic primary producers. During the macrophyte growing season 7-17% of the lagoon benthos was expected to be light limited. In the deepest areas of the lagoon (>2m) changes in bottom irradiance were related more to variations in the light attenuation than to variations in water level, but at intermediate depths (1.5 m) water level appeared to play an important role in determining benthic light availability.

The phytoplanktonic component was the main driver of the temporal dynamics in light attenuation coefficients but only accounted for 44% of light attenuation on average. Despite no correlation between DOC and K was observed, the dissolved organic matter accounted for an important fraction of light attenuation. The partitioning of light attenuation resulted in a similar contribution of the

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[2] See Chapter 6 of this thesis.

particulate and the dissolved water components, with a mean contribution of 50% and 45% to the light attenuation coefficient respectively.

3.6. Acknowledgements

BO was supported by a BRD grant from the University of Barcelona. We thank Samuel Pons and the personnel of the Albufera des Grau Nature Park for their assistance in the field work. We are especially grateful to Anna Bach for the English corrections and to Dr. Salva Pueyo for his valuable comments. Three anonymous reviewers are acknowledged for their contribution to the improvement of the original manuscript.

Chapter 4

Spatiotemporal dynamics of submerged macrophytes in a Mediterranean coastal lagoon

ABSTRACT / RESUM / RESUMEN

Obrador, B. and Pretus, JLl. 2008. Spatiotemporal dynamics of submerged macrophytes in a Mediterranean coastal lagoon. *Estuarine, Coastal and Shelf Science*, submitted

The seasonal and interannual dynamics in the biomass and spatial distribution of a macrophyte meadow was explored in a Mediterranean coastal lagoon (Albufera des Grau, Balearic Islands) during six years. The dynamics in the main limnological descriptors of the lagoon (water level, salinity, temperature, nutrient concentrations and water turbidity) were also analysed to assess the factors involved in the spatiotemporal variability of the submerged macrophytes.

The meadows were dominated by *Ruppia cirrhosa*, which showed a marked seasonal cycle with winter quiescence and complete annual regrowth. The annual production of *R. cirrhosa*, calculated from a harvesting technique, showed high interannual variability and was amongst the highest described for this species in the literature, ranging from 327 to 919 gDW m^{-2}. The spatial distribution of macrophytes was not related to horizontal salinity gradients, and appeared to be determined by light availability and wave exposure, with the highest abundances found in shallow and gently sloped areas sheltered from the strong northerly winds. The interannual variations in the macrophyte descriptors (area of occurrence, average depth of the meadows, and maximum biomass) were mainly related to water turbidity and salinity, but the effect of these variables was constrained to the spring and summer months, respectively. A significant negative correlation between the cover extent of *R. cirrhosa* and the water level at the end of the previous annual cycle was observed, suggesting a positive effect of desiccation on the cover extent of the macrophytes. After six years of apparent stability of the meadows, the macrophytes sharply disappeared from the lagoon. Although the mechanisms are not clear, this shift was likely attributable to the combination of several factors.

RESUM (*en català*)

Es va estudiar la distribució espacial i la dinàmica estacional i interanual en la biomassa dels macròfits submergits en una llacuna litoral Mediterrània (Albufera des Grau, Illes Balears). Durant els sis anys d'estudi també es van analitzar els principals descriptors limnològics de la llacuna (nivell de l'aigua, temperatura, salinitat, concentració de nutrients i terbolesa) per tal de determinar els factors implicats en la dinàmica espaciotemporal dels macròfits.

Els prats de macròfits van estar dominats per *Ruppia cirrhosa*, que mostrà un marcat cicle estacional amb quiescència hivernal. La producció anual de *R. cirrhosa*, calculada a partir de tècniques d'extracció de biomassa, es mogué, amb una elevada variabilitat interanual, en el rang 327-919 gDW m^{-2}, entre els valors més alts descrits per a aquesta espècie a la bibliografia. La distribució espacial dels macròfits no va estar relacionada amb gradients horitzontals de salinitat, sinó que vingué determinada per la disponibilitat de llum i l'exposició a l'onatge, amb les màximes abundàncies situades a les zones someres, amb pendents suaus i exposades al sud, a redossa dels forts vents de tramuntana. Les variacions interanuals en els descriptors macrofítics (extensió dels prats, fondària mitjana i biomassa màxima) van estar principalment relacionades amb la terbolesa i la salinitat de l'aigua, però els efectes d'aquestes variables quedà restringit als mesos de primavera i estiu, respectivament. S'observà una relació significativa entre l'extensió de *R. cirrhosa* i el nivell de l'aigua al final de l'any hidrològic anterior, suggerint un possible efecte positiu de la dessecació damunt la cobertura dels macròfits. Després de sis anys d'aparent estabilitat dels prats, els macròfits van desaparèixer sobtadament de la llacuna. Els mecanismes implicats en aquest canvi no estan clars, i estarien relacionats amb la combinació de diversos factors.

RESUMEN (*en castellano*)

Se estudió la distribución espacial y la dinámica estacional e interanual en la biomasa de los macrófitos sumergidos en una launa litoral Mediterránea (Albufera des Grau, Islas Baleares) durante seis años. También se analizaron los principales descriptores limnológicos de la laguna (nivel del agua, temperatura, salinidad, concentración de nutrientes y turbidez) para determinar los factores implicados en la dinámica espaciotemporal de los macrófitos.

Las praderas de macrófitos estuvieron dominadas por *Ruppia cirrhosa*, que mostró un claro ciclo estacional con quiescencia hibernal. La producción anual de *R. cirrhosa*, calculada a partir de técnicas de extracción de biomasa, mostró una alta variabilidad interanual en el intervalo 327-919 gDW m^{-2}, situándose entre los máximos valores descritos para esta especie en la bibliografía. La distribución espacial de los macrófitos no estuvo relacionada con gradientes horizontales de salinidad, sino con la disponibilidad de luz y la exposición al oleaje, mostrando las máximas abundancias en zonas someras, con pendientes suaves y expuestas al sur, protegidas de los fuertes vientos del norte. Las variaciones interanuales en los descriptores macrofíticos (extensión de las praderas, profundidad media y biomasa máxima) estuvieron principalmente relacionadas con la turbidez y la salinidad del agua, cuyos efectos se restringieron a los meses de primavera y verano respectivamente. Se observó una relación significativa entre la extensión de *R. cirrhosa* y el nivel del agua de la laguna al fin del año hidrológico anterior, sugiriendo un posible efecto positivo de la desecación sobre la cobertura del macrófito. Después de seis años de aparente estabilidad de las praderas, los macrófitos desparecieron drásticamente de la laguna. Los mecanismos implicados en este cambio no están claros y estarían relacionados con la combinación de diversos factores.

4.1. Introduction

In coastal ecosystems submerged macrophytes are key species with important structuring roles, serving as habitat and food resources not only for aquatic organisms but also for many waterbird species (Levin et al. 2001). In these highly productive systems, the primary producers are either dominated by rooted macrophytes, macroalgae or phytoplanktonic communities (Duarte 1995). In the specific context of freshwater shallow lakes the competition between benthic and pelagic primary producers has been intensely studied during the last decades, resulting in the alternative stable states theory that defines the existence of two stable states, macrophytic and phytoplanktonic, stabilised by several mechanisms that control the shift from one state to the other (Scheffer et al. 1993).

Coastal ecosystems, which are amongst the most impacted marine ecosystems (Halpern et al. 2008), have been subject to a world-wide degradation during the last century as a result of intense anthropogenic impacts (Lotze et al. 2006). Increased nutrient inputs have favoured the spread of fast-growing macroalgae, replacing the original rooted macrophytes and leading to strong environmental alterations (Valiela et al. 1997; Raffaeli et al. 1998). The characterisation of the submerged aquatic vegetation in coastal ecosystems is thus of prime importance for assessing its ecological status. Apart from this, the knowledge of the properties and dynamics of the submerged macrophytes in medium to low impacted systems must contribute to better understand the factors controlling their distribution and abundance (Duarte 2002). Many factors appear to be involved, but salinity variations and light availability have traditionally received major attention, and the need to consider other factors (physical, geological and geochemical) has been recently highlighted (Koch 2001). The knowledge of the factors involved in the dynamics of the macrophyte meadows must contribute to the conservation and management of these highly valuable ecosystems.

In this study, we work on a highly productive coastal lagoon with dense and extensive macrophyte meadows (Albufera des Grau, Western Mediterranean). Extremely high biomass of the euryhaline macrophyte *Ruppia cirrhosa* has been recently observed in the lagoon (Obrador et al. 2007), but macroalgae-dominated states without macrophytes have been also observed in the previous decades (Margalef 1952; Pretus 1989). Given the high macrophyte production in the lagoon, the properties and stability of the macrophyte-dominated state raise interest. As a part of a major research programme, this paper deals with the production and spatiotemporal dynamics of the macrophyte meadows from a seasonal and interannual perspective. Firstly, we assess the annual production of *R. cirrhosa*, determined by harvesting methods during three years. Secondly, the spatial, seasonal and interannual dynamics of the macrophyte meadows is assessed from a six-year survey together with the main physicochemical descriptors of the lagoon, in order to determine the factors involved in the dynamics of the submerged macrophytes.

4.2. Methods

4.2.1 Study site

The Albufera des Grau (surface area 78 ha, volume 1.0 hm^3) is an enclosed brackish coastal lagoon located in the northeast coast of the island of Menorca (Balearic Islands, Western Mediterranean; Fig. 4.1). The lagoon is the most extensive wetland of the island and was declared Nature Park in 1995. Currently, it does not support recreational or intense commercial activities, and only a minor familiar fishing industry is allowed to operate in the lagoon. Its average depth is 1.37 m and it reaches a maximum of 3 m (Pretus 1989). The lagoon is subject to high seasonal and interannual hydrological variability, and the water exchange with the sea is irregular and does not represent an important renewal of water in the system (Obrador et al. 2008). The freshwater inputs are frequently torrential and are supplied by two streams that drain an area of 56 km^2. The main land covers in the watershed comprises 47% woodlands, composed of Mediterranean Holm oak and Aleppo pine forests, 9% shrublands, and 41% extensive dry farming land (authors' unpublished data). Currently, the lagoon exhibits dense littoral meadows of *Ruppia cirrhosa*, which attain values of biomass of up to 1760 gDW m^{-2} in this system (Obrador et al. 2007). Macroalgae (*Polysiphonia spp.*, *Gracilaria sp.* and *Chaetomorpha crassa*) are sparsely observed. In the past, the lagoon has been described as a macroalgae-dominated system, and hyperhaline events, haline vertical stratifications, and dystrophic crises have been reported in the last decades (Margalef 1952; Pretus 1989; Cardona 2001).

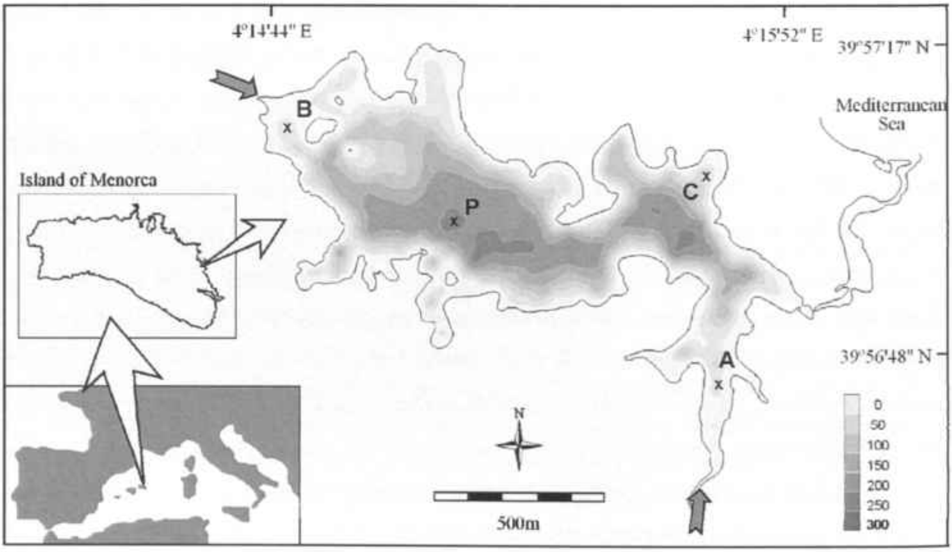


Figure 4.1. Location and bathymetric map (50 cm isobaths) of the Albufera des Grau coastal lagoon in the Island of Menorca (Western Mediterranean). The sampling sites (crosses) and the freshwater inputs (grey arrows) are shown.

4.2.2 Spatial distribution of macrophytes

The spatial distribution of macrophytes was determined from systematic surveys of the lagoon conducted annually during the period of maximum biomass (summer) for the years 2002 to 2007. Macrophyte cover was determined by visual observation from a boat, and repeated diving immersions were done in order to identify macrophyte species when necessary. The surface of the lagoon was divided in a 25x25 m grid, and the abundance of each macrophyte species was determined for each unit. Macrophyte abundance was determined by a percent cover scale with five classes (absence, <25%, 25-50%, 50-75%, >75%). For each year and species, the surface area of occurrence was calculated, together with the average depth of the meadows (weighted by the area assigned to each level of the cover index). The spatial distribution of macrophytes was compared with the basic morphometrical descriptors of the lagoon. The depth (from 0 to 300 cm), slope (from 0 to 90 degrees) and slope direction (from 0 to 360 degrees) were calculated for each grid unit from the bathymetry of the lagoon (authors' unpublished data). The effect of the environmental variables on the macrophyte cover was evaluated with a factorial regression analysis, and the cover index was treated as an ordinal multinomial variable (logit transformed). Complementary 3D graphs were used to better visualise the effects on macrophyte cover, applying a weighted least-squares smoothing method. All the statistics were performed on Statistica 8.0 software.

4.2.3 Biomass and production of *Ruppia cirrhosa*

The biomass of *R. cirrhosa* was determined at approximately monthly intervals (weekly on summer 2002) during the period 2002 to 2007. Three littoral sites located within the macrophyte beds (sites A, B, C, Fig. 4.1) were sampled by triplicate (except in the years 2005 to 2007, when site C was not sampled). The biomass was determined with a cylindrical sampler of 37 cm of diameter and above-ground biomass was sorted by hand from the core. The biomass measurements were performed until the water level was too high to work with the sampling device. After sorting and cleaning with tap water, the biomass samples were dried (70 °C to constant weight) and weighted. The carbon content of the samples was determined in a CarloErba EA1108 elemental analyser with a mean error of 1%.

The annual production of *R. cirrhosa* was determined during three years (from 2002 to 2004) at the three littoral sampling sites. We followed a harvesting technique described in Menéndez (2002). This method, hereinafter referred to as B+M, is appropriate for thin leaved macrophytes with seasonal development such as *R. cirrhosa*, and is based on biomass variations corrected for the biomass loss by mortality between two sampling times (Menéndez 2002). The increase in biomass in a given time interval i is given by:

$$\Delta B_i = P_i - M_i - G_i \qquad \text{Eq. (4.1)}$$

where ΔB_i is the observed increase in live biomass, P_i is net production, M_i is natural mortality, and G_i is grazing (all expressed in gDW m^{-2} per time interval). Assuming that grazing is negligible (Menéndez 2002), the annual production P (in gDW m^{-2} y^{-1}) was calculated as the sum of the biomass increases plus the sum of the mortality during the same time interval:

$$P = \sum_i \Delta B_i + \sum_i M_i \qquad \text{Eq. (4.2)}$$

The mortality between two sampling intervals was determined by collecting the detached biomass (D_i) in permanent enclosures of known surface area (4 m^2) made of 1 cm plastic mesh and located close to the sampling sites. The value of detached biomass was corrected for decomposition to obtain the mortality in each time interval with the equation:

$$M = D \cdot e^{-k_d t} \qquad \text{Eq. (4.3)}$$

where k_d is the decomposition rate (d^{-1}), and t is the time interval. We used a decomposition rate of 0.018 d^{-1}, previously estimated for *R. cirrhosa* in the Albufera des Grau with the litter bag method following Menéndez et al. (2004) (R^2=0.85; n=54; p<0.01, author's unpublished data).

For comparison, annual production was also calculated with the following methods: 1) from the maximum achieved biomass (Congdon and McComb 1979); 2) by summing all the positive biomass changes (Murthy et al. 1986); and 3) by summing the total mortality during a complete year cycle, assuming a turnover of 100%.

4.2.4 Water parameters

The basic limnological parameters of the lagoon were recorded at 50 cm-depth intervals at a central deep site located in the macrophyte-free area of the lagoon (site P; Fig. 4.1). Monthly vertical profiles of water salinity and temperature were obtained with field sensors (WTW Multiline-P3 and WTW Cond315i). Salinity is reported in the Practical Salinity Scale. Nutrient concentrations (nitrate, nitrite, ammonia, total phosphorus and SRP) were determined in pre-filtered water samples following standard methods (Hansen and Koroleff 1999) and provided by the Albufera des Grau Monitoring Program. Data of nitrate concentration was unavailable from January 2003 to May 2003. Phytoplankton biomass was evaluated from pigment concentrations in water, which were extracted in acetone 90% and determined by the trichromatic method (Jeffrey and Humphrey 1975). Water turbidity (K, in m^{-1}) was calculated from the Chlorophyll-a concentration with a specific equation for the light attenuation coefficient in the Albufera des Grau (R^2=0.93; n=22; p<0.001; Obrador and Pretus 2008). The percentage of surface irradiance reaching the bottom of the lagoon was calculated from K and the depth of the water column. For the period 2002-2004 an extensive survey was conducted to assess the spatial variations in salinity, performing vertical profiles at the three littoral sites (A, B and C, Fig. 4.1) and at five to seven sites distributed along the east-west axis of the lagoon (following the expected direction of maximum gradient, from the entrance of the main stream to the output channel; Fig. 4.1). The EW coordinate was categorised in eight zones 200 m wide, and the differences in salinity were tested with a non-parametric Kruskall-Wallis test.

Daily values of water level in the lagoon (in cm above sea level, cm a.s.l.) were measured with a fixed scale near the outlet channel and provided by the Albufera des Grau Nature Park, together with the time series of local precipitation. The mean, maximum and minimum monthly water temperature was obtained from a time series of daily water temperature, which was in turn calculated from an empirical relationship with air temperature ($R^2=0.93$; $n= 100$; $p<0.001$, author's unpublished data). The daily values of air temperature and wind speed were obtained from the nearest (7 Km) meteorological station (Spanish Meteorological Institute).

4.2.5 Overall changes in the macrophyte meadows

In order to work in a longer data set, the overall changes in the macrophyte meadows were evaluated including data for the period 2000-2001 reported in Obrador et al. (2007). The considered macrophyte descriptors were the total surface area of occurrence, grouped in shallow (< 1 m) and deep (>1 m) areas, the average depth of occurrence (weighted by the surface area of each level of the cover index), the maximum biomass, and the date of the biomass peak (expressed in Julian days). The relationships between the macrophyte descriptors and the limnological and climatic variables were evaluated with the nonparametric Spearman coefficient at a significance level of 0.01. The independent variables were water level (WL), salinity (S), turbidity (Turb), percent bottom irradiance (bottIrrad), total dissolved inorganic nitrogen (DIN), soluble phosphorus (SRP), water temperature (Temp), total precipitation (P_T) and mean wind speed (Wind), and were analysed considering their annual, seasonal and monthly averages. Hydrological years (from September to August) were used. Given the almost absence of macrophytes in 2007, an analysis of the whole data set was conducted to identify the variables with anomalous behaviour for that year. We selected those variables in which the 2007 value fell outside the "normal" range of variation, i.e., that observed in the period 2000-2006. For those selected variables a relative anomaly was calculated as the departure from the 2000-2006 range relative to the mean for that period, i.e. the difference between the value observed in 2007 and the minimum or maximum value of the period 2000-2006, divided by the mean for the period 2000-2006. A multivariate approach was not used given the low number of data points (8 years) in comparison with the number of variables.

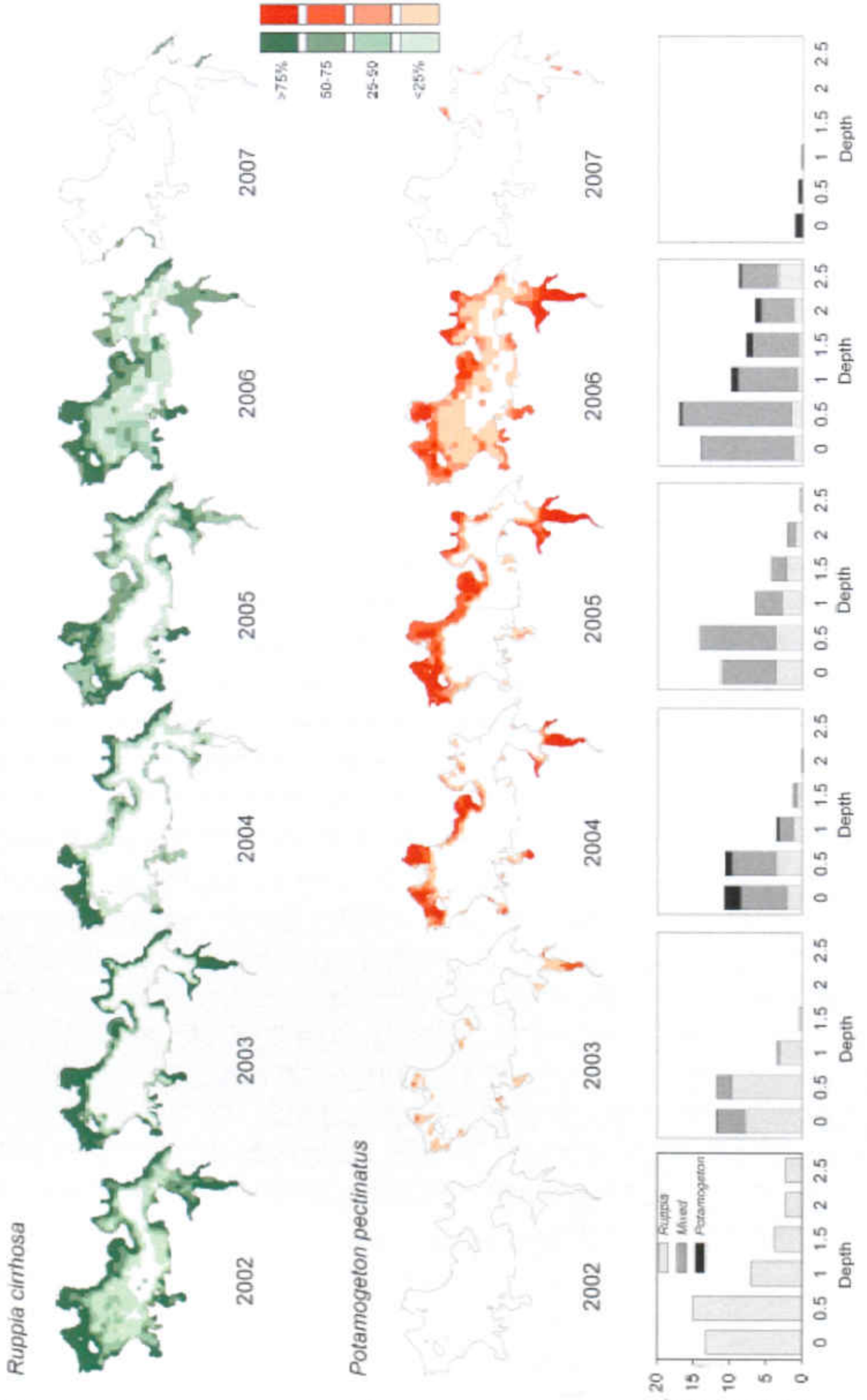


Figure 4.2. Spatial distribution of the macrophyte meadows during the period 2002-2007, with the percent cover (color scale) of a) *R. cirrhosa* and b) *P. pectinatus*. The depth distribution of the monospecific and mixed meadows (from black to light grey) is shown in c).

4.3. Results

4.3.1 Spatial distribution of macrophytes

The total surface covered by macrophytes showed considerable differences between years, but a common pattern in the spatial distribution was observed (Fig. 4.2). The maximum density of *Ruppia cirrhosa* was observed in the littoral areas, especially in the shallow extensive inlets (Fig. 4.2a and 2c). In 2003 and 2004, *R. cirrhosa* decreased its distribution, mainly in the deep areas and in the central southern coast. In 2007, this species almost disappeared from the lagoon and only occasional patches with vegetation were observed. The other macrophyte species, *Potamogeton pectinatus*, was absent in 2002, and showed a progressive increase in distribution from 2003 to 2006, to finally disappear in 2007 (Fig. 4.2b). The spread of this species started in the areas near the streams, and formed the denser beds in the littoral areas. During the maximum distribution of 2006 *Potamogeton* was present in the 75% of the lagoon, and only in the areas near the central southern coast this species was not observed. The depth distribution of the surface area covered by monospecific and mixed meadows (Fig. 4.2c) showed that the lagoon moved from monospecific *Ruppia* meadows in the littoral areas (2002), to mixed beds, firstly only in the littoral (2003 to 2005) and finally in the whole depth gradient (2006). In 2007 a drastic reduction of the macrophyte beds occurred at any depth for both species.

Table 4.1. Results of the factorial regression to assess the effect between the morphometric descriptors and the cover index of *R. cirrhosa* and *P. pectinatus*. The likelihood scores of the significant models ($p < 0.001$) for each year are shown. (n.s.: not significant).

		Likelihood score				
Model	d.f.	2002	2003	2004	2005	2006
R. cirrhosa						
Depth	1	361.2	463.4	308.1	462.6	302.3
Slope	1	52.6	61.2	12.5	n.s.	54.2
Direction	1	12.7	16.3	21.9	35.4	43.4
Depth + Slope	2	367.6	494.8	313.0	464.8	338.9
Depth + Direction	2	374.9	483.2	334.9	511.2	352.0
Slope + Direction	2	65.4	73.8	32.3	38.1	91.6
Depth + Direction + Slope	3	381.4	511.5	338.3	512.2	383.2
P. pectinatus						
Depth	1	-	109.4	303.3	295.9	423.6
Slope	1	-	46.5	62.8	11.5	33.2
Direction	1	-	n.s.	13.7	48.2	43.4
Depth + Slope	2	-	142.5	347.1	304.6	441.2
Depth + Direction	2	-	111.9	320.9	356.2	474.6
Slope + Direction	2	-	47.4	73.0	56.6	71.9
Depth + Direction + Slope	3	-	144.0	361.1	361.8	488.5

The results of the factorial regression between the cover index and the morphometrical descriptors of the lagoon showed significant effects of depth, slope and slope direction (Table 4.1). Depth was the main parameter for both *R. cirrhosa* and *P. pectinatus*, as seen for the high likelihood scores in comparison with the other models (Table 4.1). A graphical visualization of the effects of depth, slope and slope direction on the cover index of *R. cirrhosa* for the year 2006 (Fig. 4.3) showed that the highest abundances were found at shallow depths and low slopes, whereas the shallow steep areas exposed to north showed a pronounced decrease in macrophyte abundance. At higher depths (>100 cm) the abundance was lower, and whereas the north-exposed direction was poorly vegetated, the south-exposed areas showed high macrophyte abundances. In both shallow and deep areas the negative effect of the orientation to north was not restricted strictly to that direction but was detectable in the range E-N-W.

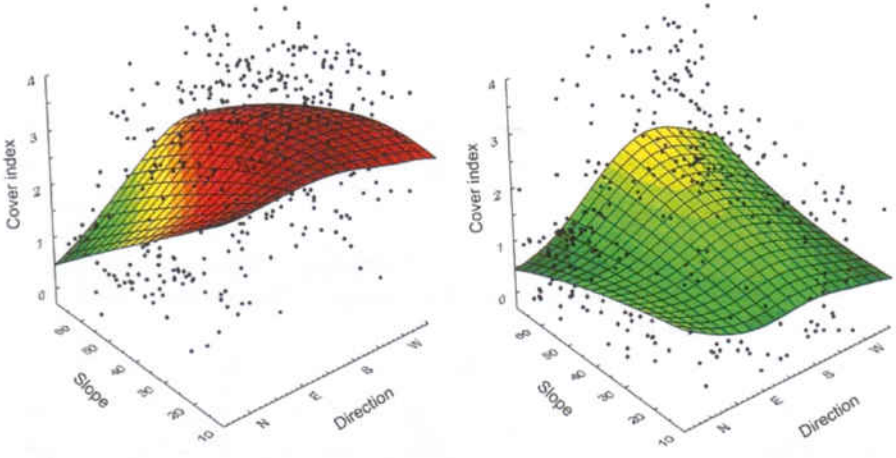


Figure 4.3. 3D plots of the effects of the morphometric descriptors on the abundance of *R. cirrhosa* for the year 2006. The equal abundance isolines in the plane defined by the slope and the slope direction are shown for the shallow (0-100 cm, left panel) and deep (>100 cm, right panel) areas of the lagoon.

4.3.2 Temporal dynamics of *R. cirrhosa* biomass and production estimates

The biomass of *R. cirrhosa* showed a clear seasonal trend with total disappearance in winter and a growing period starting in spring and leading to the maximum values in summer (Fig. 4.4). All the studied sites showed the same seasonal pattern and only differed in the peak biomass. High interannual variability was observed, with a first decrease in biomass in the period 2002-2004 (peak values ranging 718-919 gDW m^{-2} in 2002, and 327-476 gDW m^{-2} in 2004). After a recovery of the maximum biomass to values above 500 gDW m^{-2} in 2005-2006, the biomass of *R. cirrhosa* was undetectable in 2007.

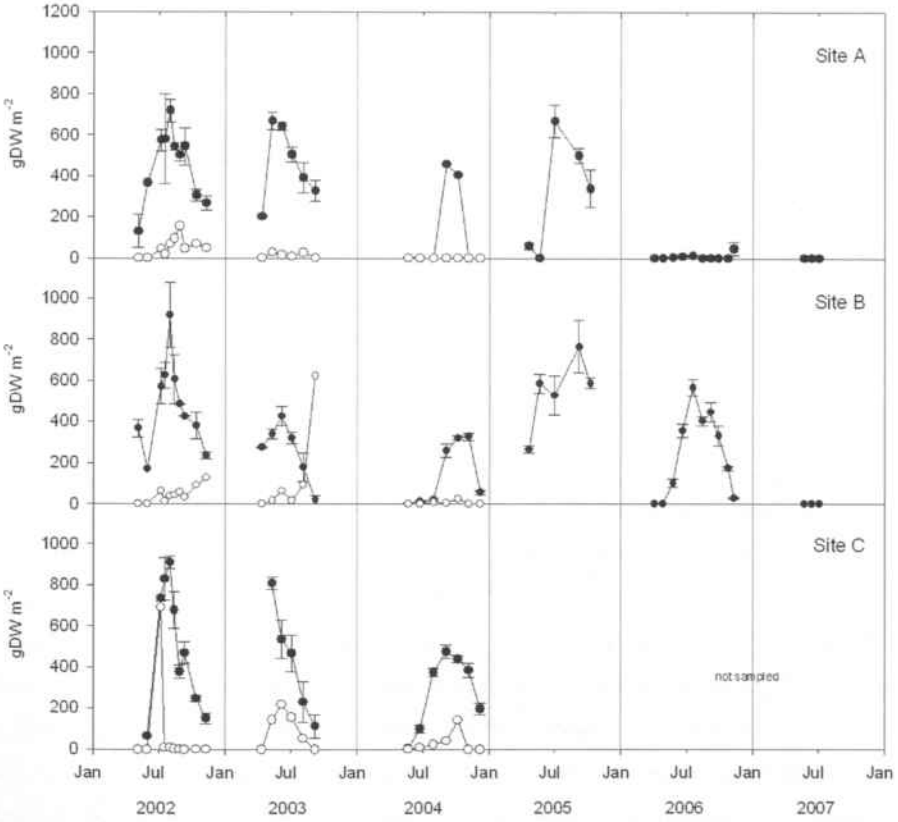


Figure 4.4. Temporal dynamics of *R. cirrhosa* biomass (mean ± s.e.) at each sampling site (filled symbols). The open symbols refer to the detached biomass (D) between two sampling intervals in the permanent enclosures used for the production estimates in the period 2002-2004. Site C was not sampled after the year 2005.

The temporal pattern of biomass loss by mortality of *R. cirrrhosa* showed high variability between sites and years. The detached biomass in the enclosures was on average less than 15% of the living biomass during the sampling interval (Fig. 4.4). Continuous biomass loss was observed during the study period every year, but some anomalous patterns were observed, such as the massive mortality at the beginning of the sampling period at site C in 2002, or at the end of the annual cycle at site B in 2003 (in which cases the production was not estimated). In 2004, the detached biomass at sites A and B was much lower than in the previous years, and visual observations showed that those enclosures did not reflect the general macrophyte density of the site. From the mean carbon content of the *R. cirrhosa* biomass (36.7 ± 2.4 %; n=70) the production estimates were expressed in gC m^{-2} y^{-1} (Table 4.2). The different methods to estimate the annual production yielded similar results (relative s.d. of 6% between methods on average) except for 2004, when the estimate based on total mortality was considerably lower than the others (Table 4.2). If this value is neglected, the production estimates ranged 154-324 gC m^{-2} y^{-1}. All the methods showed a decrease in the production of *R. cirrhosa* during the study period.

Table 4.2. Comparison of the different methods to estimate annual production (gC m^{-2} y^{-1}) of *R. cirrhosa*. The mean and s.d. of the three sampling sites is shown for each method.

	B + M	Maximum Biomass	Biomass increments	Total mortality
2002	324 ± 8	312 ± 42	291 ± 70	304 ± 57
2003	270 ± 82	233 ± 71	233 ± 71	236 ± 185
2004	180 ± 40	154 ± 31	154 ± 30	85 ± 82

4.3.3 Water parameters and pigment concentration in the water column

The chlorophyll-a concentration did not show a clear seasonal pattern, and erratic peaks were observed annually (Fig. 4.5a). A basal concentration of chlorophyll below 15-20 μg L^{-1} was observed every year, but values above 100 μg L^{-1} were reached during the peaks. Such extremes declined fast and the pulse did not last more than one or two months, but every year showed a different pattern of recovery to the basal condition. The years 2002 and 2005 were characterised by continuous low concentrations, whereas long turbid periods were observed from March 2003 to August 2004 and from July 2006 to March 2007. The calculated water turbidity, expressed as the light attenuation coefficient, ranged 0.82 - 3.32 m^{-1} (Fig 5a). The timing of the phytoplankton peaks was roughly in accordance with peaks of nutrient concentration in water, mainly nitrogen (Fig 5b). The ammonia concentration was below 5 μM most of the time, with occasional peaks above 10 μM (maximum of 28 μM on July 2006). The peaks of nitrate were typically observed in spring and autumn, with maximum values of 26 μM, whereas the rest of the year nitrate was below 1 μM. Despite the dynamics of both nutrients were highly erratic, the nitrate peaks were temporally coincident with torrential inputs from the watershed, identified by sharp increases in water level during rainy periods (Fig. 4.5c). Ammonia, instead, was uncorrelated to water inputs and was mainly associated to sediment flux after occasional events of bottom hypoxia (authors' unpublished data).

Water salinity ranged 2.7 - 18.9, and showed a clear seasonal pattern with maximum and minimum values in early autumn and late spring, respectively (Fig. 4.5c). During the transect survey of 2002 to 2004 (Fig. 4.6), no significant differences in salinity were observed between the sampling sites (Kruskall-Wallis = 0.16; N=148; p=0.98), nor between the categorized EW coordinates (K.W. = 6.4; N=339; p=0.49). The standard deviation in salinity between sites was always below 1.4 units (mean s.d. 0.33 ± 0.31).

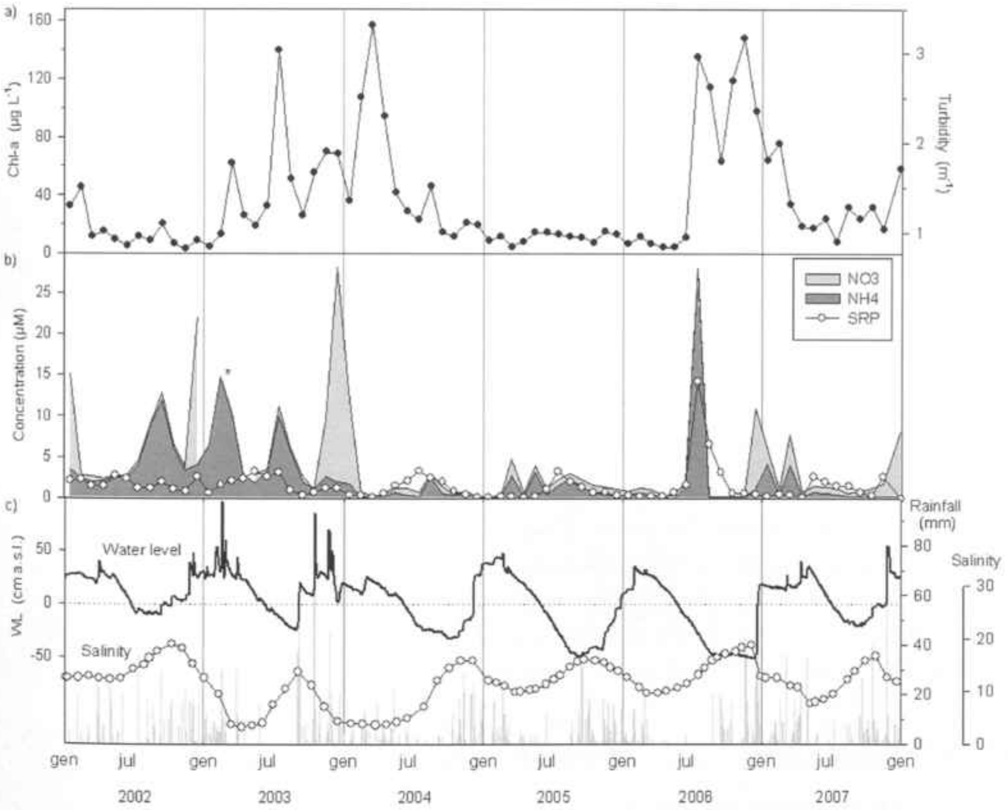


Figure 4.5. Temporal dynamics of the water parameters during the studied period. The concentration of Chlorophyll-a and the resulting calculated water turbidity are shown in (a); the nutrient concentrations are shown in (b) and the hydrological descriptors (water salinity, daily water level (WL) and daily precipitation) are shown in (c). The asterisk indicates the absence of data of nitrate concentration (see text for details).

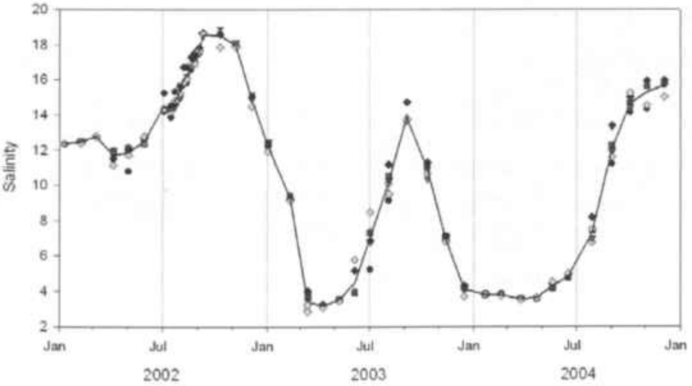


Figure 4.6. Temporal dynamics in salinity along the EW axis of the lagoon for the period 2002-2004. Each symbol corresponds to the mean salinity of a 200 m wide zone, and the line is the mean of all the sites.

4.3.4 Overall changes in the macrophyte meadows

The overall pattern of variation of the macrophyte cover for the period 2000 to 2007 is shown in Figure 4.7 by grouping the different depths into shallow (0-1m) and deep (above 1m). The decrease in the distribution of *R. cirrhosa* observed from 2001 to 2004 is mainly related to the lower presence in the deep areas of the lagoon (decrease of 86% from 2001 to 2004) rather than a decrease in the littoral (decrease of 40%). The spread of *Potamogeton* since 2003 occurred mainly in the shallow areas and only in 2006 this species was found in the whole depth gradient. The average depth of the *R. cirrhosa* and *P. pectinatus* beds was 0.87 ± 0.35 m and 0.64 ± 0.30 m, respectively, and an interannual variation in the mean depth parallel to that of the surface cover was observed for both species (Fig. 4.7). The annual maximum biomass of *R. cirrhosa* showed a decrease from 2000 to 2004, and a slight recovery in 2005-2006 that dropped to undetectable values in 2007.

Table 4.3. Spearman rank correlations between the macrophyte descriptors for *R. cirrhosa* and the limnological and climatic variables: water level (WL), salinity (S), turbidity (Turb), DIN, ammonia (NH4), water temperature (Temp) and wind speed (Wind). The codes in brackets indicate if the variable refers to the annual (AN) or monthly average (codes as in Figure 4.8). Only the significant relationships are shown ($p<0.01$). The asterisks in brackets indicate those correlations that were also significant when the year 2007 was included in the analysis. The range observed in the period 2000-2006 is also shown for reference.

Macrophyte descriptor	Predictor	Spearman R	Range
Total area of occurrence (22; 61) ha	WL (sep)	-0.96	(-65; 7) cm a.s.l.
	WL (oct)	-1.00	(-53; 22) cm a.s.l.
	S (jul)	0.89 (*)	(6; 18) g L-1
	S (aug)	0.89 (*)	(10; 22) g L-1
	Turb (mai)	-0.94	(0.8; 1.4) m-1
	bottIrrad (mai)	0.94 (*)	(1.2; 11.1) %
	bottIrrad (AN)	0.89 (*)	(1.2; 10.8) %
Area of occurrence (shallow) (18; 31) ha	WL (sep)	-0.96	(-65; 7) cm a.s.l.
	WL (oct)	-0.93	(-53; 22) cm a.s.l.
Area of occurrence (deep) (4; 31) ha	WL (sep)	-0.93	(-65; 7) cm a.s.l.
	WL (oct)	-0.96	(-53; 22) cm a.s.l.
	S (jun)	0.89 (*)	(4; 16) g L-1
Average depth (56; 104) cm	WL maximum (AN)	-0.96	(-16; 96) cm a.s.l.
	Turb (mar)	-0.89 (*)	(0.8; 3.3) m-1
	Turb (apr)	-0.96 (*)	(0.8; 2.3) m-1
	Wind (jun)	0.96 (*)	(3.6; 4.6) m s-1
	bottIrrad (mar)	0.89 (*)	(0.1; 10.5) %
	bottIrrad (apr)	0.93 (*)	(0.1; 10.3) %
Maximum biomass (476; 1760) gDW m^{-2}	Turb (aug)	-0.94	(0.9; 2.6) m-1
	SRP (jul)	-0.94	(0.7; 14.2) µM
Date of the peak (130; 249) Julian d	Temp maximum (apr)	-1.00	(18.2; 21.8) °C

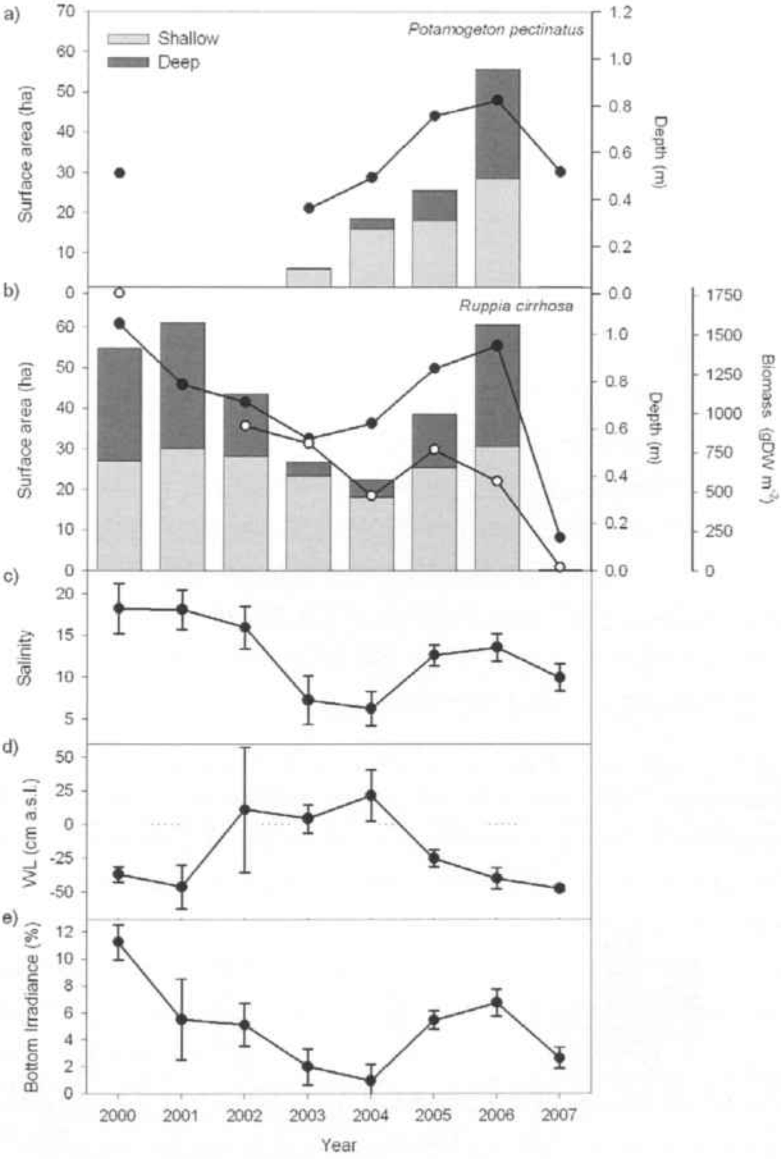


Figure 4.7. Annual changes in the macrophyte descriptors and in the main environmental variables for the period 2000-2007. The surface area covered by *P. pectinatus* and *R. cirrhosa* are shown in a) and b) respectively. The colours in the bars refer to the surface area corresponding to the shallow ($z < 1$ m) and deep ($z > 1$ m) areas of the lagoon. The lines are the average depth of occurrence (dark symbols) and the peak biomass of *R. cirrhosa* (open symbols). The mean ± s.d. of the summer salinity (c), of the water level (WL) in autumn (d), and of the percent bottom irradiance in spring (e) are also shown. See text for

The significant relationships between the macrophyte descriptors and the water and climatic variables for the period with macrophytes (2000-2006) are shown in Table 4.3. Given the low number of data points for *P. pectinatus* (4 years) the analysis was only performed for *R. cirrhosa*. The descriptors related to the area of occurrence were positively correlated with the summer salinity and the spring bottom irradiance, and negatively correlated with the water level in the previous autumn. The mean annual bottom irradiance also showed a significant relationship with the area of occurrence. The average depth showed similar relationships and was also correlated with the wind speed in summer, whereas the maximum biomass included a negative relationship with the phosphorus concentration in summer. The date of the maximum biomass was highly negatively correlated with the maximum temperature of April.

The anomalies in the environmental variables for the year 2007 are shown in Figure 4.8. The variables that in 2007 fell outside the range of variation of the period 2000-2006 were related to water level, temperature, turbidity, nutrient concentrations, rainfall and wind speed. The largest anomalies were observed in the precipitation of April, with a value 180% higher than the mean of 2000-2006, and in the turbidity of autumn and winter months (between 40% and 115% higher). The year 2007 was also characterised by low water levels in winter, by high phosphorus and nitrate concentrations in September and March respectively, and by low ammonia and total DIN in autumn and summer, despite these variables showed large variability during the reference period, as seen by the high relative standard deviation of the variable (Fig. 4.8). It was also a windy year on average, whereas the temperature anomaly was very low at any season.

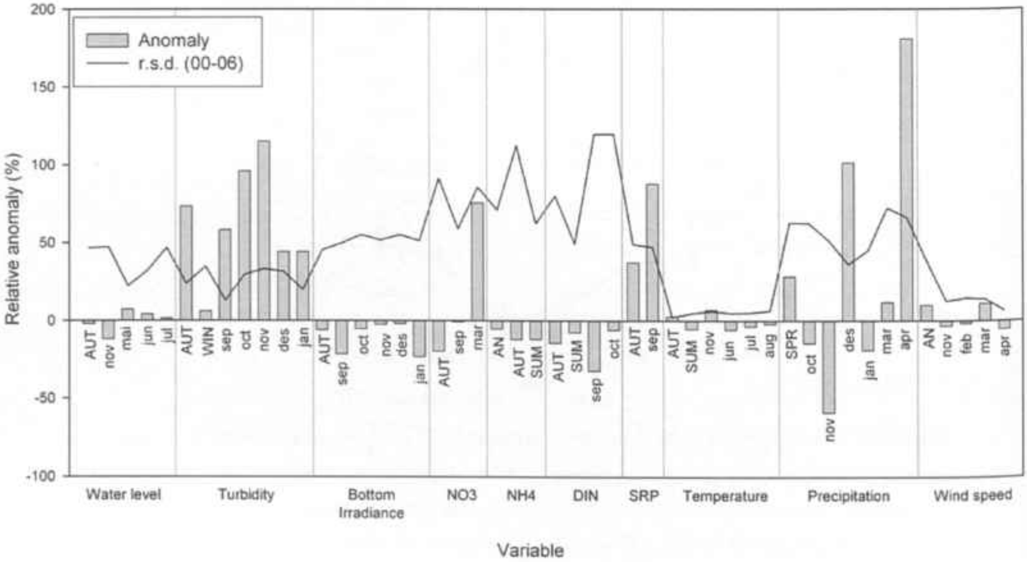


Figure 4.8. Relative anomaly of the year 2007 in relation to the period 2000-2006 for the selected climatic and limnological descriptors (see text for details). The relative anomaly is defined as the departure from the 2000-2006 range relative to the mean (see text for details). The relative standard deviation (r.s.d.) in the period 2000-2006 is also shown for comparison (line). The legend below the bars indicates if the variable is referred to the annual (AN), seasonal (uppercase) or monthly (lowercase) values (codes for season: AUT: autumn, WIN: winter, SPR: spring, SUM: summer).

4.4. Discussion

4.4.1 Biomass dynamics and production estimates

In permanent waters *R. cirrhosa* typically shows an annual life cycle with winter quiescence and vegetative growth from stolons (Verhoeven 1979), although perennial stands have also been observed elsewhere (Gesti et al. 2005). In this study, the stands of *R. cirrhosa* showed a clear seasonal development with winter disappearance and complete annual regrowth. Only occasionally *Ruppia* is able to overwinter and behave as a biannual, as occurred in 1999 to 2000 (J.P. personal observation).

With regard to the production estimates, all the methods used to estimate the annual production of *R. cirrhosa* gave similar results. The B+M method (based on biomass variations and mortality estimates) showed the highest values, as expected if considering mortality. The difference between the biomass-based methods (methods 1 and 2) and the B+M method was, however, much smaller than that reported in Menéndez (2002). It is often assumed that mortality is in the same order of magnitude than biomass variations (Menéndez 2002; Bartoli et al. 2008), but in this study the detached biomass was always below 15% of living biomass. It must be noticed, however, that in some cases the permanent enclosures used to estimate mortality did not reflect the same pattern than the adjacent meadows. Higher sampling effort would be necessary to accurately estimate the mortality, with replicate enclosures at each site, higher frequency samplings, and continuous control of the state of the enclosures. Given the complete annual regrowth of *R. cirrhosa* during the studied period, the high sampling effort, and the associated uncertainty of the B+M method, the annual production of *R. cirrhosa* appears to be appropriately estimated simply from the maximum biomass (Casagranda and Boudouresque 2007). In this sense, the maximum biomass observed during the studied period (327-919 gDW m^{-2}) was lower than that observed in 2000 (up to 1760 gDW m^{-2}; Obrador et al. 2007), but it was still in the upper range of variation reported for this species in the literature (Verhoeven 1980b; Calado and Duarte 2000; Azzoni et al. 2001; Menéndez 2002; Pasqualini et al. 2006; Pergent et al. 2006; Casagranda and Boudouresque 2007; Bartoli et al. 2008). These results highlight the importance of macrophyte production in the Albufera des Grau.

With regard to the phenology of the meadows, Verhoeven (1979) observed that the growth and flowering of *R. cirrhosa* were related to water temperature and that complex interactions of plant properties determined the decay of the vegetation, which took place after four months of exponential growth. With the methodology used in this study, we could not determine the beginning of the exponential growth, because the biomass measures started when the water level was low enough to use the sampling device. Instead, we worked with the date of the maximum biomass. The marked negative relationship between the maximum temperature of April and the date of the maximum biomass of *Ruppia* (Table 4.3) may be related to the shift from winter quiescence to exponential growth, in accordance with Verhoeven (1979). In cold years with lower spring water temperature, the exponential growth starts later in spring and the maximum biomass is achieved later. On the contrary, in years with warmer springs, the winter quiescence is stopped earlier and the maximum biomass is achieved early in the summer.

4.4.2 Spatial distribution

Horizontal salinity gradients are a common feature of many coastal ecosystems and often determine the spatial distribution of macrophytes (Menéndez et al. 2002; Agostini et al. 2003; Lirman et al. 2008). Nonetheless, the Albufera des Grau can be considered horizontally uniform in salinity, as no significant differences were observed between sites or along the seaward-landward axis during the salinity survey (Fig. 4.6). Previous intensive surveys of the lagoon had shown slight horizontal gradients in salinity after intense freshwater or seawater inflows, but the gradients were always small and never lasted more than a few days (authors' unpublished data). On the other hand, the spatial variation in water turbidity was analysed during the same period by Obrador and Pretus (2008) and no significant horizontal gradients were observed. Therefore, the spatial distribution of macrophytes cannot be explained by horizontal variations in salinity or water turbidity and must be related to other factors.

The results of the factorial regressions showed that the morphometrical descriptors of the lagoon were significantly related to macrophyte occurrence (Table 4.1). The depth was the main factor to explain the spatial distribution of macrophytes, thus suggesting the effect of light limitation on the distribution of macrophytes. This is in accordance with previous observations expecting macrophyte light limitation to occur in considerable areas of the lagoon throughout the annual cycle (Obrador and Pretus 2008). It must be noticed, however, that the best models to explain the macrophyte cover where those that included the combined effect of depth, slope and slope direction (Table 4.1). The areas exposed to north showed a clear reduction of macrophyte abundance, especially in those shallow areas with steep slopes, a situation that precludes an explanation based on direct sun exposure requirements. The results more likely reflect the avoidance to the wave stress generated by the strong northerly winds, which are dominant in frequency and strength in the island (Jansà 1979). The importance of physical factors such as slope and wave exposure on the spatial distribution of submerged macrophytes has been previously observed in other shallow lakes and coastal systems (Berglund et al. 2003; Charpentier et al. 2005; Feldmann and Noges 2007). The effect of the slope may be related not only to the associated wave stress but also to other factors such as sediment stability (Duarte and Kalff 1986). Given the combined effect of depth, slope and slope direction observed in this study, and given the low fit or even not significance of the models based only on the slope (Table 4.1), the direct effect of wave stress on the macrophyte meadows is the most plausible explanation. Such effect may include several mechanisms such as changes in plant morphology, edge erosion, direct breakage or seed accumulation (Koch 2001; Steinhardt and Selig 2007). Apart from this, it may be argued that the spread of *P. pectinatus* in the period 2003-2006 may have had an effect on the distribution of *R.*

cirrhosa by generating competition between the two species (Kautsky 1991), although at the moment this cannot be proved true, neither discarded. Remarkably indeed, the significance of the geospatial models was maintained in the different years, thus highlighting the robustness of the depth and depth-slope-direction models to explain the distribution of both species. In conclusion, the spatial distribution of macrophytes in the Albufera des Grau is mainly determined by light limitation combined with wave exposure, so that the highest abundances are found in shallow and gently sloped areas sheltered from the dominant wind stress of the area.

4.4.3 Overall trends in the macrophyte meadows

The meadows of *R. cirrhosa* in the Albufera des Grau showed considerable interannual variability and drastically disappeared in 2007. The correlations between the macrophyte descriptors and the water and climatic variables for the period with macrophytes allowed the exploration of the factors involved in the interannual dynamics of *R. cirrhosa* from a seasonal point of view. The main factors were related to water level, water salinity and light availability, and secondarily to water temperature. It must be highlighted that the hydrological descriptors of the lagoon showed a marked seasonal trend mainly driven by the precipitation-evaporation regime of the Mediterranean climate (Obrador and Pretus 2008), but the other water variables, namely nutrient and pigment concentrations and associated turbidity, showed the highly variable dynamics with erratic peaks characterizing coastal lagoons (Comín et al. 2004). The effect of water temperature on the phenology of the meadows has been already discussed, and the following discussion will focus on the factors involved in the remaining descriptors of *R. cirrhosa*, i.e. the area of occurrence, the weighted average depth of the meadows and the maximum biomass, as a measure of annual production. Interestingly, all the macrophyte descriptors showed a similar pattern of annual variation (Fig. 4.7). The positive effect of salinity was detected on the total area of occurrence and on the area of the deep meadows, and its influence was constrained to the summer months (June to August), with no effect of salinity during spring (Table 4.3). These results must be read in the context of the current range of salinity (oligo-mesohaline; Fig. 4.5), so that the relationships may become different or even opposite to the observed ones if different ranges were to be considered.

On the other hand, the effect of light availability (as seen by the water turbidity itself and by the percent bottom irradiance) was observed on the total area of occurrence and on the average depth of the meadows. In both cases the effect was constrained to the growing period during the spring months (from March to May). The absence of correlation after the initial growing period is not surprising given the relatively fast velocity at which the canopy of *R. cirrhosa* reaches the water surface, and the importance of self-shading rather than water turbidity in the attenuation of light beneath the meadows (Calado and Duarte 2000).

With regard to water level, we observed a negative correlation of the area of the meadows with the water level of the previous September and October (Table 4.3). A possible explanation for this might be related to higher bottom irradiance associated to low water levels, but this is not very likely because we did not find any significant relationship with the bottom irradiance during autumn months (Table 4.3). Moreover, the water level in September and October was in the lowest range of variation (from -65 to 7 cm a.s.l. in September; Table 4.3), what implies a considerable littoral desiccation. As an example, the desiccated area at -65 cm a.s.l. corresponds to the 68% of the littoral areas (<1 m depth). For *R. cirrhosa*, one might expect a positive relationship between water level and the macrophyte descriptors, as a result of the lethal effect of desiccation on this species (Verhoeven 1979), which tolerates only desiccations shorter than five hours (Adams and Bate 1994). Our results, however, suggest that desiccation is not only not lethal nor sub-lethal for *R. cirrhosa*, but rather favours its coverage extent in the next year. One possible explanation for this may be related to the high plasticity of the reproductive effort of this species in relation to water permanency. Gesti et al. (2005) described higher seed production in temporarily flooded environments than in permanently submerged ones, where vegetative growth from stolons dominates and plant fructification is minimal. Similar resource allocation into seed production under desiccation stress was reported for *Ruppia maritima* by Costa and Seeliger (1989). Thus, we hypothesize that the lagged negative relationship between the area of the meadows and the water level at the end of the previous annual cycle observed in this study may be related to increased seed production and a further expansion of the meadows.

With regard to the disappearance of the meadows in 2007, the mechanisms involved in such a drastic reduction are far from evident. It could be hypothesized that the disappearance of macrophytes was related to a massive mortality of the meadows due to, for example, a perturbation such as the entrance of herbicides from the watershed, largely dedicated to farming. Despite we lack information on the presence of pollutants in the streams, this extreme is not likely given the rather non-intensive agricultural and farming practises in the watershed and inside the Natural Park (M. Truyol 2008 pers. comm.). Moreover, healthy stands of *R. cirrhosa* are easily found in systems with polluted agriculture-derived water inputs, such as those found in the Ebro Delta (Menéndez et al. 2002). At this level of empirical approach, it is more plausible that the macrophyte disappearance is related to a combination of several naturally driven factors. Firstly, the correlation analysis showed that those variables that were markedly correlated with the macrophyte descriptors, namely summer salinity and spring light availability, also maintained the significance of the correlation when the year 2007 was included in the analysis (Table 4.3). More in detail the year 2007 was characterised by low levels of bottom irradiance in spring (3.2%; Fig. 4.7) and by low salinity in summer (between 8.5 and 12.1; Fig. 4.7), what could have triggered macrophyte decline. Actually none of these variables was anomalously different for the year 2007, i.e. they moved within the range observed in the previous years (Fig. 4.8). With regard to the search of anomalies for 2007, this year was specially characterised by extremely high precipitation in April. This may be related to the referred increased turbidity of May by entering nutrients into the lagoon, but, as stated above, neither the nutrient concentration nor the turbidity of May were out of range (Fig. 4.8). Apart from this, the anomalously higher turbidity mainly in autumn months could accelerate the macrophyte decline in the previous year, preventing them to perform possible phenological functions later in the life cycle, as resource reallocation in belowground tissues. This argument being plausible, both lagged (fall) and current (spring) light limitations would have combined for preventing macrophytic emergence in 2007.

Finally, it must be highlighted that the disappearance of macrophytes occurred despite the lagoon maintained the annual levels of nutrients, salinity and turbidity within the range of the previous years, and these variables only showed anomalous behaviour in their seasonal or monthly dynamics. As an example, the nitrate concentration of March in 2007 was anomalously higher than those observed in the same period during 2000 to 2006, but from an annual perspective (i.e., considering the absolute value instead of the temporality), the year 2007 only reached half the maximum concentration observed previously (in December 2003; Fig. 4.5). Moreover, the variables correlated with the macrophyte interannual dynamics only showed significant relationships for some months or seasons, reflecting the temporal variation in the relationship between the macrophytes and the environment. Approaches to coastal lagoon ecology based on annual averages are misleading because the temporal sequence of the processes involved plays a much relevant role in shifting the system components. This, together with the large interannual variability in the limnological descriptors of these systems, makes that any approach to ascertain the factors that drive the dynamics of submerged vegetation in coastal ecosystems require a temporally extended and seasonally explicit analysis of the system.

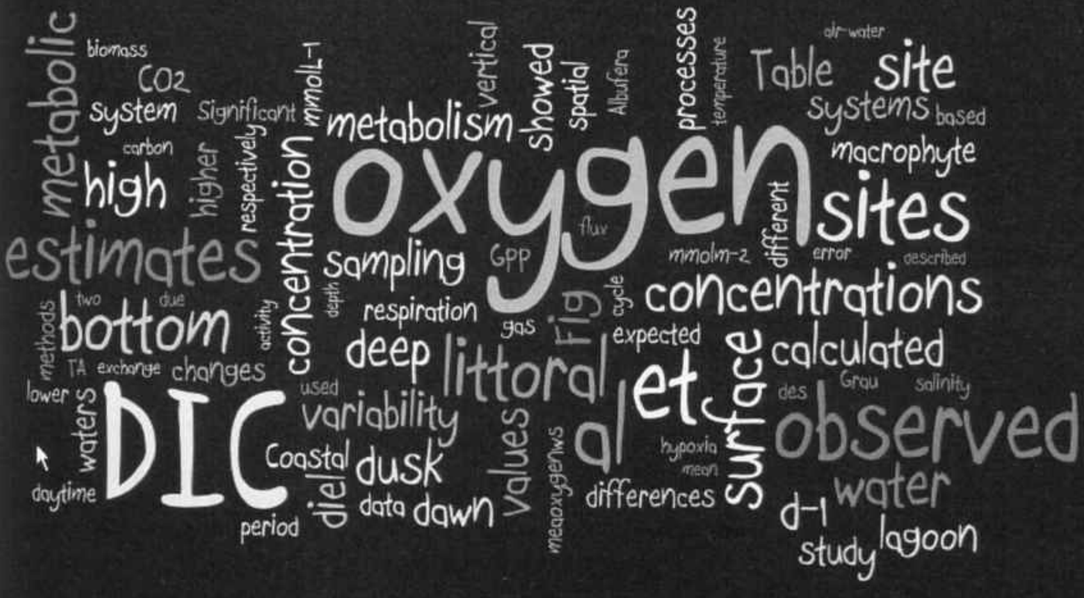
4.5. Conclusions

The macrophyte meadows in the Albufera des Grau were characterised by high values of peak biomass of *R. cirrhosa*, pointing the Albufera des Grau amongst the most productive systems for this species. The spatial distribution of macrophytes was determined by light availability and wave stress. Considerable interannual variability was observed in the annual production and in the basic descriptors of the status of the meadows, whose dynamics were mainly related to water salinity and light availability in summer and spring, respectively. Despite the apparent stability of the meadows observed during the first years, the system sharply shifted to a non-vegetated state. The meadow disappearance may be related to the combination of several factors with lagged influences along the life cycle of the macrophytes.

4.6. Ackowledgements

This study was funded by the Govern de les Illes Balears and the Consell Insular de Menorca. We acknowledge Margarita Menéndez for her help in the design of the production enclosures, and Sam

Pons, Melisa Gañán, and the staff of the Albufera des Grau Nature Park for their assistance in the field work. Valuable comments from Miquel Truyol and M. Menéndez are also highly appreciated.



Chapter 5

Variability in dissolved inorganic carbon and oxygen concentrations and ecosystem metabolism in a macrophyte-dominated Mediterranean coastal lagoon

ABSTRACT / RESUM / RESUMEN

Obrador, B. and Pretus, JLl. 2009. Variability in dissolved inorganic carbon and oxygen concentrations and ecosystem metabolism in a macrophyte-dominated Mediterranean coastal lagoon. *Estuaries and Coasts*, under revision

The spatial and temporal variability in dissolved inorganic carbon (DIC) and dissolved oxygen (DO) concentrations was explored in a macrophyte-dominated Mediterranean coastal lagoon (Albufera des Grau, Balearic Islands) in summer 2002. We made estimates of whole-system metabolic parameters (gross photosynthesis, *GPP*, community respiration, *CR*, and net ecosystem metabolism, *NEP*) with the free-water diel approach for both DIC and DO.

The results showed high spatial and temporal variability in DIC and DO. The lagoon moved from a maximum spatial homogeneity in concentration at dawn, to a double spatial gradient in the vertical and horizontal dimensions at the end of the light period. The spatial variability was driven by the photosynthetic activity in the surface waters of the macrophyte meadows, rather than by differences in sediment metabolism. Bottom hypoxia was only observed at dawn at the littoral areas of the lagoon and did not represent a critical factor in the lagoon. The metabolic estimates showed a wide range of variation with considerable differences between sites. The atmospheric exchange represented a minor fraction of the total diel change in concentration. An important discrepancy between the DIC and DO metabolism was observed, mainly due to the anaerobic processes and the chemical reactions that take place at the water/sediment interface and in the water column. High sampling effort with multiple sampling sites and coupled DIC and DO estimates appear to be fundamental if accurate quantification of whole-system metabolism with the free-water method is aimed in productive macrophyte-dominated shallow lakes and lagoons.

RESUM (*en català*)

Durant l'estiu de 2002 es va analitzar la variabilitat espacial i temporal en les concentracions de carboni inorgànic dissolt (DIC) i oxigen dissolt (DO) en una llacuna litoral Mediterrània dominada per macròfits (s'Albufera des Grau, Illes Balears). Es van fer estimes dels descriptors metabòlics a nivell de sistema (fotosíntesi, *GPP*, respiració de la comunitat, *CR*, i metabolisme net ecosistèmic, *NEP*) a partir de les variacions nictemerals de DIC i DO en aigües lliures.

Els resultats van mostrar una elevada variabilitat espacial i temporal en les concentracions de DIC i DO. La llacuna es mostrà espacialment homogènia a l'albada, mentre que a l'ocás s'observà un doble gradient espacial de concentració en les dimensions horitzontal i vertical. La variabilitat espacial estigué determinada per l'activitat fotosintètica en l'aigua superficial al si dels prats de macròfits, més que no pas per diferències en el metabolisme del sediment. Es van observar alguns valors hipòxics en l'aigua de fons de les zones litorals a l'albada, però la seva baixa ocurrència situen la hipòxia com un factor poc crític per a la llacuna. Les estimes metabòliques van mostrar un elevat rang de variació, amb importants diferències entre localitats. L'intercanvi atmosfèric de CO_2 i O_2 va suposar un flux menor en comparació amb la magnitud dels canvis nictemerals de concentració observats. Es va observar un discrepància important entre el metabolisme basat en carboni i el basat en oxigen, com a conseqüència dels processos anaeròbics i de reaccions químiques a la interfase sediment/aigua i a la columna d'aigua. Donada l'elevada variabilitat observada, es conclou que les estimes precises de metabolisme basades en el mètode de canvi de concentració en aigües lliures requereixen múltiples localitats d'estudi i aproximacions conjuntes entre DIC i DO en sistemes soms dominats per macròfits.

RESUMEN (*en castellano*)

Durante el verano de 2002 se analizó la variabilidad espacial y temporal en las concentraciones de carbono inorgánico disuelto (DIC) y de oxígeno disuelto (DO) en una laguna litoral Mediterránea dominada por macrófitos (s'Albufera des Grau, Illes Balears). Se estimaron los descriptores metabólicos a nivel de sistema (fotosíntesis, *GPP*, respiración comunitaria, *CR*, y metabolismo neto ecosistémico, *NEP*) a partir de las variaciones nictemerales de DIC y DO en aguas libres.

Los resultados mostraron una elevada variabilidad espacial y temporal en las concentraciones de DIC y DO. La laguna se mostró espacialmente homogénea al amanecer, mientras que en al final de día se observó un doble gradiente espacial de concentración en las dimensiones vertical y horizontal. La variabilidad espacial vino determinada por la actividad fotosintética en el agua superficial de las zonas con macrófitos. A pesar de que se observaron algunos valores hipóxicos en el agua de fondo de las zonas litorales al amanecer, su baja ocurrencia descarta la hipoxia como un factor crítico en la ecología de la laguna. Las estimas metabólicas mostraron un elevado rano de variación, con importantes diferencias entre localidades. El intercambio atmosférico de CO_2 y O_2 supuso un flujo de menor importancia en comparación con la magnitud de los cambios de concentración observados a escala nictemeral. Se observó una importante discrepancia entre el metabolismo basado en oxígeno y el metabolismo basado en carbono, a consecuencia de los procesos anaeróbicos y las reacciones químicas en la interfase sedimento/agua y en la columna de agua. Dada la elevada variabilidad observada, se concluye que la estimación precisa del metabolismo a partir del método de cambio de concentración en aguas libres requiere múltiples localidades de estudio y la combinación de DIC y DO en sistemas someros dominados por macrófitos.

5.1. Introduction

Coastal lagoons are highly productive systems with primary producers either dominated by rooted macrophytes, macroalgae or phytoplanktonic communities (Duarte 1995). The high accumulation of biomass in these systems can occasionally lead to summer hypoxias and dystrophic crisis with dramatic ecological and economical consequences (Bachelet et al. 2000; Diaz 2001; Rabalais and Turner 2001), and in some coastal lagoons, macrophyte biomass harvesting has even been suggested as a management practice addressed to minimize summer anoxia (Duarte et al. 2002). On the other hand, the intensity of carbon cycling in these highly productive systems has been a subject of study since the earliest whole-system metabolic works (Odum and Hoskin 1958, in Swaney and Hall 2004).

The metabolic approach to the study of aquatic ecosystems deals with the balance between the two major pathways of carbon (primary production and respiration) and is a useful indicator of ecosystem function. The balance between gross primary production (*GPP*) and community respiration (*CR*) is the net ecosystem production (*NEP*), and is used to define the trophic status of the system, i.e. autotrophic or heterotrophic for positive or negative *NEP*, respectively (Odum 1956). The metabolic estimates can be obtained by different methods, each one subject to advantages and limitations, the use of which can lead to different conclusions (Hanson et al. 2003). The traditional enclosure incubation methods in bottles, benthic chambers or its variations are difficult to extrapolate to whole-system values due to the isolation and consequent alteration of the biological activities (Hall and Moll 1975). On the other hand, the free-water methods are based on diel variations of dissolved inorganic carbon (DIC) or dissolved oxygen (DO) concentrations, assuming that their dynamics are mainly controlled by biological processes rather than by physical processes (Kemp and Boynton 1980). The major drawback of the free-water method is that the observed changes in concentrations must be corrected with estimates of the gas exchange with the atmosphere, which are subject to high degree of uncertainty (Gazeau et al. 2005b). The advantage of the free water methods over incubation methods is that the results are more easily extrapolated and include the benthic and pelagic components of ecosystem metabolism (Hanson et al. 2003). This is particularly important in coastal lagoons, and in generally all the shallow aquatic systems, where the physicochemical and nutrient dynamics are highly influenced by intense sediment-water interactions (Scheffer 1998). In these systems, the coupled analysis of DIC and DO metabolic estimates can be used to estimate the contribution of anaerobic processes to total metabolism (Torgersen and Branco 2007). With the currently available instruments, continuous measurements of DIC and DO can be performed to make more reliably estimates of metabolic parameters based on high-frequency and temporally extended data sets. However, it has been recently shown that the usual restriction of the metabolic estimates to a single sampling site within the studied system may neglect the within-system spatial heterogeneity and lead to erroneous conclusions (Van de Bogert et al. 2007; Russell and Montagna 2007).

In this work we study the DIC and DO variability and metabolic estimates based on the diel free-water method in a Mediterranean coastal lagoon. The Albufera des Grau (Balearic Islands, Western Mediterranean) is an enclosed coastal lagoon with dense and extensive meadows of the euryhaline macrophyte *Ruppia cirrhosa*. Given the very high biomass accumulation observed in the lagoon (Obrador et al. 2007), the question of the intensity of carbon cycling in this system raises interest. In this study, we analyse the spatial and temporal variability in DIC and DO during the period of maximum biomass of the macrophyte meadows. For DO, the severity and extent of bottom hypoxia is assessed, and for DIC, the potential carbon limitation of *R. cirrhosa*'s photosynthesis is explored, as previous observations had shown possible carbon limitation of macrophytes during a diurnal summer cycle (authors' unpublished data). Whole system metabolic estimates are calculated from discrete diel changes in both DIC and DO concentrations at different sites to discuss the spatial heterogeneity and representativity of the metabolic estimates. We use an approximation based on both DIC and DO, and not only on DIC, for two reasons. Firstly, the variability in oxygen levels is by itself informative of the ecological status of the system, yielding information on the extent of hypoxias and consequent risk of dystrophic crisis (Viaroli et al. 2001; Russell et al. 2006). Secondly, in shallow systems where intense bacterial activity takes place in the sediment, carbon and oxygen metabolic estimates are not expected to follow the classical Redfield stoichiometry, and the coupled analysis of DIC and DO can yield information on the extent of bacterial metabolism (Torgersen and Branco 2007).

Our objectives were 1) to assess the spatial and temporal variability in DIC and DO concentrations, 2) to determine the magnitude and variability of whole-system metabolism in the period of maximum macrophyte activity, and 3) to assess the agreement between the DIC and DO measures of metabolism.

5.2. Methods

5.2.1 Study site

The Albufera des Grau (surface area 78 ha, volume 1 hm^3) is a brackish coastal lagoon located in the northeast coast of the island of Menorca (Balearic Islands, Western Mediterranean, Fig. 5.1). The main limnological features are summarised in Table 1. The average depth is 1.37 m with a maximum of 3 m (Pretus 1989). The lagoon is subject to high seasonal and interannual hydrological variability, and the water exchange with the sea is irregular and does not represent an important renewal of water in the system (Obrador et al. 2008). Currently, the lagoon exhibits dense littoral meadows of *Ruppia cirrhosa*, which can attain values of biomass of up to 1760 gDW m^{-2} in this system (Obrador et al. 2007). Macroalgae (*Polysiphonia spp.*, *Gracilaria sp.* and *Chaetomorpha crassa*) are sparsely observed in the deeper areas of the lagoon. Intense phytoplankton peaks are observed every year usually in relation to the entrance of nutrients from the watershed or from the decomposition of the macrophyte meadows (Obrador et al. 2007). In the past, the lagoon has been described as a macroalgae-dominated system (Margalef 1952; Pretus 1989), and hyperhaline events, haline vertical stratifications, and dystrophic crises have been reported (Pretus 1989; Cardona et al. 2001).

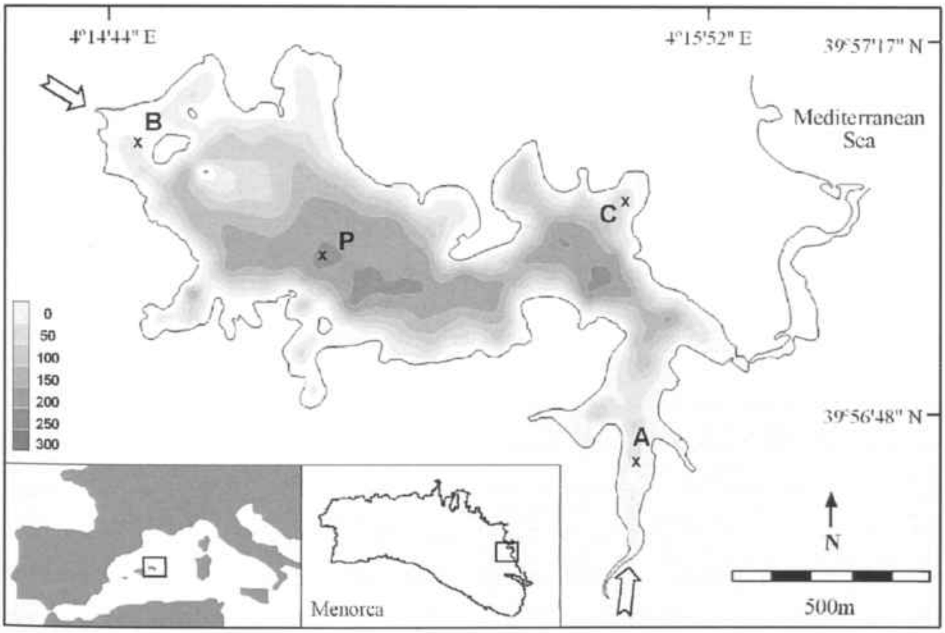


Figure 5.1. Location and bathymetric map (50 cm isobaths) of the Albufera des Grau coastal lagoon. The sampling sites (crosses) and the freshwater inputs (arrows) are shown.

Table 5.1. Summary of the limnological characteristics of the Albufera des Grau coastal lagoon during the study period. The range of the climatic data is also shown

	Range
Temperature (°C)	19.8 – 31.9
Salinity (g L^{-1})	12.5 – 19.1
pH	8.71 – 10.35
Alkalinity (meq L^{-1})	1.786 – 3.347
NH_4 (µM)	2.3 – 9.1
NO_3 (µM)	0.1 – 0.6
SRP (µM)	0.9 – 2.8
TP (µM)	2.9 – 8.2
DOC (mg L^{-1})	13.01 – 19.26
Ca^{2+} (mmol L^{-1})	3.49 – 5.29
SO_4^{2-} (mmol L^{-1})	8.49 – 12.82
Chlorophyll-a (µg L^{-1})	3.49 – 10.64
Sediment organic content (%DW)	9 – 19
Air temperature (°C)	23.8 ± 1.6
Wind speed (m s^{-1})	3.7 ± 1.2

5.2.2 Field and laboratory work

The study was carried out weekly during summer 2002 at four different sites in the lagoon: three littoral sites located beneath macrophyte meadows (A, B, C, Fig. 5.1), and a central deep site located in the macrophyte-free area of the lagoon (P, Fig. 5.1). During the sampling period, the depth of the sampling sites ranged 0.5-0.7 m at the littoral sites and 2-2.5 m at the central site. A total of 10 diel cycles were surveyed at each site from 3 July to 9 September 2002. Each survey consisted on three duplicate water measurements over a complete diurnal cycle (at dusk, dawn and dusk). The water samples at each site were taken every 50 cm from surface to bottom, and the four sampling sites were sampled within 45 min. The concentration of dissolved oxygen (mM), together with water temperature (°C) and pH (NBS scale), were determined in situ with a WTW Multiline-P3 sonde fitted with a CellOx 325 sensor calibrated in vapour-saturated air before each deployment. The mean error of the oxygen and pH measures was below 0.003 mM and 0.01 pH units, respectively. Water salinity was measured with a WTW Cond315i sonde. Water samples for physicochemical analyses were filtered and analyzed in the laboratory as soon as possible. Total alkalinity (TA) was determined by potentiometric titration with H_2SO_4 (Stumm and Morgan 1996), with an analytical reproducibility of 0.03 meq L^{-1}. The concentrations of the DIC species were calculated from the pH and alkalinity values using the dissociation constants of Cai and Wang (1998) for the measured salinity and temperature. The concentration of total DIC, i.e. the sum $CO_2 + HCO_3^- + CO_3^{2-}$, was subject to a mean reproducibility of 0.087 mM.

To calculate the metabolic parameters, the volumetric gas concentrations (mM) were integrated over the entire water column and expressed in areal concentrations (mmol m^{-2}). The TA of bottom water samples was not determined because previous observations showed that vertical variations in TA are below 4% (authors' unpublished data). Thus, the concentration of DIC for bottom waters was calculated from the TA of the corresponding surface water sample, assuming that bottom TA equalled surface TA. The error in DIC associated to this assumption is 0.064 mM and 0.004 mM for the littoral and deep sites respectively, which in terms of areal concentrations is less than 1% and 3% respectively. These estimates were done at the same sites by comparing the concentrations calculated from the measured bottom and surface alkalinities with those calculated assuming surface alkalinity at bottom in different summer samplings.

5.2.3 Numerical and statistical methods

The differences in concentration between sampling sites were evaluated with the non parametric Mann-Whitney U test. The difference between surface and bottom waters was evaluated with the non parametric paired test of Wilcoxon. All the statistical analysis were evaluated to a significance level of 0.05 and performed in the STATISTICA software.

The change in the areal concentration of DIC or DO during the night (from dusk to dawn) was assumed to be due to nighttime community respiration and exchange with the atmosphere. The change in DIC or DO during the day (from dawn to dusk) was assumed to be caused by gross primary production, daytime respiration and exchange with the atmosphere. Thus, the night community respiration (CR_n) and the daytime net ecosystem production (NEP_d) were estimated from the equations:

$$CR_n = \Delta C_{a.n} - F_i \qquad \text{Eq. (5.1)}$$

$$NEP_d = \Delta C_{a.d} - F_i \qquad \text{Eq. (5.2)}$$

where $\Delta C_{a.n}$ and $\Delta C_{a.d}$ are the change in the areal concentration of DIC or DO during night and day respectively, and F_i is the flux of CO_2 or O_2 across the air-water interface (mmol m^{-2} d^{-1}) multiplied by the length of the sampling interval.

Daytime community respiration, CR_d, was assumed to equal nighttime CR_n, despite it is likely to be higher. This widely used assumption can underestimate gross primary production and *CR*, but would not have an effect on the *NEP* estimates (Cole et al. 2000). Gross primary production (*GPP*) was then calculated as the sum of CR_d and NEP_d. Finally, the estimates of *NEP* for the 24-hour period were calculated from:

$$NEP = GPP - CR \qquad \text{Eq. (5.3)}$$

where *CR* is the daily community respiration, defined as the sum of CR_n and CR_d. The values of CR_n, NCP_d, *GPP* and *NEP* are expressed in mmol m^{-2} d^{-1}. To compare metabolism between sites the areal estimates were converted to volumetric values (mmol L^{-1} d^{-1}) by dividing by the depth of the water column at each site.

The whole-system metabolic estimates were calculated from a surface-weighted average of the values at the littoral and deep sites for each date. The surface area corresponding to littoral (depth < 1 m) and deep (depth > 1 m) areas was calculated from the hypsographic curve for the lagoon (author's unpublished data). The whole-system metabolism was finally expressed in mmol m^{-2} d^{-1}.

Ideally, free-water estimates of metabolism should be based on high-frequency measurements to prevent the errors associated to inflections in the gas curves near dawn and dusk (Hanson et al. 2003). In the absence of the necessary equipment to perform continuous gas measurements, and given the high spatial variability observed in the lagoon (authors' unpublished data), our sampling strategy was designed to favour replication instead of sampling frequency. The main cause of error in our sampling design can arise from the fact that the time of sampling was not exactly coincident with dusk and dawn at all sites. To assess this error, on 21 august we performed a complete diel cycle at site B with water measurements every 2 hour. With the smoothed rate of change observed for DO and DIC, we estimated the error in sampling within 45 minutes around dawn and dusk. The error of the metabolic parameters estimated in this way was 39 mmol m^{-2} d^{-1} for DO and 116 mmol m^{-2} d^{-1} for DIC. We discuss the effect of this error later.

Atmospheric exchange: calculation of gas air-water fluxes

The flux of CO_2 or O_2 across the air-water interface was calculated from:

$$F = \varepsilon\, k\left(C_{atm} - C_w\right) \qquad \text{Eq. (5.4)}$$

where F is the flux (mmol m^{-2} d^{-1}), ε is the chemical enhancement factor for CO_2 (dimensionless), k is the gas transfer velocity (m s^{-1}), and C_w and C_{atm} are the concentration of gas (CO_2 or O_2) in surface water and in atmospheric equilibrium respectively (mmol m^{-3}). The concentration of CO_2 in atmospheric equilibrium was calculated from Henry's law: $CO_{2atm} = \alpha \cdot pCO_2$, where α is the solubility constant for CO_2 at given salinity and temperature (mol m^{-3} atm^{-1}), obtained from Weiss (1974), and pCO_2 was assumed to be constant at 380 μatm. The concentration of DO in atmospheric equilibrium was calculated from salinity and temperature following Weiss (1970). The k in Eq. (5.4) is the most problematic term for the calculation of air-water fluxes, and several equations have been proposed to estimate k as a function of wind speed in open oceans and estuaries (Raymond and Cole 2001). In this study we calculated k following two different methods. The first parameterization was the proposed by Liss and Merlivat (1986) as described in Frankignoulle et al. (1996). This method, from now on referred to as LM86, assumes a lineal dependence of k on wind-speed. The second method was the parameterization of Borges et al. (2004) for microtidal estuaries with low influence of water current on k. A specific k-wind slope for the lagoon was calculated from the lagoon surface area (0.7 km^2) following the equations in Borges et al. (2004). The values of k were corrected for the observed in situ salinity and temperature with the Schmidt numbers (the ratio of the kinematic viscosity to the diffusion coefficient) for each gas (CO_2 and O_2). The Schmidt numbers for freshwater and for seawater were calculated from water temperature following the formulations of Wanninkhof (1992). A linear relationship with salinity was assumed to calculate the Schmidt numbers at the observed water salinity (Borges et al. 2004). Daily values of wind speed (m s^{-1}) were obtained from the closest (7 Km) meteorological station (Spanish Meteorological Institute). To account for the chemical enhancement of the air-water flux of CO_2 at high values of pH, a chemical enhancement factor for the in situ values of salinity, temperature and pH, was calculated from the theoretical model of Hoover and Berkshire (1969), as described in Wanninkhof and Knox (1996).

5.3. Results

5.3.1 Variability in DIC and DO concentrations

From the total number of diel cycles surveyed, one sampling date was discarded because of intense rainfall (26 august). Two diel cycles showed anomalous behaviour in DIC and DO because of equipment malfunction, and were also discarded. Thus, a total of 36 diel cycles were analysed.

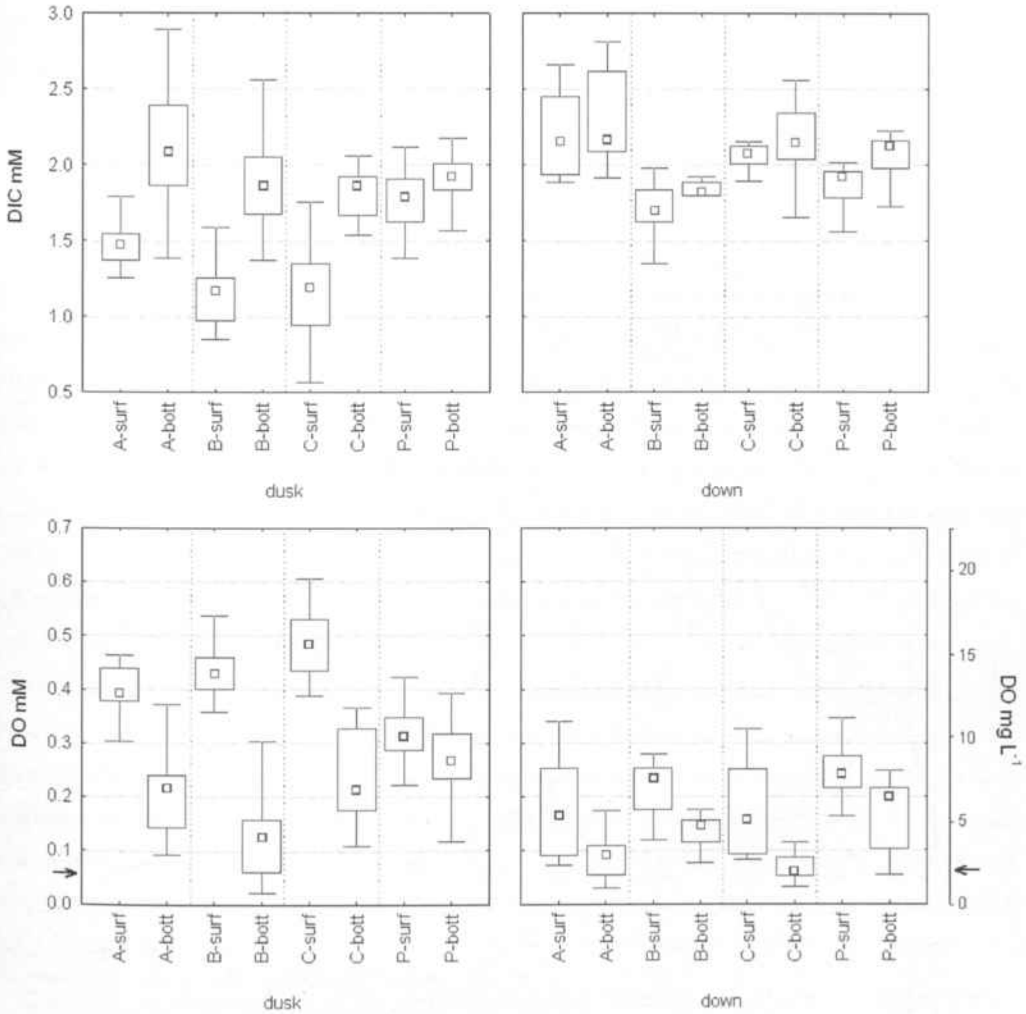


Figure 5.2. Variability in DIC and DO concentrations. The median (point), the range (whiskers), and the 25% and 75% percentiles (box) are shown for each site and depth, for the dawn and dusk samplings. The arrows indicate the 2 mg L^{-1} definition of hypoxia.

The concentration of DIC and DO ranged 0.57-2.89 mM and 0.02-0.61 mM, respectively, and high spatial and temporal variability was observed (Fig. 5.2). Significant differences in DIC and DO concentrations were observed for the three considered factors: sampling time (dusk or dawn), type of site (littoral or deep) and depth (surface or bottom) (Fig. 5.2). All the diel surveys showed the expected variation in DIC, with high values at dawn and low values at dusk, and the inverse trend was observed for DO (low and high values at dawn and dusk, respectively; Fig. 5.2).

Table 5.2. Vertical concentration gradient (bottom-surface) of DIC and DO for each sampling site. The mean ± s.d. is shown for the dusk and dawn samplings. The depth and the mean biomass of *R. cirrhosa* are also shown for each site. Significance levels (Wilcoxon matched pairs test for the differences between surface and bottom): *: $p<0.05$; **: $p<0.01$; ***: $p<0.001$; n.s.: not significant.

Site	Depth cm	Biomass gDW m^{-2}	DIC gradient (mmol L^{-1} m^{-1})		DO gradient (mmol L^{-1} m^{-1})	
			dusk	dawn	dusk	dawn
A	50	576 ± 74	$1.20 \pm 0.68^{***}$	$0.22 \pm 0.28^{*}$	$-0.38 \pm 0.20^{***}$	$-0.16 \pm 0.18^{*}$
B	50	606 ± 171	$1.21 \pm 0.48^{***}$	$0.26 \pm 0.18^{**}$	$-0.52 \pm 0.25^{***}$	$-0.16 \pm 0.11^{*}$
C	50	667 ± 206	$1.19 \pm 0.45^{***}$	$0.28 \pm 0.25^{**}$	$-0.48 \pm 0.23^{***}$	$-0.19 \pm 0.18^{**}$
P	250	-	$0.05 \pm 0.05^{**}$	0.07 ± 0.06 (n.s.)	$-0.03 \pm 0.03^{**}$	-0.03 ± 0.04 (n.s.)

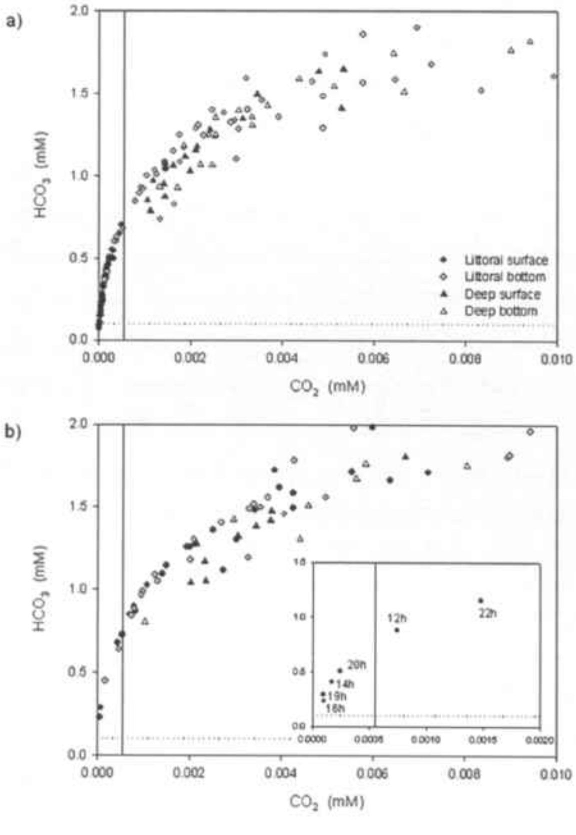


Figure 5.3. Carbon dioxide and bicarbonate concentrations observed during the studied period at dusk (a) and dawn (b). Each point corresponds to a sampling time, and different symbols represent the depth (surface or bottom) and type of site (littoral or deep). The inset shows a detail of the diel cycle of 21 August at site B. The lines are the compensation points for CO_2 (solid line) and HCO_3 (dotted line) described for *R. cirrhosa* in Peñuelas and Menédez (1990).

Bottom hypoxia at the littoral sites was observed on the 37% of the dawn surveys and on the 4% of the dusk surveys, whereas at the deep site only one survey showed bottom hypoxic values (Fig. 5.2). On the complete diel cycle of 21 august at site B, bottom hypoxia disappeared one hour after dawn (data not shown). With regard to the possible carbon limitation of macrophytes' photosynthesis, the CO_2 and HCO_3 concentrations are shown in Figure 3. At dusk, all the surface waters of the littoral sites showed concentrations below the CO_2 compensation point for *R. cirrhosa* and were only occasionally below the compensation point for HCO_3. At dawn, only a few points were below CO_2 compensation point. From the complete diel cycle of 21 august, CO_2 concentrations below the compensation point were observed from 2p.m. to 8p.m. (Fig. 5.3, inset).

The concentration gradient between surface and bottom (in mmol L^{-1} m^{-1}) was always positive for DIC (i.e., higher concentration at bottom than at surface) at all sites (Fig. 5.2; Table 5.2). The contrary was observed for DO, with lower concentrations at bottom than at surface. No significant vertical gradients in salinity were observed during the study period. The temperature vertical gradient ranged from 3.2 to -10.2 °C m^{-1} and from 0.36 to -0.44 °C m^{-1} for the littoral and deep sites, respectively (data not shown). The surface-bottom difference in DIC and DO was always significant at the littoral sites (Wilcoxon test $p<0.05$), whereas at the deep site, significant vertical gradients were only observed at dusk (Table 5.2). The DIC vertical gradient at dusk was significantly higher at the littoral sites than at the deep site ($U=26$; $p<0.001$; Table 5.2, Table 5.3b). Similarly, the DO vertical gradient at dusk was significantly higher at the littoral sites than at the deep site ($U=67$; $p<0.001$). The difference in gradient between littoral and deep sites was not evaluated at dawn because the vertical gradient at the deep site was not significant (Table 5.2).

With regard to the differences in concentration between littoral and deep sites, at dusk, surface water DIC was significantly lower at the littoral sites than at the deep site, whereas no significant differences between deep and littoral sites were observed in surface water at dawn or in bottom DIC concentrations at anytime (Fig. 5.2; Table 5.3a). The inverse pattern was observed for DO at dusk, with higher surface concentrations at the littoral sites than at the deep site. The bottom DO concentration was however significantly lower at the littoral sites than at the deep site both at dusk and dawn (Table 5.3a).

With regard to the amplitude of the diel change in concentration, at the littoral sites the surface waters always showed higher amplitudes than bottom waters for both components (Fig. 5.4). For surface waters, the deep site showed significantly lower amplitudes than the littoral sites for both DIC and DO (Fig. 5.4 and Table 5.3c). No significant differences in the DIC and DO changes in bottom waters were observed between deep and littoral sites.

Table 5.3. Summary of the Mann-Whitney U tests for the differences between littoral (L) and deep (D) sites. The tests for the differences in a) concentrations (mM), b) in the absolute vertical concentration gradient (mmol L^{-1} m^{-1}), and c) in the absolute diel change in concentration (mmol L^{-1} d^{-1}) are shown. Significance levels are as in Table 2

a)	DIC		DO	
	dusk	dawn	dusk	dawn
Surface	$L < D^{***}$	n.s.	$L > D^{***}$	n.s.
Bottom	n.s.	n.s.	$L < D^{*}$	$L < D^{**}$

b)	DIC gradient		DO gradient	
	dusk	dawn	dusk	dawn
	$L > D^{***}$	-	$L > D^{***}$	-

c)	Amplitude DIC cycle		Amplitude DO cycle	
	day	night	day	night
Surface	$L > D^{***}$	$L > D^{***}$	$L > D^{***}$	$L > D^{***}$
Bottom	n.s.	n.s.	n.s.	n.s.

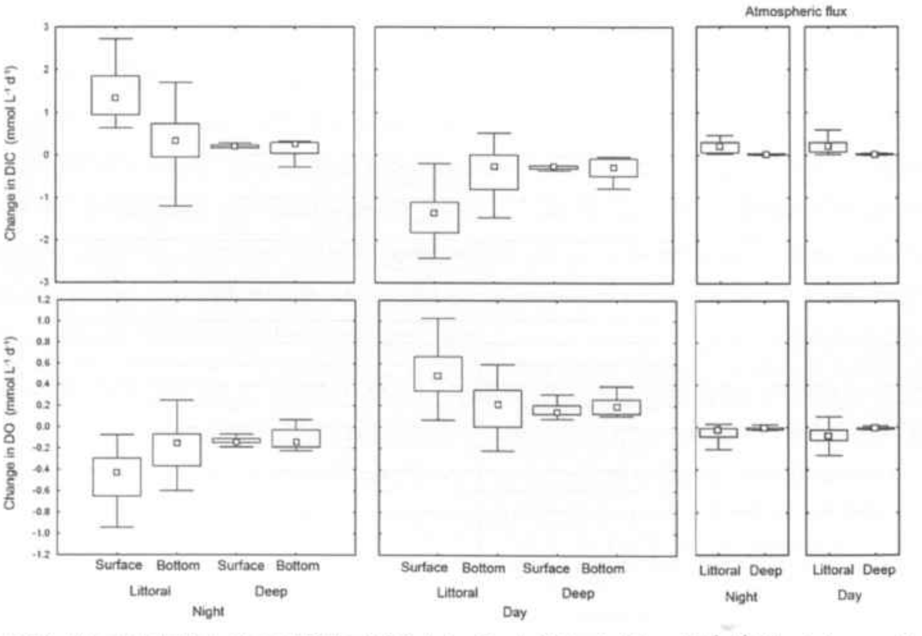


Figure 5.4. Observed diel incursions of DIC and DO during the studied period (mmol L^{-1} d^{-1}). Symbols are as in Figure 5.2. The right hand panels are the calculated air-water fluxes of CO_2 and O_2 during night and day, expressed in mmol L^{-1} d^{-1} for comparison (positive and negative numbers denote, respectively, invasion and evasion). 5.

The calculated air-water fluxes showed high variability. The daily flux of CO_2 was always positive (invasion) and ranged 0.021-1.259 mmol L^{-1} d^{-1} (26-315 mmol m^{-2} d^{-1}). The mean difference in the daily flux calculated with the two k-wind parameterizations used (B04 and LM86) was 0.141 mmol L^{-1} d^{-1} (43.3 mmol m^{-2} d^{-1}), which represents a relative standard deviation (r.s.d.) of up to 64%. For DO, positive and negative fluxes were observed, but oxygen evasion was the most frequent case (87% of the surveys). The daily flux of oxygen ranged from -0.444 to 0.078 mmol L^{-1} d^{-1} (-111 to 31 mmol m^{-2} d^{-1}), and the mean difference between the two methods was 0.071 mmol L^{-1} d^{-1} (22.8 mmol m^{-2} d^{-1}), which represents a mean r.s.d. of 34%.

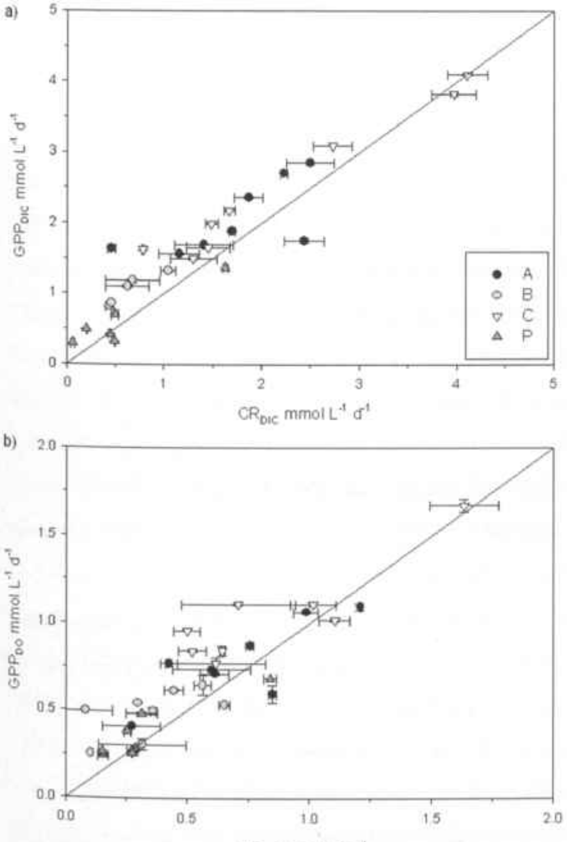


Figure 5.5. Estimates of community respiration (*CR*) against gross primary production (*GPP*) based on DIC (a) and DO (b) estimates. The error bars refer to the standard deviation of *CR* and *GPP* for the two methods used to estimate the atmospheric exchange.

With regard to the diel changes in the depth-integrated concentration, a small number of the surveys did not show the expected pattern of variation. For DIC one survey showed night decrease in concentration, and another one showed day increase in concentration, and for DO, one night showed unexpected increase in concentration. These anomalous surveys were not considered in the metabolic estimates, and its significance will be discussed later. The metabolic estimates (in mmol L^{-1} d^{-1})

showed a wide range of variation (Fig. 5.5). All the metabolic parameters are expressed in terms of the mean and s.d. of the two calculations, and the mean difference in *CR* and *GPP* between the two estimates of the atmospheric exchange was 0.075 mmol L^{-1} d^{-1} for DIC, and 0.037 mmol L^{-1} d^{-1} for DO. The community respiration (*CR*) ranged 0.058-4.109 mmol L^{-1} d^{-1} for DIC and 0.081-1.634 mmol L^{-1} d^{-1} for DO (Fig. 5.5). The photosynthesis was very close to *CR*, and ranged 0.295-4.098 mmol L^{-1} d^{-1} for DIC and 0.244-1.670 mmol L^{-1} d^{-1} for DO. The deep site showed the lowest values of *GPP* and *R*, and high variability was observed within the littoral sites (Fig. 5.5). The lagoon was turned towards net autotrophy most of the surveys, but some negative NEP values (net heterotrophy) were observed. NEP ranged from -0.681 to 1.172 mmol L^{-1} d^{-1} for DIC and from -0.251 to 0.456 mmol L^{-1} d^{-1} for DO. Both GPP and R were much smaller when calculated from DO changes than when based on DIC changes.

5.4. Discussion

High spatial and temporal variability was observed in the DIC and DO concentration during the studied period. The dusk-dawn variations in DIC and DO concentrations reflect the expected diel cycle in the dominance of the production-respiration processes following the diel light cycle. The DIC and DO vertical concentration gradients can be attributed to the vertical distribution of the dominant biological activity. This distribution, with surface and bottom waters dominated by photosynthetic and respiratory processes, respectively, is the expected pattern in shallow systems dominated by canopy forming macrophytes like *R. cirrhos*a, where the canopy reaches water surface and generates intense self-shading and high vertical gradients in temperature (Carpenter and Lodge 1986; Duarte et al. 2002). A different pattern is expected in systems dominated by benthic non-canopy-forming macrophytes or by bottom macroalgae (D'Avanzo and Kremer 1994).

The main driver of spatiotemporal variability can be attributed to the macrophyte photosynthetic activity at the littoral surface waters. This is reflected by several evidences. Firstly, the differences in surface concentrations between littoral and deep sites are only evident at dusk (Fig. 5.2 and Table 5.3a), i.e., after the period of carbon-demanding and oxygen-releasing photosynthetic activity. Secondly, the DIC and DO vertical gradients were higher at dusk than at dawn (Table 5.2), and were higher at the littoral sites than at the deep site (Table 5.3b). The higher vertical gradients at dusk are again related to the photosynthetic activity at surface waters in the littoral sites. Thirdly, the diel changes in DIC and DO were higher at the littoral sites than at the deep site only for surface waters (Table 5.3c). It must be noted that these littoral-deep differences at surface were not only observed during the day but also during the night (Table 5.3c). The night differences in the diel changes may be attributed to a higher respiration from the macrophyte biomass of the meadows. The absence of difference in the bottom diel changes (Table 5.3c) suggests that common metabolic processes take place at all the sites, independently of the depth and of the presence or absence of rooted macrophytes.

This is confirmed for DIC because bottom concentrations are not significantly different between littoral and deep sites (Fig. 5.2 and Table 5.3a). In the case of DO, however, bottom differences in concentration between littoral and deep sites were observed at dawn and dusk (Table 5.3a). It must be noticed that the significance of these differences is less important than for the surface waters, but they are anyway significant. A possible explanation for this differential pattern between DIC and DO concentrations in bottom waters may be attributable to differences in bacterial metabolism and chemical processes taking place at the sediment/water interface, as discussed below.

In conclusion, the variability in DIC and DO was determined by the diel cycle of biological activity within the macrophyte meadows. The maximum spatial heterogeneity was observed at dusk, while more homogenous conditions for both DIC and DO were observed at dawn (Fig. 5.2). During nighttime there is a homogenization of the biogeochemical processes; while during daytime differences in the dominant processes appear between surface and bottom waters, and between deep and littoral sites. This double spatial pattern (vertical and horizontal) is in accordance with the expected physicochemical variability within macrophyte beds (Carpenter and Lodge 1986; Barko and James 1998).

Concerning the significance of the DO levels, the frequency of bottom hypoxia was low in comparison with other coastal systems (Kuo and Neilson 1987; Breitburg 1990; Castel et al. 1996; Souchu et al. 1998; Rabalais et al. 2001; Viaroli et al. 2001; Duarte et al. 2002; Harzallah and Chapelle 2002; Viaroli and Christian 2003). Bottom hypoxia was observed at dawn at the littoral sites, and only occasional hypoxias were observed at dusk (Fig. 5.2). Complementarily, the complete diel cycle of 21 august showed that bottom hypoxic concentrations disappeared soon after dawn, indicating a fast recovery of oxygen. The sampling period was not especially hot in comparison with the average of the last thirty years (Table 5.1), what could have contributed to lower the extent and severity of bottom hypoxia. Moreover, the range of macrophyte biomass observed in the macrophyte meadows (Table 5.2; data from an authors' ongoing study[3]) was lower than the extreme values reported by Obrador et al. (2007) but were still in the upper range for coastal lagoons with *Ruppia cirrhosa* (Obrador et al. 2007). In other coastal embayments, bottom hypoxia is related to water stratification (Breitburg 1990; Ritter and Montagna 1999; Hearn and Robson 2001). In our study the water column was homogenous in salinity, and vertical temperature gradients were observed at the littoral sites, as is expected beneath macrophyte meadows (Barko and James 1998). From our results, bottom hypoxia does not seem to be a critical factor in the Albufera des Grau. It must be highlighted, however, that in this study we used the most common definition of hypoxia (DO < 2 mg L^{-1}; Rabalais and Turner 2001), but adverse effects on benthic communities can occur at higher concentrations (Ritter and Montagna 1999).

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[3] See Chapter 4 of this thesis

With regard to the ecological significance of the observed DIC concentrations, the available data showed that CO_2 limitation in *R. cirrhosa* is expected to occur during typical summer days, a suggested by the presence of almost all the surface littoral concentrations below the compensation point for CO_2 at dusk (Fig. 5.3). This species is highly adapted to low CO_2 concentrations and has the ability to use bicarbonate (Hellblom and Axelsson 2003). The concentration of bicarbonate only occasionally dropped below the compensation point (Fig. 5.3). These results give a first idea of the intensity of the carbon cycling beneath the dense meadows of *Ruppia cirrhosa* in this system.

With regard to the metabolic estimates, the discrete sampling approach in the free-water method was subject to certain inaccuracy due to the assumption that dusk and dawn coincides with the inflexion of the diel gas curves, which is not always necessarily true (Hanson et al. 2003). To prevent this, the free-water method should ideally be based on continuous measurements, and sampling frequencies of 5-30 minutes are common (Maberly 1996; Cole et al. 2000; Hanson et al. 2003). Nonetheless, approaches based on a small number of data points are common in the literature (Kemp and Boynton 1980; Carmouze et al. 1991; Swaney et al. 1999; Bachmann et al. 2000). McKellar (1977) compared the abbreviated dusk-dawn measurements with complete diel cycles in a Florida estuary and did not found significant differences except under rainy or cloudy conditions. Cronk and Mitsch (1994) also found identical results with the dusk-dawn approach than with a complete diel cycle. In the context of our instrumental limitation, it must be noted that we aimed to assess the spatial variability in the estimates and to explore the discrepancy between the DIC and DO estimates. In this sense, we favoured precision over accuracy. The precision of our estimates resulted from the errors associated to the measurements of the concentrations, to the lag of 45 minutes between the sampling at the different sites, and, for DIC only, to the assumption of surface alkalinity in bottom water samples. The overall precision of our estimates of *CR* and *GPP* was 11% for DIC and 7% for DO. We believe that this error is acceptable and ensures the validity of the results discussed here.

The metabolic estimates and the atmospheric exchange showed high spatial and temporal variability. The calculated atmospheric exchange was very sensitive to the k-wind parameterizations used, and extremely high differences in the flux were observed between the two methods, with mean r.s.d of up to 64% for DIC and 34% for DO. It is known that metabolic estimates are strongly affected by the methods used to estimate the air-water flux, and even antagonist conclusions with regard to the autotrophy or heterotrophy of the system can arise depending on the k-wind parameterization used (Gazeau et al. 2005b). However, during the studied period the magnitude of the air-water exchange was small in comparison with the magnitude of the biological fluxes (Fig. 5.4). The k-wind parameterizations used resulted in differences of only 6% in our estimates of *GPP* and *CR* on average. Thus, the uncertainty in the calculation of the air-water flux due to the inaccuracy in the estimation of the gas transfer velocity had a relatively small influence on the metabolic estimates in this study.

The estimates of *GPP* and *CR* showed a wide range of variation between dates and sites. The deep site showed the lowest values of the volumetric *GPP* and *CR*, and high variability was observed within the littoral sites (Fig. 5.5). When the metabolic estimates were converted to areal units, site P became the site with the highest metabolism, due to the higher depth. This will be discussed later in the context of site representativity of whole-system metabolism.

With regard to the comparison of the DIC and DO metabolism, the estimates based on DO were much smaller than those based on DIC. Calculated from the relationship between the nighttime corrected changes in DIC and DO, the respiration quotient ($RQ = \Delta DIC/\Delta DO$) averaged 2.4, which falls outside the rage described by Williams and del Giorgio (2005) for the respiration of different types of organic matter (RQ between 0.67 and 1.24). Deviations from this range of RQ may be expected if the stoichiometric C:N:P ratios of the organic matter being processed were extremely different from the typical aquatic (106:16:1) or terrestrial (790:7.6:1) organic matter (Torgersen and Branco 2007). This is, however, not the case in the Albufera des Grau, where the aerobic respiration of either macrophyte biomass (236C:8N:1P, authors' unpublished data) or sedimentary organic matter (1000C:102N:1P, author's unpublished data and López (2004a) would yield respiratory quotients of 0.94 and 0.83, respectively.

The low DO consumption in relation to the DIC emission must thus be related to other factors than organic matter composition, and the presence of anaerobic metabolic processes is the most plausible explanation. We assessed the qualitative contribution of anaerobic metabolism from the paired relationships between the TA and DIC changes (Fig. 5.6). The TA-DIC diagrams are used to identify biogeochemical processes in a wide variety of systems, including coral reefs (Watanabe et al. 2006), mangroves (Borges et al. 2003), aquifers (Cai et al. 2003), and estuarine waters and sediments (Forja et al. 2004; Bouillon et al. 2007). Because in this study the vertically integrated TA was subject to some error (see methods section) we complemented the TA-DIC diagrams with coupled analysis with DIC and DO. All these vector diagrams allow the comparison of the paired dynamics of the two considered variables (DIC, DO or TA) with the theoretical vectors describing the well-known stoichiometry of the biological and chemical reactions, including the bacterially-mediated metabolism of organic matter and the further chemical reactions of the resulting reduced species in the water column. The main biogeochemical processes and their corresponding DIC, DO and TA stoichiometry are listed in Table 4.

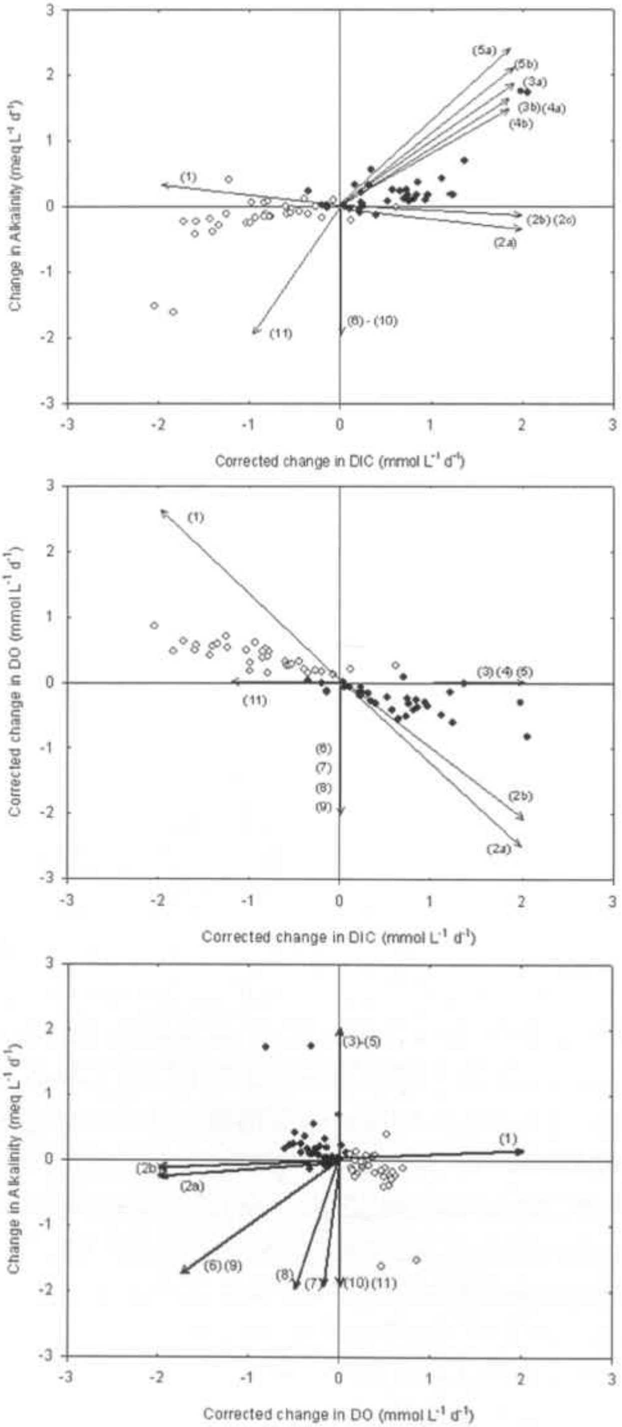

Figure 5.6. Paired diagrams of the diel changes (vertically integrated) in DO (mmol L^{-1} d^{-1}), DIC (mmol L^{-1} d^{-1}) and TA (meq L^{-1} d^{-1}) during the studied period. The DIC and DO changes are corrected for atmospheric exchange. The daytime (open circles) and nighttime (filled symbols) changes are shown. The numbers in brackets refer to the expected vectors for the biogeochemical processes listed in Table 4.

Table 5.4. Stoichiometry of the main biogeochemical reactions and impact on DO (mmol L^{-1}), on DIC (mmol L^{-1}) and on total alkalinity (meq L^{-1}).

Reaction	ΔDIC	ΔDO	ΔTA
(1) Photosynthesis $106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \rightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2$	-106	+138	+18
(2) Aerobic respiration of organic matter $(CH_2O)_x(NH_3)_y(H_3PO_4) + (x+2y)O_2 \rightarrow xCO_2 + yNO_3^- + HPO_4^{2-} + (x+y)H_2O + (y+2)H^+$	+x	-x-2y	-y-2
(2a) Redfield stoichiometry (x = 106; y = 16)	+106	-138	-18
(2b) *Ruppia* biomass (x = 236; y = 8)	+236	-252	-10
(2b) Sediment organic matter (x = 1000; y = 102)	+1000	-1204	-104
(3) Denitrification (Mechanism 1) $(CH_2O)_x(NH_3)_y(H_3PO_4) + 0.8xNO_3^- + (0.8x-2)H^+ \rightarrow xCO_2 + 0.4xN_2 + yNH_3 + HPO_4^{2-} + 1.4xH_2O$	+ x	0	0.8x-2+y
(3a) Redfield stoichiometry (x = 106; y = 16)	+106	0	+98.8
(3b) *Ruppia* biomass (x = 236; y = 8)	+236	0	+194.8
(3c) Sediment organic matter (x = 1000; y = 102)	+1000	0	+900
(4) Denitrification (Mechanism 2) $(CH_2O)_x(NH_3)_y(H_3PO_4) + (0.8x+0.6y)NO_3^- + (0.8x+0.6y-2)H^+ \rightarrow xCO_2 + (0.4x+0.8y)N_2 + HPO_4^{2-} + (1.4x+1.8y)H_2O$	+x	0	0.8x+0.6y-2
(4a) Redfield stoichiometry (x = 106; y = 16)	+106	0	+92.4
(4b) *Ruppia* biomass (x = 236; y = 8)	+236	0	+191.6
(4c) Sediment organic matter (x = 1000; y = 102)	+1000	0	+859.2
(5) Sulphate reduction $(CH_2O)_x(NH_3)_y(H_3PO_4) + 0.5xSO_4^{2-} + (0.5x-2)H^+ \rightarrow xCO_2 + yNH_3 + 0.5xHS^- + HPO_4^{2-} + xH_2O$	x	0	x-2
(5a) Redfield (x = 106; y = 16)	+106	0	+120
(5b) *Ruppia* biomass (x = 236; y = 8)	+236	0	+242
(5c) Sediment organic matter (x = 1000; y = 102)	+1000	0	+1100
(6) Nitrification $NH_3 + 2O_2 \rightarrow NO_3^- + H_2O + H^+$	0	-2	-2
(7) Oxidation of iron $4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$	0	-1	-8
(8) Oxidation of manganese $2Mn^{2+} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^+$	0	-1	-4
(9) Oxidation of sulphide $HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$	0	-2	-2
(10) Precipitation of iron sulphide $Fe^{2+} + HS^- \rightarrow FeS + H^+$	0	0	-2
(11) Precipitation of $CaCO_3$ $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$	-1	0	-2

The three vector diagrams located all the nighttime changes between the respiration line and the denitrification and sulphate reduction lines (Fig. 5.6). In this sense, it is known that sulphate reduction can account between 10% and 90% of organic matter remineralization in coastal systems (Jørgensen 1982), and high sulphate reduction rates have been specifically described in the sediments of the Albufera des Grau (López 2004b). For daytime, on the contrary, the lower DO change in comparison to the DIC change are not the expected under a combination of photosynthetic oxygen demand and anaerobic sediment respiration, and all the points fell between the photosynthesis and the calcite precipitation lines (Fig. 5.6). The $CaCO_3$ saturation index was always in supersaturation for calcite and aragonite during the studied period. However, we did not find any evidence of calcite precipitation in the field, and the calcification rates reported by López (2003) in the waters of the Albufera des Grau (6 μmol L^{-1} d^{-1} and 70 μmol L^{-1} d^{-1} at salinities of 10 and 37 respectively) are small in comparison with the DIC changes observed here (Fig. 5.4). It is hypothesized that the high concentration of DOC observed in the lagoon (up to 19.26 mg L^{-1}; Table 5.1) may have inhibited calcite precipitation, due to its inhibiting effect on calcite nucleation at concentrations above 1.8 mg L^{-1} (Lebron and Suarez 1996).

In the absence of significant DIC losses due to calcification, a complementary explanation for the low DO/DIC daytime ratios is needed. The precipitation as FeS in the sediment, or the reoxidation of the reduced sulphide generated from sulphate reduction are possible explanations (de Wit et al. 2001; Azzoni et al. 2001). The precipitation of FeS is the most likely explanation, in accordance with previous observations in the Albufera des Grau (López 2004b). However, a reoxidation of up to 80-90% of the sulphides produced by sulphate reduction was reported in a shallow estuary (Chambers et al. 1994). Another plausible explanation may be related to the transport of oxygen from leaves to roots and further release in the rhizosphere, a process that has been described for several macrophytes and specifically for *Ruppia* (Thursby 1984; Azzoni et al. 2001). This could influence by itself the DO and DIC dynamics (Kemp et al. 1986) and hence explain the lower DO/DIC daytime ratios, but it is likely that its effect is more related to the coupling and uncoupling of nitrification and denitrification at the sediment/water interface. The daytime oxygen release from the roots could enhance microbial nitrification, which may counteract the photosynthetic oxygen demand and hence result in a lower net oxygen change. In this sense, the vector diagrams for the daytime points (Fig. 5.6) could be explained by daytime processes dominated by photosynthesis and nitrification. This is in accordance with López (2003), who observed that nitrification played a role in the nitrogen cycle in the water of the Albufera des Grau. Against this argument, the enhancement of coupled nitrification/denitrification by benthic photosynthesis (An and Joye 2001) could mask this effect, as a CO_2 release from denitrification would occur and hence maintain or even reduce the DO/DIC ratio. This is, however, not the case in vegetated sediments. During light exposition, the macrophyte vegetated sediments show decreased denitrification rates by expanding the oxic sediment area and thus uncoupling the nitrification/denitrification activities (Risgaard-Petersen and Jensen 1997). In this sense, Bartoli et al. (2008) described total denitrification rates being lower in *Ruppia*-vegetated sediments than in bare sediments in a non tidal coastal lagoon in the Adriatic. Thus, the higher daytime bottom oxygen levels as a result of oxygen release in the roots, and the consequent enhancement of nitrification but not denitrification, together with a degree of calcite precipitation, FeS precipitation and sulphide reoxidation, may be responsible for the lower DO changes in relation to DIC changes during daytime.

In conclusion, the DIC and DO dynamics were highly uncoupled in this study, as is expected in a shallow aquatic system with intense sediment-water interaction and large variations in oxygen concentrations (Torgersen and Branco 2007). High discrepancies between DIC and DO dynamics, similar to those observed in this study, were attributed to differential impact of water movement on DIC and DO by Ziegler and Benner (1998) in a seagrass-dominated coastal lagoon. Despite the Albufera des Grau is a non tidal lagoon and despite it did not receive significant riverine inputs during the sampling period, we cannot discard a similar explanation here. However, as discussed before, we believe that the DIC and DO uncoupling is more likely related to bacterial-mediated processes together with further chemical reoxidation of the resulting reduced species in the water column or in the oxic upper portion of the sediment. As stated by Torgersen and Branco (2007), this complexity in the biogeochemical processes generates significant deviations from the traditional photosynthesis/respiration stoichiometry in the DIC and DO dynamics in shallow aquatic systems. The immediate consequence of this is that any estimation of metabolic parameters by free-water methods based solely on oxygen measurements is not recommended, and that coupled DIC and DO estimates of metabolism should be performed and comparatively interpreted. The paired diagrams with the process vectors of the known reactions are a useful tool to explore this variability and even allow quantitative approaches (Watanabe et al. 2006; Torgersen and Branco 2007).

Table 5.5. Summary of the whole system metabolism based on DIC changes during the study period (mean ± s.d., in mmol C m^{-2} d^{-1}). The estimates based on the surface-weighted average, the central sampling site, and the littoral sampling sites are shown

	Surface-weighted average	Deep site	Littoral sites
GPP	1169 ± 619	1426 ± 914	1056 ± 341
CR	1027 ± 747	1273 ± 1183	834 ± 421
NEP	136 ± 351	108 ± 561	162 ± 184
F	60 ± 31	46 ± 26	107 ± 55

Given the high discrepancy between the DIC and DO metabolism, we calculated the surface-weighted whole-system metabolism only from the DIC estimates. The whole system *GPP* was 1169 ± 619 mmol m^{-2} d^{-1}, and *CR* was 1027 ± 747 mmol m^{-2} d^{-1} (Table 5.5). These estimates were in the upper range of the reported values for coastal systems (Duarte and Agustí 1998). *GPP* and C*R* were in close balance, slightly turned into net autotrophy, as is expected in a macrophyte-dominated system (Duarte and Cebrian 1996). Thus, the net ecosystem production was a small fraction of the magnitude of the *GPP* and *CR* fluxes (12% on average), and the *GRR*/*R* ratio was 1.21, a value that falls well within the expected values in coastal systems (Duarte and Agustí 1998). The analysis of the net autotrophic or heterotrophic character of the system from the results of a single season makes no sense in systems with high metabolic seasonality such as the macrophyte-dominated coastal systems (Gattuso et al. 1998) and will not be discussed here. During the studied period, coincident with the period of maximum macrophyte biomass and activity, the magnitude of the fluxes was very high. From the calculated carbon fluxes, we calculated the residence time for DIC as 3.7 days, and for DO as 0.9 days. These small values are similar to those obtained by Ziegler and Benner (1998) in a seagrass-dominated costal lagoon.

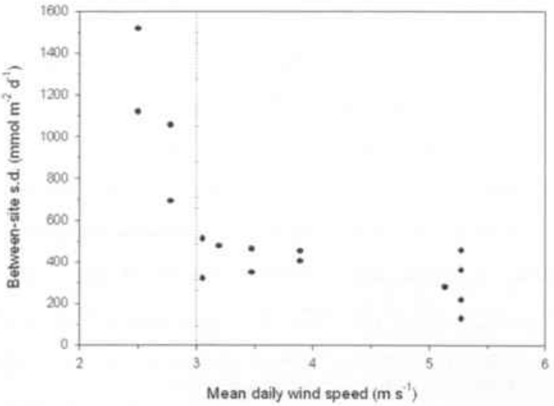

Figure 5.7. Spatial variability in the metabolic estimates in relation to the mean daily wind speed (m s^{-1}). The spatial variability for each date is defined as the standard deviation of the *GPP* and *CR* estimates at all the sampling sites.

Finally, the whole-system values based on surface-weighted averages differed from those calculated only from the deep site estimates by 32%, and from those at the littoral sites by 55% on average (Table 5.5). The use of single site estimates of metabolism in lakes and estuaries has been criticised because it neglects the spatial metabolic heterogeneity of the system, and the adoption of multiple sampling sites is highly recommended (D'Avanzo et al. 1996; Russel et al. 2006; Russell and Montagna 2007; Van de Bogert et al. 2007). In macrophyte-dominated systems, this extent is probably even more necessary, as not only the physical processes influence, but also spatial differences in biomass take place along the meadows. Van de Bogert et al. (2007) proposed the study of spatial metabolic heterogeneity in lakes in order to partition the metabolic signal detected in a central sampling site into benthic and pelagic sources. They also detected the presence of a wind threshold below which the between-sites deviations in metabolism were higher due to reduced homogenising water circulation. More in detail, the threshold described by Van de Bogert et al. (2007) in Peter Lake was one hour with wind speeds above 2.75 m s^{-1} and the authors suggest that larger benthic-pelagic differences in metabolism could raise this threshold. With the number and distribution of the sampling sites used in this study, we cannot quantify the portion of benthic or littoral metabolism detected in a central-pelagic site in the Albufera des Grau, but we explored the relationship between the mean daily wind speed and the standard deviation of the *GPP* and *CR* estimates. Despite more data would be needed to confirm our observations, we observed a threshold at daily wind speeds of c.a. 3 m s^{-1} (Fig. 5.7). The high site-to-site variation in metabolism observed in this study is not only due to the higher metabolic rates observed in the Albufera des Grau but also to the distinctive presence of macrophytes as a heterogenising factor. Despite the methodological approach was substantially different from that used by Van de Bogert et al. (2007), and despite our wind speed values correspond to daily averages, the threshold observed here is close to that reported in Peter Lake. Interestingly, this similar threshold value occurs despite different physical properties of lakes exist (morphometry, size, maximum fetch, depth), and despite wind speed is the main but not the only driver of horizontal mixing in aquatic systems.

5.5. Conclusions

The concentrations of DIC and DO showed high spatiotemporal variability, mainly driven by the macrophyte photosynthetic activity at surface waters beneath the littoral meadows. A double vertical and horizontal gradient was observed, but fast homogenization took place during nighttime. Bottom hypoxia was observed only in the littoral areas at dawn and does not appear to be a threat in this system. Our metabolic estimates were in the upper range described for coastal systems, and showed high spatial variability. An important discrepancy between the DIC and DO metabolism was observed, mainly due to anaerobic processes and pure chemical reactions taking place in the sediment and in the water column. Given the high spatiotemporal variability found in this study, high sampling effort and coupled DIC and DO analyses are fundamental if precise and accurate quantification of whole-system metabolism with the free-water method is aimed in productive macrophyte-dominated shallow lakes and lagoons.

5.6. Ackowledgements

BO was supported by a BRD grant from the University of Barcelona. We acknowledge Miquel Truyol, Melysa Gañán and the staff of the Albufera des Grau Nature Park for their assistance in the field work.

Chapter 6

The carbon cycle in a macrophyte-dominated coastal lagoon (Albufera des Grau, Western Mediterranean)

ABSTRACT / RESUM / RESUMEN

Obrador, B. and Pretus, JLl. 2009. The carbon cycle in a macrophyte-dominated coastal lagoon (Albufera des Grau, Western Mediterranean). *in prep.*

The dynamics of dissolved inorganic carbon, DIC, and its stable isotope composition, $\delta^{13}C_{DIC}$, were studied during three years in relation to estimates of whole-system fluxes in a highly productive macrophyte-dominated Mediterranean coastal lagoon (Albufera des Grau, Balearic Islands). We quantified the main carbon compartments and performed seasonal and annual carbon budgets. The results were complemented with an annual budget of organic carbon (OC) and a stable isotope approach along the food web to evaluate the fate of organic matter production.

The observed seasonal cycle of DIC was explained by several fluxes that were much higher in magnitude than the resulting net balance. The DIC cycling was extremely intense (residence time of 3.7 days and 18.6 days in the vegetated and unvegetated periods, respectively) in comparison with the water residence time. Due to the high turnover of carbon, the $\delta^{13}C_{DIC}$ little contributed to trace carbon fluxes, and showed a temporal dynamics more related to the isotope composition of the carbon sources than to the magnitude of the fluxes. The metabolic fluxes in the lagoon were very high, but calcite precipitation, hydrological carbon fluxes and atmospheric exchange were also important on the seasonal and annual budgets. The pCO_2 was clearly related to the production and decomposition cycle of the macrophyte meadows, but hydrological perturbations and phytoplankton peaks highly perturbed its dynamics. The lagoon was a sink of atmospheric CO_2 during the vegetated period, and a source during the unvegetated one. The net emission of CO_2 was more related to internal metabolism (likely due to the decomposition of macrophytic biomass) than to a heterotrophic activity fuelled by allochthonous inputs of OC.

The water inputs were occasionally responsible for the development of phytoplankton peaks and altered the water column stability and oxygenation, what highly affected the carbon cycling in the lagoon, but on the contrary, the watershed and marine water inputs did not represent a net input of OC, and neither did the lagoon export organic matter produced within the system. The high macrophytic production in the lagoon did not play a significant role in the food-web, which apparently relied on other organic matter sources. The decomposition of macrophytic biomass appeared to be the main destiny of the high macrophytic production, together with burial in the sediments, which represented a 15-30% of the annual macrophytic production.

RESUM (*en català*)

Es va estudiar la dinàmica del carboni inorgànic dissolt, DIC, i la seva composició isotòpica, $\delta^{13}C_{DIC}$, en una llacuna litoral Mediterrània dominada per macròfits (Albufera des Grau, Illes Balears) durant tres anys. Es van quantificar els compartiments de carboni i els fluxos de DIC a nivell de sistema per a realitzar balanços anuals i estacionals de DIC. També es va avaluar el destí de la producció primària mitjançant balanços anuals de carboni orgànic, OC, i d'una exploració isotòpica dels principals compartiments orgànics de la llacuna.

La dinàmica del DIC va estar determinada per la combinació de fluxos molt majors en magnitud que els canvis observats de concentració, en especial els fluxos metabòlics però també la precipitació de carbonats, l'intercanvi amb l'atmosfera o els fluxos hidrològics. El ciclat del DIC va ser molt intens (temps de residència del DIC de 3.7 dies i 18.6 dies en els períodes amb i sense macròfits, respectivament) en comparació amb el temps de residència de l'aigua. Aquesta elevada taxa de renovació va emmascarar la senyal de la $\delta^{13}C_{DIC}$. La pCO_2 va mostrar una dinàmica molt lligada al cicle estacional dels prats de macròfits, però també va ser intensament pertorbada per pics de fitoplàncton i esdeveniments d'entrada d'aigua. El flux atmosfèric de CO_2 va oscil·lar estacionalment, absorbint netament CO_2 en els mesos amb macròfits i emetent-ne en l'època no vegetada, en relació a la descomposició de biomassa macrofítica.

El paper dels fluxos hidrològics en els balanços de carboni va estar associats a la desestabilització de l'estructura i oxigenació de la columna d'aigua i al desenvolupament de pics fitoplanctònics, més que no pas a l'entrada de OC. L'elevada producció dels prats de macròfits no sembla tenir un paper rellevant en la xarxa tròfica, de manera que el principal destí del carboni produït internament seria la descomposició, molt ràpida a la llacuna, i l'enterrament al sediment, que va suposar un 15-30% de la producció anual macrofítica.

RESUMEN (*en castellano*)

Se estudió la dinámica del carbono inorgánico disuelto, DIC, y su composición isotópica, $\delta^{13}C_{DIC}$, en una laguna litoral Mediterránea dominada por macrófitos (Albufera des Grau, Islas Baleares) durante tres años. Se cuantificaron los compartimentos de carbono i los flujos de DIC a nivel de sistema para realizar balances anuales y estacionales de DIC. También se evaluó el destino de la producción primaria mediante balances anuales de carbono orgánico, OC, y mediante una exploración isotópica en los principales compartimentos orgánicos de la laguna.

La dinámica del DIC estuvo determinada por la combinación de flujos muy superiores a los cambios observados de concentración. Los flujos principales fueron metabólicos, pero también fueron significativos la precipitación de carbonatos, el intercambio atmosférico y los flujos hidrológicos. El ciclado de DIC fue muy intenso (tiempos de residencia de 3.7 y 18.6 días para los periodos con y sin macrófitos, respectivamente) en comparación con el tiempo de residencia del agua. Esta elevada tasa de renovación enmascaró la señal de los distintos procesos sobre la $\delta^{13}C_{DIC}$. La dinámica de la pCO_2 estuvo asociada al ciclo estacional de actividad de las praderas de macrófitos, pero fue intensamente perturbada por picos fitoplanctónicos y por entadas de agua al sistema. Se observó una oscilación estacional en el flujo atmosférico de CO_2, actuando la laguna como sumidero de CO_2 en los meses vegetados, y como una fuente en los meses sin macrófitos, en relación con la descomposición de la biomasa macrofítica.

El papel de los flujos hidrológicos en los balances de carbono estuvo más asociado a la desestabilización de la estructura y oxigenación de la columna de agua que a la entrada de OC. La red trófica de la laguna aparentemente no se sustenta en la elevada producción de las praderas de macrófitos, cuyo destino sería la rápida descomposición y el enterramiento en el sedimento, que supuso entre un 15 y un 30% de la producción anual macrofítica.

6.1. Introduction

Coastal ecosystems are amongst the most biogeochemically active areas of the biosphere (Gattuso et al. 1998). After being historically neglected in global carbon budgets, the carbon balance in coastal waters has been subject to intense study during the last decades, and it is now well documented that they play a significant role in the global carbon cycle despite their comparatively small surface area (Smith and Hollibaugh 1993; Frankignoulle et al. 1998; Thomas et al. 2004; Borges 2005). The intrinsic complexity of coastal environments results in large uncertainties in the determination of the direction and magnitude of carbon fluxes in these systems (Gattuso et al. 1998), and the heterogeneity and diversity of coastal ecosystems has been recently stressed as a factor that introduces further uncertainty in the quantitative integration of CO_2 fluxes at regional and global scales (Cai and Dai 2004; Borges et al. 2005). Particularly, and despite the effort done in particular ecosystems (e.g. Smith and Hollibaugh 1997; Gazeau et al. 2005a), there is a lack of comprehensive approaches to carbon cycling and its inter-annual variability in both tidal and non-tidal lagoons and in macrophyte-dominated ecosystems (Borges et al. 2005; Borges et al. 2006; Delille et al. 2009). Macrophytic beds are believed to play a significant role in the global carbon cycle due to their high biomass, long turnover time and high burial rates (Smith 1981; Duarte et al. 2005). However, little is known about the effect of macrophytic beds on air-water carbon fluxes and on the dynamics of dissolved inorganic carbon (DIC), and it is still undetermined their quantitative role in the global carbon cycle. In this sense, the budget of inorganic carbon in aquatic systems can be much improved by the analysis of the stable isotope composition of DIC, which can substantially contribute to better understand carbon-cycling by tracing sources and fluxes of carbon among interacting compartments (Bade et al. 2004).

On the other hand, the understanding of the role macrophytes play on carbon cycling in coastal environments requires an assessment of the fate of the carbon production within the system (Duarte and Cebrian 1996). The stable isotopes of carbon and nitrogen are a useful tool to trace the pathways of carbon among consumers in food webs (Post 2002; McCutchan et al. 2003), and have been used to study carbon cycling in many coastal ecosystems (Michener and Schell 1994), but little data is still available for Mediterranean coastal lagoons (Vizzini and Mazzola 2008).

In this paper we study the carbon dynamics in a highly productive coastal lagoon dominated by macrophytes. The Albufera des Grau (Balearic Islands, Western Mediterranean) is an enclosed coastal lagoon which exhibits dense and extensive meadows of the macrophyte *Ruppia cirrhosa*, with peak biomass values of up to 1760 gDW m^{-2} (Obrador et al. 2007). During three years, we studied the dynamics of DIC and its stable isotope composition, and quantified the main carbon compartments and fluxes in the lagoon. The main objective of this paper is to quantify the dynamics of DIC in relation to the main carbon pools and to perform seasonal and annual carbon budgets through estimates of whole-system carbon fluxes. We also evaluated the fate of organic matter production in the lagoon with a stable isotope approach along the food web and performed an exploratory budget of organic carbon, to better understand the carbon dynamics in the system.

6.2. Methods

6.2.1 Study site

The Albufera des Grau (surface area 78 ha, volume 1.0 hm^3) is a brackish coastal lagoon located in the northeast coast of the island of Menorca (Balearic Islands, Western Mediterranean; Fig. 6.1). The average depth is 1.37 m with a maximum of 3 m (Pretus 1989). Climate is typically Mediterranean, with mean air temperature of 17 ºC and 549 mm annual precipitation. The lagoon is located on Palaeozoic siliciclastic turbidites and receives only surface water inputs from inland. It is connected to the sea by a narrow channel, but the water exchange with the sea is irregular and does not represent an important renewal of water (Obrador et al., 2008). The lagoon is subject to high seasonal and interannual hydrological variability, with torrential freshwater inputs supplied by two streams that drain an area of 56 km^2. The watershed, mainly composed of Palaeozoic siliciclastic sands and silts and Mesozoic dolomites and sandstones, comprises extensive dry farming land (41%), Mediterranean Holm oak and Aleppo pine forests (47%) and shrublands (9%) as the main land covers (authors' unpublished data).

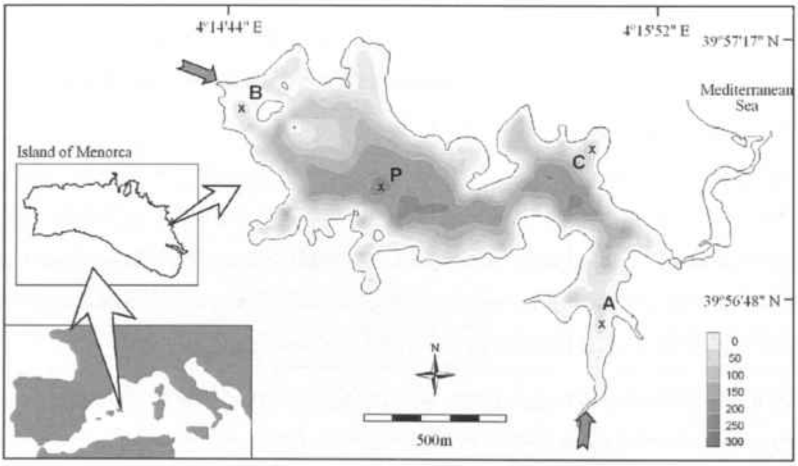

Figure 6.1. Location and bathymetry (50 cm isobaths) of the Albufera des Grau in the Island of Menorca (Western Mediterranean). The four sampling sites (crosses) and the freshwater inputs (grey arrows) are shown.

Currently, the lagoon is a macrophyte-dominated system with *Ruppia cirrhosa* and *Potamogeton pectinatus* which show a marked seasonal cycle (Obrador et al. 2007; Obrador and Pretus 2009a). Macroalgae (*Polysiphonia spp.*, *Gracilaria* sp. and *Chaetomorpha crassa*) are only sparsely observed in the deepest areas of the lagoon. Intense phytoplankton peaks are observed typically related to nutrients inputs from the watershed or from the decomposition of the macrophyte meadows (Obrador et al. 2007; Obrador and Pretus 2009a). In the past, the lagoon has been described as a macroalgae-dominated system (Margalef 1952; Pretus 1989); and hyperhaline events (up to 60 g L^{-1} in 1995, authors' unpublished data), haline vertical stratifications, and hypoxic crises have also been reported (Pretus 1989; Cardona 2001).

6.2.2 Field and laboratory work

The study period ranged from January 2002 to December 2004. Water samples for physicochemical analyses were taken monthly at a 3m-depth site in the central area of the lagoon (site P; Fig. 6.1). All samplings were conducted at the same time of the day and six water samples were taken at different depths every 50 cm from surface to bottom. Complementarily, three littoral sites (sites A, B and C; Fig. 6.1) were also sampled from May 2002 to address the spatial variability in the selected variables. Water salinity (reported in the practical salinity scale), pH (NBS scale), temperature (°C) and oxygen concentration (mg L^{-1}) were determined in situ with field sensors (WTW Multiline P3 and WTW Cond315i). Water samples were filtered and analyzed in the laboratory as soon as possible. Alkalinity was determined by potentiometric titration with H_2SO_4 and Gran evaluation (Stumm and Morgan, 1996), with an analytical reproducibility of 0.03 meq L^{-1}. The parameters of the carbonate system (total dissolved inorganic carbon and partial pressure of CO_2) were calculated from the pH and alkalinity values using the CO2SYS software (Lewis and Wallace, 1998). The CO_2 solubility of Weiss (1974) and the dissociation constants of Millero et al. (2006) for the in situ salinity and temperature were used. The mean reproducibility of the [DIC] and pCO_2 measurements was 0.087 mM and 30 μatm, respectively. The concentration of calcium, $[Ca^{2+}]$, was determined by ICP-OES and was used to the determine the saturation state with respect to calcium carbonate, Ω, calculated as:

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K_{cal} \qquad \text{Eq. (6.1)}$$

where $\left[CO_3^{2-}\right]$ is the concentration of the carbonate ion and K_{cal} is the solubility product for calcite at the observed salinity and temperature (Mucci 1983).

The phytoplankton biomass was evaluated from pigment concentrations in water, which were extracted in 90% Acetone and determined by the trichromatric method (Jeffrey and Humphrey 1975). The concentration of phytoplanktonic carbon, [Phyt-C], was determined assuming a carbon/chlorophyll ratio of 50 (Reynolds 1984), a value within the range reported by Cloern et al. (1995). The concentration of detritic carbon, [Det-C], was calculated from the difference between Particulate Organic Carbon, [POC], and [Phyt-C]. [POC] was determined in a CarloErba EA 1108 elemental analyser on pre-combusted fibre filters after the filtration of a known volume of water. The concentration of Dissolved Organic Carbon, [DOC], was determined in a TOC-500 Shimadzu in the water samples from sites B (littoral) and P (deep).

The stable isotope composition of DIC, $\delta^{13}C_{DIC}$, was measured by direct precipitation of $BaCO_3$ under basic conditions (pH between 10-12) and further analysis of the precipitates by IRMS (Bishop 1990). Briefly the method consists on the addition of NaOH 0.6M to raise the pH and further addition of $BaCl_2$ 0.25M in excess to ensure the complete precipitation of all the DIC and sulphate present in the sample. The precipitate was cleansed with NaClO 5% and deionised water to eliminate organic residuals and analysed in a Finnigan MAT DeltaC with a mean reproducibility of 0.4‰ for these samples (based on 22 duplicate measurements). We followed the recommendations concerning sample and reagent handling and processing given in the literature (Bishop 1990; Szynkiewicz et al. 2006). The accuracy of our $\delta^{13}C_{DIC}$ estimates, based on the analysis of 67 duplicate samples taken within 1 m distance, was 0.6‰. We also analysed the $\delta^{13}C_{DIC}$ in the streams entering the lagoon, but methodological constraints did not allow a complete isotopic characterization of the runoff inputs and only a reduced data set was available for discussion.

The data for the stable isotope characterisation of the food web was obtained from an authors' ongoing project dealing with the seasonal variations in stable isotope composition in the lagoon, and here we only show the mean values. Briefly, the study was based on specific samplings of selected trophic compartments in the period 2002 to 2004. The selected compartments were sampled seasonally and a significant number of individuals/samples were taken for each compartment. The organic matter sources considered were macrophytes (*R. cirrhosa* and *P. pectinatus*), macroalgae (*C. crassa*, *Polysiphonia sp.* and *Gracilaria* sp.), POC (as a surrogate of phytoplankton) and sedimentary organic matter (SOM). Macrophyte and macroalgal samples were sampled by hand and cleaned with tap water prior to drying. Surface sediments (upper 1-2 cm) were sampled with an Ekman dredge in spring 2006 during an intense survey that covered the whole lagoon (67 samples). Only the uppermost 1-2 cm were sampled, and the samples were treated with HCl 2N to remove carbonate debris and rinsed with deionised water prior to analysis (Kennedy et al. 2005). The benthic invertebrates were sampled with a 1 mm net in the littoral areas of the lagoon and included *Gammarus aequicauda*, *Sphaeroma hookeri* and *Pseudoammnicola gasulli*. The zooplankton was sampled with a 53 µm net in the central part of the lagoon. Up to nine fish species (*Anguilla anguilla*, *Atherina boyeri*, *Chelon labrosus*, *Dicentrarchus labrax*, *Gambusia holbrooki*, *Liza aurata*, *Liza ramado*, *Liza saliens* and *Mugil cephalus*) were sampled with a trammel net and a only muscle tissue was analysed. All samples were dried (70 °C to constant weight), powdered and weighted, and were analysed in a Finnigan MAT DeltaC with a mean reproducibility of 0.3‰ for both carbon in nitrogen in these samples (based on 20 duplicate measurements). All the data on the stable isotope composition was expressed in delta units (‰) relative to the PDB and N_2 standards for carbon and nitrogen, respectively.

6.2.3 Determination of the main carbon compartments

The main carbon pools in the lagoon (DIC, MC, PHYT-C, DET-C and DOC) were determined from the mean concentration of each compartment in water ([DIC], [PHYT-C], [DET-C] AND [DOC]) and the water volume at each sampling date, obtained from the bathymetry of the lagoon. In the specific case of macrophytic carbon, MC, we used the carbon content, the mean monthly biomass and the annual surface cover of *R. cirrhosa* during the studied period reported in Obrador and Pretus (2009a).

As a first evaluation of the hydrological influence on DIC dynamics, we calculated the DIC expected under conservative behaviour, i.e. we calculated the [DIC] by simple mixing between a riverine and a marine endmembers. In the constructed mixing model the concentration of a given constituent in a sample of salinity S, C_s, was determined by:

$$C_s = C_{sw} f + C_R (1 - f) \qquad \text{Eq. (6.2)}$$

where C_R and C_{sw} are the concentrations of the riverine and marine end members respectively, and f is the fraction of seawater in the sample, obtained from:

$$f = \frac{(S - S_R)}{(S_{sw} - S_R)} \qquad \text{Eq. (6.3)}$$

where S_R and S_{sw} are the salinities of the riverine and marine end members respectively. The salinities and concentrations used to construct the mixing model (Table 6.1) were taken from literature data (marine endemember) and from specific samplings in the streams entering the lagoon (riverine endmember). To account for the variability in the runoff concentrations, we used upper (mean + s.d.) and lower (mean - s.d.) estimates for S_R and C_R. We evaluated the total mass of DIC (calculated from the expected concentration and the observed lagoon water volume). The mixing model was also used to determine the dynamics of Ca and Na, with calculations performed in the same way than DIC. The calculated Ca served to mass-balance total calcium to estimate the fluxes of calcite precipitation and dissolution, and the Na was used to evaluate of the accurateness of the mixing model due to its expected conservative behaviour with salinity.

6.2.4 Estimates of the DIC fluxes

The estimated fluxes of carbon into and from the lagoon include the hydrological fluxes (runoff inputs, seawater inputs and lagoon outflow to the sea) and the atmospheric flux of CO_2. Site-specific internal fluxes such as calcite precipitation and dissolution, sediment fluxes and system metabolism were also estimated. Despite some fluxes were calculated on a daily (hydrological and atmospheric) or monthly (calcite fluxes) basis, the results were analysed on an annual and seasonal basis to minimize the effect of inaccuracies in our estimates. The seasons considered were the vegetated and unvegetated periods, defined from the presence or absence of *R. cirrhosa*. The residence time of DIC for each period was calculated from the mean pool size and the total inputs.

Table 6.1. Salinity and concentration data of the riverine and marine end members used in the mixing model and to estimate DIC and OC hydrological fluxes in the lagoon. The numbers in brackets indicate the number of samples analysed in the streams entering the lagoon

End member	Seawater (SW)	Riverine (FW)
Salinity	38 [a]	2.27 ± 1.15 (176)
Alkalinity meq L-1	2.568 [a]	5.89 ± 2.61 (70)
DIC mM	2.260 [a]	5.92 ± 2.79 (64)
Na mM	523 [c]	12.79 ± 10.36 (16)
Ca mM	11 [c]	3.47 ± 2.22 (116)
DOC mM	0.07 [b]	0.82 ± 0.49 (6)
POC mM	0.01 [b]	0.01-0.08 [d, e]

[a]: Bethoux et al. (2005), [b]: Doval et al. (1999), [c]: Millero (1996), [d]: Vidal-Abarca et al. (2001) [e]: Meybeck (2006)

Hydrological fluxes

The carbon fluxes from runoff, $FDIC_{runoff}$, seawater inflow, $FDIC_{sw}$, and lagoon outflow, $FDIC_{outflow}$, were calculated from the water fluxes and the mean concentration in each flow. The water fluxes were obtained from a specific dynamic hydrological model for the Albufera des Grau (Obrador et al. 2008). Briefly, the model consists on daily water balances in the watershed and the lagoon coupled to a salt mass balance in the lagoon. The model was calibrated during the same period studied here and allows a correct estimation of the daily water fluxes in the lagoon. The concentrations in stream runoff and seawater were the same that we used in the simple mixing model (Table 6.1). To account for the variability in the stream runoff concentrations, we used upper (mean + s.d.) and lower (mean - s.d.) estimates of the concentration in runoff. For the budgetary analysis, however, we only used the lower estimate given the results of the calcium mass balance (see section 2.4.3). The fluxes were calculated on a daily basis and integrated between the monthly sampling dates. For a higher accuracy, the outflow was calculated daily by interpolating the DIC concentration in the lagoon from our monthly original data. This makes sense since the water fluxes are available on a daily basis and the DIC concentration followed a marked seasonal cycle. Additional data points available in some periods (authors' unpublished data) were added during the interpolation to better adjust the seasonal behaviour.

Atmospheric exchange: calculation of gas air-water fluxes

The flux of CO_2 across the air-water interface was calculated daily from the interpolated concentration of CO_2 as:

$$FDIC_{atm} = \varepsilon\, k\left(C_{atm} - C_{w}\right) \qquad \text{Eq. (6.4)}$$

where $FDIC_{atm}$ is the flux (mmol m^{-2} d^{-1}), ε is the chemical enhancement factor for CO_2 (dimensionless), k is the gas transfer velocity (m d^{-1}), and C_w and C_{atm} are the concentration of CO_2 in surface water and in atmospheric equilibrium respectively (mmol m^{-3}). The concentration of CO_2 in atmospheric equilibrium was calculated from Henry's law: $CO_{2_{atm}} = \alpha \cdot pCO_2$, where α is the solubility constant for CO_2 at given salinity and temperature (mol m^{-3} atm^{-1}), obtained from Weiss (1974), and pCO_2 is the atmospheric partial pressure of CO_2. The value of pCO_2, assumed to be constant at 379 μatm (IPCC, 2007), was corrected for water vapour following Zeebe and Wolf-Gradow (2005). The k in eq. (4) is the most problematic term for the calculation of air-water gas fluxes, and several equations have been proposed to estimate k as a function of wind speed in open oceans and estuaries (Raymond and Cole 2001). In this study we calculated k following a parameterization for microtidal estuaries with low influence of water current on k (Borges et al. 2004). A specific k-wind slope for the Albufera des Grau was calculated from the lagoon surface area (0.7 km^2) following the equations in Borges et al. (2004). The values of k were corrected for the in situ salinity and temperature with the Schmidt number for CO_2 (the ratio of the kinematic viscosity to the diffusion coefficient). The Schmidt numbers for freshwater and for seawater were calculated from water temperature following the formulations of Wanninkhof (1992). A linear relationship with salinity was assumed to calculate the Schmidt number at the observed water salinity (Borges et al. 2004). The daily values of wind speed (in m s^{-1}) were obtained from the closest (7 Km) meteorological station (Spanish Meteorological Institute). As a reference we also estimated the air-water fluxes using literature minimum (0.72 m d^{-1}) and maximum (1.68 m d^{-1}) estimates for k in estuaries (Raymond and Cole 2001). To account for the chemical enhancement of the air-water flux of CO_2 at high values of pH, a chemical enhancement factor ε for the in situ values of salinity, temperature and pH, was calculated from the theoretical model of Hoover and Berkshire (1969), as described in Wanninkhof and Knox (1996).

Internal fluxes

We included in the internal fluxes all the processes affecting DIC within the lagoon: biological metabolism, calcite precipitation and dissolution, and sediment efflux. The net internal flux, $FDIC_{ni}$, was estimated as the difference between the observed DIC and the DIC expected by hydrological and atmospheric fluxes, $DIC_{h.a}$. The $DIC_{h.a}$ was calculated by summing the hydrological and atmospheric fluxes to the observed DIC at the previous time step.

The calcite precipitation and dissolution fluxes were estimated from a mass balance of total calcium in the lagoon and were compared with site-specific literature data. The difference between the observed mass of calcium and that expected by the simple mixing model (section 2.3) was assumed to correspond to calcite precipitation or dissolution. Calcite precipitation was previously estimated for the Albufera des Grau from incubation experiments by López (2003). This author describes supersaturation in calcite and reports calcite precipitation rates of 0-2 and 30-40 mmol m^{-2} d^{-1} at salinities of 10 and 37, respectively (López 2003). Given that our upper estimate for calcite precipitation was unrealistically out of the range described by López (2003), we only used the fluxes obtained from the lower estimate. This also applies to the estimation of the DIC fluxes, and is justified as a substitute of the unavailable data on the concentration - discharge relationship in stream runoff.

The metabolism during the vegetated period was calculated from previous estimates of community respiration, *CR*, and Gross Primary Production, *GPP*, in the Albufera des Grau (Obrador and Pretus 2009b). The mean daily areal metabolism, determined in summer 2002 through free-water diel variations in DIC at the same sites studied here, were 1169 ± 619 mmol C m^{-2} d^{-1} and 1027 ± 747 mmol C m^{-2} d^{-1} for *GPP* and *CR* respectively (Obrador and Pretus 2009b). On the other hand, it is noteworthy that these metabolic rates refer to whole system metabolism, and hence also include calcite precipitation and sediment respiration. As a reference sediment efflux in the Albufera des Grau was estimated in 21-55 mmol m^{-2} d^{-1} by López (2004b). As no metabolic data was available in winter, we performed a rough estimate of the planktonic metabolism during the unvegetated period using generic relationships with the water constituents. For planktonic community respiration, *R*, we used the relationship between *R* and [Chlorophyll] given in Williams and del Giorgio (2005) for estuaries. The planktonic *GPP* was estimated from the ratio *GPP/R*, which was calculated as a function of [Chlorophyll] and [DOC] following del Giorgio and Peters (1994).

6.2.5 Estimates of the main organic carbon fluxes

To perform an exploratory annual budget of organic carbon, OC, we estimated whole-system fluxes from sampling and literature data. The estimated OC fluxes into and from the lagoon include the hydrological fluxes of POC and DOC (runoff and seawater inputs and outflow to the sea), the biological metabolism and the burial of organic matter. The hydrological OC fluxes were calculated in the same way than the hydrological DIC fluxes (section 2.4.1 and see the concentrations in seawater and runoff in Table 6.1). The burial of organic matter was calculated from mean sedimentation rates in the lagoon and the organic carbon content in sediments (Middelburg et al. 2004). The sediment accretion rate (0.2-0.4 cm y^{-1}) was obtained through ^{210}Pb and ^{137}Cs dating of a sediment core taken in the central part of the lagoon (results of an author's ongoing project). The organic carbon content of sediments was determined on the above-described surface sediment samples in a CarloErba EA1108 elemental analyser, and averaged 7.6 ± 2.1 % in dry weight. To avoid the assumption of steady state conditions in the OC compartments, we calculated the net change in the mass of the carbon pools between sampling dates.

6.3. Results

6.3.1 Main hydrological and production events

The hydrological dynamics in the lagoon was based on a seasonal pattern of precipitation - evaporation broken by intense rainfall events entering significant amounts of water from stream runoff. Two main torrential events were observed during the studied period, as shown by the water fluxes (Fig. 6.2b) and by the daily changes in water level (Fig. 6.2a). Both events were recorded in 2003 (March and November). The torrential event of March 2003 resulted in a slight vertical salinity gradient (Fig. 6.2a). Other significant water inputs of minor importance occurred despite they were not always evident from the visualisation of the runoff flux from the hydrological model. This is the case of the sharp water level increases of April 2002, December 2002, September 2003, March 2004 and December 2004.

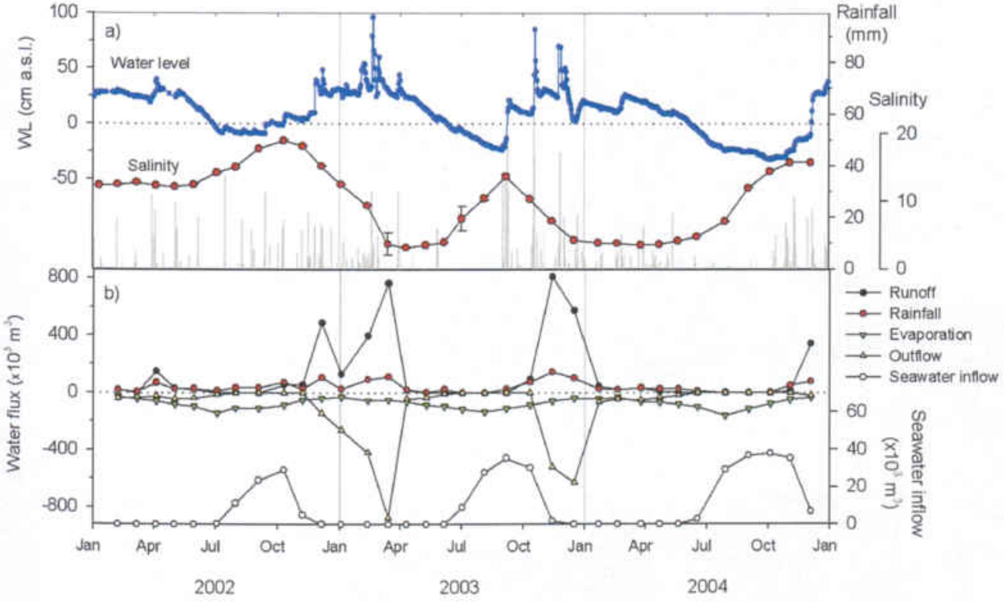

Figure 6.2. Temporal dynamics of the hydrological descriptors during the period 2002-2004. a) Water salinity (mean ± s.d. at the deep site), daily water level (in cm a.s.l.) and daily precipitation (mm). b) Water fluxes into and from the lagoon between sampling dates (note the different right axis for seawater inputs)

With regard to the dynamics of the primary producers, the phytoplankton peaked on March 2003 simultaneously to the torrential event (Fig. 6.3). The high phytoplanktonic biomass accumulation together with the slight salinity gradient probably caused the observed bottom hypoxia in spring 2003 (Fig. 6.3d). In summer 2003 another slight vertical salinity gradient, this time generated after the entrance of seawater (Fig. 6.2a and 6.2b), coincided with a new phytoplankton peak (Fig. 6.3a), and started a bottom hypoxia that lasted until the end of summer (Fig. 6.3). The chlorophyll concentration was above 50 µg L^{-1} during the autumn of 2003 and peaked again on February-March 2004, after another intense rainfall (see the daily water level in Fig. 6.2a). The macrophyte meadows showed a marked seasonal cycle with a growing period in spring leading to maximum biomass in summer and winter disappearance (Fig. 6.3a). In 2004 the macrophyte biomass decline started later and healthy stands were observed until December.

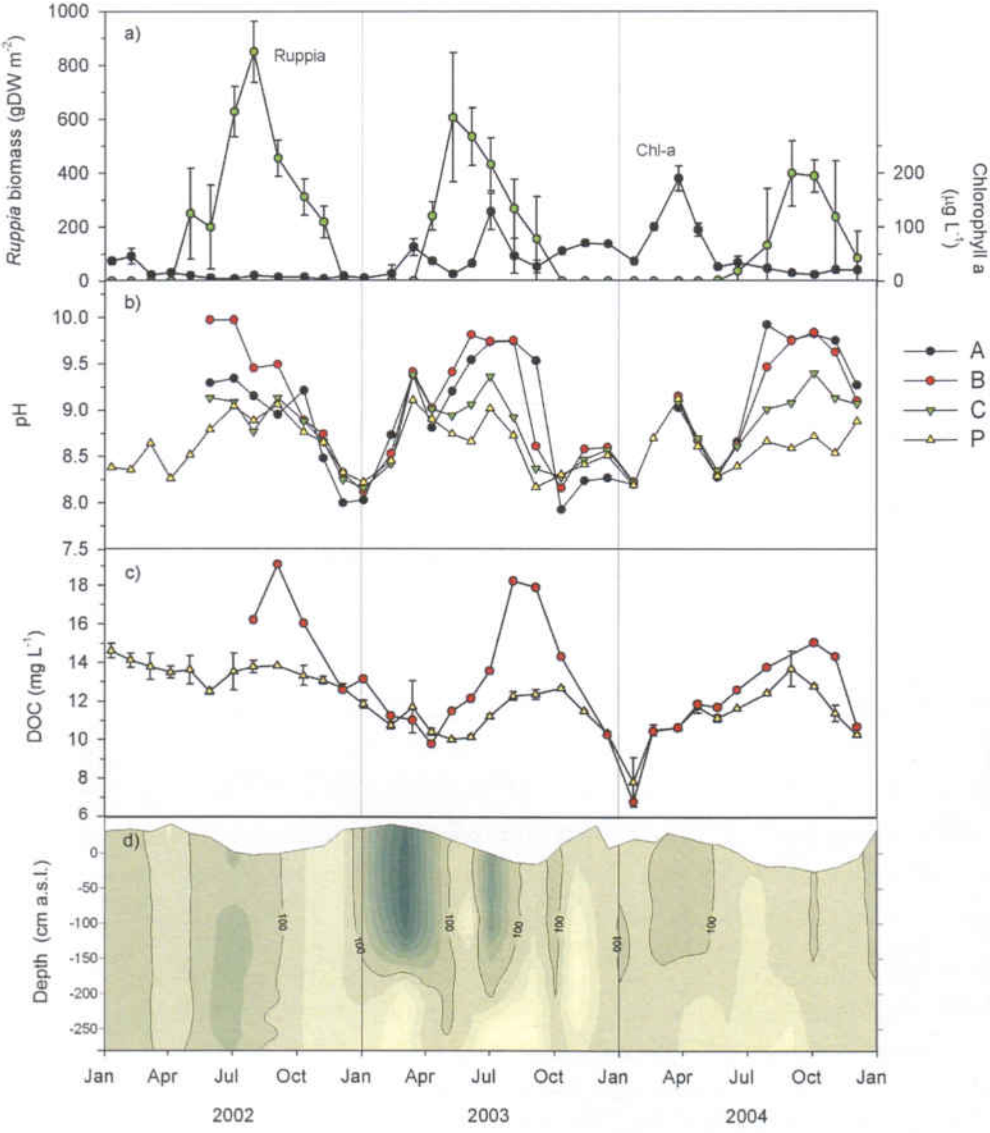

Figure 6.3. Temporal dynamics in the mean biomass of *R. cirrhosa* and Chlorophyll-a concentration (mean +- s.d.) (a), and in pH at the four sampling sites (b). In (c) the [DOC] is shown for sites B and P. In (d) the oxygen dynamics in a time-depth contour plot is shown for the central site.

The pH ranged 7.9-10 and showed a basic seasonal cycle with low values in winter (between 8.0 and 8.2) and maximum values in summer or early autumn (up to 9.97). Significant pH inflexions were observed during the spring months of 2003 and 2004, with a sharp increase followed by immediate decrease in pH. The same temporal pattern was observed in all the sampling sites, but the littoral ones, especially sites A and B, exhibited higher values than the deep site during the summer maximum. In winter all the sites showed similar values and temporal behaviour.

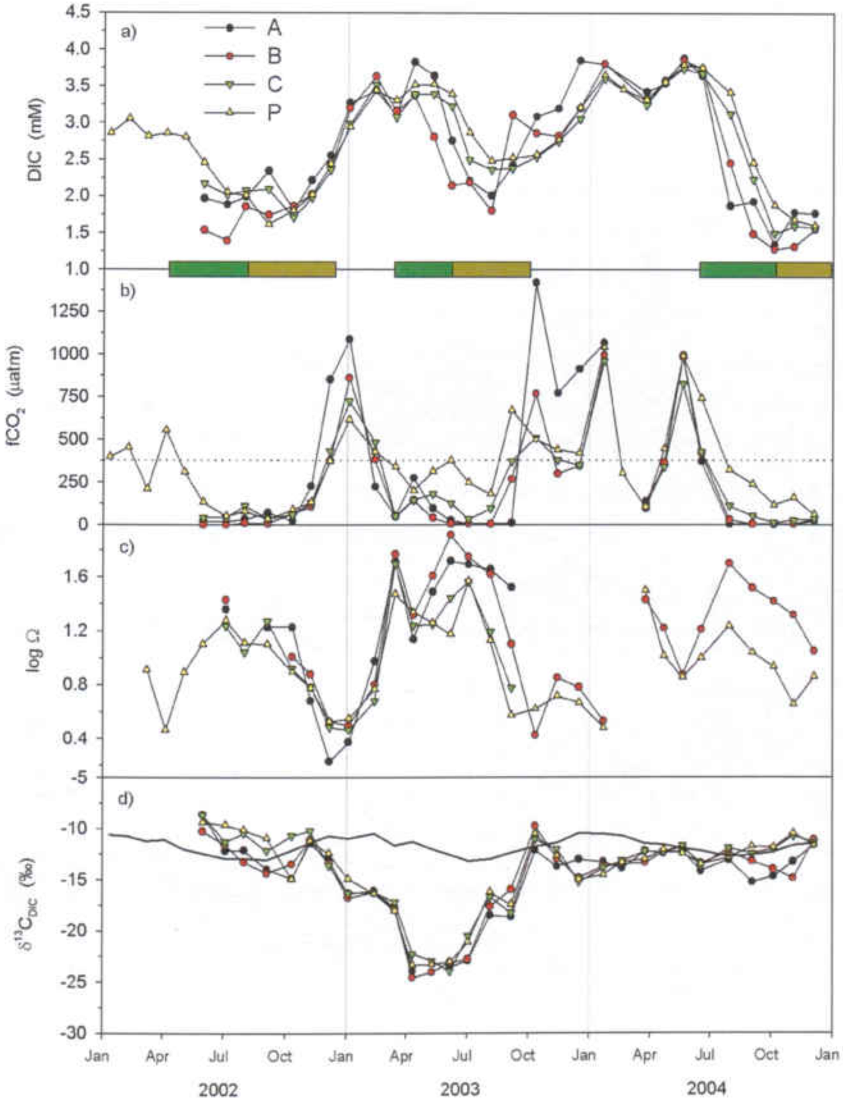

Figure 6.4. Temporal dynamics in DIC (a), pCO$_2$ (b), log Ω (b) and δ^{13}C$_{DIC}$ (c) at the four sampling sites during the period 2002-2004.

6.3.2 DIC] and $\delta^{13}C_{DIC}$ dynamics

The [DIC] ranged 1.28-3.88 mM and showed a marked seasonal pattern, with minimum values in summer or early autumn, and maximum values in winter and early spring (Fig. 6.4). The same dynamics was observed in all the sites, but the littoral ones showed lower summer values than the central site. The pCO_2 showed a wide range of variation (1-1419 µatm) with a temporal dynamics inverse to that of pH. During summer and most of spring the lagoon pCO_2 was below atmospheric equilibrium. In late autumn a sharp increase lead the lagoon above atmospheric equilibrium (up to 1000 µatm). In 2004, a peak in pCO_2 in spring broke this general seasonal pattern. Despite a seasonal trend in the saturation state of calcite was observed, the four sampling sites were supersaturated during the whole period (Fig. 6.4c).

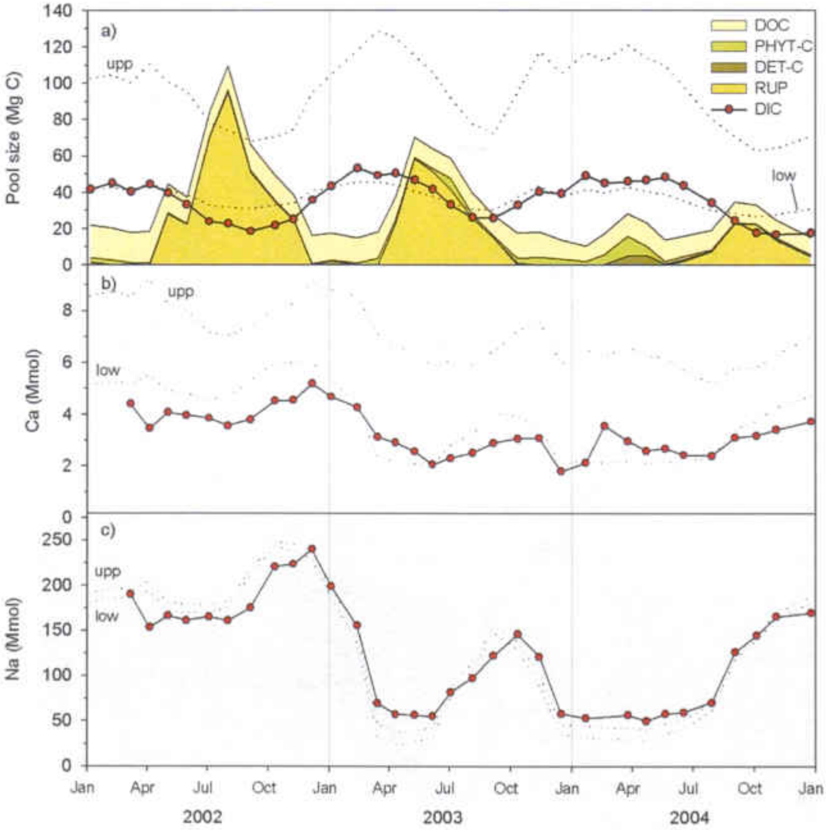

Figure 6.5. Dynamics in the main carbon pools in the Albufera des Grau during the studied period (Mg C). Note the cumulative representation of the organic carbon pools (MC, Phyt-C, Det-C and DOC). The dotted lines are the upper (upp) and lower (low) estimates of DIC by conservative mixing. In b) and c) the dynamics of the pools of Ca and Na (circles) are shown together with the mixing estimates (dotted lines).

The $\delta^{13}C_{DIC}$ did not show seasonal trend and moved in a high range of variation (from -24.5‰ to -9.4‰). A basal value of between -10‰ and -15‰ was observed during most of the year, except in the period March-August 2003, with values lower than -22‰. The isotopic deployment in DIC to values of $\delta^{13}C$ below that basal range started in December 2002 and was maintained until September 2003. All the sampling sites showed the same temporal dynamics. The few data available from streams yielded a tentative $\delta^{13}C_{DIC}$ in runoff of -12.9 ± 0.7‰ (n=5).

6.3.3 Carbon pools

The main carbon compartments in the lagoon were MC, DOC and DIC (Fig. 6.5). MC reflected the seasonal dynamics of the meadows and was the largest carbon compartment in the lagoon during the vegetated period, with maximum values of 95 Mg C, except in 2004, when DIC was the largest pool. The Phyt-C and Detri-C pools peaked in spring 2004, and ranged 0.2-11 Mg C and 0-5 Mg C, respectively. The DOC pool was quite constant in magnitude and ranged 9-18 Mg C. The inorganic pool, DIC, showed a seasonal behaviour in the range 17-53 Mg C. Both the range and the dynamics in DIC were fairly described by the mixing model, which consistently described the conservative dynamics of the sodium and the calcium pools (Fig. 6.5). For both DIC and Ca, the lower estimate by the mixing model was the most accurate prediction, and the upper estimate fell out of range. The mean seasonal contribution of the different carbon pools to total OC is summarised in Table 6.2. During the vegetated period MC accounted for more than two thirds of OC, followed by DOC. On the contrary, during the unvegetated period DOC was the dominant OC pool.

Table 6.2. Average carbon budgets (mean ± s.d.) during the vegetated and unvegetated periods (Mg C)

		Organic carbon pools					
Period	Days	MC	PHYT-C	DET-C	DOC	OC	DIC
Unvegetated	138 ± 17	0 (0%)	3.3 ± 2.3 (18%)	1.3 ± 1.2 (7%)	14 ± 3 (75%)	19 ± 2	44 ± 3
Vegetated	227 ± 17	31 ± 19 (70%)	1.2 ± 1.0 (3%)	0.2 ± 0.2 (<1%)	12 ± 2 (27%)	45 ± 20	31 ± 6

6.3.4 DIC fluxes

The estimated monthly hydrological fluxes followed the temporal dynamics of the water fluxes and were dominated by runoff inputs and lagoon outflow, both centred in the rainy periods (Fig. 6.6). The total seasonal and annual hydrological fluxes showed high interannual variability (Table 6.3). Annual runoff inputs were between 18 and 32 Mg C y^{-1} except in 2003, with values above 100 Mg C y^{-1}. A similar pattern was observed in the $FDIC_{outflow}$, with annual values around 10 Mg C (except, again, in 2003, with 101 Mg C y^{-1}). The annual $FDIC_{sw}$ was always below 4 Mg C y^{-1}.

Table 6.3. Estimates of the seasonal and annual DIC fluxes (in Mg C per period) in the Albufera des Grau. The mean mass of DIC (in Mg C) and the observed net change in DIC (ΔDIC) are also shown for each period. For $FDIC_{atm}$ the numbers in brackets correspond to the minimum and maximum estimates. *Unv*: unvegetated period, *veg*: vegetated period

		Observed conditions		Physical fluxes						Internal fluxes						
Period	Days	DIC	ΔDIC	Runoff	Outflow	Inflow	Net hydrol.	Atmospheric exhange	Net physical	Net internal^1	GPP^2	CR^2	GPP plankton^3	R plankton^3	Calcite precipitation^4	Sediment respiration^5
2002																
Unv	120	43 ± 2	3	7	-3	0	4	-1 (-1; -1)	3	0	n.a.	n.a.	-48	138	-34	(17; 43)
Veg	245	28 ± 8	-9	25	-7	2	20	81 (53; 124)	101	-110	-2397	2106	-26	160	-104	(44; 113)
	365	33 ± 10	-6	32	-10	2	24	80 (52; 123)	104	-110			-74	298	-138	(61; 156)
2003																
Unv	154	45 ± 6	20	101	-98	0	3	-27 (-14; -33)	-24	44	n.a.	n.a.	-253	360	-9	(32; 83)
Veg	211	37 ± 10	-16	4	-3	3	4	11 (6; 15)	15	-31	-2010	1766	-297	425	-24	(37; 95)
	365	40 ± 9	4	105	-101	3	7	-16 (-8; -18)	-9	13			-550	785	-33	(69; 178)
2004																
Unv	140	47 ± 2	7	4	-8	0	-4	-14 (-10; -24)	-18	25	n.a.	n.a.	-608	481	14	(24; 62)
Veg	226	29 ± 13	-29	14	-1	4	17	-2 (-2; -4)	15	-44	-1990	1748	-99	256	-22	(37; 94)
	366	35 ± 14	-22	18	-9	4	13	-16 (-12; -28)	-3	-19			-707	737	-8	(61; 156)

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[1]: Estimated from the difference between DIC and $DIC_{h,a}$

[2]: Whole-system values including calcite and sediment fluxes (Obrador and Pretus 2009b)

[3]: Planktonic metabolism calculated from [DOC] and [Chlorophyll] (del Giorgio and Peters 1994; Williams and del Giorgio 2005)

[4]: Estimated from the calcium mass balance

[5]: Site-specific rates from López (2004b)

The daily air-water flux of CO_2 averaged 8.1 mmol m^{-2} d^{-1} and ranged from -265 to 231 mmol m^{-2} d^{-1}, where positive and negative values denote air-to-water fluxes (CO_2 invasion) and water-to-air fluxes (CO_2 evasion), respectively (Fig. 6.6). The direction of the flux between sampling intervals (c.a. monthly, Fig. 6.6) changed seasonally, with invasion taking place during the vegetated months (from spring to early autumn) and evasion during the unvegetated months. In spring 2004 this pattern was broken with a significant CO_2 invasion in the unvegetated period. The total seasonal $FDIC_{atm}$ (Table 6.3) showed that during the unvegetated period, the lagoon was a source of CO_2 to the atmosphere (between 1 and 27 Mg C) and during the vegetated period it was a sink of CO_2 (11-81 Mg C) except in 2004, when the atmospheric exchange was nearly balanced.

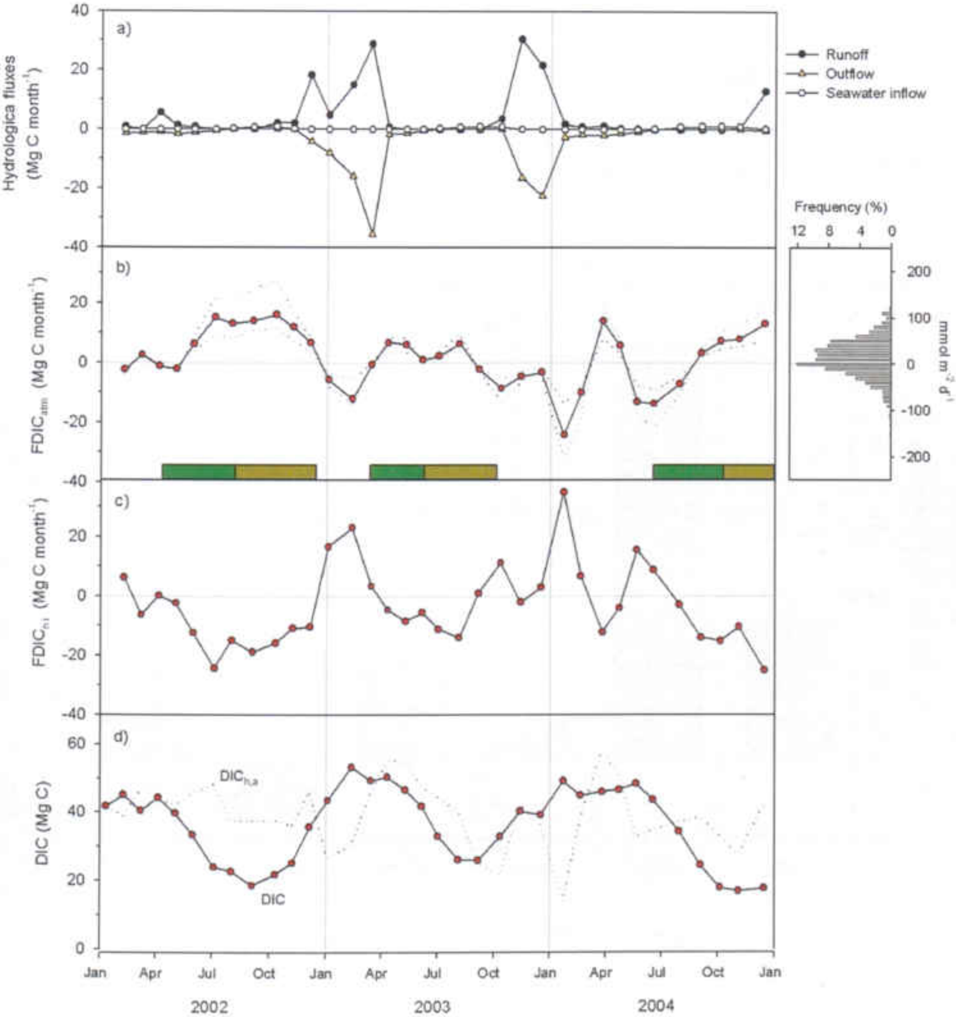

Figure 6.6. Monthly hydrological (a), air-water (b) and net internal (c) fluxes of DIC in the Albufera des Grau (Mg C per sampling interval). In d) the observed DIC (circles) and DIC_{h}a (line) curves used to calculate the net internal fluxes are shown. The dotted lines in b) correspond to the air-water fluxes using literature minimum and maximum estimates for k. The right-hand panel in b) shows the frequency distribution of the daily areal atmospheric fluxes (in mmol m^{-2} d^{-1}). The horizontal coloured boxes indicate the vegetated period (the growing and decreasing months of macrophytes are in light and dark colours, respectively).

The net internal flux, estimated from the difference between the observed DIC and the physical fluxes, ranged seasonally from -25 to 35 Mg C per month (Fig. 6.6c). The lagoon was a net source of inorganic carbon during the unvegetated months and a sink during the vegetated months (Fig. 6.6, Table 6.3). The annual net internal flux was highly variable and ranged from -110 to 12 Mg C (Table 6.3). The calcite fluxes estimated from the calcium mass balance were always negative (calcite precipitation) except for the unvegetated period of 2004 (Fig. 6.7). The daily calcite precipitation rates were between -7 and -51 mmol m^{-2} d^{-1} and showed a clear relationship with water salinity (Fig. 6.7). The total seasonal precipitation of calcite was higher in the vegetated period (-22 to -104 Mg C) than in the unvegetated one (-9 to -34 Mg C). With regard to the metabolic fluxes, the whole-system estimates of *GPP* and *CR* were clearly the highest fluxes of DIC during the vegetated period, with values around 2000 Mg C per season (Table 6.3). The planktonic metabolism was much smaller, and ranged from -74 to -707 Mg C per season for *GPP* and from 298 to 785 Mg C per season for *CR*. The mean residence time of DIC was estimated in 18.6 ± 9.8 days in the unvegetated period and 3.7 ± 0.6 days in the vegetated one.

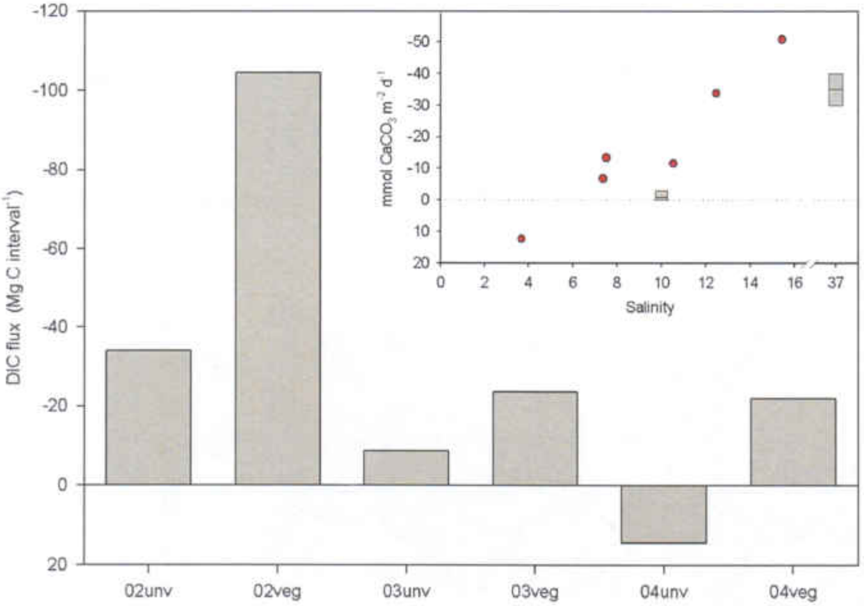

Figure 6.7. Estimates of the seasonal $CaCO_3$ precipitation and dissolution (in Mg C per season). The inset shows the relationship between the water salinity and the estimated daily areal rates of calcite fluxes (circles), in comparison with the López (2003) estimates (boxes). Positive and negative values stand, respectively, for dissolution and precipitation (note the inverse axis for a better visualization of calcite precipitation).

6.3.5 Annual OC fluxes and exploration of the trophic flows

The allochthonous inputs of OC were primarily from runoff and were dominated by the dissolved (DOC) form (Table 6.4). The annual hydrological inputs of OC were below 10 MgC y^{-1} except in 2003, with annual inputs above 30 Mg C y^{-1}. The net hydrological flux of OC was always lower than 10 Mg C y^{-1}, and only in 2003 it was negative. The annual burial of organic matter was estimated in between 38 and 75 Mg C y^{-1}.

Table 6.4. Estimates of the annual net fluxes of organic carbon in the Albufera des Grau (Mg C y^{-1}). The numbers in brackets are rough estimates and should only be considered tentatively.

Flux	2002	2003	2004
Observed changes in OC	0	0	4.8
ΔMC	0	0	4.8
ΔDet-C	-1.7	2.9	-2.5
ΔPhyt-C	-1.7	-0.2	0
ΔDOC	-2.3	-5	-1
Net OC change	-5.6	-2.2	1.3
Hydrological fluxes			
Runoff			
DOC	8.3	27.5	4.6
POC	1.5	5.1	0.9
Seawater inflow			
DOC	0.1	0.1	0.1
POC	0	0	0
Total hydrol. inputs	9.9	32.7	5.6
Outflow			
DOC	-2.5	-32	-2.3
POC	-0.2	-6.3	-1.3
Total hydrol. outputs	-2.7	-38.3	-3.3
Net hydrol. flux	7.2	-5.6	2.3
Internal fluxes			
Net internal flux[1]	-12.8	3.4	-1.0
Burial (OC)	-38 to -75	-38 to -75	-38 to -75
Burial (MC)	-10 to -20	-10 to -20	-10 to -20
Annual production of *R. cirrhosa*	94	61	24
Exudation of *R. cirrhosa*[2]	2.9	4.4	1.1

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[1]: Estimated from the difference between observed change and net hydrological and atmospheric flux

[2]: Estimated from the DOC dynamics in the littoral and deep sites

The isotopic exploration of the food web showed a clear discrimination of the primary producers by their average carbon stable isotope composition. The main primary producers *R. cirrhosa* and phytoplankton, showed clearly distinct carbon isotope compositions (δ^{13}C of -16.8‰ and -27.5‰, respectively). The macroalgae showed species-specific δ^{13}C values (ranging from -216‰ to -29.2‰), and SOM showed a narrow range of variation around -24.6‰. The most ^{13}C-enriched and ^{13}C-depleted values corresponded to *Potamogeton* (-16.2‰) and *Polysiphonia* (-29.2‰) respectively. The δ^{13}C of consumers ranged from -25.3‰ to -18.1‰, laying between the phytoplankton and *R. cirrhosa* signatures. The benthic invertebrates (*Sphaeroma*, *Gammarus* and *Pseudoamnicola*) showed more enriched values (-18.1‰ to -20.7‰) than the pelagic ones (zooplankton, -25.3‰, *Palaemon*, -20.8‰). The stable isotope ratios of nitrogen did not discriminate all the primary producers. The δ^{15}N of *Ruppia*, phytoplankton and *Chaetomorpha* overlapped around 9‰, whereas *Polysiphonia*, SOM and *Gracilaria* showed δ^{15}N values below 7‰. *Potamogeton pectinatus* was the most ^{15}N-depleted source (5.4‰). Among consumers, the benthic invertebrates showed, together with *Mugil cephalus* and *Liza aurata*, the most depleted values (δ^{15}N below 10‰). The highest δ^{15}N corresponded to *Anguilla anguilla* and *Dicentrarchus labrax* (14.9‰).

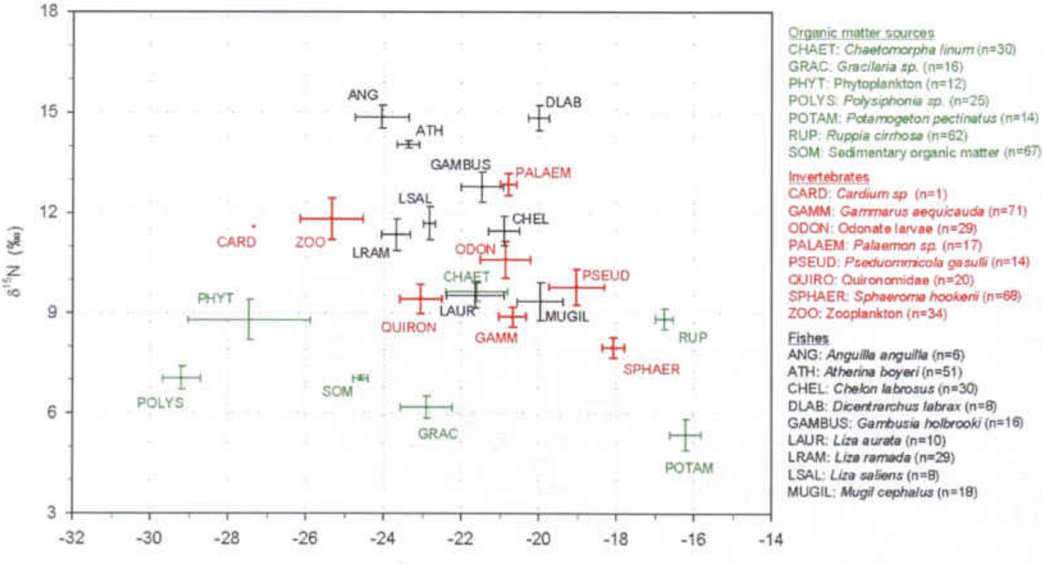

Figure 6.8. Carbon and nitrogen stable isotope composition of the main trophic compartments in the Albufera des Grau (mean ± s.e.).

6.4. Discussion

6.4.1 DIC dynamics and fluxes

The temporal dynamics of pCO_2 showed a marked seasonal cycle mainly related to the seasonality of the macrophyte meadows. During the vegetated period the lagoon was below atmospheric equilibrium due to intense photosynthesis within the macrophyte beds. The lowest pCO_2 values were observed in the littoral sites, but the pattern was common in all the sampling sites. When the macrophyte meadows started to decline, the pCO_2 increased above atmospheric equilibrium, achieving the highest values in the littoral sites, probably due to the respiration of macrophytic biomass. In summer 2003, the deep central site showed a slight increase in pCO_2, likely due to the release of CO_2 from the anoxic bottom of the lagoon, a condition that was not observed in the littoral sites. It was in autumn 2003 when the four sampling sites showed more differences, which could be explained by the summed carbon inputs from macrophytic respiration and from torrential inputs (Fig. 6.6). The torrential event observed in spring 2003 did not generate spatial variability in pCO_2, probably because it did not imply such a high net input of carbon, as there was a simultaneous high compensating outflow (Fig 2). The huge pCO_2 decrease of February-March 2004 (Fig. 6.4) was clearly related to the intense phytoplankton bloom of those months. Thus, the pCO_2 dynamics could be explained by a robust seasonal cycle in the absorption and release of carbon from the macrophyte meadows, punctually perturbed by hydrological and phytoplanktonic events.

The dynamics in the total DIC could be roughly interpreted in a similar way, but the agreement between the observed dynamics and the prediction of the simple mixing model (Fig. 6.5) alternatively raises the idea that the DIC is highly controlled by hydrological processes. The observed changes in DIC were, however, not easily explained by a single dominant flux, as they were the result of balancing fluxes that were much higher in magnitude than the resulting net balance (Fig. 6.6, Table 6.3).

The monthly hydrological, atmospheric and net internal fluxes of DIC were similar in magnitude (from -30 to 30 Mg C month^{-1}, Fig. 6.6). The hydrological DIC fluxes were dominated by runoff inputs, whereas the $FDIC_{sw}$ remained as a minor flux in the carbon cycling of the lagoon. The low seawater influence on the carbon dynamics is not surprising given the enclosed character of the Albufera des Grau (Obrador et al. 2008). However, although not directly, the seawater inflow did substantially influence the carbon cycling in the lagoon by altering water column stability and oxygenation, as discussed later. The three studied years showed a similar balance with regard to the hydrological DIC fluxes. Despite not exactly balanced, the $FDIC_{outflow}$ was close in magnitude to the $FDIC_{runoff}$, what resulted in a relatively small net hydrological annual input into the lagoon (7-24 Mg C y^{-1}, Table 6.3). It must be noticed that the disproportionate torrential inputs of 2003 (Fig. 6.2) render this year a singular character with regard to the DIC budget (the unusual magnitude and frequency of the torrential events in 2003 is confirmed by temporally extended observations in the lagoon, authors' unpublished data).

The air-water CO_2 flux also played a significant role in the net DIC balance in the lagoon. The daily areal fluxes were within the reported values in estuarine and coastal systems (Frankignoulle et al. 1998; Cai et al. 1999; Raymond and Cole 2001). The difference between our estimate and the minimum and maximum estimates of $FDIC_{atm}$ (from literature minimum and maximum values of k) was small in comparison with the observed range, with a mean uncertainty of 15 mmol m^{-2} d^{-1}. The temporal dynamics of the flux was related to the seasonal dynamics of the macrophyte meadows, and shifted seasonally in direction depending on the presence or absence of submerged vegetation (Fig. 6.6). Thus during the vegetated period, the lagoon was a sink of atmospheric CO_2, which was probably directed to support macrophytic production, and during the unvegetated period the lagoon was a source of CO_2 to the atmosphere. Superimposed to this seasonal macrophyte-based pattern, the peaks of phytoplankton sharply altered the atmospheric CO_2 exchange. Thus, during phytoplankton peak of spring 2004 (Fig. 6.3) there was a marked CO_2 invasion (Fig. 6.6), which resulted in a CO_2 input of 20 Mg C. The huge pCO_2 increase observed in the following months (Fig. 6.4b) and the consequent shift to negative air-water fluxes (Fig. 6.6) suggests a significant carbon flux from lagoon respiration immediately before the development of macrophytes. This probably contributed to raise the DIC availability during the macrophyte growing period, what may be related to the anomalous negative air-water flux (-2 Mg C) during the vegetated period of 2004 (Table 6.3). The analysis of the temporal evolution of the CO_2 flux does not clarify if the CO_2 efflux in the months after the decay of the meadows is mostly due to the decomposition of macrophytic biomass or related to the injection of CO_2 supersaturated waters from stream runoff, because both processes are time-coincident in late autumn (Fig. 6.6). In 2002, the total air-water flux during the unvegetated period (-1 Mg C) was similar in magnitude to the net hydrological flux (input of 4 Mg C, Table 6.3) what would support the hypothesis of stream CO_2 injection. On the contrary, on 2003 the net atmospheric flux in the unvegetated period was much higher (-27 Mg C) than the net hydrological inputs (3 Mg C), and on 2004 there was net CO_2 evasion (-14 Mg C) despite the net hydrological flux was negative, supporting the idea that lagoon metabolism is main driver of the CO_2 emission. It is difficult to determine if this respiration flux is due to sediment release, to the respiration of autochthonous OC (likely macrophytic biomass) or to the respiration of allochthonous OC. The OC balance must help distinguish between the two latter options (see below).

With regard to the internal fluxes, despite the net internal flux was on the same range than the hydrological and atmospheric fluxes, the magnitude of the specific internal fluxes was much higher than the physical fluxes (Table 6.3). Thus, *GPP* and *CR* pumped carbon at extremely high rates leading to fluxes around 2000 Mg C per season (Table 6.3). It must be noticed that the whole-system *GPP* and *CR* were the least precise of our estimates because they were based on highly variable daily metabolic rates (Obrador and Pretus 2009b). Nonetheless, the magnitude of the metabolic fluxes during the vegetated period was responsible for the low residence time (3.7 days). Despite such low residence times are similar to those reported in other macrophyte-dominated ecosystems (Ziegler and Benner 1998), the relationship between carbon turnover time and the mean water residence time in the Albufera des Grau (8 months, Obrador et al. 2008) yields an extremely high turnover of carbon in relation to that of water. The DIC cycling is c.a. 65 times faster than the water cycling during the vegetated period and c.a. 13 times higher during the apparently less dynamic unvegetated period, which to the best of our knowledge are unusually high values.

On an annual basis, macrophytic and planktonic metabolism were clearly the main contributor to total internal fluxes, given the comparatively lower values of calcite precipitation (-8 to -138 Mg C y^{-1}, Table 6.3) and sediment efflux (61 to 178 Mg C y^{-1}, Table 6.3). With regard to calcite fluxes, our estimates were in the range described by López (2003) from sediment incubations, but were somewhat higher, especially in 2002 (Fig. 6.7). Such slight overestimation of the calcite precipitation could be explained by the high abundance of the reef-forming polichaete *Ficopomatus enigmaticus*, which forms dense and productive carbonate reefs in the lagoon (Fornós et al. 1997) and in summer 2002 was especially abundant (B.O. personal observation). We cannot, however, discard methodological inaccuracies in our estimates, which should be considered tentatively. For instance the resulting positive flux in the unvegetated period of 2004 (dissolution of 14 Mg C, Table 6.3) is contradictory with the calcite supersaturation observed during the study period (despite there was a month with lack of data, Fig. 6.4). Nonetheless, calcite fluxes in the lagoon appear to be a significant carbon flux similar in magnitude to the hydrological and atmospheric fluxes, but much smaller than the pure metabolic fluxes.

6.4.2 $\delta^{13}C_{DIC}$ dynamics

The $\delta^{13}C_{DIC}$ dynamics was apparently more related to the isotope signature of the flows than to the magnitude of the fluxes by themselves. The existence of a basal value between -10 and -15‰ could be explained by the combination of several processes. Firstly, the DIC inputs from stream runoff showed, despite the few available data, $\delta^{13}C_{DIC}$ values well within this basal range (-12.9‰). Secondly, the atmospheric fluxes could have contributed to maintain such negative range. The expected $\delta^{13}C_{DIC}$ under isotopic equilibrium with the atmosphere is ~0‰ because of the enrichment of about 8‰ with respect to atmospheric CO_2 that takes place in the well-known temperature-dependent equilibrium fractionations (Zhang et al. 1995). The gas transfer, i.e., invasion and evasion of CO_2, between air and water is subject to minimal (~1‰) kinetic fractionations when diffusion is the dominant process (Zhang et al. 1995). However, in situations that favour rapid exchange of CO_2 in open-system conditions, a much higher isotopic fractionation between gaseous and dissolved CO_2 appears to occur (Doctor et al. 2008, Myrbo and Shapley 2006). This is the case of the CO_2 invasion at high pH, when the CO_2 reacts with OH ions to form HCO_3 in the so-called chemical enhancement of CO_2 (Wanninkhof and Knox 1996). The observed isotope fractionation during such reaction is in the range -13‰ to -15‰ and yields a $\delta^{13}C_{DIC}$ of about -10‰ to -13‰ (Herczeg and Fairbanks 1987; Bade and Cole 2006; Doctor et al. 2008). In this study the air-water transfer was far from isotopic equilibrium, as indicated by the extreme variability in pCO_2 (1 - 1419 μatm), and hence it is realistic to expect an effect of the chemical enhancement fractionation on the $\delta^{13}C_{DIC}$. The basal value of $\delta^{13}C_{DIC}$ of -10 to -15‰ could thus be explained by the combination of runoff and atmospheric inputs. On the other hand the respiration of macrophytic biomass, would add DIC to the water with a $\delta^{13}C$ very similar to this range ($\delta^{13}C$ for *R. cirrhosa* = -16.8 ± 1.8, Fig. 6.8). This input of carbon could explain the decrease in $\delta^{13}C_{DIC}$ observed from December 2002 to February 2003, where the pCO_2 sharply increases due to the decomposition of *Ruppia* biomass. The drastic depletion in DIC observed from April to July 2003 to values of -25‰ was probably related to intense sediment respiration during the bottom anoxia that took place in sprig and summer (Fig. 6.3). The carbon isotope signature of SOM ($\delta^{13}C$ = -24.6 ± 1.5 ‰, Fig. 6.8) and the concomitant increase in pCO_2 observed at the central site of the lagoon during that period makes this explanation the most plausible. However, the coincidence in the $\delta^{13}C$ of SOM with that of phytoplankton (-27.5 ± 5.4, Fig. 6.8) and that of C3-derived terrestrial organic matter (~ -27‰, Boutton 1991; Michener and Schell 1994) does not allow to discard other explanations, especially considering the large duration of the ^{13}C depletion. After the isotopic depletion in DIC summer 2003, the increase in $\delta^{13}C$ would be explained firstly by the respiration of macrophytic biomass (see increase in pCO_2 in September 2003, Fig. 6.4c), followed by runoff inputs (Fig. 6.6), what would have lead again the $\delta^{13}C_{DIC}$ to the -10 to -15‰ range.

In conclusion, the analysis of $\delta^{13}C_{DIC}$ to outline the dominant processes of carbon cycling is quite limited in the Albufera des Grau, likely due to the intense cycling of carbon in this system, what may obscure process signalling. The use $\delta^{13}C_{DIC}$ in the study of the carbon cycle in aquatic systems has been typically restricted to less dynamic systems such as the open ocean or large temperate lakes (Quay et al. 1986; Stiller and Nissenbaum 1999; Gruber et al. 2002), and its use in carbon balances in shallow coastal systems where carbon cycling is very dynamic is of lower utility.

6.4.3 Carbon pools and fate of OM

The carbon budget in the lagoon shifted between a clear dominance of MC in the vegetated period to a dominance of DOC in the unvegetated period. The most dynamic compartment was MC, which resulted in large seasonal changes in OC. The OC during the vegetated period doubled that during the unvegetated one. The ratio DIC/OC shifted between below 1 in the vegetated period (ratio ~ 0.8) to above 2 in the unvegetated period (ratio ~ 2.4).

The stable isotope exploration of the food web resulted in a good discrimination of the main autochthonous sources of organic matter, with a low overlapping in the $\delta^{13}C$ of the primary producers

(Fig. 6.8). This clear discrimination in OM sources is not always observed and appears to be restricted to simple systems with few different sources of organic matter (Cloern et al. 2002). There is a large growing literature outstanding the stable isotope seasonal and spatial variability in coastal environments (Stephenson et al. 1984; Hemminga and Mateo 1996; Deegan and Garritt 1997; Middelburg and Nieuwenhuize 1998; Boyce et al. 2001; Cloern et al. 2002; Keats et al. 2004; Vizzini and Mazzola 2003; Vizzini et al. 2005; Vizzini and Mazzola 2006; Garcia et al. 2007; Bucci et al. 2007). This variability is attributed to several environmental factors including temperature, salinity, irradiance, DIC availability for primary producers and anthropogenic inputs of organic matter or nutrients. In this sense it must be noticed that the results shown here are the mean values from a major project dealing with stable isotope variability in the Albufera des Grau and should thus be considered carefully. Despite with the present data we could not discriminate phytoplanktonic carbon from allochthonous OM sources, the signal of the major component in terms of biomass, MC, was clearly different of all the other considered sources. In this sense, the $\delta^{13}C$-$\delta^{15}N$ plane described a low dependency of the food web on macrophytic biomass, and most of the food web compartments were characterised by $\delta^{13}C$ values more similar to those of phytoplankton (-27‰), macroalgae (-22‰ to -29‰), SOM (-26‰) or allochthonous carbon (-27‰, Thornton and McManus 1994), likely relying largely on such carbon sources. Even the invertebrates living on the macrophyte meadows, *G. aequicauda* and *S. hookeri*, were supported by other sources than macrophytic organic matter. The small transfer of *Ruppia* biomass through grazing is in accordance with previous studies, which highlighted that herbivores had, however, a pronounced role in accelerating decomposition by means of macrophyte biomass fragmentation (Verhoeven 1980b; Menéndez and Comín 1990) and that feeding of epifauna herbivores was highly based on epiphytic algae rather than on macrophytic biomass (Kitting et al. 1984; Klumpp et al. 1992). Unfortunately the scarce epiphytic community did not allow us to determine its stable isotope composition and discern its role in this study.

Nonetheless, it is worth mentioning that not only the epifauna herbivores but also the whole consumers of the food web did not rely on MC. This likely discards a possible trophic role of macrophytes via the detritic pathway and through DOC exudates. The exudation of DOC, a common feature of many submerged macrophytes, can represent a substantial fraction of macrophytic production (Khailov and Burlakova 1969; Brylinsky 1977; Penhale and Smith 1977) and represent an important pathway of carbon flow in coastal communities (Robertson et al. 1982; Mann 1988; Alber and Valiela 1994; Ziegler and Benner 1999). We observed high differences between the littoral and deep [DOC] only in the vegetated period, especially during senescence (Fig. 6.3), what suggests an unambiguous macrophytic origin of DOC in the lagoon. From the differences between littoral and deep [DOC] we estimated DOC production within the system in 3 Mg C y^{-1}. The DOC production is surprising given its low contribution to the food web. DOC has been described to play a substantial role in the underwater light climate in the Albufera des Grau (Obrador and Pretus 2008) and could thus significantly influence macrophyte dynamics by affecting light availability (Obrador and Pretus 2009a). Further research in determining the sources of DOC through optical characterization and the analysis of its carbon stable isotope composition should help confirm the macrophytic origin of DOC in the lagoon.

On the other hand, the small contribution of *Ruppia* to the lagoon food web contrasts with its dominant role in the carbon pools. Such discrepancy between pool size and significance for secondary production has been previously shown in other macrophyte-dominated ecosystems (Kaldy et al. 2002) and may be related to the low palatability of macrophytic biomass. However, Vizzini and Mazzola (2008) recently highlighted the importance of the dominant primary producer in determining the diet of consumers in three Mediterranean coastal lagoons. The food web in the Albufera des Grau, a confined lagoon, was not based on macrophytic organic matter, what would be in accordance with the conclusions of Vizzini and Mazzola (2008) who stressed the importance of confinement and hydrological regime in determining the trophic structure.

Discarding the trophic consumption as a main destiny of the macrophyte meadows, the fate of the huge macrophyte production raises interest. Duarte and Cebrian (1996) depicted that the main pathways of organic matter production in macrophyte-based ecosystems were decomposition, export and sediment burial, although there was high variability between ecosystems. The annual production of *R. cirrhosa* during the period 2002-2004 was between 24 and 94 Mg C y^{-1} (Table 6.8), but higher productions of up to 140 Mg C y^{-1} were attained in other years (Obrador and Pretus 2009a). A tentative mean value of the annual production of *R. cirrhosa* would thus be 70 Mg C y^{-1}. The export of OC ranged between 3 and 38 Mg C y-1, but had similar values to the OC inputs, what resulted in nearly balanced net hydrological OC fluxes (below 10 M C y^{-1}, Table 6.8), thus discarding the export as a significant destiny for macrophytic production.

Our estimate of the annual burial of organic matter was 38-75 Mg C y^{-1}, a value within reported burial rates in other coastal lagoons or macrophyte-dominated ecosystems (Knoppers 1994; Duarte et al. 2005). The isotope composition of SOM, which showed a very narrow range of variation around -24.6‰, was in accordance with the $\delta^{13}C$ of organic matter in a short core extracted for palaeolimnological purposes in the lagoon (data from an author's ongoing project) and is thus a robust measure of the $\delta^{13}C$ of SOM in the system. The value of -24.6‰ can be interpreted by simple mixing of two isotopically distinct organic matter sources: macrophytic biomass ($\delta^{13}C \sim -17$‰), and phytoplanktonic or allochthonous biomass ($\delta^{13}C \sim -27$‰ in both cases), which are expected to be the most important OM sources in the system. From this simple model we estimated that 27% of SOM derives from macrophytic carbon. With the available data we cannot elucidate if the remaining 73% is produced within the system (phytoplankton) or is allochthonous, especially considering the high interannual variability in both macrophyte production (Obrador and Pretus 2009a) and hydrological OC inputs (Table 6.4). Nonetheless, considering that the hydrological inputs and outputs of OC are nearly balanced (Table 6.4) one may expect that most of the OC burial was related to autochthonous carbon. This makes sense because the outflow of water (and hence of OC) in the lagoon usually takes place immediately after high runoff inputs (Fig. 6.2). Thus, a large faction of OC burial in sediments must proceed from phytoplanktonic production, whose metabolic rates have not been yet estimated in the lagoon. Further work is thus required to satisfactorily complete the puzzling annual carbon cycle in the Albufera des Grau.

With regard to the burial of OC, considering the fraction of SOM that derives from macrophytic biomass, the resulting specific burial rate for MC is the 27% of the burial rate for total OC, i.e. between 10 and 20 Mg C y^{-1}. Taking 70 MgC y^{-1} as the mean annual production of *R. cirrhosa*, the burial of macrophytic biomass would thus represent between 15 and 30% of annual production. Knoppers (1994) described that on average 10-25% of total primary production of coastal lagoons was directed to sediment storage, and Duarte and Cebrian (1996) reported an average burial of 16% of the production in seagrasses. Thus, considering the inherent uncertainties in our approach, the burial of MC in Albufera des Grau would be within the expected values for coastal systems. Nonetheless, there is a large fraction of macrophytic production that can not be assigned to grazing, export or storage and should hence correspond to decomposition. From site-specific decomposition rates of *Ruppia* biomass previously estimated in the Albufera des Grau ($k=0.018\ d^{-1}$, unpublished data), the time to decompose the 90% of macrophyte biomass is only 128 days. Despite decomposition rates of macrophytic material can be variable depending on several environmental factors (Menéndez et al. 2003; Menéndez et al. 2004) this high decomposition rate suggests that decomposition is the main destiny of macrophytic production in the Albufera des Grau, what is in accordance with the interpretation of the DIC dynamics and the CO_2 efflux to the atmosphere during the unvegetated period seen in previous section.

In this paper we did not aim to define the net autotrophic or heterotrophic character of the lagoon, what would require a different approach with more detailed and temporally extended metabolic measures. Nonetheless, some conclusions can be inferred from our results. Firstly, the lagoon's annual metabolic balance is likely close to zero or slightly autotrophic with regard to macrophytic production, as discussed before. This is of course not opposite to the existence of a seasonal shift between autotrophy and heterotrophy, a typical feature of many coastal lagoons dominated by macrophytes (Knoppers 1994; Gattuso et al. 1998). An annual net heterotrophic character may be generated by the interaction of hydrological and planktonic extreme dynamics. Runoff inputs may turn aquatic systems towards net heterotrophy by entering large amounts of OC, mainly as DOC (Duarte and Prairie 2005). This is not the case here, because the hydrological OC fluxes were nearly balanced, what reduces a significant role of allochthonous DOC inputs in the net metabolism of the lagoon. Rather than that, the main driver of heterotrophic metabolism apart from the macrophyte production and decomposition cycle is likely the stability and oxygenation of the water column. The mechanism is quite more complex but may lead to a similar result than the fuelling of community respiration by DOC external inputs. Intense runoff may enhance phytoplankton blooms which in turn may result in enhanced bottom hypoxia and higher sediment efflux, as occurred in 2003. Thus, the annual heterotrophic character of the lagoon is probably determined by the degree of amplification of the sediment efflux rather than by the variability of the allochthonous OC inputs, as seen in other coastal systems (Smith and Hollibaugh 1997). Despite the bottom anoxia can be generated by both seawater inflow and runoff inputs, it is noteworthy the influence of the runoff inputs on the ecology of the lagoon, as seen by the fast response of phytoplankton to runoff inputs.

The influence of the watershed in the carbon cycling of the lagoon would thus be based on the close relationship between the timing and intensity of the runoff inputs and the phytoplankton growth, the generation of vertical stratification and the onset of bottom hypoxias. All these processes are overlapped to the seasonal cycle of the macrophyte meadows, which is more robust and inertial in front of hydrological perturbations. In conclusion, much effort is needed for a complete outline of the carbon cycling in highly dynamic Mediterranean coastal lagoons subject to unpredictable hydrological influence.

6.5. Conclusions

The DIC cycle in the lagoon was subject to very intense metabolism and secondarily affected by calcite, atmospheric and hydrological fluxes. DIC showed a extremely high turnover in comparison to that of water. The dynamics of the pCO_2 in the Albufera des Grau could be explained by a basic seasonal cycle of production and decomposition of the macrophyte meadows punctuated by phytoplanktonic peaks and hydrological torrential inputs.

The air-water flux of CO_2 was mainly driven by internal metabolism rather than to external inputs of CO_2-saturated water. As in other macrophyte-dominated coastal systems, the lagoon shifted seasonally in the direction of the air-water CO_2 flux, being a sink of atmospheric CO_2 during the vegetated period and a source of CO_2 during the unvegetated period. The neat annual balance of DIC showed high interannual variability likely depending on the degree of perturbation of the basal macrophytic cycle. The effect of watershed and marine water inputs was more related to the development of phytoplankton peaks and to the alteration of water column stability and oxygenation than to the effect of organic matter inputs by themselves.

The high macrophytic production in the lagoon was mainly decomposed, and macrophytic biomass had a small role in the food web of the lagoon. Similarly, the burial of macrophytic organic matter was small in comparison to the annual macrophytic production, and the organic matter buried appeared to have a phytoplanktonic origin.

Ackowledgements

This study received funding from the Institut Menorquí d'Estudis, the Govern de les Illes Balears and the Island Council of Menorca. For the valuable field and lab assistance we thank Lídia Cañas, Júlia Garcia and Sam Pons. Helpful comments from P. López are also greatly acknowledged.

Overall discussion and synthesis

Overall discussion

The previous set of chapters consist on specific approaches to different domains by which processes and patterns shape the ecosystem functioning in the Albufera des Grau, as a case study of a Mediterranean coastal lagoon dominated by macrophytes. As stated in the introduction, the thesis is outlined around the results of the first chapter, in fact an introductory chapter to the ecology of the lagoon. What follows is an overall discussion and synthesis of the results obtained all along, aimed to map the links between each particular aspect dealt with, thus providing the frame for the main conclusions of the thesis. I will also analyse in detail how the hypothesis suggested in Chapter 1 are confirmed or rejected along the other chapters, as well as outline the issues which should receive major attention in the future research of equivalent ecosystems, and particularly in this lagoon.

Hydrology

The hydrological behaviour of the lagoon has been studied from a dynamic modelling approach in order to determine the main drivers of the hydrological descriptors from a robust and temporally extended data set. Despite its simplicity, the model correctly simulated the temporal dynamics of salinity and water level, adjusting both the timing and the range of these variables. Despite many coastal lagoons are hydrologically more complex than the Albufera des Grau, our results should help encourage the use of dynamic modelling approaches in coastal lagoon research, an area where much effort is being done at present (Chapelle et al. 2005). Providing a validated hydrological model for a given lagoon can be very useful for further biogeochemical budgetary approaches, as done in Chapter 6, but also because it can serve as a basis for more complex ecological models, such as those developed in other Mediterranean coastal lagoons with promising results (Arhonditsis et al. 2002; Plus et al. 2003; Zaldívar et al. 2003; Giusti and Marsili-Libelli 2005; Giusti and Marsili-Libelli 2006; Plus et al. 2006; Hull et al. 2008; Marinov et al. 2008).

The complexity of any hydrological model (time scale considered, spatial approach, number of dimensions) would depend on both the objectives of the modelling approach and on the hydrological characteristics of the site. We believe that the limitations of the model for the Albufera des Grau are acceptable given the aim of the finally established model. The possible improvements discussed in Chapter 2, namely the spatially explicit treatment of the watershed and the incorporation of a salinity-discharge relationship in stream runoff, might contribute to a better simulation of the torrential events, which is the main limitation of the model. However, we believe that the model outputs adequately reflect the dynamics of both water level and salinity, especially when considering a seasonal perspective and the range of salinity instead of the precise daily values of the variables. We felt thus confident to analyse the hydrology of the lagoon from the results of a simulation for a historical period. The assumption that these results appropriately reflect the behaviour of the lagoon are sustained on the temporal extension of the calibration and validation data sets, and on the complementary qualitative validation of the model outputs with the historical salinity data. The ability of the model to predict salinity changes above the range of calibration must be seen also as an indication of its robustness.

The hydrological characterisation of the lagoon from a 30-year simulation showed that the main behaviour was related to the precipitation/evaporation regime rather than to seawater exchange, and provided a mean water residence time of 8 months. In this sense, the Albufera must be considered an enclosed lagoon with limited marine influence. The importance of the hydrological regime and the degree of confinement in the ecological functioning of Mediterranean coastal lagoons is widely recognised (Quintana et al. 1998a; Quintana et al. 1998b; Quintana 2002; Pérez-Ruzafa et al. 2005; Viaroli et al. 2005; Badosa et al. 2006; Badosa et al. 2008). In this thesis, we have depicted a specific hydrological framework for the Albufera des Grau which is likely different from that described a few decades ago (Pretus 1989) and definitely different from that expected a few centuries ago (Habsburg Lorena 1890), with higher marine influence on the lagoon dynamics.

The salinity regime of the Albufera des Grau during the whole period studied in the different chapters of this thesis ranges 2.7-25 g L^{-1}, and the lagoon should thus be classified as oligo-polyhaline following the Venice classification system (Table D.1; IUBS 1959). However, there was a hyperhaline period in the 1990s, and the model allowed to depict such raise in salinity as a naturally-driven process associated to the consecution of dry years with annual precipitation below 400 mm (Chapter 2). Thus the hyperhaline range should also be considered within the lagoon's spectrum, despite being less frequent. With regard to the lower limit of salinity, the interesting relationship between the mean annual salinity and the total annual precipitation observed from the 30 years simulation (Fig, 2.7) yielded a minimum value of mean salinity of 5.6 g L^{-1}, which is believed to be an acceptable lower limit for the lagoon given the temporal extension of the simulation. The minimum simulated daily salinity during the historical period was 3.9 g L^{-1}, very close to observed minimum value for that period (3.1 g L^{-1}; Fig. 2.5). Salinities below 2 g L^{-1} would have actually been very unlikely given the currently measured high solute concentrations of the streams in the watershed (c.a. 2 g L^{-1}; see Tables 2.3 and 6.3), although much lower values are presumed under higher rainfall regimes. The lower limit of salinity for the Albufera des Grau is thus in the oligohaline range.

Table D.1. Salinity ranges following the Venice classification system (IUBS 1959)

Division	Salinity
Limnetic (Freshwater)	< 0.5
Oligohaline	0.5 – 5
Mesohaline	5 – 18
Polyhaline	18 – 30
Euhaline	30 – 40
Hyperhaline	> 40

The results of the developed dynamic model have direct applications in management practices, apart from the uses employed in this thesis. Firstly, the model itself can be a useful tool as it can serve as a basis to design management strategies under changing climatic scenarios. In a day to day activity, the model can also be useful to predict and prevent undesirable situations (littoral desiccation, hypersalinization) before the critical period of summer, when the water management is highly limited (Pretus 2003). Secondly, the marked relationship between water salinity and precipitation allowed the definition of the salinity in equilibrium with the average local precipitation (17.7 g L^{-1}), indicating the range of mesopolyhalinity as the most appropriate target for the management of the lagoon under current rainfall regimes. Thirdly, the conclusion that the hypersalinisation observed in 1990s was driven by natural processes rather than by anthropogenic alterations of the watershed hydrology or by inadequate management of the lagoon system, should dissuade the need of supplementary freshwater inputs to maintain the lagoon within adequate ecological status, in accordance with previous observations (Pretus 2003).

The results of Chapter 2 have been used implicitly and explicitly in other chapters. The conceptual scenario of an enclosed lagoon has been used to judge the appropriateness of the use of the free-water diel approach to estimate carbon and oxygen metabolism in Chapter 5. The model itself, or more specifically the resulting water fluxes into and from the lagoon, has been used to mass-balance the carbon flows in Chapter 6, in a integrative chapter aimed to describe the patterns carbon cycling in the lagoon.

Macrophyte dynamics

In Chapter 4 we have observed considerable interannual variability in the descriptors of the macrophyte meadows, independently of their reference to production (maximum biomass) or to spatial distribution (area of occurrence, average depth). Such variability appears to be determined by salinity, water level and light availability, being their effects restricted to a particular period of the annual cycle. Salinity may affect macrophytes only in summer, when it is higher; light availability may only affect macrophytes in spring, at the onset of macrophyte growing period, and water level may have a double role through the interference on the bottom light availability in spring and through a lagged effect at the end of the previous annual cycle.

The role of water level and salinity variations on the spatiotemporal dynamics of the macrophyte meadows was already suggested in Chapter 1. With regard to the water level, in the introductory chapter we described a fast recovery of the meadows after a huge littoral desiccation. It was quite a unexpected result, since our hypothesis was that littoral desiccation could generate massive mortality of the meadows, as a result of the lethal effect of desiccation on *R. cirrhosa* (Verhoeven 1979), which tolerates desiccation but only for less than five hours (Adams and Bate 1994). The non lethal effect of desiccation on the macrophyte meadows has been confirmed in Chapter 4. We have shown that littoral desiccation not only does not negatively affect the meadows, but also have found a positive relationship between macrophyte cover and summer desiccation at the end of the previous annual cycle. Although the mechanisms are not clear, we hypothesize a possible explanation for this positive effect based on higher seed production, what would be in accordance with previous observations on *R. cirrhosa* and *R. maritima* (Costa and Seeliger 1989; Gesti et al. 2005). The effect of desiccation on the macrophyte meadows should be explored in detail, ideally through field observations or experimentation rather than in laboratory small-scale experiments.

With regard to the role of horizontal salinity gradients on the spatial distribution of the macrophytes, this hypothesis has been discarded in Chapter 4. Contrary to other coastal lagoons (Menéndez et al. 2002; Agostini et al. 2003; Lirman et al. 2008), we have showed that the Albufera can be considered spatially homogenous in salinity, and that the spatial distribution of macrophytes is determined by other factors, namely light availability and wave exposure. The role of light availability is not new since it is the classical factor to be considered when studying macrophyte spatial distribution in coastal ecosystems (Dennison 1987; Duarte 1991; Koch 2001). The role of wave exposure, which would be in accordance with the suggestions of Verhoeven (1980b), is quite surprising given the enclosed character of the lagoon and the higher depth of the lagoon in comparison with the systems described by Verhoeven (1980b). An explanation for this might be the high intensity of the northerly winds characteristic of the island of Menorca (Jansà 1979).

Less well understood is the almost disappearance of macrophytes after six years of apparent stability, which would be attributed to a combination of several factors. With the available data we cannot perform analysis of possible thresholds in the factors that drive macrophyte interannual dynamics, and thus it is not possible to better understand the macrophyte disappearance in 2007. Future research on the macrophyte dynamics based on palaeolimnological approaches might contribute to better understand the factors driving macrophyte stability in the lagoon.

Macrophytic production

In this thesis we have estimated the production within the macrophyte meadows from two different approaches. In Chapter 5 the net ecosystem production was assessed by means of a diel free-water approach, and in Chapter 4 the net annual production of *R. cirrhosa* was determined through a biomass harvesting technique.

The diel metabolic approach has yielded highly variable *NEP* values at both littoral and deep sites (Table 5.5). By assuming that the volumetric metabolic rates (mmol m^{-3} d^{-1}) in the littoral sites reflect the sediment plus planktonic plus macrophytic metabolism, and that the volumetric rates in the deep site correspond solely to planktonic plus sediment metabolism, we have estimated the metabolism corresponding to macrophytes as the difference between the littoral and deep volumetric metabolic rates. When expressed in areal units, the resulting *GPP* and *R* estimates corresponding to macrophytes are 681 ± 205 mmol m^{-2} d^{-1} and 516 ± 273 mmol m^{-2} d^{-1}. These values are approximately 60% of the total metabolism in the littoral sites (Table 5.5).

From these estimates, the *NEP* corresponding to macrophytes would be 165 ± 129 mmol m^{-2} d^{-1}. It must be noted that this production mainly corresponds to the net production of *R. cirrhosa* in summer, but also includes the epiphytic production. As a rough evaluation, assuming that it corresponds solely to *R. cirrhosa* metabolism and that this value is not changing during the macrophytic growing period (4-5 months, Chapter 4), this estimate would correspond to a macrophytic net annual production of 238-297 gC m^{-2} y^{-1}. These values are very close to the annual production of *R. cirrhosa* determined through biomass harvesting methods for that year (312 ± 42 gC m^{-2} y^{-1} for 2002; Table 4.2). Despite this is a very rough evaluation, we believe that the close agreement between both approaches validates our results and encourages the further use of these metabolic estimates later in Chapter 6. Being these estimates plausible, our results point the macrophyte meadows of the Albufera des Grau in the upper range of production in macrophyte-dominated coastal ecosystems, which are typically in the range 150-400 gC m^{-2} y^{-1} (Knoppers 1994; Gattuso et al. 1998; Duarte and Chiscano 1999).

The estimates of the macrophyte production from harvesting techniques (taking the maximum biomass as an estimate of annual production) are in the range 154 – 651 gC m^{-2} y^{-1} for the whole period (Fig. 4.7). This points the production of *R. cirrhosa* in the Albufera des Grau amongst the highest values for this species in the literature (Verhoeven 1980b; Calado and Duarte 2000; Azzoni et al. 2001; Menéndez 2002; Pasqualini et al. 2006; Pergent et al. 2006; Casagranda and Boudouresque 2007; Bartoli et al. 2008). We have not recognized a clear explanation for such high production especially considering the potential limitation by light in spring (Chapter 3) and by carbon in summer (Chapter 5). This issue is briefly discussed in the next section.

Light climate and macrophytes

In Chapter 3 we have explored the underwater light climate in the lagoon in a sufficiently extended data set to cover much of the expected temporal variability.

Unexpectedly the lagoon has been spatially uniform with regard to the light attenuation coefficient. This makes that the spatial variations in the underwater light regime are only related to the depth of the water column rather than to local differences in the behaviour of light in the aquatic medium.

Also interesting are the results of the light attenuation partitioning (section 3.4.2). The equation derived to calculate *K* as a function of the water components explains a large fraction of its variance, and has been used later in Chapter 4 to determine, together with the water level, the effect of bottom irradiance on the macrophyte meadows. Unlike most estuarine and coastal systems and contrary to the prevailing view of light attenuation in freshwater shallow lakes where sediment resuspension highly determines light climate (Cristofor et al. 1994; van Duin et al. 2001; Jackson 2003), the light attenuation coefficient in the Albufera des Grau has been found to be poorly determined by inorganic tripton. Given the above-mentioned effect of wave stress, and hence of wind exposure, on the macrophyte meadows, the small role of ISS, expected to be largely originated by wind-driven sediment resuspension, is at least surprising, and may be related to the time scale considered in the light climate exploration (Banas et al. 2005). Further work on the variability in K and its components at shorter time scales will probably contribute to better understand such unexpected result. It is noteworthy the role of DOC in the light attenuation, which has been reported in estuaries but is not common in coastal lagoons (Bracchini et al. 2005; Branco and Kremer 2005; Xu et al. 2005). Given the macrophytic origin of DOC depicted in Chapter 6 (Fig. 6.3), the role of DOC in the underwater light regime could suppose a mechanism through which benthic and pelagic primary producers interact, and should be explored in detail. Further work is needed to characterize the optical properties of DOC and confirm its role on the light climate in the lagoon.

Our results highlight the potential light limitation in a significant fraction of the lagoon benthos during the macrophyte growing period based on the evaluation of bottom irradiance. As discussed, these results do not demonstrate by themselves the light limitation on the macrophyte meadows, but rather suggest it, as our arguments have relied on macrophytic light requirements taken from the literature. Nonetheless, these results agree with those of Chapter 4, where the depth of the water column has been identified as the main factor determining the spatial distribution of macrophytes, thus highlighting the effect of light limitation through a more mechanistic approach. It is noteworthy that the potential light limitation would even be higher if the self-shading effect of the macrophyte canopy was considered (Carr et al. 1997; Calado and Duarte 2000).

Knoppers (1994) depicted a positive relationship between water depth and annual production in macrophyte dominated lagoons without light limitation. Given the light limitation at the bottom of the Albufera des Grau, it is not likely that its high maximum depth (3m) is behind the high production of *R. cirrhosa* in this system, as hypothesized in Chapter 1. However, it is noteworthy that the biomass and production estimates were performed in the littoral rather than in the deep areas of the lagoon. We have shown that for K lower than 1.8 m^{-1} all the areas shallower than 1.5 m would not be light limited (Fig. 3.8). Given that the 80% of the values of K were below 1.8 m^{-1} (Fig. 3.2), it is concluded that light limitation is unlikely in shallow areas. In conclusion, light limitation is expected to occur only in the deep areas of the lagoon, but not in the littoral areas where biomass estimates are performed. The correlation analysis performed in Chapter 4 can be interpreted in accordance with these observations: a detailed evaluation shows that the macrophyte descriptors that were correlated with light availability in spring were those based on cover metrics but not those referring to production measures (Table 4.3, note that the maximum biomass was not significantly related to light availability in spring months). This would agree with the previous observations, suggesting that light availability does not determine macrophyte production in the Albufera des Grau.

With regard to the role of water depth on macrophyte production, it should be analysed considering the depth at the same sampling sites where production estimates are performed, and not on the mean or maximum depth of a given system. A tentative bibliographic exploration of the relationship between water depth and the annual macrophyte production in different Mediterranean coastal lagoons dominated by *R. cirrhosa* is shown in Fig. D.1. When possible, we used the depth at the sampling sites rather than the mean depth of each lagoon. The annual production was assumed to equal maximum biomass in those systems for which only biomass data was reported, in accordance with the results of Chapter 4. We assumed 20% ash content (Menéndez 2002) and 37% carbon content (Chapter 4) to convert data in original units to gC m^{-2} y^{-1} when these factors were not reported. Despite the results must be considered tentatively, a clear negative relationship between water depth and maximum biomass is observed (Fig. D.1), contrary to the observations of Knoppers (1994). This may depict light limitation as an important factor determining the annual production of *R. cirrhosa* in Mediterranean coastal lagoons. For the Albufera des Grau, the production estimates fall above the expected values for the depth at which samples were taken. This suggests again that light limitation is not playing a role in the production of *R. cirrhosa* in the littoral areas of the lagoon, contrary to other similar Mediterranean systems. It is noteworthy the extreme production of the year 2000, with a value close to 500 gC m^{-2} which is clearly out of range. A possible explanation for this may be related to the fact that *R. cirrhosa* appeared to overwinter and behave as biannual in 1999 to 2000 (J.P. personal observation), but this extreme is not easily demonstrated.

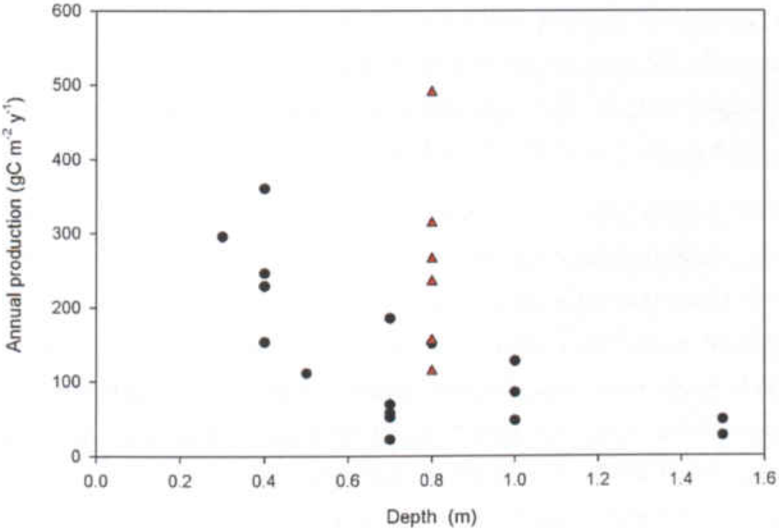

Figure D.1. Biomass of *R. cirrhosa* as a function of depth for different coastal lagoons (black circles) in comparison with the Albufera des Grau (red triangles). The lagoons corresponding to bibliographic data are Valle Smarlacca, Italy (Azzoni et al. 2001; Bartoli et al. 2008); Llacuna de la Tancada, Spain (Menéndez and Comin 1989; Menéndez 2002); Lake Ichkeul, Tunisia (Casagranda and Boudouresque 2007); Tvärminne, Finland (Verhoeven 1980b), Camargue, France (Verhoeven 1980b), Coastal ponds, Netherlands (Verhoeven 1980b), Certes fishponds, France (Viaroli et al. 1996; Bachelet et al. 2000); Santo André lagoon, Portugal (Calado and Duarte 2000); Biguglia lagoon, Italy (Pasqualini et al. 2006; Pergent et al. 2006); Sta Giulia lagoon, Italy (Pergent et al. 2006); Fra Ramon, Spain (Gesti et al. 2005).

In conclusion, light availability is a key factor that determines the variability in the spatial distribution of macrophytes (area of occurrence, average depth) by affecting macrophyte development in the deep areas of the lagoon, but would not play a significant role on the meadows located at shallow depths. Interestingly, the potential light limitation at intermediate depths would depend on both water level and light attenuation (Fig. 3.8) thus linking the hydrological dynamics and the underwater light regime.

Carbon cycling

The consequences of the high macrophytic production on the carbon cycling in the lagoon have been studied in Chapters 5 and 6.

On Chapter 5 we have assessed the variability in the concentration of the metabolic gases during the period of maximum activity of the meadows. We have concluded that the diel metabolic activity of macrophytes is responsible for a high small-scale variability in the DIC and DO concentrations in the lagoon. Our estimates of the metabolic parameters are in the upper range for coastal ecosystems (Smith and Hollibaugh 1997; Ziegler and Benner 1998; McGlathery et al. 2001; Duarte et al. 2002; Santos et al. 2004; Barrón et al. 2006), and have showed high temporal variability. An important contribution of anaerobic metabolism and chemical reactions taking place at the sediment/water interface or in the water column to total metabolism has been highlighted, as expected in a shallow aquatic system (Torgersen and Branco 2007). On the contrary atmospheric flux would be of minor importance at this scale. We have also concluded that the application of the free-water diel approach to estimate metabolic parameters in macrophyte-dominated coastal lagoons should be based on multiple sites and on the combined analysis of DIC and DO variations.

In chapter 6 we have observed high differences in the DIC and OC annual balances between years. The lagoon is thus exhibiting large variability in the carbon processing on both space and time at multiple time scales, from between days to interannual. This variability may be attributable to differences in internal metabolism (as shown in Chapter 5), in calcite precipitation (as suggested in Chapter 6), or in the hydrological-based fluxes of carbon (as described in Chapter 6). The atmospheric carbon flux, which despite being a significant flux on the annual budgets is of lower importance in comparison with the metabolic fluxes, is mainly driven by the pCO_2 in the lagoon, i.e. its dynamics is largely controlled by the resulting dynamics in the lagoon processes and hence must not be considered an additional source of variability to carbon cycling.

The seasonal dynamics of DIC is explained by the combination of several fluxes that are much higher in magnitude than the resulting net balance. The DIC cycling in the lagoon is extremely fast, with a mean residence time of only 3.7 days during the vegetated period. This value, despite in accordance with other macrophyte-dominated systems (Ziegler and Benner 1998), highlights the intensity of carbon cycling in the lagoon, as it corresponds to a turnover between 13 and 65 times the turnover of water. The main fluxes determining DIC dynamics are the intense internal metabolic fluxes, but calcite precipitation and atmospheric and hydrological fluxes are also important.

Interestingly, the role of the watershed and the sea processes on the lagoon carbon cycling appears to be poorly linked to the delivery of organic material by itself. This contrasts with the prevailing view of carbon cycling in coastal lagoons, which are usually highly affected by marine and terrestrial carbon inputs (Smith and Hollibaugh 1997; Buddemeier et al. 2002). Despite the relatively small number of annual cycles considered and despite being subject to some inaccuracies (section 6.4), our estimates of carbon cycling in the Albufera des Grau depict a system where hydrological fluxes are more responsible of indirect effects on carbon cycling than of direct organic or inorganic carbon delivery. Thus, the role of the freshwater and marine inputs is related to the development of phytoplankton peaks, to the alteration of the water column stability and to the triggering of bottom hypoxia.

The results of Chapter 6 suggest that the food web within the lagoon is not sustained on macrophytic carbon, but on other organic matter sources. Decomposition appears to be the main destiny of the high macrophyte production, although sediment burial would account for between 15 and 30% of total macrophyte production, whereas grazing and export would be negligible. Waterfowl consumption might be also a destiny to be considered (Verhoeven 1980b), but was not evaluated here. Our results are in accordance with the expected pattern in macrophyte-dominated coastal systems (Knoppers 1994; Duarte and Cebrian 1996). The fast decomposition of the macrophyte meadows, in accordance with the high decomposition rates estimated in the lagoon, are reflected in the dynamics of DIC and pCO_2 in water. Despite intensely punctuated by phytoplankton blooms and torrential and marine inputs, the pCO_2 dynamics follows a seasonal cycle related to the production and decomposition of the meadows. The atmospheric flux of CO_2 is thus seasonally shifting, and the lagoon acts as a source or sink of CO2 depending on the presence of submerged vegetation. Such seasonal shift in the direction of atmospheric carbon fluxes is a typical feature of many macrophyte-dominated coastal lagoons (Knoppers 1994; Gattuso et al. 1998)

Significance of hypoxia

The hypoxic conditions in a typical summer period have been concluded to be of minor importance in the Albufera des Grau in Chapter 5, contrary to what happens in many Mediterranean coastal lagoons, where episodic hypoxic events[4] seriously affect the status of the system and the survival of animals and vegetation due to the low oxygen levels and sulphide release from anaerobic metabolism (Castel et al. 1996; Souchu et al. 1998; Giordani et al. 2008).

The summer hypoxic events are usually related to the accumulation of large amounts of organic matter, largely of macroalgal origin, together with meteorological favouring conditions (Harzallah and Chapelle 2002). Despite macroalgal biomass is more prone to reduce oxygen levels, the accumulation of macrophytic biomass has also been reported to lead to summer hypoxic crisis in some coastal lagoons (Duarte et al. 2002). In other coastal embayments, bottom hypoxia has also been related to vertical stratification in the water column (Ritter and Montagna 1999; Hearn and Robson 2001).

Apart from the biomass based hypoxia described in Chapter 5, in Chapter 6 we have described the occurrence of stratification-based hypoxias. These appear to play a significant role in the annual carbon balance and highly determine the stable isotope composition of DIC. We have observed vertical stratifications generated after high freshwater inputs (e.g. spring 2003) or after the entrance of seawater in summers with low salinity in the lagoon (e.g. summer 2003; Fig. 6.2 and Fig. 6.3). In both cases there is a need for calmed weather with low winds, but the latter case (seawater inputs) is potentially expected to last longer because the high temperatures in summer may contribute to enhance density stratification. Moreover, given the oligo-haline range during the studied period, the difference in salinity between the lagoon water and seawater is likely to be much higher than the difference between lagoon water and freshwater, thus facilitating vertical density stratification. The summer vertical stratifications are thus expected to be more critical than the others and to generate more intense bottom hypoxias, also because of the higher temperatures in summer and the consequent decrease in oxygen solubility and enhanced bacterial metabolism. The change in sediment metabolism due to increased bottom salinity may also contribute to favour summer hypoxia (López 2003).

All these factors where combined in 2003, when we assisted to the most intense hypoxic event, which, as mentioned above, highly modified the carbon fluxes in the lagoon, and despite not evaluated, likely impacted the aquatic biota. The high temperatures observed that summer (27 ± 2.1 °C, much higher than the long-term mean summer temperatures, 24 ± 1 °C; Table D.2) probably

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[4] Such events are commonly referred to as *dystrophic crises* (e.g. Bartoli et al. 1996; Lardicci et al. 1997; Viaroli et al. 2001; Duarte et al. 2002; Frascari et al. 2002; Harzallah and Chapelle 2002; Viaroli and Christian 2003; Marinov et al. 2006; Obrador et al. 2007; Magni et al. 2008). The term *dystrophy* originally refers to those aquatic ecosystems characterised by high loading of allochthonous organic matter, largely as DOM (see discussion in Wetzel 2001 p813), and therefore should probably better not be used to refer to summer oxygen depletions in coastal ecosystems.

favoured the hypoxia. Moreover, the intense phytoplankton peak in summer 2003 highly contributed to enhance bottom hypoxia by increasing biomass accumulation and by lowering bottom light availability (see Fig. 3.4). In contrast, the even more intense phytoplankton peak observed in spring 2004, which also highly reduced bottom light availability (Fig. 3.4), only generated a minor bottom hypoxia (Fig. 6.3). Such lower hypoxia may be due to the lower temperatures in spring than in summer, and to the homogenous vertical salinity profile in the water column (Fig. 6.2).

Table D.2. Summary of the hydrological, meteorological and physical features of the summer period (June, 1-August, 31) for the years 2002 to 2004 and for the long-term average. Some descriptors of seawater input (daily flows, duration of the period with inputs) are also reported. The asterisk indicates modelled data. n.a.: not available

	2002	2003	2004	1975-2001
Rainfall mm	117 mm	1 mm	14 mm	45 ± 44 mm
Wind speed	3.7 ± 1.4 m s^{-1}	3.5 ± 1.2 m s^{-1}	3.8 ± 1.4 m s^{-1}	3.9 ± 0.5 m s^{-1}
Air temperature	24 ± 2.3 °C	27 ± 2.1 °C	24 ± 2.5 °C	24 ± 1 °C
Observed WL	-2 ± 8 cm a.s.l.	-12 ± 8 cm a.s.l.	-16 ± 9 cm a.s.l.	-15 ± 10 *
Water salinity	15.4 ± 1.2	8.9 ± 4.1	7.8 ± 3.1	20.0 ± 10.8 *
Max bottom salinity	16.5	14	12	n.a.
Max salinity gradient	0.0 ± 0.2 (0.3) m^{-1}	1.3 ± 2.0 (4.4) m^{-1}	0.4 ± 0.8 (1.9) m^{-1}	n.a.
Salt input	4 886 Mg	10 089 Mg	7659 Mg	3352 ± 871 Mg *
Mean daily flow *	532 $m^3 d^{-1}$	820 $m^3 d^{-1}$	772 $m^3 d^{-1}$	784 ± 155 $m^3 d^{-1}$
Maximum daily flow *	753 $m^3 d^{-1}$	1167 $m^3 d^{-1}$	1128 $m^3 d^{-1}$	1071 ± 150 $m^3 d^{-1}$
Duration*	129 d	125 d	158 d	185 ± 70 d

The bottom hypoxia observed of summer 2004 was related to another slight vertical salinity gradient after seawater input (see Fig. 6.2), but it was much minor than that of 2003, lasting only one month. The lower extent of this hypoxia was probably related to the less extreme temperature of summer 2004, which equalled the long-term average, and to a lower vertical salinity gradient in comparison to that observed in summer 2003 (Table D.2). Independent estimates based on salt mass balance between sampling intervals showed a smaller input of seawater in summer 2004 with respect to that of 2003 (Table D.2), in accordance with the daily water flows simulated with the hydrological model. The summer 2004 also showed higher wind speeds than the summer 2003, what may have also contributed to avoid a more intense hypoxia. It is clear from the analysis of the summer meteorological and lagoon data, that summer 2002 was not especially prone to show hypoxic events, given the cool temperatures and high wind speeds, the low seawater inputs (shown by both the model results and the independent salt-balance estimates) and the higher salinity at the beginning of summer (Table D.2).

In conclusion the significance of bottom hypoxias largely depends on the combination of several factors, in accordance with previous observations (Harzallah and Chapelle 2002). The main factors here were the salinity levels of the lagoon in summer, the magnitude and intensity of the seawater inflow, the wind and temperature regimes, and the development of phytoplanktonic peaks. From our results, we believe that bottom hypoxic events in the Albufera des Grau are only occasionally critical, and that the huge hypoxia undergone in summer 2003 was due to the singular combination of several critical factors, especially favoured by low salinity. The minor importance of both biomass-based and stratification-based hypoxias in the Albufera des Grau contrasts with many other coastal lagoons (Castel et al. 1996; Viaroli et al. 2001; Harzallah and Chapelle 2002; Viaroli and Christian 2003; Giordani et al. 2008), and also with reported hypoxic crisis in the same Albufera des Grau in the 1980s, a period of macroalgal dominance (Pretus 1989; Cardona and Pretus 1991).

Sources of variability

We have used a number of different methodologies to fulfil the specific objectives of the different chapters of this thesis, as well as multiple temporal scales of analysis, from the study of the diel cycles to the yearly analysis of a long-term hydrological simulation. In Chapter 6 we have integrated information of carbon flows from data at different temporal scales: we have used diel metabolic data together with monthly and annual carbon budgets, and combined these results with estimates of carbon flows at more integrative scales, such as the stable isotope characterization of the food web or the estimates of burial rates in the sediment. We truly believe that integrating such diversity of sources of information results in a better understanding of the functioning of the studied. The temporal variability of the external forcings that take place in coastal lagoons (Kjerfve 1994) requires that the basic information of the physical properties of the system (e.g. water fluxes) be available on as high a temporal resolution as possible. Estimates of water flows (and of associated materials) from monthly analysis may lead to erroneous interpretations due to the obscuration of small scale processes that take place between samplings, what makes that working on daily water fluxes is highly advantageous.

In Chapter 6 we have used daily water flows to study carbon cycling at seasonal and annual scales. Despite this highly contributed to a more precise estimation of the hydrological carbon fluxes in the lagoon, there are some important inaccuracies in our approach. The most important one is the lack of a discharge-concentration relationship in our calculations (this deficit was also evident in the construction of the hydrological model itself, as discussed above), and has been compensated by assuming the lower of our estimates as representative. Despite these caveats, we believe that our approach is much more precise than performing budgetary calculations based on rough non-modelled estimates of the water fluxes performed on a monthly basis.

Another important issue arising from the results of Chapter 6 is the temporal extension considered. Given the high interannual variability observed in the pattern of carbon cycling in the lagoon, the temporal extension of our approach, based on an analysis of three years, appears to be insufficiently short. Nonetheless, we have drafted a first detailed description of carbon cycle in the system, outlining the role of internal processes over hydrological processes in the carbon cycling. The analysis of long-term data appears to be fundamental for a correct depiction of those processes that vary over multiannual scales, or, what is the same, to reveal the 'invisible present' of the ecological systems (Magnuson 1995). To our knowledge, long-term high quality data allowing the determination of carbon fluxes in coastal lagoons are scarce, and complete studies such as the Smith and Hollibaugh (1997) in Tomales Bay are very singular given the huge effort and resources required. One interesting line of future research in the Albufera des Grau might be the development of a coupled ecological-hydrological model (based on the hydrological model developed in Chapter 2) that allowed the analysis of carbon balances from a temporally-extended data set. As introduced above, coupled ecological-hydrological models have been developed in other Mediterranean lagoons, with promising results (Arhonditsis et al. 2002; Plus et al. 2003; Zaldívar et al. 2003; Giusti and Marsili-Libelli 2005; Giusti and Marsili-Libelli 2006; Plus et al. 2006). The very first step in the Albufera des Grau should definitely be the improvement of the characterisation of the carbon concentrations in the end-members, which at their present knowledge have only allowed the rough estimates performed in Chapter 6. In conclusion, the diversity of approaches used in this thesis resulted in a higher multi-scale understanding of the processes that shape the functioning of the lagoon.

Despite the spatial pattern of the processes has been treated less intensely than its temporal dynamics, we have intended to characterise the spatial variability in most of the processes considered along this thesis. The assessment of the spatial variability in the different considered variables (turbidity, macrophytes, salinity, metabolism) have considered the pure spatial variability (i.e. the change in the salinity or turbididy along the horizontal dimension, or the vertical gradient in DIC) but also the variability between and within sites differing in their depth (e.g. in the biomass and production estimates or in the analysis of the diel metabolism). Unexpectedly, the lagoon can be considered homogenous with regard to salinity and light attenuation in water. This lack of intense horizontal gradients is not common in most coastal lagoons, which are frequently subject to large spatial gradients in salinity (Menéndez et al. 2002; Agostini et al. 2003; Lirman et al. 2008). Interestingly, the results of Chapter 5 have depicted the existence of small-scale horizontal and vertical gradients linked to the diel light cycle with regard to the concentrations of the metabolic gases and the water temperature (data not shown). The lagoon moves from almost homogenous conditions at down to a double spatial gradient at dusk, as a response of macrophytic metabolic activity during daytime.

Given the high variability on both space and time observed, and the diversity of scales at which this variability is manifested, the very first conclusion of this thesis is that any approach to coastal lagoon ecology must be based on sampling designs that cover as much of this variability as possible, in order to avoid misinterpretations. To our opinion, high inaccuracies can be expected if this variability is not considered, as is inevitably common in broad scale studies dealing with the identification of patterns along continental gradients. In the case of the Albufera des Grau, for example, a sampling design aimed to characterize any of the processes studied here, may result in equivocal results if based simply on annual or seasonal samplings.

On the other hand the approach used in this thesis puts especial emphasis on those processes that affect or are mediated by macrophytes, given their fundamental role in the ecology of coastal lagoons (Sand-Jensen and Borum 1991; Kjerfve 1994; Viaroli et al. 1996; Levin et al. 2001; Plus et al. 2003; Nielsen et al. 2004). We have characterised the hydrological and underwater light regimes, described the spatial and temporal dynamics of submerged macrophytes in relation to several environmental factors, and drafted the basic pattern of carbon cycling in the lagoon. The reader might recall the absence of biotic interactions and their effects in this thesis, given that we have focused on those factors that shape the ecological functioning of the lagoon from a *bottom-up* perspective. The influence of trophic interactions on ecosystem functioning have been intensely studied in freshwater shallow lakes under the light of the regime shifts theory (Scheffer et al. 1993), with some incursions in oligo-mesohaline systems (Moss 1994; Jeppesen et al. 1994; Jakobsen et al. 2003; Romo et al. 2005; Cardona 2006; Badosa et al. 2007; Jeppesen et al. 2007). Our focus on the *bottom-up* processes does not imply in absolute a belief of a predominance of the *bottom-up* processes over *top-down* effects. Rather than that, we have set this research in a background that was in accordance with the main processes outlined as regulatory of the stability of coastal lagoons, suggested to be of biogeochemical rather than biotic nature (Viaroli et al. 2008). It must be noted that in one of the best documented evidences of regime shift in mesohaline coastal lagoons, Petersen et al. (2008) recently reported a salinity-induced change from a bottom-up controlled turbid state into a top-down controlled clear-water state. There are few well documented examples of regime shifts in meso-polyhaline lagoons in the literature. In this context, we have the impression that the ecological processes that take place in coastal lagoons with salinities above the mesohaline range need further attention by ecologists, in order to properly situate them in more general ecological theories. Part of this disattendance may be related to the presence of intuitive boundaries in the range of application of such theoretical backgrounds. The term *brackish* has a wide meaning, and refers to all waters with salinity lower than seawater and higher than freshwater (Elliot and McLusky 2002). It is our impression that coastal lagoons such as the Albufera des Grau, which can move from the oligohaline to the polyhaline ranges appear to be in a no mans' land between the notion of brackish as understood by pure limnologists (which rarely reaches mesohalinity) and the notion of brackish for marine biologists (which rarely goes below polyhalinity).

Conclusions

Conclusions

The general conclusions of this thesis can be summarised as follows:

1. The Albufera des Grau is a simple system with regard to the hydrological processes that take place. A simple dynamic model with few data requirements specifically developed for the Albufera des Grau correctly simulated the temporal dynamics of the main hydrological descriptors of the lagoon at a daily scale.
2. From the analysis of a hydrological dynamic simulation run for the last 30 years, the Albufera des Grau is defined as an enclosed lagoon with limited marine influence, with water mostly in the oligo-polyhaline range and a water residence time of 8 months. The precipitation-evaporation seasonal cycle and the torrential punctuation of this basic pattern are responsible for the temporal dynamics of both water level and water salinity.
3. The lagoon is dominated by submerged vegetation, with dense and extensive meadows dominated by *Ruppia cirrhosa*. The annual production of this species is amongst the highest reported in the literature, and portrays the Albufera des Grau as a highly productive coastal ecosystem.
4. The spatial distribution of macrophytes is determined by light availability and wave stress, rather than by horizontal salinity gradients, which are insignificant in the lagoon. The interannual dynamics of the macrophyte meadows is determined by salinity, water level and light availability, with their effects restricted on particular periods of the annual cycle. Light availability is an important factor for macrophytes in the deepest areas of the lagoon, but would not play an important role in the macrophyte dynamics in shallow areas.
5. The lagoon can be considered spatially uniform with regard to the light attenuation in water. The spatial variation in the underwater light regime would thus be only related to the depth of the water column. The temporal variation in the underwater light regime at intermediate depths would be related to light attenuation and to water level fluctuations.
6. The phytoplankton is the main driver of the light attenuation in the water column, but there is an important contribution of DOC, which appears to have a macrophytic origin. The inorganic suspended solids play a minor role in the light attenuation at the considered temporal scale.
7. The intense diel metabolic activity within the macrophyte meadows is responsible for high small-scale variability in the DIC and DO concentrations. The lagoon moves from almost homogenous conditions at down to a double spatial gradient at dusk, manifested in the vertical and horizontal dimensions.
8. The metabolism of the lagoon is highly variable at a daily scale and between sites, and is highly influenced by anaerobic metabolism and chemical oxidation reactions. The atmospheric flux of both DIC and DO is a minor contribution in comparison with internal fluxes.

9. The application of the free-water diel approach to perform metabolic estimates in macrophyte-dominated coastal lagoons should be based on multiple sites and on the combined analysis of DIC and DO variations.

10. The DIC cycling in the lagoon is extremely fast, with a turnover between 13 and 65 times higher than that of water. The seasonal dynamics of DIC is explained by the combination of several fluxes that are much higher in magnitude than the resulting net balance, of which the most important are the internal metabolic fluxes, but is also highly affected by calcite precipitation and by atmospheric and hydrological fluxes.

11. The dynamics of pCO_2 in the lagoon is largely explained by the seasonal cycle of production and decomposition of the macrophyte meadows, with intense punctuations driven by phytoplankton peaks and hydrological inputs. The atmospheric flux of CO_2 exhibits a seasonal shift, and the lagoon acts as a source or sink of CO_2 depending on the presence of submerged vegetation.

12. The high macrophytic production does not support neither the pelagic nor the benthonic food web in the lagoon, which would rely on other sources of organic matter. The fate of macrophyte production appears to be decomposition and secondarily sediment burial, whereas trophic consumption and export would be of minor importance.

13. The annual balance of DIC and OC is highly variable, likely depending on the degree of perturbation of the basal seasonal cycle of macrophytes. The effect of torrential inputs and seawater inflow on the annual carbon balances is based on the development of phytoplankton peaks or the alteration of the vertical structure of the water column and the occasional enhancement of bottom hypoxia, rather than to the delivery of allochthonous carbon.

14. Despite the high biomass accumulation in the lagoon in summer, littoral hypoxic conditions are of minor importance, as are stratification-based hypoxias in the deepest areas of the lagoon.


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ANNEX

Assumpte: SM 2216
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Estimado Dr. Obrador

Ref. Scientia Marina manuscrito SM 2216

Me complace informarle que su manuscrito "Spatial distribution and biomass of aquatic rooted macrophytes and its relevance in the metabolism of a Mediterranean coastal lagoon" por Biel Obrador; Joan Lluís Pretus and Margarita Menéndezha sido aceptado para su publicación en *Scientia Marina.*

El manuscrito será sometido a la revisión final de inglés. Si los cambios son pocos, nosotros los introduciremos en el texto. Si fueran muchos, se los enviaremos a Vd. para su inclusión en la versión final.

Recibirá las galeradas unas semanas después de nuestra recepción de la versión corregida del manuscrito.

Muchas gracias por considerar *Scientia Marina* para la publicación de su trabajo.

Cordialmente,

Dra. M. Pilar Olivar
Director
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Dear Biel Obrador:

We are pleased to inform you that your manuscript, "A Dynamic Model to Simulate Water Level and Salinity in a Mediterranean Coastal Lagoon" has been accepted for publication in Estuaries and Coasts.

For queries regarding your accepted paper, please click the following link, complete the query form and click "Submit".

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Title: Light regime and components of turbidity in a Mediterranean coastal lagoon

Estuarine, Coastal and Shelf Science

Dear Biel Obrador,

My evaluation of your revised manuscript indicates that you have satisfactorily dealt with the suggestions of the reviewers. I am, therefore, pleased to accept the manuscript, as revised, for publication in Estuarine, Coastal and Shelf Science.

I have today prepared it for the publisher and forwarded it to the Journal Manager at Elsevier Production Department who will deal with it further.

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